POLYMERISATION OF SURFACTANT LYOTROPIC LIQUID CRYSTALLINE PHASES

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A thesis submitted for the degree of Doctor of Philosophy of The Australian National University.

Department of Applied Mathematics
Research School of Physical Sciences and Engineering

NATURAM PRIMUM COGNOSCE RERUM
Polymerisation of Surfactant Lyotropic Liquid Crystal Phases

A Thesis submitted for the degree of Doctor of Philosophy

to the Australian National University

Department of Applied Mathematics
Research School of Physical Sciences and Engineering

[Diagram]
For my Father.  
Whom I will never forget.

Mo tōku Matua.  
Kiā mau mahara ake tonu atu.  
Te Kōtuku ka moe whakaāio.

Pour mon Père.  
Qui je n'oublierai jamais.
Preface

This dissertation is an account of work carried out from March 1991 to July 1994 in the Department of Applied Mathematics, Research School of Physical Sciences and Engineering, The Australian National University, Canberra for the degree of Doctor of Philosophy.

The work included in this thesis has for the most part been solely performed by myself, the long boring hours of making ampoules, staring down a microscope and playing with the X-ray camera were all part of the joy of doing a Ph. D. Acknowledgment must though be extended to my collaborators.

The initial work on the surfactants ADAB and ADDAB discussed in chapter 4 was performed in conjunction with Calum Drummond (Division of Chemicals and Polymers, Ian Wark Laboratories, CSIRO, Melbourne, who was helped by Krister Fontell, Ali Khan and Olle Söderman during his visit to Physical Chemistry I, University of Lund, Sweden in May and June of 1991).

Surface tension measurements performed on DTAB (chapter 3) and ω-UTAB (chapter 5) were obtained at CSIRO, Melbourne by Nicole Moriarty and Calum Drummond.

The work included in chapter 6 on the formation of the spiral texture was performed in collaboration with Maurice Kléman (Laboratoire de Minéralogie-Cristallographie, Universités de Paris-6 (Pierre et Marie Curie) et de Paris-7, France) and Patrick Kékicheff. Janelle Kennard was also involved in some of the early experimental work.

The dendritic polymer studied in chapter 8 was synthesised by Dr Craig Hawker (IBM, Almaden, USA), with the subsequent work being performed in collaboration with David Antelmi.

The remaining work reported in this thesis was performed by myself.

None of the work presented here has been submitted to any other institute of learning for any degree.

Kathryn M. McGrath
Canberra,
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Publications

1. K.M. McGrath, P. Kékicheff and M. Kléman
   Spiral textures in lyotropic liquid crystals: first order transition between normal hexagonal and lamellar gel phases

2. K.M. McGrath
   Phase behaviour of dodecyltrimethylammonium bromide/water mixtures.
   In preparation

3. K.M. McGrath and C.J. Drummond
   Polymerisation of liquid crystalline phases in binary surfactant/water systems.
   Part I. Allyldodecyltrimethylammonium bromide and allyldidodecylmethylammonium bromide.
   In preparation

4. K.M. McGrath
   Polymerisation of liquid crystalline phases in binary surfactant/water systems.
   Part II. ω-Undecenyltrimethylammonium bromide.
   In preparation

5. K.M. McGrath
   Polymerisation of liquid crystalline phases in binary surfactant/water systems.
   Part III. Sodium 10-undecenoate.
   In preparation

6. K.M. McGrath and C.J. Drummond
   Polymerisation of liquid crystalline phases in binary surfactant/water systems.
   Part IV. Dodecyldimethylammoniummethacrylate bromide.
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7. Calum J. Drummond, Craig J. Hawker, Katrina M. Drummond, K.M. McGrath, D.A. Antelmi, Karen L. Wooley and Jean M.J. Fréchet
   Solution and interfacial properties of a water soluble dendritic macromolecule.
   In preparation
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Chapter 1

INTRODUCTION

1.1 SURFACTANT SELF-ASSEMBLY

Amphiphilic molecules (surfactants, lipids, soaps or detergents as they are commonly known) have the unique characteristic of being composed of both a lyophilic (apolar associating) and a lyophobic (polar associating) group. In the case of aqueous solution these groups are termed hydrophobic and hydrophilic, respectively. Surfactants may therefore take on several forms by varying both the nature of the hydrophilic (also known as the polar head group, containing either nonionic, ionic or zwitterionic groups) and hydrophobic regions (which in general consists of either a single- or double-chain hydrocarbon which may be branched or unbranched). Figure 1.1.1 shows a schematic diagram of a single-chain ionic surfactant, whose dimensions are characterised by three parameters: the length of the hydrocarbon chain (l), its area per polar head group at the interface (a) and its volume (v).

The dual nature of surfactants enables these molecules to self-assemble in many polar and apolar solvents and also in mixtures of the two (i.e. surfactants may be used to promote mixing of oil and water). As such, amphiphilic molecules show a diverse range of solution properties. Their self-assembling behaviour in binary, ternary and multicomponent systems, generally termed lyotropic self-assembly, often closely resembles the self-assembly of pure substances with changes in temperature alone, known as thermotropic self-assembly. Both types of aggregation have been extensively studied over the past one hundred years [1-20].

Due to their hydrophilic/hydrophobic nature enabling self-assembly which results in molecular organisation and compartmentalisation, surfactants reduce the air/water surface tension and the interfacial tension between polar and apolar solvents. These properties
are an advantage in synthetic reactions where the surfactant mesophase may be used as a host, for reactivity control [21], catalysis [22], transport [23, 24], recognition [23], drug delivery [25-27], artificial photosynthesis [28-31] and a wide range of other applications. This diversity of uses means that surfactants are extensively used in both research and industry. They also have a large commercial usage, examples of which are washing powders, soaps and shampoos. Although they are already substantially exploited, the inherent instability of these surfactant assemblages to perturbations (e.g. variations in temperature, composition and additives) does in fact limit their wider range of applicability. This could perhaps be overcome by 'locking in' the structure of the phases and therefore, making them less susceptible to perturbations. The feasibility of this procedure is examined in this thesis.

![Figure 1.1.1 Schematic diagram of a single-chain ionic surfactant.](image)

Many reviews have been written regarding the different types of liquid crystalline phases formed by surfactants in lyotropic systems [1-3, 6-8, 10-13, 16-20, 32-38] and only a brief discussion will be given here.

For single-chained surfactants above a critical concentration, 'critical micelle concentration' (cmc) and temperature, 'Krafft temperature' a micellar phase forms. Note
that the formation of a micellar phase is dependent upon the nature of both the head group and hydrophobic chain. At concentrations above the cmc, micellar solutions are comprised of free surfactant molecules in conjunction with surfactant aggregates randomly distributed throughout the solution [10, 11, 18]. The exact structure of the surfactant aggregate/micelle was debated for several decades. The concept of micelle formation by surfactant molecules in solution was first proposed by McBain [39, 40] who assumed that the structure was based on surfactant bilayers. However, it has now been established that the micelle is not of one specific geometry but rather the shape of the aggregates varies with both temperature and composition as well as fluctuating with time. But it is most certainly based on a closed globular monolayer. For a single-chain surfactant with a medium length hydrocarbon chain the micellar aggregates formed at the cmc are spherical with several distinct regions being incorporated in the structure [41, 42].

The interior core of all single-chained surfactant aggregates consists of pure hydrocarbon, water being completely excluded [43-47]. Gruen has shown [44] that on average all carbon atoms in the hydrocarbon chain will be found at some time to be in a hydrophilic environment. That is, it is not necessary to have water penetration into the interior of the micelle for there to be water contact with each section of the paraffinic chains. The reason that each carbon atom spends some time in a hydrophilic environment is a consequence of the large surface-to-volume ratio and the high flexibility of the hydrocarbon chains.

A considerable amount of work has been performed on determining the degree of conformational freedom that the surfactant hydrocarbon chains have upon aggregation in comparison to that in a pure nonpolar liquid. It has been shown that while the chains can definitely not be considered to be frozen and therefore, highly ordered, they do have a reduced mobility compared with those in a pure hydrocarbon liquid [44-46, 48-52]. The chains have associated with them an intrinsic lateral pressure [51] which is dependent upon the area per polar head group. This lateral pressure enforces chain ordering even when the polar heads are fully hydrated. Ordering of the paraffinic chains is evidenced by the presence of only one or two gauche configurations being adopted per chain and the increased probability of finding a chain in the all-trans configuration in comparison to pure hydrocarbon fluids [49]. Hence, in a micelle the hydrocarbon chains have conformational freedom, albeit reduced from that in a pure hydrocarbon fluid, but still sufficiently high for the chains to be considered fluid. Evidence for the fluid-like state of the hydrocarbon chains may be obtained from wide-angle X-ray scattering, which shows one diffuse ring only at \( Q = 2\pi/4.5 \text{ Å}^{-1} \) [53]. The chains are also found to be (on average) oriented perpendicular to the hydrophobic/hydrophilic interface (due to the imposition of the head groups being fixed to the surface of the micelle) and the degree of disorder in the paraffinic chain increases with increasing distance from the surface.
The exact position of the hydrophilic/hydrophobic interface and also, where the area per polar head group \(a\) should be calculated is still under much debate but it is conventional to assume that no more than two carbon atoms penetrate the hydrophilic region [43-47]. This assumption of having a region formed entirely of nonpolar aggregates is a general one, and has been demonstrated for the case of micelles [54]. Hence, the interface is defined as being the surface that separates the water from the paraffinic medium, which is covered by the polar head groups [55, 56]. This still leaves the question as to where the head group area should be calculated. There are in general, four interfaces at which a value for \(a\) may be determined. The hydrophilic/hydrophobic interface, the water/surfactant interface, at the end of the hydrocarbon chains or at the pivotal interface (which is also known as the 'neutral' interface and is defined as being that of constant area during the bending deformation, i.e. the surface has zero elastic modulus of mixed deformation [57]). The calculated value for the head group area will differ for each of these interpretations. It should also be noted, that as the composition is increased and the surfactant passes through a phase transition the area per head group will only remain constant in the case of the pivotal interface, according to a currently popular theory [57]. This theory states that as the conditions of the surfactant system are varied the value of the head group area, calculated at the pivotal interface will remain constant.

There is though a hydrophilic and a hydrophobic region in each of the surfactants' aggregated states. The hydrophilic side of the interface contains several distinct regions, the first layer consists of the head groups of the surfactant molecules, water of hydration and undissociated hydrated counterions (in the case of ionic/zwitterionic surfactants) and may also consist of one to two carbon atoms from the hydrocarbon chain. This layer is generally called the "Stern layer". The "Gouy-Chapman" (or "diffuse double") layer is found at further distances from the interface and consists of dissociated counterions, free surfactant and water. At still further distances there is bulk water with an undisturbed hydrogen-bonding network and free surfactant molecules. This picture is only true, though for very dilute solutions where the micellar aggregates are separated by large distances. At higher concentrations the double layer disappears and the counterions are concentrated between the surfactant aggregates.

The micellar aggregate cannot be considered to be a static entity as there is continual association (rate constant \(k_1\)) and dissociation (rate constant \(k_2\)) of the surfactant molecules such that, there is no precise aggregation number for the micelle and only an average value can be defined (i.e. the micelles are polydisperse). The mean residence time for a surfactant molecule is approximately \(10^{-4}\) s and the lifetime of the surfactant aggregate as a whole is found to have a maximum value of the order of \(10^{-2}\) s [58]. These two values are of course dependent upon the surfactant involved in the aggregation. Both the micelle as a whole and the individual surfactant molecules diffuse
freely throughout the solution. Note that, the individual surfactant molecules can diffuse both within the micelle and as free surfactant.

Figure 1.1.2 shows a schematic diagram of a normal spherical micelle (defined as type I where v/\text{al} < 1, i.e. the interface is bent towards the paraffinic chains). Reverse micelles (type II where v/\text{al} > 1) are also observed to form, though generally not at low surfactant concentrations in a binary surfactant/water system for single-chain surfactants. In the reverse micelle, the surfactant molecules are oriented such that, the head groups and water are confined to the centre of the sphere with the hydrocarbon chains forming a continuum.

Changes in either the composition or temperature will affect the geometry of the aggregates and the extent of these changes will depend upon the numerous interactions between the surfactant molecules and aggregates. This will be discussed in more detail in § 1.2.2.

As the surfactant concentration is increased, it is generally observed (again this will depend upon the surfactant involved) that the micellar aggregates are no longer spherical but become distorted in an oblate or prolate fashion to form discs (comprised of surfactant bilayers) or rods, respectively. It should be noted that this deformation is due to the geometrical constraint that the radius of the micelle cannot be greater than the length of the fully extended hydrocarbon chain. If this constraint is not met the criterion of uniform density in the hydrophobic interior would no longer hold and "holes" would be produced at the centre of the sphere. Therefore, as the concentration of surfactant increases, either there is an increase in the number of micelles and the average aggregation number remains constant or the aggregation number increases and the micellar aggregate shape distorts. The latter alternative is observed most generally.

An increase in surfactant concentration also leads to changes in the nature of the hydrocarbon interiors, head group hydration and counterion dissociation (this is also true for changes in temperature). Hence, any perturbation of the system disturbs the delicate balance of the interactions involved in surfactant self-assembly, altering the aggregated state of the surfactant molecules. Micellar solutions remain isotropic for all concentrations even though the individual aggregates may no longer be isotropic, their anisotropy is averaged out by the rapid tumbling/rotation of the aggregates in solution. The viscosity of these solutions can vary considerably with concentration depending upon the shape of the surfactant aggregates (e.g. living polymer micellar solutions can have viscosities comparable to cubic phases [59]).

A variant on the micellar phase formed by double-chain surfactants is the vesicular phase (figure 1.1.3), here, the surfactant molecules are aggregated in a bilayer which closes in on itself. As with the micellar phase the vesicular phase is a dynamic entity and may also
Gouy-Chapman Layer

Hydrocarbon Core

Stern Layer

Polar Head Group

Counterion

Water of Hydration

Free Water

Water Molecules

Free Surfactant

Figure 1.1.2 Schematic diagram of a spherical micelle formed by a $C_{12}$ single-chain ionic surfactant, showing the central hydrocarbon core where all water is excluded and the chains are fluid and oriented on average perpendicular to the interface. The Stern layer consists of surfactant head groups, water of hydration, undissociated hydrated counterions and one to two carbon atoms from the hydrocarbon chain. The Gouy-Chapman layer contains dissociated counterions. The micelle is surrounded by free water and surfactant. There is continual association/dissociation of surfactant molecules, into and out of the micellar aggregate, with rate constants $k_1$ and $k_2$, respectively. Both the water of hydration and counterions are also in rapid exchange between the Stern and Gouy-Chapman layers.
be explained in terms of discrete layers (i.e. hydrocarbon core, "Stern" and "Gouy-Chapman" layers).

![Diagram](Image)

**Figure 1.1.3** Vesicular phase formed by double-chain surfactants at low surfactant composition.

At higher surfactant compositions the conditions begin to favour the formation of lyotropic liquid crystalline phases. The three most commonly observed liquid crystalline phases are the lamellar, hexagonal and cubic, which are periodic in one, two or three dimensions, respectively.

Figure 1.1.4 shows a schematic diagram for both the normal and reverse hexagonal phases [1, 12, 13, 19]. The normal hexagonal phase (type I) consists of indefinite straight cylinders packed in a two-dimensional hexagonal array. The cylinders are comprised of surfactant molecules oriented radially out from the centre with the head groups located at the surface of the cylinders, water fills the space in between the cylinders. Again, as for micelles, the radius of the cylinders must be less than or equal to the length of the extended hydrocarbon chain. For a reverse hexagonal phase (type II), as is the case for the reverse micellar phase, the head groups and water are confined to the centre of the cylinders and the hydrocarbon chains form a continuum. The cylinders in both normal and reverse hexagonal phases are aligned along a common normal (n) and the system is uniaxial. Note that the diagrams have been simplified by not including the counterions, water of hydration, etc, but the interface in the hexagonal phase may be considered to be similar to that observed in the micellar phase. The hydrocarbon chains, here, are also found to be in a fluid-like state.
Three variations of the hexagonal phase have been observed in surfactant systems while maintaining the underlying two-dimensional lattice, producing distinct liquid crystalline phases.

The complex hexagonal liquid crystalline phase (either normal or reversed) \[12, 15, 19, 60-63\] is similar to the hexagonal phase in that, it is comprised of cylinders packed in a two-dimensional hexagonal array but, here, the cylinders are built up from surfactant bilayers (figure 1.1.5). The rectangular liquid crystalline phase, in contrast, is formed by lowering the symmetry of the hexagonal phase (p6m). The cylindrical aggregates also, no longer have spherical symmetry but instead are more elliptical in shape \[1, 12, 15, 62, 64\]. Figure 1.1.6 shows the primitive rectangular phase. Other types of lattices have also been observed including the centred rectangular and the rectangular herring-bone (where the cylindrical aggregates are tilted with respect to the underlying rectangular matrix). The final variation on the hexagonal phase is the deformed hexagonal or monoclinic \[60, 61, 65\] (figure 1.1.7). Here the cylinders, as in the case of the rectangular phase, are no longer spherically symmetric. They are also tilted with respect to the original hexagonal lattice and the p6m symmetry of the hexagonal phase is lost (i.e. the unit cell is now a deformed regular hexagon with \(a \neq b\) and \(\gamma \neq 120^\circ\)). Hence, even with the limitation of the surfactant molecules aggregating to form cylinders, a vast array of different liquid crystalline phases may be formed.

Imposing regularity in the third dimension, gives rise to a second class of liquid crystalline phases. The cubic phases belong to this class. These phases have generated a
A considerable contribution to the elucidation of the six different cubic phases, found to date, originating from Luzzati and collaborators [1, 13, 32-35, 37, 38, 66-83].

Figure 1.1.5 Complex hexagonal liquid crystalline phase. The surfactant molecules aggregate into bilayers forming cylinders, which are packed in a hexagonal array. The phase exists as either a) normal or b) reverse.

Figure 1.1.6 Cross section of the primitive rectangular liquid crystalline phase. The symmetry is lowered in comparison with the hexagonal phase and the cylindrical aggregates are no longer spherically symmetric.
Although, each of these six phases are defined as cubic phases due to their symmetry, they are often classified as either discrete or bicontinuous. The discrete cubic phases are the $Q^{223}$, (figure 1.1.8 a) [74, 75, 77, 83-85]) and $Q^{227}$ (figure 1.1.8 b) [82]), in the notation of Luzzati, these phases are also known as Pm3n and Fd3m, respectively, following the International Tables for Crystallography [86]. The bicontinuous cubic phases are the $Q^{224}$ (Pn3m, figure 1.1.9 [73]), $Q^{229}$ (Im3m, figure 1.1.10 [13, 78]) and $Q^{230}$ (Ia3d, figure 1.1.11 [13, 67, 68, 87, 88]). The remaining cubic phase that has been observed is the $Q^{212}$ (P432) [78] which belongs neither to one class nor the other having characteristics of both (figure 1.1.12). The assignments of each of the cubic phases to a specific space group is a difficult process since in general from the available
X-ray data several space groups are plausible. But the structures assigned to each of these phases has come about via considerable debate and experimental evidence supporting the structures shown in figures 1.1.8 - 1.1.12.

A further classification imposed on these surfactant aggregates is that they are either normal (type I) or inverse (type II). Type I has only been observed so far for \( Q^{230} (Ia3d) \) and \( Q^{223} (Pm3n) \), whereas \( Q^{230} (Ia3d) \) may be either type I or type II.

The two discrete cubic phases consist of a cubic packing of two types of disjointed micellar aggregates, whereas, the bicontinuous cubic phases are comprised of two crystallographically equivalent three-dimensional labyrinths. These cubic phases may be explained by the skeletal graph representation where the \( Q^{230} (Ia3d) \) consists of rods linked three by three, figure 1.1.11 a), the \( Q^{224} (Pn3m) \) consisting of four rods tetrahedrally oriented, figure 1.1.9 a) and the \( Q^{229} (Im3m) \) with rods joined six by six and oriented along the sides of a cube, figure 1.1.10 a). These three phases have also been represented by a unique infinitely periodic minimal surface (IPMS) \([32, 33, 73, 89-94]\); \( Q^{224} (Pn3m) \), the double diamond IPMS (D surface, figure 1.1.9 b)), \( Q^{229} (Im3m) \) the primitive IPMS (P surface, figure 1.1.10 b)) and \( Q^{230} (Ia3d) \) the Gyroid IPMS (G surface, figure 1.1.11 b)).

**Figure 1.1.8** Representations of the two discrete cubic phases, both consisting of two types of disjointed micelles (represented here by spheres). The cubes indicate one unit cell which is primitive in the case of \( Q^{227} \) a) and face-centred for \( Q^{227} \) b). \( Q^{227} (Pm3n, \text{ type I}) \) : the micelles which are filled by the hydrocarbon chains are embedded in a polar matrix. The unit cell contains six micelles of symmetry 42m (white), centred at positions c and two micelles of symmetry m3 (black), centred at positions a. \( Q^{227} (Fd3m, \text{ type II}) \) : the micelles, filled by the polar medium are embedded in the hydrocarbon matrix. The unit cell contains eight micelles of symmetry 43m (white), centred at positions a and sixteen micelles of symmetry 3m (black) centred at positions d.
Figure 1.1.9 \( Q^{224} (Pn3m) \) bicontinuous cubic phase. a) Skeletal graph representation, where the rods are tetrahedrally oriented forming two diamond-like labyrinths. b) Corresponding double-diamond IPMS (D surface).

Figure 1.1.10 \( Q^{229} (I m3m) \) bicontinuous cubic phase. a) Skeletal graph representation: the rods are joined six by six and oriented along the sides of a cube, with the vertices of one labyrinth located at the centres of the cubes of the others. b) Related primitive IPMS (P surface).
Cubic phases, like micellar phases, are optically isotropic but their viscosity can be much higher than that of micellar phases. Bicontinuous cubic phases are typically extremely viscous (generally with a viscosity greater than that of the hexagonal phase of the same system) whereas, the discrete cubic phases are often found to have a viscosity similar to or slightly lower than that of the hexagonal phase. The discrete cubic phases are also generally observed to be located in the phase diagram (temperature, composition) between the micellar and hexagonal phases whereas, bicontinuous cubic phases form
between the hexagonal and lamellar phases. The conformation of the chains in the cubic phases is found to be similar to that in the hexagonal and micellar phases (i.e. fluid-like and oriented on average perpendicular to the interface).

As with the hexagonal phase it is possible to relate other liquid crystalline phases to the cubic phase by way of a distortion of the cubic lattice. Hence, some variants on the cubic phase are the tetragonal and rhombohedral phases [65, 95, 96]. The tetragonal liquid crystalline phase is comprised of a continuous polar medium while the apolar medium is made up by an infinite number of perforated sheets, each of which consists of finite connected rods arranged on a square network, the centre of a square overhangs the vertex of the square below. Hence, the tetragonal structure may be obtained by a stratification of the original cubic structure [65], i.e. the topology of the original cubic phase has been changed. In comparison, the rhombohedral phase is obtained by an angular distortion of the cubic phase [65, 97].

The final class of surfactant aggregates is the lamellar liquid crystalline phase (figure 1.1.13). Here, the surfactant molecules pack into indefinite planar bilayers which are intercalated with water. Variants on the lamellar phase can take the form of ripples, holes and pinches among other distortions, at high surfactant compositions [97-112], or at low surfactant concentrations the lamellar bilayers may be swollen to form the so-called "sponge" and L₃ phases [113-119]. Unlike the previous phases the lamellar phase is also found to be susceptible to ordering of the paraffinic chains, forming the so called "lamellar gel" phases (L₇, L₇' , L₅ and L₇ see also § 2.8). Here, the chains are frozen in the all-trans configuration, they are highly ordered and may be interdigitated, tilted, coiled or a combination of these. The chains may also be found to pack in a cubic array instead of the more common hexagonal array (i.e. the chains are ordered hexagonally) [120-126]. All of these lamellar phase variants are characterised by a bilayer structure and one-dimensional "smectic" ordering.

In addition to the phases described above a number of other phases termed "intermediate phases" have also been reported to be observed in surfactant/water systems. These phases are normally located between the hexagonal and lamellar phases in the phase diagram (temperature, composition). They have been observed to either replace the bicontinuous cubic phase or form in conjunction with it. Intermediate phases are, though, generally formed at lower temperatures for surfactants with longer chains with the formation of a cubic phase occurring at the expense of the intermediate phases as the temperature is increased [20, 127-129]. The structures of these phases is generally not eluded to, but due to their placement in the phase progression they must be related in some way to the hexagonal, cubic or lamellar phases which surround them.

It should be noted, that the phases described above are found to form as pure phases only above a certain temperature (the Krafft discontinuity), which varies as a function of the
composition. Below this solubility curve the liquid crystalline phases may coexist with hydrated forms of the surfactant (of which there may be several) or with the gel and coagel phases [122-124, 130]. Where the gel and coagel phases are structures which are intermediate between the wholly liquid crystalline and the crystalline state, note that in addition the coagel contains poorly developed crystals. Both the gel/coagel and hydrated surfactant may also exist as pure phases below this solubility curve.

Figure 1.1.13 Lamellar liquid crystalline phase ($L_\alpha$). The surfactant molecules form a bilayer which is locally planar, the hydrocarbon chains are fluid-like and on average oriented perpendicular to the interface.

Therefore, the general phase progression in a binary surfactant/water system with increasing surfactant composition above the solubility curve/Krafft discontinuity is micelles, discrete cubic, hexagonal, bicontinuous cubic/intermediate phases, lamellar, bicontinuous cubic/intermediate phases, reverse hexagonal, discrete cubic and reverse micellar. The variants on the hexagonal, cubic and lamellar phases (as described above) appearing in the sequence alongside, or in place of the phase to which they are related. This information is usually presented diagrammatically as a phase diagram where for a binary surfactant/water system the axes represent composition and temperature. In any given binary surfactant/water system all of these phases will generally not be observed but the order of appearance of the phases is maintained.

Transitions between two phases as a function of composition can occur in two different ways. The first is via a first order transition where the two phases coexist over a finite composition range and therefore must have from thermodynamic arguments the same chemical potential (i.e. a miscibility gap exists due to isothermal discontinuities in the free energy of mixing). The second type of phase transition is a second order transition.
where the phases do not coexist and the discontinuity arises in the first derivative of the free energy with respect to composition.

When, following any isothermal or isoplethal trajectory within a binary phase diagram it is necessary to pass through an odd and even number of phases alternatively (rule of alternation [131, 132]). The phase rule states that for a binary system only two phases may coexist. Hence combining these two rules means that, on passing from one two-phase region to another separate two-phase region following an isopleth, a three-phase line must exist between the two. The temperatures at which these three-phase line isothermal discontinuities occur are defined uniquely [132, 133].

There are, three types of phase discontinuities in binary systems where either the three phases differ in composition or two of the phases have the same composition. For the case where each phase differs in composition the intervening phase may exist only at temperatures above the three phase discontinuity or only at temperatures below it. The eutectoid line is an example of where two phases coexist with a third phase existing only above the eutectoid line (i.e. \( C = A + B \) in figure 1.1.14). In contrast, the peritectoid line is such that, the third phase exists only below the peritectoid line (i.e. \( C + D = B \) in figure 1.1.14). The third discontinuity occurring when two phases have the same composition and is called the polytectoid line. This occurs when one phase exists both above and below the polytectoid line but the second phase with which it coexists changes in the two situations (i.e. \( A + B = A + C \), or \( A + B = C + B \), or \( C + B = C + D \), or \( B + D = C + D \) in figure 1.1.14) [132, 134].

![Graphical representation of a eutectoid, peritectoid and polytectoid discontinuity.](image)

**Figure 1.1.14** Graphical representation of a eutectoid, peritectoid and polytectoid discontinuity.
All of the phases described above will not in general be observed in one surfactant/water system. Which phases are formed over particular compositional and temperature ranges for a given surfactant is dependent upon a delicate balance between numerous interactions. These interactions will vary for each different surfactant studied. It is possible, though, to categorise the surfactants according to head group, counterion and chain length and in a limited sense predict their phase progression.

1.2 THEORY OF SURFACTANT SELF-ASSEMBLY

Despite much work having been performed on these systems very little is actually known about the precise mechanism of surfactant self-assembly and the nature of the phase transitions. To date there have been three major theoretical approaches used to solve this problem, the elastic continuum theory, the local steric model and film curvature and global topology.

1.2.1 Elastic continuum theory

In an ideal liquid crystalline phase the structural units comprising the global geometry (e.g. the cylinders of the hexagonal phase) are, on average, aligned along one common direction $\pm \mathbf{n}$, the system is then classified as uniaxial. Deformations from this ideal picture may occur due to incompatibility of this structure with the constraints imposed by external influences acting on the molecules. These deformations or distortions of the director field take the form of splays (modelled by an elastic constant $K_1$ where the conformations obey $\text{div} \mathbf{n} \neq 0$), twists ($K_2$ - conformations with $\mathbf{n} \cdot \text{curl} \mathbf{n} \neq 0$) and bends ($K_3$ - conformations with $\mathbf{n} \times \text{curl} \mathbf{n} \neq 0$) \[4, 9\]. Figure 1.2.1.1 illustrates cases where pure deformations of the liquid crystals occur (a-c) as well as a combination of the three (d) forming the saddle splay.

These deformations may be described by a continuum theory which disregards the details of the structure on the molecular scale. A starting point for this theory is that in a weakly distorted system, at any point, the local optical properties are still those of a uniaxial crystal (i.e. the magnitude of the anisotropy is unchanged), only the orientation of the optical axis ($\mathbf{n}$) has been rotated. This distorted state is then described by a variable vector field $\mathbf{n}(\mathbf{r})$. This approach was instigated by Oseen \[135\] and Zocher \[136\] and examined more recently by Frank \[137\]. Following this method the free energy of the distortion (per cm$^3$) is, given by

$$F_d = \frac{1}{2} K_1 (\text{div} \mathbf{n})^2 + \frac{1}{2} K_2 (\mathbf{n} \cdot \text{curl} \mathbf{n} + q_0^2)^2 + \frac{1}{2} K_3 (\mathbf{n} \times \text{curl} \mathbf{n})^2$$ \[1.2.1.1\]

which is the fundamental formula of the continuum theory, where $q_0 = 2\pi/p$ is the natural twist of the system and $p$ is its pitch.
Figure 1.2.1.1 Possible deformations of the director field, a) pure splay, \( K_1 \), b) pure twist, \( K_2 \), c) pure bend, \( K_3 \), and d) saddle splay which is one of the possible outcomes obtained by combinations of the pure deformations.

In conjunction with deformations of the director field numerous defects will be observed in the liquid crystalline phases. These may be dislocations (breaks in translational symmetries) and/or disclinations (breaks in rotational symmetries) [4, 138-141]. Figure 1.2.1.2 shows the different types of dislocations and disclinations commonly observed in both lyotropic and thermotropic liquid crystalline phases. The line defects (either dislocations or disclinations) are produced by the process of Volterra, as in solids [142,
The perfect medium is cut along an arbitrary surface and the two newly exposed surfaces are displaced relative to each other by a translation (defined by Burgers vector, $\mathbf{b}$), rotation (defined by rotation axis, $\mathbf{v}$) or a combination of the two. Following the displacement the medium is reconnected along the two surfaces, with perfect material being inserted or removed in the case of gaps or overlaps. Using this procedure, internal stresses are created producing a line discontinuity along $\mathbf{L}$. According to Friedel [143] this dislocation line has three properties:

**Figure 1.2.1.2** Dislocations and disclinations generated by the Volterra process commonly observed in lyotropic and thermotropic liquid crystalline phases. The z-axes of the cylinders coincide with the direction of the line discontinuity $\mathbf{L}$. a) and b) edge dislocations where $\mathbf{b}$ (Burgers vector) is normal to $\mathbf{L}$, c) screw dislocation $\mathbf{b}$ is parallel to $\mathbf{L}$, d) and f) disclinations and e) twist disclination, where $\mathbf{v}$ is the rotation axis.
A dislocation line cannot end in the interior of a crystal. It must close on itself or end at another defect (outer surface, grain boundary or node formed with other dislocations).

The displacement ("strength") which defines the dislocation has the same value along its whole length (translation symmetry along the dislocation line).

All displacements can be analysed in terms of translational and rotational components. Accordingly, one can have translational or rotational dislocations, or combinations of these.

It should be noted that each defect introduces an increase in the potential energy of the system and that the disclination core is a singularity in the structure. Figure 1.2.1.3 shows schematically the topology of the surfactant aggregates near the centres of some of the line disclinations (i.e. at the singularities) produced in the Volterra process. The strength of the disclination is given by the parameter $s$. Where, $2\pi s$ yields the angle by which the director turns on a closed curve around the centre. Hence, for $s = \pm 1/2$ the corresponding angle is $\pi$ and the line is called a $\pi$-line, that is, in moving around the line disclination the director is rotated about an angle of $\pi$. The structure within these defects is still unknown but it is generally assumed that they are comprised of either centres of disordered isotropic fluid or perfect mesophase [144].

Not all of these deformations or defects are in general found in each of the liquid crystalline phases formed. Those present can often be determined by the optical texture observed (in the case of a birefringent phase) when a sample of the phase is viewed under a crossed polarising microscope, as each of the defects interacts uniquely with plane polarised light [2, 4-6, 9, 139-141, 145-150]. Hence, the texture produced by the liquid crystalline phases holds a large amount of information on the underlying local and global geometry of the surfactant molecules.

1.2.2 Local steric model

The thermodynamically stable aggregated states formed by surfactant molecules, arise due to interactions between the surfactant molecules and the solvent. The surfactant molecules interact such that the extent of contact between the alkyl chains and the water is reduced. This interaction is known as the hydrophobic effect [151], and it is dependent upon the length of the hydrocarbon chain and the degree of unsaturation or branching. The hydrophobic effect acts to promote aggregation. Interactions between the surfactant molecules include primarily the repulsion between adjacent head groups. This is effected by the strength of the head group hydration, steric requirements of both the head groups
and alkyl chains and the electrostatic interaction in the case of ionic surfactants, this interaction, therefore, tends to oppose aggregation. These two interactions, therefore, compete against each other such that, one is tending to increase the head group area and the other to decrease it. Hence, at some optimal value of the head group area the two are balanced (i.e. there is a hydrophilic/lipophilic balance). Although an understanding of these interactions is crucial in developing a theory for surfactant self-assembly they are not the only factors, geometric packing constraints and entropy are also necessary considerations for a full theoretical determination. Which of the available geometries will be formed for a given set of conditions is that which has the lowest free energy in conjunction with enforced packing constraints and entropy.

Figure 1.2.1.3 Topology near the centres of defect lines. The strength of the disclination is given by the parameter $s$.  

a) $s = + \frac{1}{2}$, b) $s = - \frac{1}{2}$, c) $s = - 1$, 
d) $s = + 1$, $\Phi = 0$, e) $s = + 1$, $\Phi = \pi/6$ and f) $s = + 1$, $\Phi = \pi/2$ where $\Phi$ is the angular distribution of the director.

The contributions to the free energy of the system include:

a) electrostatic forces (in the case of ionic surfactants),
b) interfacial tension arising from the hydrophobic effect,
c) steric repulsion,
d) alkyl chain packing,
e) solvation effects,
f) entropy effects due to the mixing of the components in the aggregates and in the solution and mixing of the aggregates themselves, and
g) molecular packing constraints including location of the head groups at the surface of the aggregates.

The theory for surfactant self-assembly using a purely equilibrium thermodynamic approach took its foundations from McBain [39, 40], Hartley [152], Debye [153, 154] and Tartar [155], during the first half of this century. It was noticed that each surfactant did not behave uniquely in solution, but instead their solution properties could be explained by a series of interactions characteristic of the class of amphiphilic molecules as a whole. In the early 1970s Tanford [151, 156, 157] extended this theory using a phenomenological model for the repulsive interactions between the head groups and for the hydrophobic effect which is attractive.

In the late 1970s Israelachvili, Mitchell and Ninham [158-162] introduced packing constraints in conjunction with the work of Tanford. Though this idea had been put forward by Hartley [163] in the 1940s, it had never been fully exploited previously. Using this classical steric and thermodynamic approach the dimensionless surfactant parameter (p) was introduced, which utilises the three parameters characterising the surfactant (v, α and I, see § 1.1). The surfactant parameter is defined to be equal to v/a₀lₑ where v the hydrocarbon core volume can be calculated using the equation v = 27.4 + 26.9nₑ where nₑ is the number of embedded carbons developed by Tanford [156], a₀ is the optimal surface area per amphiphile at the interface (set by the balance of attractive and repulsive interactions) and lₑ is the critical length of the hydrocarbon chains which are assumed to be fluid and incompressible, lₑ is generally found to be shorter than the maximum length given by Tanford, lₑ = 1.5 + 1.265nₑ [156]. Hence, using this parameter, which is assumed to be concentration independent, the self-assembling properties of the surfactant molecules are characterised. Evaluation of the surfactant parameter shows that there are four characteristic surfactant aggregation states:

- p < 1/3 spherical micelles
- 1/3 < p < 1/2 non-spherical micelles
- 1/2 < p < 1 planar bilayers
- p > 1 inverted structures

Formation of this steric model, although able to predict the dilute solution behaviour of surfactants successfully involves a series of major assumptions, which severely limits its applicability. Some of the important contributions which it does not consider are:

a) The area per polar head group is a function of both the composition and temperature and also varies depending upon the interface at which, it is calculated.
b) On increase of surfactant concentration inter-aggregate interactions begin to be important [164].

c) The extent of counterion association which affects differently the area per polar head group and the length and volume of the hydrocarbon chains varies as a function of concentration and temperature.

This model therefore fails to predict the dependence of phase behaviour upon changes in composition and temperature. The formation of aggregates based on structures other than spheres, cylinders or planes was also not considered (e.g. bicontinuous cubic and L3 phases were disregarded).

Since the introduction of the surfactant parameter considerable theoretical work has been performed on predicting the phase behaviour of surfactants as a function of temperature and composition [165-180]. These works have typically, restricted themselves to the geometrical packing of the surfactant molecules into spheres, cylinders or planes and have thus been of limited success.

1.2.3 Film curvature and global topology

The final approach in some ways tries to combine the previous two, by using the ideas of film deformations and local surfactant geometry.

The concepts of bending, curvature and surfactant film rigidity were first introduced by Helfrich [165, 167, 174, 175] in the 1970s. An extension of this work [47, 93, 94, 181-186] lead to the introduction of the concept that the topology at the interface is determined uniquely by combined local (surfactant parameter) and global constraints. Here, geometric relations are used to link the local molecular shape of the aggregating surfactant molecules to the global compositions of the surfactant/water system.

The assumptions inherent in this geometric model include the local curvatures of the interface being determined by the value of the surfactant parameter and global constraints imposed by the sample composition. That is, the curvature is allowed to vary and the surfactant parameter is no longer fixed but is instead dependent upon the curvature of the interface. For each point on the interface a Mean (H) and Gaussian (K) curvature may be assigned, where these curvatures can be related to the surfactant parameter by the following equation

\[
\frac{\gamma}{\alpha l} = 1 + HI + \frac{KL^2}{3}
\]
Hence, when the interface is a) bent towards the paraffinic chains, v/al < 1 and H < 0, b) flat, v/al = 1 and H = K = 0 and c) bent towards the polar medium, v/al > 1 and H > 0 (figure 1.2.3.1).

![Diagram of interface orientations](image)

**Figure 1.2.3.1** Variation of Mean curvature (H) with surfactant parameter (v/al). a) Interface curved towards hydrocarbon chains, v/al < 1, H < 0. b) Flat interface, v/al = 1, H = 0. c) Interface curved towards polar region, v/al > 1, H > 0.

From the defined curvature of the interface it is therefore possible to express the energy of deformation of the surfactant film in terms of deviations about the preferred curvatures \( H_0 \) and \( K_0 \). Figure 1.2.3.2 shows the variation of the surfactant self-assembly as a function of the surfactant parameter and volume fraction of the chains. This theory, though, still ignores inter-aggregate interactions but is now capable of predicting bicontinuous phases and also develops the importance of rigidity and curvature of the surfactant film in determining the stability of the surfactant mesophases. Hence, while still limited in its predictive ability this approach is able to account for all the known surfactant assemblies.

However, there is currently no complete theory for surfactant self-assembly and it is therefore not possible to predict fully the phase progression of a surfactant molecule. Some general conclusions may however be drawn for different groups of surfactant molecules.

### 1.3 POLYMERISATION OF LIQUID CRYSTALLINE PHASES

Due to the sensitivity of the surfactant liquid crystalline phases to changes in their environment the range of applications in which these systems can be used are in fact limited. Were it possible to "lock in" the structure of the phase either completely or partially (i.e. increase its stability as a function of temperature, concentration and pressure) this could lead to the development of new uses for surfactants in commercial, industrial and scientific research.
Increasing the stability of the liquid crystalline phases may be accomplished in two ways, either via stabilisation or rigidification. Stabilisation involves the addition of a component to the system such that the presence of this component reduces the effects of changes in temperature and/or composition on the phase. This additional component may take several forms, including water or oil soluble polymers, salts or the surfactant itself may be polymerised prior to aggregation. Rigidification, in contrast, can only be achieved subsequent to surfactant self-assembly. Hence, it must involve polymerisation of one or more of the components in the system. Using this method, the aim is to "lock in" the underlying structure of the phases by covalently bonding one or more of the components. It is hoped that this will yield polymers with precise geometries ordered in one-, two- or three-dimensions (in the case of lamellar, hexagonal and cubic phases, respectively) which could be tailored by altering the characteristics of the surfactant monomers (e.g. paraffinic chain length). Polymerisation of such systems could, therefore, give rise to unique polymeric materials not previously synthesised which have a regular partitioning
of polar and apolar regions. This defined polymer geometry could then subsequently be used as model membranes, molecular sieves (where the radius of the cavities can be fine tuned by variation of the surfactant chain length), organic and inorganic templates, as well as in many other types of systems.

1.3.1 Stabilisation of liquid crystalline phases

The addition of a polymer or salt to the surfactant system in order to enhance the stability of the liquid crystalline phases will not be discussed here, instead only the self-assembly of polymerised surfactants.

The concept of polymerisation prior to surfactant self-assembly has been known for many years [187-199] with the polymers being termed polysoaps or amphiphilic polymers. These types of polymers, which are essentially a polar backbone with hydrophobic side chains or a hydrophobic backbone with surfactant-like side chains, may also be compared with some polyelectrolytes (in the case where either the backbone or side chains contain charged groups). Hence, their solution behaviour is often similar [200]. Results using this method have shown that the liquid crystalline phases formed by the polymer do indeed have an increased stability to both changes in temperature and composition.

A problem inherent in this type of approach is that the polymers, due to the methods of synthesis (i.e. in general free radical polymerisation), are polydisperse. Hence in comparing the monomeric phase behaviour with that of the polymer, it must be taken into consideration that while the monomer/water system will be a binary system, the polymeric system will be comprised of several amphiphilic components, each of which will have different self-assembling properties. Thus, for example a hexagonal phase may be formed in both the monomeric and polymeric systems, however it is likely that the two phases will be both locally and globally different.

1.3.2 Rigidification of liquid crystalline phases

In a ternary system the polymerisation may be carried out in the oil or aqueous phase (i.e. either a component has been added to the oil or water, yielding a quaternary system, or the oil is polymerisable) or the surfactant itself may be polymerised.

The bulk of the work performed for ternary systems has involved a polymerisable oil or water soluble monomer, and results have indicated various degrees of success [201-209]. Polymerisation of the full range of surfactant mesophases obtainable in a single system
has not been studied. Most work has been performed within the three bicontinuous cubic phases or in micellar and vesicular solution. The ultimate aim, of these studies has largely been to polymerise the monomeric component, and then remove the non-polymerisable components, leaving a rigid three-dimensional labyrinth (in the case of the bicontinuous cubic phases).

Using this approach, Ström and Anderson have reported successful polymerisation in the bicontinuous cubic phase regions of ternary didodecyldimethylammonium bromide ((CH$_3$-(CH$_2$)$_{11}$)$_2$-N+((CH$_3$)$_2$Br)/water/polymerisable oil systems, such that, the original structure was maintained upon removal of the water and surfactant [202, 205-207]. Likewise, Laversanne has reported successful polymerisation of lamellar, hexagonal and cubic phases via polymerisation of acrylamide inside the water region [204]. In contrast, Glatzhofer et al. have reported limited success using both a polymerisable oil and surfactant with polymerisation either not occurring or to an extent not greater than approximately 50% [208].

Similarly, Holtzscherer et al. showed that polymerisation of acrylamide in a swollen lamellar mesophase resulted in a phase transition to an isotropic fluid [203]. Finally, Herz et al. showed that polymerisation of the oil phase (which was one of styrene, isoprene or dimethylbutadiene) in both hexagonal and lamellar phases of fatty acid soaps always resulted in destruction of the structure with the polymer being expelled [201].

These results leave the reader confused as to whether full polymerisation in these types of systems is feasible or not and how it is possible to reconcile the above differences.

Several problems are intrinsic within this method since liquid crystalline phases are formed by a unique balance between a series of interactions with the curvature of the interface being an important factor in phase formation. In an oil/water/surfactant system three distinct substances, having vastly different solution properties, coexist such that, a stable interface is formed dividing the oil and water regions into a variety of geometries ($\S$ 1.1). By altering the nature of one of the components the curvature of the interface will correspondingly be changed. This change in curvature, therefore, affects the balance of interactions increasing the probability that a phase transition or separation will occur upon polymerisation.

In order to simplify the problem binary systems have been studied which are comprised of either surfactant plus oil [201, 210, 211], where either the surfactant and/or the oil may be polymerisable or surfactant plus water systems where the surfactant itself is polymerised. The latter have been extensively studied, particularly in the case of micellar or vesicular polymerisation [58, 193, 201, 212-244]. This interest arises since the polymeric micelles or vesicles may be used to mimic biological systems, in the study of transportation, slow release of chemicals trapped in the core of the polymer (applicable
for slow release drug delivery or chemical reactions) and many other processes involved in biological systems. A sub class of this last category occurs for binary surfactant/water systems where the counterions are polymerisable [245, 246].

By using these binary systems the problem of changing the nature of one of the components upon polymerisation may not introduce as severe a disturbance to the system as in ternary systems and it is therefore, presumed to be easier to obtain polymerised phases. These simplified systems may also yield answers to the fundamental problems associated with polymerisation of surfactant mesophases.

Following this approach, Herz et al. [201] and Friberg et al. [210, 211] have shown that polymerisation of lamellar type phases (i.e. phases based on surfactant bilayers) in surfactant/polymerisable oil systems, resulted in retention of the underlying surfactant phase with an increase in the interlayer spacing.

Most reports on polymerisation in polymerisable surfactant/water systems for the micellar or vesicular regions have indicated that retention of the original phase is possible (i.e. intra-aggregate polymerisation occurs) [193, 213, 215-242, 244]. There remain, though, doubts as to whether, particularly in the micellar case, polymerisation of an individual surfactant aggregate is possible. Recent results reported by Cochin et al. [58, 243] have indicated that it is likely that polymerisation via a group of low reactivity will produce polymers of low molecular weight, which are often of similar molecular weight to that of the micellar aggregate. But these polymers are not necessarily formed via intra-micellar polymerisation due to the rates of polymerisation, surfactant dissociation and micellar dissolution varying with composition, temperature and the nature of the surfactant. Therefore, it has often been mistakenly concluded, using comparison of micellar aggregation numbers and polymer molecular weights only, that intra-micellar polymerisation has occurred. Surfactants containing a highly reactive polymerisable group in contrast, yield polymers of high molecular weight, even at low surfactant composition, thus excluding the possibility of intra-micellar polymerisation occurring.

Two groups, Herz et al. [201] and Friberg et al. [212, 214], have studied polymerisation of the surfactant monomer in lyotropic liquid crystalline phases. Both reported that polymerisation was possible but indicating varied results. Friberg et al. [212, 214] showed that polymerisation of a hexagonal phase resulted in a transformation to a lamellar phase and that the polymerisation went to completion whereas, Herz et al. [201] showed that a gel phase was retained upon polymerisation.

Hence, despite a considerable amount of work having been performed on the polymerisation of surfactant mesophases (particularly the micellar and vesicular phases in binary systems and the bicontinuous cubic phases in ternary systems) it remains unclear
as to whether it is possible to rigidify a surfactant liquid crystalline phase such that, the underlying surfactant geometry is retained.

There are several complications involved in the polymerisation of surfactant lyotropic liquid crystalline phases, many of which are still not fully resolved, due to the lack of a complete picture of the mechanism of surfactant self-assembly. The major difficulty seems to be the different physical properties, introducing changes to the interactions between the molecules and aggregates, of the polymer as compared with the monomer. Since the mechanism for polymerisation is via free radicals, the polymer formed will be polydisperse. Hence, the system will not necessarily be a binary one, instead the number of amphiphilic components in the system may be large. Therefore, an understanding of polymer/monomer interactions and their affect upon the self-assembly of the monomeric surfactant is also an advantage. Determination of the self-assembly properties of the polymerised form of the surfactant is also important, so that a comparison between the monomeric and polymeric self-assembling behaviour can be performed. Any common features between the two phase diagrams would increase the probability of retention of the liquid crystalline geometry upon polymerisation.

A full account of the polymerisation of surfactant lyotropic liquid crystalline phases is very involved and requires first an understanding of the monomeric surfactant's self-assembly (i.e. determining the phase progression with composition and temperature). Following this, one must attempt to quantify the affect that introduction of a polymerisable group into the surfactant has on its observed self-assembly. This can be achieved by relating its phase behaviour with that of an equivalent non-polymerisable surfactant. It is also necessary to understand the polymeric surfactants phase behaviour and then, how the two are related. It is therefore, preferable, to choose polymerisable moieties which introduce a minimal perturbation into the make-up of the surfactant. Hence, reducing not only its affect on the self-assembly of the monomer but also the difference between the natures of the polymer and monomer. The approach adopted here was therefore, to simplify the systems in an attempt to understand the chemical and physical process involved during polymerisation. The conditions under which polymerisation of surfactant lyotropic liquid crystalline phases, leading to the formation of completely polymerised phases such that, the underlying surfactant geometry remains undisturbed, throughout the polymerisation could therefore be determined. This process, thereby producing new polymers with defined geometries which can be subtly modified by changes to the original surfactant.

There is, a vast array of surfactants and polymerisable groups to choose from, but surfactants which are available synthetically in high purity and polymerisable groups which are well defined are more amenable.
To this end, two polymerisable groups were chosen: the allyl (R-CH₂-CH=CH₂) and the ethyl methacrylate (CH₂=C(CH₃)-CO₂-CH₂-CH₂-R) groups. These two groups differ considerably. The allyl group, although known to be difficult to polymerise [247-253], should introduce minimal perturbations into the system both before and after polymerisation. In comparison, the ethyl methacrylate group polymerises readily but has an increased flexibility and the characteristics of this group will have a considerable influence on the subsequent behaviour of any surfactant into which it is incorporated.

Not only, is the nature of the polymerisable moiety important, but the position of the surfactant molecule into which it is incorporated is also crucial, as this will change both the ease of polymerisation and also the physical characteristics of the polymers obtained. Hence, the allyl and ethyl methacrylate groups were incorporated into either the polar head group of the surfactant or at the end of the hydrocarbon chain. In this way, the polymer backbone will either be confined to the surface of the aggregate or to the hydrocarbon core (assuming that the surfactant geometry is maintained throughout the polymerisation). Polymerisation at the head group position will introduce problems due to the constraints of curvature, position and repulsive head group interactions all of which will tend to oppose polymerisation. Placement at the end of the chain also has the problem of increased mobility, where the correct orientation of two carbon-carbon double bonds, required for polymerisation to occur, may not be able to be obtained in the time available before the free radical is lost.

The ionic class of surfactants was chosen since these have been extensively studied (with their self-assembly being reasonably well understood) and can be synthesised to high purity. In particular, surfactants based on either a quaternary ammonium or carboxylate head group.

In this thesis, results for the following series of surfactants are reported:

**ADAB**: allyldodecyldimethylammonium bromide, CH₃-(CH₂)₁₁-N⁺(CH₃)₂(CH₂-CH=CH₂)Br⁻
A single-chain quaternary ammonium surfactant with the allyl group incorporated into the head group of the surfactant (chapter 4).

**ADDAB**: allyldidodecylmethylammonium bromide, (CH₃-(CH₂)₁₁)₂-N⁺(CH₃)(CH₂-CH=CH₂)Br⁻
The double-chain analogue of ADAB (chapter 4).

**ω-UTAB**: ω-undecenyltrimethylammonium bromide, CH₂=CH-(CH₂)₉-N⁺(CH₃)₃Br⁻
A single-chain quaternary ammonium surfactant with the allyl group incorporated at the end of the hydrocarbon chain, this surfactant is therefore, analogous to ADAB with the position of the polymerisable moiety altered (chapter 5).

**Na-10**: sodium 10-undecenoate, CH₂=CH-(CH₂)₈-CO₂⁻Na⁺
A single-chain fatty acid soap with the allyl group incorporated at the end of the hydrocarbon chain, this surfactant is analogous to ω-UTAB but with a change of head group (chapter 6).

**DDAM**: dodecyldimethylammoniumethylmethacrylate bromide, $\text{CH}_3(\text{CH}_2)_{11}-\text{N}^+(\text{CH}_3)_2(\text{CH}_2\text{-CH}_2\text{-O-CO-C(CH}_3}\text{)=CH}_2)\text{Br}^-$

This surfactant is analogous to ADAB with a change in the polymerisable moiety from the allyl group to the ethylmethacrylate group (chapter 7).

In an attempt to quantify the affects of addition of a polymerisable moiety to these surfactants the self-assembling behaviour of the non-polymerisable surfactant dodecyltrimethylammonium bromide (DTAB, $\text{CH}_3(\text{CH}_2)_{11}-\text{N}^+(\text{CH}_3)_3\text{Br}^-$) was also studied (chapter 3). Therefore, not only from this series is it possible to determine the affect of changes of position and nature of the polymerisable moiety on polymerisation but, also on the self-assembly of the surfactant itself.

The final molecule studied is from a new class of macromolecules called dendritic polymers which due to their spherical or near spherical shape and defined molecular weight may be compared to a "polymerised micelle" (chapter 8).
1.4 REFERENCES

91. Larsson, K., *J. Colloid Interface Sci.* **113** 299-300 (1986).
2.1 MATERIALS

The following surfactants were used for the experimental work of this thesis.

**DTAB**

Dodecyltrimethylammonium bromide (DTAB, \(\text{CH}_3-(\text{CH}_2)_{11}-\text{N}^+\text{(CH}_3)_3\text{Br}^-\), > 99 % pure) was purchased from Kodak Eastman Fine Chemicals. It was further purified by washing in hot ethyl acetate followed by hot filtration to remove any organic contaminants. The surfactant was then recrystallised several times from absolute ethanol and dried under vacuum over phosphorus pentoxide yielding a white powder.

Elemental Analysis: Calculated for \(\text{C}_{15}\text{H}_{34}\text{NBr}\): C 58.43 %; H 11.12 %; N 4.54 %; Br 25.91 %. Found C 58.29 %; H 10.88 %; N 4.44 %; Br 26.39 %. Decomposition temperature -135 °C.

NMR Analysis: Proton \(\text{CH}_3-(\text{CH}_2)_{11} 0.88 \delta; \text{CH}_3-(\text{CH}_2)_{8} 1.26 \delta; \text{CH}_3-(\text{CH}_2)_{8}-\text{CH}_2 1.35 \delta; \text{CH}_2-\text{CH}_2-\text{N} 1.75 \delta; (\text{CH}_3)_3\text{N} 3.48 \delta; \text{CH}_2\text{-N} 3.61 \delta.\) Carbon 13 \(\text{CH}_3\text{-CH}_2 8.54 \delta; \text{CH}_3\text{-CH}_2 9.10 \delta; \text{CH}_2\text{-CH}_2\text{-N} 12.06 \delta; \text{CH}_3-(\text{CH}_2)_{2}(\text{CH}_2)_{7} 15.33 \delta; \text{CH}_3\text{-CH}_2\text{-CH}_2 17.76 \delta; (\text{CH}_3)_3\text{N} 39.25 \delta; \text{N-CH}_2 52.82 \delta.\)

FTIR Analysis: \(\text{CH}_2\text{ rock} 728.7 \text{cm}^{-1}; \text{C-H bend} 1463.8 \text{cm}^{-1}; \text{H-C stretch} 2918.6 \text{cm}^{-1}.\)

**ADAB**

Allyldodecyltrimethylammonium bromide (ADAB, \(\text{CH}_3-(\text{CH}_2)_{11}-\text{N}^+\text{(CH}_3)_3\text{Br}^-\), was prepared by reacting dodecyltrimethylamine (> 95 % purity, purchased from Tokyo Kasei Kogyo Co., Ltd.) with allyl bromide (99 % pure, purchased from Aldrich Chemical Co., Inc.) in a mole ratio of 1:1.25, respectively. Both
reagents were initially dissolved in ethyl acetate before mixing, and the reaction was performed at 0 °C. The resulting quaternary ammonium compound, which precipitates immediately, was filtered, recrystallised several times from ethyl acetate and dried under vacuum [1].

Elemental Analysis: Calculated for C\textsubscript{17}H\textsubscript{36}NBr: C 61.08 %; H 10.78 %; N 4.19 %; Br 23.95 %. Found C 61.58 %; H 10.88 %; N 3.85 %; Br 23.69 %. m.p. 74 °C.

NMR Analysis: Proton CH\textsubscript{3}-(CH\textsubscript{2})\textsubscript{11} 0.86 δ; CH\textsubscript{3}-(CH\textsubscript{2})\textsubscript{8} 1.23 δ; CH\textsubscript{3}-(CH\textsubscript{2})\textsubscript{9}-CH\textsubscript{2} 1.32 δ; CH\textsubscript{2}-CH\textsubscript{2}-N 1.73 δ; (CH\textsubscript{3})\textsubscript{2}-N 3.36 δ; CH\textsubscript{2}-CH\textsubscript{2}-N 3.50 δ; =CH-CH\textsubscript{2}-N 4.38 δ; CH\textsubscript{2}=C doublet of doublets centred at 5.75 δ; CH=CH\textsubscript{2} 5.96 δ. Carbon 13 CH\textsubscript{3}-CH\textsubscript{2} 14.02 δ; CH\textsubscript{3}-CH\textsubscript{2} 22.58 δ; CH\textsubscript{2}-CH\textsubscript{2}-N 22.73 δ; CH\textsubscript{2}-(CH\textsubscript{2})\textsubscript{2}-N 26.23 δ; CH\textsubscript{3}-(CH\textsubscript{2})\textsubscript{2}-CH\textsubscript{2} 29.15 δ; CH\textsubscript{3}-(CH\textsubscript{2})\textsubscript{3}-(CH\textsubscript{2})\textsubscript{5} 29.50 δ; CH\textsubscript{3}-CH\textsubscript{2}-CH\textsubscript{2} 31.82 δ; (CH\textsubscript{3})\textsubscript{2}-N 50.42 δ; N-CH\textsubscript{2}-(CH\textsubscript{2})\textsubscript{10} 63.84 δ; C-CH\textsubscript{2}-N 65.96 δ; C=CH\textsubscript{2} 124.44 δ; CH=CH\textsubscript{2} 129.96 δ.

FTIR Analysis: C=C stretch 1467.1 cm\textsuperscript{-1}; H-C= stretch 3015.6 cm\textsuperscript{-1}.

**ADDAB**

Allyldidodecylmethylammonium bromide (ADDAB, (CH\textsubscript{3}-(CH\textsubscript{2})\textsubscript{11}h-N+(CH\textsubscript{3})(CH\textsubscript{2}-CH=CH\textsubscript{2})Br) was used from two sources; it was purchased from SOGO pharmaceutical Co., Ltd., but also had to be prepared due to limited availability of the surfactant from SOGO. It was prepared by reacting dodecylamine (99+ % pure, purchased from Aldrich Chemical Co., Inc.) at 200 °C, in a reaction vessel fitted with an air condenser, with active Raney nickel (50 % slurry in water, pH > 9, purchased from Aldrich Chemical Co., Inc., activity tested by ignition of litmus paper by dry Raney nickel) in a weight ratio of 25:1 respectively. The resulting didodecylamine was taken up in ethyl acetate, the solution was then filtered to remove the Raney nickel, and the didodecylamine crystallised from the solvent. Further purification involved repeated recrystallisation from ethyl acetate. The didodecylamine was dissolved in ethanol (20 g to 50 ml respectively), to which 12.25 ml of 85 % formic acid was added slowly while the temperature was maintained at 40 °C. Following this addition, 11.5 ml of 36 % aqueous formaldehyde solution was added and the temperature was raised to 60 °C. When the evolution of carbon dioxide could no longer be detected, the temperature was maintained at the reflux point for half an hour. The solution was then neutralised by the addition of aqueous sodium hydroxide, the top layer was drawn off and dried with anhydrous potassium carbonate, followed by filtration and then distillation (b.p. 183 °C at 0.35 Torr), yielding didodecylmethylamine [2]. The didodecylmethylamine was then dissolved in ethyl acetate and reacted with allyl bromide in a mole ratio of 1:1.25 respectively, the reaction mixture was stirred at room temperature for several hours, the solvent was removed yielding a white precipitate [3-5]. Purification involved repeated recrystallisation from
ethyl acetate, the surfactant was then dissolved in water which was removed via freeze drying.

Elemental Analysis: Calculated for C_{28}H_{58}NBr : C 68.82 %; H 11.96 %; N 2.87 %; Br 16.35 %. Found C 68.73 %; H 11.90 %; N 2.83 %; Br 16.54 %. m.p. 72 °C.

NMR Analysis: Proton CH_{3}-(CH_{2})_{11} 0.87 δ; CH_{3}-(CH_{2})_{8} 1.24 δ; CH_{3}-(CH_{2})_{8}-CH_{2} 1.34 δ; CH_{2}-CH_{2}-N 1.70 δ; CH_{3}-N 3.32 δ; CH_{2}-CH_{2}-N 3.39 δ; =CH-CH_{2}-N 4.34 δ; CH_{2}=C doublet of doublets centred at 5.7 δ; CH=CH_{2} 5.9 δ. Carbon 13 CH_{3}-CH_{2} 14.56 δ; CH_{3}-CH_{2} 22.91 δ; CH_{2}-CH_{2}-N 23.11 δ; CH_{2}-(CH_{2})_{2}-N 26.80 δ; CH_{3}-(CH_{2})_{2}-CH_{2} 29.77 δ; CH_{3}-(CH_{2})_{3}-(CH_{2})_{5} 29.90 δ; CH_{3}-CH_{2}-CH_{2} 32.34 δ; CH_{3}-N 48.82 δ; N-CH_{2}-(CH_{2})_{10} 61.44 δ; C=CH_{2}-N 61.44 δ; C=CH_{2} 124.60 δ; CH=CH_{2} 130.26 δ.

FTIR Analysis: C=C stretch 1465.4 cm⁻¹; H-C= stretch 3003.7 cm⁻¹.

ω-UTAB

ω-Undecenyltrimethylammonium bromide (ω-UTAB, CH_{2}=CH-(CH_{2})_{9}-N+(CH_{3})_{3}Br⁻) was prepared by reacting ω-undecenol (99 % pure, purchased from Aldrich Chemical Co., Inc.) with allyl bromide in dry acetonitrile in the presence of 1,1'-carbonyldiimidazol (97 % purity, purchased from Fluka Chemie) in the mole ratio of 1:5:1 respectively [6]. The reaction mixture was stirred for one hour at room temperature and then refluxed for a further two hours. After cooling, ether and water were added to the solution and the aqueous layer removed. The organic layer was washed with dilute hydrochloric acid, aqueous sodium carbonate and water and then dried over anhydrous magnesium sulfate. The solvent was then removed and the resulting ω-undecenyl bromide was vacuum distilled (b.p. 60 °C at 1x10⁻³ Torr). This reaction is employed to convert alcohols to bromides where the alcohol contains a secondary functional group which is potentially affected by the presence of the bromide, for example addition to the double bond as is the case in the above reaction. The final step in forming ω-UTAB involves bubbling trimethylamine gas through a solution of ω-undecenyl bromide in ethyl acetate at room temperature for several hours. The resulting ω-UTAB forms as a precipitate which is filtered and purified by repeated recrystallisation from absolute ethanol.

Elemental Analysis: Calculated for C_{14}H_{30}NBr : C 57.53 %; H 10.34 %; N 4.79 %; Br 27.34 %. Found C 57.6 %; H 10.25 %; N 4.57 %; Br 27.58 %. Decomposition temperature 192 °C.

NMR Analysis: Proton (CH_{2})_{5}-(CH_{2})_{2}-N 1.27 δ; CH_{2}-CH_{2}-CH=C 1.36 δ; CH_{2}-CH_{2}-N 1.75 δ; CH_{2}-CH=C 2.04 δ; (CH_{3})_{3}N 3.47 δ; CH_{2}-N 3.63 δ; CH=C doublet of doublets centred at 4.96 δ; CH=C 5.80 δ. Carbon 13 CH_{2}-CH_{2}-N 22.97 δ; CH_{2}-CH_{2}.
CH=C 25.92 δ; (CH$_2$)$_5$-(CH$_2$)$_2$-CH=C 29.04 δ; CH$_2$-CH=C 33.51 δ; (CH$_3$)$_3$-N 53.10 δ; CH$_2$-N 66.57 δ; =CH$_2$ 113.95 δ; =CH 138.83 δ.

FTIR Analysis : C=C stretch 1638.0 cm$^{-1}$; H-C= stretch 3017.2 cm$^{-1}$.

**Na-10**
Sodium 10-undecenoate (Na-10, CH$_2$=CH-(CH$_2$)$_8$-CO$_2$Na$^+$) was prepared by reacting equimolar amounts of 10-undecenoic acid (> 99 % pure, purchased from Tokyo Kasei Kogyo Co., Ltd. and vacuum distilled before use) and 50 % sodium hydroxide solution. The precipitate was filtered and washed with ethanol, washed with ether to remove any traces of the parent acid, redissolved in water and finally freeze dried. Further purification was achieved by repeated recrystallisation from absolute ethanol [5, 7].

Elemental Analysis : Calculated for C$_{11}$H$_{19}$O$_2$Na : C 64.08 %; H 9.22 %; O 15.53 %; Na 11.17 %. Found C 64.16 % and H 9.38 %. Decomposition temperature 220 °C.

NMR Analysis : Proton (CH$_2$)$_4$-(CH$_2$)$_2$-C=O 1.31 δ; CH$_2$-CH$_2$-CH=C 1.38 δ; CH$_2$-CH$_2$-C=O 1.56 δ; CH$_2$-CH=C 2.05 δ; CH$_2$-C=O 2.18 δ; CH$_2$=C doublet of doublets centred at 5.01 δ; CH=C 5.87 δ. Carbon 13 CH$_2$-C=O 25.78 δ; (CH$_2$)$_5$-CH$_2$-C=O 28.64 δ; CH$_2$-CH$_2$-C=O 33.12 δ; CH$_2$-CH=C 37.36 δ; =CH$_2$ 113.83 δ; =CH 139.67 δ; C=O 183.55 δ.

FTIR Analysis : Symmetric C=O carboxylate stretch 1462.5 cm$^{-1}$; asymmetric C=O carboxylate stretch 1560.0 cm$^{-1}$; C=C stretch 1642.8 cm$^{-1}$; H-C= stretch 3083.3 cm$^{-1}$.

**DDAM**
Dodecyldimethylammoniummethacrylate bromide (DDAM, CH$_3$-(CH$_2$)$_{11}$-N$^+${(CH$_3$)$_2$}(CH$_2$-CH$_2$-O-CO-C(CH$_3$)=CH$_2$)Br$^-$) was prepared by reacting methacrylic acid 2-dimethylaminoethyl ester (98 % pure : Tokyo Kasei Kogyo Co., Ltd., containing 2000 ppm of methylhydroquinone, to prevent polymerisation) with n-dodecyl bromide (99 % pure : Tokyo Kasei Kogyo Co., Ltd.) in a ratio of 1:1.1 mole respectively in acetone at room temperature (< 25 °C) for two days. Both reagents were used as received, after their purity had been verified by gas chromatography and NMR spectroscopy. The acetone was then removed and the precipitated product was washed with dry ether to remove any remaining methacrylic acid 2-dimethylaminoethyl ester, recrystallised several times from ethyl acetate and dried under vacuum [8-11].

Elemental Analysis : Calculated for C$_{20}$H$_{40}$O$_2$NBr : C 59.10 %; H 9.92 %; N 3.45 %. Found C 58.27 %; H 10.05 %; N 3.27 %. m.p. 87-89 °C.

NMR Analysis : Proton CH$_3$-(CH$_2$)$_{11}$ 0.89 δ; CH$_3$-(CH$_2$)$_8$ 1.23 δ; CH$_3$-(CH$_2$)$_8$-CH$_2$ 1.32 δ; CH$_2$-CH$_2$-CH$_2$-N 1.75 δ; CH$_3$-C= 1.94 δ; (CH$_3$)$_2$-N 3.50 δ; CH$_2$-CH$_2$-CH$_2$-N 3.84 δ; O-CH$_2$-CH$_2$-N 4.16 δ; CH$_2$-O 4.85 δ; H-C=C(CH$_3$) 5.85 δ proton trans to
methyl group, 6.13 δ proton cis to methyl group. Carbon 13 CH₃-CH₂ 13.47 δ; CH₃-C= 17.66 δ; CH₃-CH₂ 22.06 δ; CH₂-CH₂-CH₂-N 22.35 δ; CH₂-(CH₂)₂-N 25.65 δ; CH₃-(CH₂)₂-CH₂ 28.68 δ; CH₃-(CH₂)₃-(CH₂)₅ 28.98 δ; CH₃-CH₂-CH₂ 31.26 δ; (CH₃)₂-N 51.24 δ; N-CH₂-CH₂-O 57.63 δ; N-CH₂-(CH₂)₁₀ 61.57 δ; CH₂-O 64.83 δ; =CH₂ 126.69 δ; C= 134.55 δ; C=O 165.70 δ.

FTIR Analysis: C=C stretch 1633.7 cm⁻¹; C=O stretch 1720.8 cm⁻¹; H-C= stretch 3019.3 cm⁻¹.

Non-polymerisable surfactants
Hexadecyltrimethylammonium chloride (CTAC, CH₃-(CH₂)₁₅-N⁺(CH₃)₃Cl⁻, 99 % pure), dodecyltrimethylammonium chloride (DTAC, CH₃-(CH₂)₁₁-N⁺(CH₃)₃Cl⁻, 99 % pure) and hexadecyltrimethylammonium bromide (CTAB, CH₃-(CH₂)₁₅-N⁺(CH₃)₃Br⁻, 99%+ % pure) were purchased from Kodak Eastman Fine Chemicals. Sodium tetradecanoate (C₁₄Na, CH₃-(CH₂)₁₂-CO₂-Na⁺, purity 99%) was purchased from Sigma Chemical Co. Potassium oleate (KO, CH₃-(CH₂)₇-CH=CH-(CH₂)₇-CO₂-K⁺) and sodium di(2-ethylhexyl) sulfosuccinate (AOT, CH₃-(CH₂)₃-CH(CH₂-CH₃)-CH₂-O-CO-CH₂-CH(SO₃-Na⁺)-CO₂-CH₂-CH(CH₂CH₃)-(CH₂)₃-CH₃, > 95 % pure) were purchased from Tokyo Kasei Kogyo Co., Ltd. Octaethyleneglycol mono n-hexadecyl ether (C₁₆EO₈, CH₃-(CH₂)₁₅-(O-CH₂-CH₂)₈-OH, 98 % pure), octaethylene glycol mono n-dodecyl ether (C₁₂EO₈, CH₃-(CH₂)₁₁-(O-CH₂-CH₂)₈-OH, 98 % pure) and hexaethylene glycol mono n-dodecyl ether (C₁₂EO₆, CH₃-(CH₂)₁₁-(O-CH₂-CH₂)₆-OH, 98 % pure) were purchased from Nikko Chemicals Co., Ltd. Sodium dodecyl sulfate (SDS, CH₃-(CH₂)₁₁-SO₄-Na⁺, special purity 99 % pure) was purchased from BDH Chemicals Ltd. All these surfactants were used as received.

Dendritic polymer
The dendritic polymer, ((K⁺O₂C)₁₆-[G-4])₂-[C] (molecular weight 9353) was prepared by Dr Craig Hawker (previously at the Department of Chemistry, University of Queensland, Australia now situated at IBM, Almaden, USA) using the method described in chapter 8 and was subsequently dried before use.

AIBN
α,α'-Azobis(isobutyronitrile) (AIBN, (CH₃)₂C(CN)=N=NC(CH₃)₂), extra pure, was purchased from Tokyo Kasei Kogyo Co., Ltd. and further purified by recrystallisation from methanol.

Water
Water used in all experimental work was purified by one of two methods. Firstly it was passed through a Krystal Klear reverse osmosis system, followed by distillation after which it was passed through a four cartridge Milli Q plus water system. The first cartridge in this system contains activated carbon followed by a mixed bed, cartridges two
and three contain a mixed bed and the fourth cartridge contains organex, the water is then passed through a final pre-sterilised, vented microporous membrane filter at the point-of-use, giving water with a conductivity of $5.5 \times 10^{-8}$ S cm$^{-1}$. The second method of purification was triple distillation, involving filtration through activated charcoal incorporated prior to the second-stage distillation from alkaline permanganate to give water with a conductivity < $8 \times 10^{-7}$ S cm$^{-1}$ (water prepared by this method was used in surface tension experiments only).

**Ampoule preparation**

Bulk samples for all surfactant/water systems were prepared by adding weighed amounts of the surfactant and purified water into a glass ampoule which was flame sealed. The samples were homogenised by continual heating (where the actual temperature depended upon the thermal stability of the surfactant being used, but was below 90 °C for all surfactants) and centrifugation over a period of several weeks.

**2.2 NMR MEASUREMENTS**

Proton and carbon 13 nuclear magnetic resonance (NMR) spectrum were obtained using a Varian VXR300S spectrophotometer (University Nuclear Magnetic Resonance Centre, Research School of Chemistry, The Australian National University) operating at 25 °C. The solvent used was either deuterated chloroform with tetramethylsilane (TMS) as an external reference or deuterated water.

D$_2$O deuterium quadrupolar NMR studies, performed on the liquid crystalline phases of the ADDAB/D$_2$O system (chapter 4, § 4.2.4), were accomplished using a modified Varian XL 100-15 pulsed spectrometer working in the Fourier transform mode using an external lock and operated at a resonance frequency of 15.351 MHz (Physical Chemistry 1, University of Lund, Sweden).

Quadrupole NMR spectra are obtained by measuring the average anisotropy encountered by the molecules during their journey through the liquid crystalline phase, using the magnetic resonance of the deuterium nuclei. The splitting of the spectra may be explained to arise as follows. Nuclei having spin quantum numbers, $I$, greater than 1/2 (in the case of deuterium $I = 1$) have associated with them nuclear electric quadrupole moments. These quadrupole moments, $eQ$, interact with electrical field gradients, $eq$, to produce shifts in their magnetic energy levels (this being the dominant interaction). That is, the magnetic energy levels of the nuclei are perturbed by the interaction of the quadrupole moments with the electrical environment of the nuclei.

The perturbation depends upon the orientation of the electrical environment of the deuterium nucleus with respect to the external magnetic field of the experiment; this
angular dependence is described by second-order spherical harmonics $P_2(\theta)$. When the time average of $P_2(\theta)$ is non-zero, the perturbation splits the magnetic resonance lines by an amount

$$\Delta \nu = \nu_Q(P_2(\theta))$$

where $\Delta \nu$ and $\nu_Q$ are frequencies, and the average of $P_2(\theta)$ is taken over scales comparable to $1/\nu_Q$. If the sample is non-oriented, i.e., the mesophase contains a large number of domains of random orientations $\theta$, then the deuterium quadrupole spectrum will be a "powder" spectrum showing the distribution of splittings $\Delta \nu$; this distribution has peaks for $\theta = \pm \pi/2$; from the separation of those peaks the values of $P_2(\theta)$ can be extracted just as in the case of oriented samples [12].

In a homogeneous anisotropic medium (such as the lamellar and hexagonal phases) the mean value of the quadrupolar Hamiltonian is non-zero due to the static quadrupole interaction not being averaged out by the molecular motion. This residual interaction manifests itself as a splitting of the magnetic resonance lines [13-23].

In the case of a pure lamellar liquid crystalline phase for example, this quadrupole interaction generates a spectrum with two equally intense peaks. In a region where two phases coexist the spectrum is comprised of a superposition of the two individual phases spectrum.

An isotropic phase like a micellar solution or a cubic liquid crystalline phase yields only one rather sharp singlet peak, provided the static quadrupole interaction is averaged out to zero.

Spectra from D$_2$O molecules can also be used to identify the various phases present in samples. The width of the quadrupolar doublet can be analysed as

$$\Delta \nu = \nu_Q \frac{n_b}{n_f + n_b} P_2(\beta)$$

where $n_b$ and $n_f$ are the fractions of the D$_2$O molecules which are, respectively, "bound" to the interfaces separating the polar-apolar moieties, and "free" within the bulk water, and $P_2(\beta)$ describes the orientation of the OD bonds with respect to the normal of the interfaces [24]. The quadrupole splitting is then defined as the distance (in Hz) between two adjacent peaks and is equal to $4qQ/\hbar$.

Self-diffusion proton NMR measurements were performed on the ADAB cubic phase (chapter 4, § 4.2.3) using the Fourier transform pulsed gradient spin-echo technique on a modified JEOL FX60 spectrometer (Physical Chemistry 1, University of Lund, Sweden).
In this technique the diffusion coefficient, $D$, of the water is determined by performing proton NMR spectroscopy upon a sample. The proton NMR is measured using a Fourier transform pulsed gradient spin-echo pulse sequence [25-28], which is an extension of the original spin-echo experiments developed by Hahn [29], with the addition of the pulsed field gradients of McCall [30] and then later extended by Stejskal and Tanner [14].

Figure 2.2.1 shows the pulse sequence used in this experiment which consists of two radio frequency pulses, $90^\circ$ and $180^\circ$ which are separated by a time $\tau$, which produce an echo at time $2\tau$. In order to measure the self-diffusion, magnetic field gradients are applied as two short pulses of equal duration. The first is between the $90^\circ$ and $180^\circ$ pulses and the second between the $180^\circ$ pulse and the spin-echo. In the Fourier transform mode of the experiment the second half of the spin-echo is Fourier transformed.

\[ \frac{E_g}{E_o} = \exp\left(-\gamma G \delta \right)^2 D \left( \Delta - \frac{\delta}{3} \right) \]  

2.2.3

If the spin bearing molecules are able to diffuse between the two field gradient pulses, the spin-echo amplitude, $E_g$, will be reduced from its value, $E_o$, when the experiment is performed without a field gradient. The amplitude of the spin-echo by this pulse sequence is given by [31]
where \( \gamma \) is the magnetogyric constant, \( G \) the strength of the gradient pulse and \( \Delta \) is the time interval between the gradient pulses.

Hence the diffusion coefficient is obtained by measuring the peak amplitude of the echo at different lengths of the gradient pulse, \( \delta \) and fitting equation 2.2.3 to the obtained data. By plotting \( \ln \frac{E_g}{E_o} \) against \( \delta^2(\Delta - \delta/3) \), where \( \gamma, \Delta \) and \( G \) are constant throughout the experiment, the diffusion coefficient of the water is obtained from the slope of the curve which is determined by a least squares fit.

### 2.3 FTIR MEASUREMENTS

Fourier transform infrared (FTIR) analysis was performed on a Perkin Elmer 1600 series FTIR (Chemistry The Faculties, The Australian National University). Samples were prepared as a nujol mull using NaCl plates.

### 2.4 ELECTRICAL CONDUCTIVITY

Electrical conductivity measurements were obtained using a TPS Conductivity Meter Model 2102A (Auto-Ranging, Auto Cell, K factor) which was calibrated using standard potassium chloride solutions (0.1 M KCl, conductivity 1.290x10^{-2} S.cm^{-1} and 1x10^{-3} M KCl, conductivity 1.471x10^{-4} S.cm^{-1}). All samples were equilibrated to 25 °C using a Julabo SW-20C thermostated water bath which has an accuracy of \( \pm 0.1 \) °C.

Conductivity measurements are extremely sensitive to impurities in either the water or the electrolyte used and this can cause inaccuracies in measurements obtained, particularly in the concentration region where aggregation of surfactant molecules is first seen. These impurities may be in the form of ammonia, carbon dioxide, traces of dissolved substances derived from containing vessels, air or dust. Impurities in the water can influence the ionisation of the electrolyte and hence the resulting conductivity, it is necessary, therefore, to use highly purified water and ultra clean vessels when performing conductivity experiments.

The electrical conductivity of a solution is a measure of the solution's ability to conduct electricity (i.e. to transmit current through the solution). The conductivity is determined by measuring the resistance (R) of a solution of the electrolyte which is under the influence of a constant electric field. The resistance will, therefore, be directly proportional to the length of the solution along the field (l, cm) and inversely proportional to the cross sectional area which is perpendicular to the field (a, cm^2), hence
where $\rho$ is termed the resistivity ($\Omega \cdot \text{cm}$) and is a constant for a particular electrolyte, at a given concentration. The reciprocal of the resistivity is known as the specific conductance or conductivity ($\kappa$, $\Omega^{-1} \cdot \text{cm}^{-1}$ or $\text{S} \cdot \text{cm}^{-1}$).

Since, the conductivity ($\kappa$), is a measure of the electrolytes ability to transmit current through the solution (which is achieved via the independent migration of charged species) it comprises contributions from all ionic species ($i$) present in solution. Where each contribution to $\kappa$ will be proportional to the concentration of the ionic species ($c_i$), the magnitude of its charge ($z_i$) and its mobility ($\mu_i$, the limiting velocity of the species in a unit electric field ($\text{cm}^2 \cdot \text{s}^{-1} \cdot \text{V}^{-1}$)), hence

$$\kappa = \text{const} \sum_i |z_i| \mu_i c_i$$  \hspace{1cm} (2.4.2)

where the constant of proportionality is equal to the Faraday (F) [32].

Einstein’s relation shows that the diffusion coefficient ($D$, a measure of the rate at which molecules spread down a concentration gradient) is directly proportional to the ionic mobility, i.e.

$$D = \frac{\mu kT}{ez}$$  \hspace{1cm} (2.4.3)

where $e$ is the electronic charge, and from the Stokes-Einstein relationship it may also be related to the frictional coefficient ($f$) via an inverse proportionality

$$f = \frac{kT}{D}$$  \hspace{1cm} (2.4.4)

The frictional coefficient is a measure of how strongly the surrounding fluid resists the motion of the particle and is dependent upon both the molecular geometry of the ionic species and the viscosity ($\eta$) of the solvent. For a spherical particle of radius, $r$, Stokes showed that

$$f = 6\pi r \eta$$  \hspace{1cm} (2.4.5)

$r$ here is the hydrodynamic radius of the ionic species. From equations 2.4.4 and 2.4.5 above it should be noted that the Stokes-Einstein relation is independent of the charge of the diffusing particle. Equating equations 2.4.3 and 2.4.4 relates the ionic mobility to the frictional coefficient via an inverse relationship

$$\mu = \frac{ez}{f}$$  \hspace{1cm} (2.4.6)

Hence, the conductivity of an electrolyte may be expressed as [32]
Although not explicit in equation 2.4.6 the mobility is dependent upon both the concentration and temperature, (due to interactions between the ions) which leads to a corresponding dependence of the conductivity on both the concentration and temperature of the electrolyte solution.

Ionic surfactants in solution act as electrolytes, hence measurement of the specific conductivity as a function of concentration may be used to determine the concentration at which aggregation of the surfactant molecules begins (the critical micelle concentration, cmc). As aggregation of the surfactant molecules occurs the nature of the ionic species in solution changes and, as a consequence, the solutions ability to conduct electricity is also altered leading to a change in slope of the specific conductivity versus surfactant concentration curve. The cmc is taken to be the concentration at which there is the maximum change in the change of the slope (i.e. the concentration where the slope is changing most rapidly).

\[
\frac{d^2 K}{dc^2} = 0 \quad c = \text{cmc}
\]

This definition can be applied to any ideal colligative property which is a linear function of the concentration above and below the cmc [33].

For a uni-univalent surfactant, RX, where X is the counterion, forming a micelle \((R_nX_m)^{n-m}\), with charge \((n - m)\), aggregation number \(n\), bound counterions \(m\) and degree of dissociation \(\beta\) equal to \(m/n\), a monodisperse mass action-model may be used [34-36], where it is assumed that at each concentration there is exclusively an average/monodisperse micelle (i.e. polydispersity in \(n\) and \(\beta\) is ignored), to set up the following equilibrium:

\[
nRX \rightleftharpoons nR^{+/−} + nX^{+/−} = (R_nX_m)^{n-m} + (n - m)X^{+/−}
\]

Hence the conductivity equations for the micellar system treat the aqueous monomers and micelles as a solution of mixed electrolytes.

An equation for the specific conductivity of this equilibrium above the cmc can be written by knowing that the equivalent conductivity is a measure of the specific conductivity per unit concentration of charge [37, 38]

\[
\Lambda = \frac{1000k}{c}
\]
where \( c \) is the concentration in gram equivalents per litre. From the law of independent migration every ion contributes a definite amount towards the equivalent conductivity, irrespective of the nature of the other ion with which it is associated in the electrolyte

\[
\Lambda = \Lambda_c + \Lambda_a
\]

where \( \Lambda_c \) and \( \Lambda_a \) are the equivalent conductances of the cation and anion respectively. Equating 2.4.10 and 2.4.11, yields

\[
\Lambda = \Lambda_c + \Lambda_a = \frac{1000\kappa}{c}
\]

and the conductivity equation for the micellisation equilibrium may be written as [35]

\[
1000\kappa = c_0(\Lambda_R + \Lambda_X) + \frac{c - c_0}{n} \Lambda_{\text{mic}} + \frac{c - c_0}{n}(n - m) \Lambda_X
\]

where \( c_0 \) is the cmc. At \( c = c_0 \) and \( \kappa = \kappa_0 \)

\[
1000 \frac{\kappa - \kappa_0}{c - c_0} = \frac{1}{n} \Lambda_{\text{mic}} + \frac{n - m}{n} \Lambda_X
\]

where \( n, m \) and \( \Lambda_{\text{mic}} \) are unknown, \( \Lambda_R \) is taken to be its value at infinite dilution (\( \Lambda_{0R} \)) due to the low concentrations employed (for the bromide and sodium counterions at 25 °C \( \Lambda_{Br} = 77.44 \) and \( \Lambda_{Na^+} = 50.53 \) [37]). Hence, to solve this equation for \( m \), it is necessary to determine the aggregation number of the micelles and their equivalent conductance. The aggregation number may be determined experimentally using light scattering [39, 40], fluorescence quenching [41-44] or a number of other techniques. It is useful at this stage to approximate \( n \) by assuming that the volume of the hydrocarbon interior of a spherical micelle is equal to \( 4/3\pi l^3 \), where \( l (\text{Å}) \) is the length of the longer portion of the hydrocarbon chain. Its value may be calculated from Tanford's equation [45] for the maximum length that the hydrocarbon chain can have, i.e. \( l_{\text{max}} = 1.5 + 1.265n_c \), where \( n_c \) is the number of embedded carbons in the hydrocarbon chain. Hence the volume of one molecule of hydrocarbon having molecular weight \( M \) and density \( \rho \) will be equal to \( 10^{24}M/N\rho \) where \( N \) is Avogadro's number, hence

\[
n = \frac{4}{3} \pi l^3 \frac{N\rho}{10^{24}M}
\]

This approximation of the aggregation number assumes that \( n \) is determined purely by the length of the hydrocarbon chain and is independent of the nature of the head group (i.e. two surfactants having identical hydrocarbon chain length but different head groups will have the same aggregation number). The aggregation number may also be determined using a variation of the above method, where \( n \) is determined by calculating the volume of the surfactant which may be approximated from head group surface area measurements and \( l_{\text{max}} \) assuming a cone-like shape and 100 % packing in the micelle. Both of these
latter two techniques are comparable with each other and also with aggregation numbers determined experimentally.

$\Lambda_{\text{mic}}$ may be eliminated from equation 2.4.14 by using equation 2.4.7, if the micelle is assumed to be spherical with radius $r_{\text{mic}}$ (this assumption being not too drastic near the cmc). The frictional coefficient is given by equation 2.4.5

$$f_{\text{mic}} = 6\pi r_{\text{mic}} \eta$$ \hspace{1cm} 2.4.16

and the specific conductivity due to the micelle with charge $n - m$ is

$$\kappa_{\text{mic}} = \frac{(n - m)^2 \text{Fec}}{6\pi r_{\text{mic}} \eta}$$ \hspace{1cm} 2.4.17

Assuming a long rod-like geometry for the dissociated surfactant ($z = \pm 1$) with length, $l$, radius, $a$, and frictional coefficient given by [46, 47]

$$f_R = \left( \frac{1}{2} a \right)^2 \left( \frac{3}{2} \right)^{\frac{1}{3}} \left( \frac{1}{2} a \right)^{\frac{2}{3}} \frac{6\pi \eta \left( \frac{3}{4} a^2 \right)^{\frac{1}{3}}}{\left( 2\ln \left( \frac{1}{a} \right) - 0.11 \right)}$$ \hspace{1cm} 2.4.18

the specific conductivity for the surfactant will be

$$\kappa_R = \frac{\left( \frac{3}{2} \right)^{\frac{1}{3}} \left( 2\ln \left( \frac{1}{a} \right) - 0.11 \right) \text{Fec}}{6\pi \eta \left( \frac{3}{4} a^2 \right)^{\frac{1}{3}} \left( \frac{1}{2} a \right)^{\frac{2}{3}}}$$ \hspace{1cm} 2.4.19

Hence

$$\frac{\kappa_{\text{mic}}}{\kappa_R} = \frac{(n - m)^2}{r_{\text{mic}}} \left( \frac{\left( \frac{3}{4} a^2 \right)^{\frac{1}{3}} \left( \frac{1}{2} a \right)^{\frac{2}{3}}}{\left( \frac{3}{2} \right)^{\frac{1}{3}} \left( 2\ln \left( \frac{1}{a} \right) - 0.11 \right)} \right)$$ \hspace{1cm} 2.4.20

If it is assumed that the solvation of both the monomer and aggregate are the same, the volume of the aggregate including the solvation layer is $n$ times the effective volume of the monomer, hence

$$V_{\text{mic}} = nV_R$$ \hspace{1cm} 2.4.21

Since the micelle is assumed to be spherical, $V_{\text{mic}} = \frac{4}{3}\pi r_{\text{mic}}^3$ and for a rod-like surfactant, $V_R = \pi a^2 l$, therefore $r_{\text{mic}} = (3/4na^2)^{1/3}$ and

$$\frac{\kappa_{\text{mic}}}{\kappa_R} = \frac{(n - m)^2}{r_{\text{mic}}} \left( \frac{\left( \frac{1}{2} a \right)^{\frac{2}{3}}}{\left( 2\ln \left( \frac{1}{a} \right) - 0.11 \right)} \right) = \frac{\Lambda_{\text{mic}}}{\Lambda_R}$$ \hspace{1cm} 2.4.22
$l_{\text{max}}$ may be used as the value for $l$ and correspondingly the maximum value of the volume may also be calculated following Tanford, $v_{\text{max}} = 27.4 + 26.9n_c$. Using $l_{\text{max}}$ and $v_{\text{max}}$ the radius of the rod-like surfactant, $a$, may be determined, $a = (v_{\text{max}}/\pi l_{\text{max}})^{1/2}$, hence

$$\frac{\Lambda_{\text{mic}}}{\Lambda_R} = \frac{(n - m)^{1/2} \left( \frac{1/2}{\pi l_{\text{max}}} \right)^{1/3}}{\left( \frac{3}{2} n \right)^{1/3} \ln \left( \frac{\pi l_{\text{max}}^3}{v_{\text{max}}} \right) - 0.11}$$  \hspace{1cm} 2.4.23

But $\Lambda = \Lambda_R + \Lambda_X = 1000\kappa/c$ from equation 2.4.12, therefore at the cmc, $\Lambda_R + \Lambda_X = 1000\kappa_0/c_0$, but $1000\kappa_0/c_0$ is equal to the slope of the specific conductivity versus concentration curve below the cmc ($S_1$), therefore $\Lambda_R = 1000S_1 - \Lambda_X$ and $1000(\kappa - \kappa_0)/(c - c_0) = S_2$, the slope of the specific conductivity versus concentration curve above the cmc, hence

$$1000S_2 = \frac{1}{n} \left( \frac{n - m)^{1/2} \left( \frac{1/2}{\pi l_{\text{max}}} \right)^{1/3}}{\left( \frac{3}{2} n \right)^{1/3} \ln \left( \frac{\pi l_{\text{max}}^3}{v_{\text{max}}} \right) - 0.11} \right) (1000S_1 - \Lambda_X) + \frac{n - m}{n} \Lambda_X \hspace{1cm} 2.4.24$$

Using this equation, an approximation of the number of bound counterions may be determined and from this the degree of dissociation $\beta$.

A second method for determining the degree of dissociation of the micelle is to merely take the ratio of the slopes $S_1$ and $S_2$. Here the slope below the cmc is assumed to be determined predominantly by the intrinsic mobilities of the various counterions whereas the slope above the cmc measures contributions due to counterions, monomers and micelles. Any difference in the two slopes is attributed as being entirely due to variations in the counterion "binding", aggregation number and interactions, calculation of the degree of dissociation using this method compares favourably with other methods used for extracting this parameter.

Hence, measurement of the specific conductivity as a function of concentration can be used to determine both the concentration at which aggregation occurs and also the degree of counterion binding.

### 2.5 SURFACE TENSION MEASUREMENTS

Surface or interfacial tensions arise due to the short-range forces of attraction which exist between molecules. Molecules located in the bulk solution are influenced, on average, by equal forces of attraction in all directions. In contrast, those situated at interfaces are
subjected to unbalanced attractive forces causing a net inward pull resulting in an overall movement of molecules away from the interface towards bulk solution causing a spontaneous contraction of the interface. From this the surface tension ($\gamma$) of a pure liquid or solution is defined as the force acting on the surface at right angles and inward from the boundaries of the surface tending to minimise the area of the interface. That is, the surface tension is equal to the work per unit area required to produce a new surface. This definition yields two equivalent interpretations of the surface tension; as the force per unit length of the boundary of the surface or the energy per unit area of the surface. Therefore

$$\gamma = \left( \frac{\partial G}{\partial A} \right)_{T,p}$$

i.e. the surface tension is identical to the excess Gibbs free energy per unit area arising from the surface.

If two phases $\alpha$ and $\beta$ divided by a surface $s$ are in equilibrium the Gibbs free energy is assumed to be additive, therefore

$$G = G^\alpha + G^\beta + G^s$$

where $G$ is the total Gibbs free energy and $G^\alpha$, $G^\beta$ and $G^s$ are the Gibbs free energies of phases $\alpha$ and $\beta$ and the surface respectively.

For a bulk solution the Gibbs free energy is defined to be

$$G = E + pV - TS + \sum_i \mu_i n_i$$

where $E$ is the internal energy, $p$ the pressure, $V$ the volume, $T$ the absolute temperature, $S$ the entropy, $\mu_i$ the chemical potential of component $i$ and $n_i$ the number of moles of component $i$. The corresponding term for a surface is then obtained by replacing the volume term by an area term, hence

$$G^s = E^s + \gamma A - TS^s + \sum_i \mu_i n_i$$

where $A$ is the surface area and $\gamma$ is the surface tension. Substituting equation 2.5.3 for $G^\alpha$ and $G^\beta$ and equation 2.5.4 into equation 2.5.2 gives the change in Gibbs free energy of the system as

$$dG = \sum_{\alpha,\beta,s} \left( dE + pdV + Vdp - TdS - SdT + \sum_i \mu_i dn_i + \sum_i n_i d\mu_i \right)$$

$$+ Ad\gamma + \gamma dA$$
From the first law of thermodynamics for a reversible process

\[ dE = \delta q - \delta w = \sum_{\alpha, \beta, S} dE = \sum_{\alpha, \beta, S} (T dS - (p dV + \delta w_{\text{non}} - p V)) \]

2.5.6

where \( q \) is the heat, \( w \) the work and \( dw_{\text{non}} - p V \) the non-pressure volume work, hence

\[ dE = \sum_{\alpha, \beta, S} \left( V dP - S dT + \sum_i n_{i} d\mu_i + \sum_i n_{i} d\mu_i - \delta w_{\text{non}} - p V \right) \]

+ \( Ad\gamma + \gamma dA \)

2.5.7

From the definition of the surface tension, \( \gamma dA \) may be equated to the work (non-pressure volume) per unit area, hence

\[ dE = \sum_{\alpha, \beta, S} \left( V dP - S dT + \sum_i n_{i} d\mu_i + \sum_i n_{i} d\mu_i \right) + Ad\gamma \]

2.5.8

then, from the first and second laws of thermodynamics it is known that

\[ dG = V dP - S dT + \sum_i n_{i} d\mu_i \]

2.5.9

therefore,

\[ \sum_i n_i^\alpha d\mu_i + \sum_i n_i^\beta d\mu_i - \sum_i n_i^\gamma d\mu_i + Ad\gamma = 0 \]

2.5.10

From this relationship the Gibbs-Duhem equation is obtained by considering the case of an equilibrium of just one bulk phase, i.e.

\[ \sum_i n_i d\mu_i = 0 \]

2.5.11

This then permits the evaluation of the activity of one component from measurements made on the other in a binary system. Substituting the Gibbs-Duhem equation into equation 2.5.10 yields

\[ \sum_i n_i^\alpha d\mu_i + Ad\gamma = 0 \]

2.5.12

which is known as the Gibbs adsorption equation, relating the surface tension to the number of moles and chemical potentials of the components in the interface. For a two component system (e.g. surfactant plus water)

\[ n_1^\alpha d\mu_1 + n_2^\alpha d\mu_2 + Ad\gamma = 0 \]

2.5.13

or
The quantity $\frac{n_i^S}{A}$ is called the "surface excess" of component $i$ and is given the symbol $\Gamma_i$, therefore in general the Gibbs adsorption equation may be stated in the form

$$d\gamma = -\frac{n_i^S}{A} d\mu_1 - \frac{n_i^S}{A} d\mu_2$$  \hspace{1cm} 2.5.14

How is the "surface excess" defined? Consider a general property $P$ while moving from phase $\alpha$ to $\beta$. The interface is then a region of thickness $\tau$ across which the properties of the system vary from those characteristic of $\alpha$ ($P_\alpha$) to those of $\beta$ ($P_\beta$). Despite this definition no volume is assigned to the interface, it is instead as if the properties of $\alpha$ and $\beta$ apply right up to some dividing plane situated at a specific value of $x$ ($x_0$). In principle this "surface" may be located at any value of $x$ such that the shaded areas shown in figure 2.5.1 (indicating how much $P$ has been over or underestimated by extending to $P_\alpha$ or $P_\beta$, respectively) compensate for one another, this position will differ though with each property considered. Hence choosing the dividing surface for a particular property means that the profiles of the other properties of the system will be divided differently yielding a "surface excess" due to an inequivalence of the over and underestimations. Choosing the property for defining the dividing surface to be the number of surface moles of solvent per unit area in a slice of solution at some value of $x$ has the consequence that $\Gamma_1 = 0$, hence the Gibbs adsorption equation is reduced to

$$d\gamma = -\Gamma_2 d\mu_2$$  \hspace{1cm} 2.5.16

![Figure 2.5.1](image)

*Figure 2.5.1 Position of the Gibbs dividing surface at $x = x_0$ between pure phases $\alpha$ and $\beta$ in the interface of thickness $\tau$. The dividing surface is placed so as to minimise the over and underestimation (i.e. make equivalent the shaded areas) in the value assigned to a general property $P$ having values $P_\alpha$ and $P_\beta$ in pure phase $\alpha$ and $\beta$, respectively.*
That is a physical understanding of the surface excess of component 2 ($\Gamma_2$) is made available by the arbitrary placement of the mathematical surface which sets the surface excess of component 1 ($\Gamma_1$) to zero and is generally given the notation $\Gamma_2^\perp$ (in the case of a surfactant/water system $\Gamma_{H_2O} = 0$ and $\Gamma_2$ is the surface excess of surfactant at the interface).

A definition of the chemical potential of any component states that it is dependent upon the activity ($a$) of that component as follows

$$\mu = \mu_0 + RT \ln a$$  \hspace{1cm} 2.5.17

but $a = fc$ where $c$ is the concentration and $f$ the corresponding activity co-efficient, therefore

$$d\mu = RT \frac{da}{a} = RT \ln(fc)$$  \hspace{1cm} 2.5.18

In most cases of interest the solutions are in the dilute regime where it is assumed that $f$ tends to 1 and is constant over the entire concentration range used, hence

$$\Gamma_2^\perp = -\frac{1}{RT} \frac{1}{d\ln c} \frac{dy}{dy}$$  \hspace{1cm} 2.5.19

That is, the surface excess of component 2 can be determined by measuring the change of surface tension with concentration. This form of the Gibbs equation can be applied to a solution of a non-ionic surfactant but in the case of a solution of an ionic surfactant, in the absence of any added electrolyte, Haydon and co-workers [48-50] have argued that the equation must be modified to allow for the fact that both the anions and cations of the surfactant will adsorb at the solution surface in order to maintain local electroneutrality (even though not all of these ions are surface-active in the amphiphilic sense). Hence for a solution of a 1:1 ionic surfactant a factor of 2 is required to allow for the simultaneous adsorption of cations and anions, therefore

$$\Gamma_2^\perp = -\frac{1}{2RT} \frac{1}{d\ln c} \frac{dy}{dy} = -\frac{1}{4.606RT} \frac{dy}{d\log c}$$  \hspace{1cm} 2.5.20

From its definition the reciprocal of the surface excess concentration gives the area of surface occupied by a mole of adsorbed molecules, therefore division by Avogadro's number converts the reciprocal of $\Gamma_2^\perp$ into a value of the surface area per molecule ($10^{20}$ is a conversion factor to give the units in Å$^2$).

$$A = \frac{10^{20}}{N\Gamma_2^\perp}$$  \hspace{1cm} 2.5.21
Hence, measurement of the change in surface tension with concentration may be used to
determine both the surface excess of a component at the interface and the surface area per
molecule at the interface.

A traditional technique used for measurement of surface tension is the du Noüy ring
method [51] where the surface tension is determined from the maximum force exerted on
a ring without detachment of the meniscus. A circular ring of radius, R, made from
platinum or a platinum/iridium alloy is suspended from a balance, the ring which has been
cleaned by flaming is assumed to be perfectly wetted by the solution and to make perfect
contact with the solution (i.e. the contact angle is zero and constant). The ring is then
slowly withdrawn from the surface while monitoring the change in weight measured by
the balance. Corrections are made for the "∞ interface" case by way of dimensionless
correction factors (B) which have been determined by Harkins and Jordan [52] and Huh
and Mason [53]. The correction factors also allow for the non-vertical direction of the
tension forces, the complex shape of the liquid supported by the ring and the nature of the
interface. The surface tension of a given liquid is then

\[ \gamma = \frac{F_{\text{max}} B}{4\pi R} \]  

2.5.22

where \( F_{\text{max}} \) is the maximum equilibrium force required to detach the ring from the liquid
surface and \( F \) is the force acting upon the ring as it is withdrawn from an interface. This
force, \( F \) is equal to the sum of 1) the weight of the ring, 2) the vertically resolved
component of the surface tension acting on the inner and outer three phase contact lines
and 3) the buoyancy or upthrust due to the hydrostatic pressure difference around the
ring's circumference [54]. The sum of these three forces results in a net downwards
force which must be opposed experimentally by an equal and opposite applied force on
the ring to maintain the system at a height, h [54, 55].

For a surfactant/water system the surface tension is determined at the air/water interface
and, therefore, calculations of the surface area per molecule at the interface cannot be
directly compared with the hydrophilic/hydrophobic interface of the surfactant aggregates,
which is a fluid/fluid interface. The surface tension, as measured above, is found to
decrease with an increase in the surfactant concentration until a plateau is reached. The
onset of this plateau being the concentration at which aggregation of the surfactant
molecules begins (i.e. the cmc). From equation 2.5.19 the surface excess concentration
of the surfactant can be determined in the limit as the concentration tends towards the cmc
and from this the surface area per surfactant molecule at the interface determined.

It has been shown recently [56, 57] that the use of a linear fit to the data prior to
micellisation causes an underestimation of the surface excess concentration which is
evidenced by an adsorption plateau not being reached at the cmc. This implies that the
surface excess continues to increase above the cmc as seen in plots of pressure versus area deduced from surface tension measurements. Hence a polynomial of degree two or higher should be used when fitting data. It should be noted, that this feature of increasing surface excess concentration above the cmc is not necessarily a point of contamination.

Surface tension measurements are also a very sensitive technique for determining the purity of a surfactant. Surface-active impurities manifest themselves as either a) a minimum in the surface tension versus log of the concentration curve (i.e. the impurity is more surface active than the major component and is solubilised into the micelles of the major component, the lack of a minimum is therefore a necessary but not sufficient criterion of purity for surface active agents), b) two distinct, almost linear regions are observed prior to surfactant aggregation or c) a variation of surface tension with time.

All surface tension measurements were performed using a du Noüy tensiometer where a platinum ring was employed (Division of Chemicals and Polymers, CSIRO, Ian Wark Laboratories, Clayton, Melbourne). All samples were equilibrated to 25 °C.

2.6 pH MEASUREMENTS

pH measurements were obtained using a Metrohm 654 pH Meter which had been calibrated using pH 4.0 and 7.0 buffers. All samples were equilibrated to 25 °C.

2.7 POLARISING OPTICAL MICROSCOPY

All phase behaviour was investigated initially by polarising optical microscopy using the isothermal concentration gradient method [58]. A small amount of the powder or melt was placed on a slide with a free cover slip, water was allowed to penetrate completely, at constant temperature. The phases were observed as bands of variable birefringence as the water evaporated. An Olympus BH-2 polarising optical microscope with a Mettler FP82HT hot stage attached to a Mettler FP80HT Central Processor capable of temperature control to ± 0.1 °C was used. For each given temperature a new concentration gradient was performed. The temperature range was between 20 and 90 °C for the various surfactant/water systems studied. Bulk samples of a given composition were also viewed under crossed polarising filters (where all samples were sealed using Eccobond* 286, a general purpose epoxy adhesive purchased from W.R. Grace and Co.) and the temperature was varied between 20 and 100 °C. Photographic work was obtained using an Olympus C-35 camera that was fitted onto the microscope.
Polarising optical microscopy has long been used in the study of liquid crystals, both for thermotropic and lyotropic forms. The first reported optical textures, shown by thermotropic liquid crystals, were by Lehmann in 1889 [59, 60] and the birefringent nature of some liquid crystalline phases was established.

This birefringence in some liquid crystalline phases is related to their molecular aggregate architecture which can also be used to explain why some phases are optically isotropic. When all three refractive indices are equal, the liquid crystal is isotropic, as for micellar and cubic lyotropic liquid crystals, where each direction in space is equivalent and therefore indistinguishable. The refractive index of the phase is then, \( n = n_1 = n_2 = n_3 \). If instead at least one of the refractive indices is not equivalent to the others the system is birefringent. If the case is such that \( n_1 = n_2 \neq n_3 \) the liquid crystal is called uniaxial and the birefringence is given as \( \Delta n = n_3 - n_1 \). This is the case for lamellar, hexagonal and some intermediate liquid crystalline phases.

If the amphiphilic molecules are arranged such that they have both a randomness in lateral distribution and also in the orientation around the long axes (the direction of the unit normal, as is the case for lamellar phases) the liquid crystal will have its maximum refractive index along the mean direction of these axes (\( n_3 \)) and its minimum (\( n_1 \)) in all directions normal to this. The phase is then said to have positive birefringence. When instead the amphiphilic molecules have an architecture such that the maximum refractive index is now in any direction across the long units (i.e. \( n_1 > n_3 \)) of the phase, (as is the case for hexagonal liquid crystalline phases where the average orientation of the amphiphiles is transverse and they radiate from the central axis) the phase is said to have negative birefringence. Phases (e.g. distorted hexagonal or rectangular phases) in which none of the refractive indices are equal are said to be biaxial.

A description of the observed optical textures produced by lamellar and hexagonal liquid crystalline phases has been given by Rosevear in 1954 and again in 1968 [61, 62].

An attempt to relate the microstructure of the liquid crystals to their textures by using models of the birefringent phases and tracing ray paths through was performed by Friedel and Grandjean [63-65] and later extended by Bragg in 1934 [66]. Much work is still being done on quantifying the link between the underlying geometry of the phase with the texture produced [67-73] but as yet it is still a difficult process to understand this relationship and determine the surfactant architecture from the texture that is observed.

### 2.8 X-RAY SCATTERING

The structure of the liquid crystalline phases was checked by small-angle X-ray scattering (SAXS) measurements using a Kiessig camera [74], with point collimation. All
diffraction patterns were recorded on X-ray sensitive film (CEA Reflex 25, double coated high speed film for direct X-ray exposure purchased from CEA AB Sweden). The camera is capable of recording simultaneously both small-angle (sample to film distance of 200 or 400 mm) and wide-angle (film placed in the range of 40 to 70 mm) scattering detection. The camera is attached to a Philips generator 1120/00 with either a $^{60}$Co ($K_\alpha$ line with $\lambda = 1.79285$ Å) fine focus high intensity source PW2216/20 using an iron filter or a Cu ($K_\alpha$ line with $\lambda = 1.54439$ Å) fine focus high intensity source PW2213/20 using a nickel filter.

Samples used for X-ray analysis were loaded into thin walled X-ray transparent capillaries of internal diameter 0.7 or 1.0 mm which were sealed. Bulk samples were also sealed between two mylar or mica windows, resulting in an approximate sample thickness of 1 mm. Powder diffraction patterns obtained using all four of the different methods to house the sample were identical (apart from reflexions due to the mica or mylar windows). Oriented samples were prepared by placing the bulk samples between two concentric X-ray capillaries of diameter 1.0 and 0.7 mm or in flattened X-ray capillaries (obtained in-house by slow melting, see § 2.10 for design details) of approximately 0.1 to 0.6 mm thickness, which were then sealed. The samples were then heat cycled in order to obtain a well oriented sample (approximately ten cycles). Oriented samples of unknown composition were obtained in the same way but by placing a micellar solution between the capillaries. The capillaries remained unsealed to allow water to evaporate. When the required liquid crystalline phase had formed (as determined by formation of the appropriate optical texture seen using polarised microscopy) the capillaries were sealed.

Considerable research has been performed on the scattering of X-rays by atoms, crystalline compounds and assemblages of molecules and many reviews on the theory of X-ray crystallography have been written [75-81]. These general details will not be discussed here, but instead only those which apply directly to the structures studied in this work.

Liquid crystalline phases have been studied by both small- and wide-angle X-ray crystallography for many years with the first work being performed by Stauff in 1939 [82]. Since that time the theory and recognition of the X-ray diffraction patterns produced by these liquid crystalline phases has improved such that it is now possible to extract large amounts of information about the structure of the liquid crystals from the diffraction pattern which they produce [83-88].

Each class of liquid crystalline phase (e.g. hexagonal, cubic or lamellar) produces a characteristic diffraction pattern in the form of Debye-Scherer rings for every Bragg reflexion in the small-angle region of the X-ray scattering (with the maximum detectable spacing for the camera used here being 120 Å or $Q \sim 0.05$ Å$^{-1}$). These rings coupled
with the variation of the intensities of the peaks and any systematic absences defines a space group to the phase being considered [89], as long as the number of rings observed is sufficient (i.e. the X-ray camera and generator being used have a sufficiently large flux so as to produce rings of detectable intensity).

The reciprocal spacing ($\AA^{-1}$) of a reflexion ($Q$) is calculated as follows: since $n\lambda = 2d\sin\theta$, $\theta = 1/2(\tan^{-1}x/D)$ and $Q = 2\pi/d$.

$$Q = \frac{4\pi\sin\left(\frac{1}{2}\tan^{-1}\frac{x}{D}\right)}{\lambda}$$  

Here $x$ is the radius of the Debye-Scherer ring (mm), $D$ is the sample to film distance (mm), $\lambda$ is the radiation wavelength ($\AA$), $2\theta$ is the angle of reflexion and $d$ is the spacing in $\AA$ of the Bragg planes.

The micellar phases ($L_1$ and $L_2$), (see §1.1 for a full description of the liquid crystalline phases formed upon surfactant self-assembly) usually produce one diffuse ring only in the small-angle region [86], the diameter of which is related to the average distance between the aggregates. The diffusiveness of the ring indicates the absence of any long-range order.

Hexagonal phases produce patterns with diffraction peaks in the ratios $1:\sqrt{3}:\sqrt{4}:\sqrt{7}...$, the lamellar phase is characterised by $Q$-values in the ratios of $1:2:3:4:5...$ [86] and each of the six known cubic phases also produce characteristic diffraction patterns dependent upon their structure [85, 90-104]. A summary of these characteristic $Q$-value ratios for these common liquid crystalline phases is given in table 2.8.1, where I indicates a body-centred cubic, F face-centred cubic and $P$ a primitive cubic lattice. Note that the space group $Q_{230}$ (Ia$3d$) is the only cubic phase which is unambiguously defined by its X-ray powder spectrum. The remaining cubic phases can often be fitted to several space groups e.g. the cubic phase known as Im$3m$ may also be fitted to the space groups I$43m$, I$432$, Im$3$, I$2_13$ and I$23$ [97].

In conjunction with these sharp Bragg peaks, diffuse peaks or spots may also be observed which yield further information on the exact surfactant aggregate geometry. The complete structure of the surfactant mesophases can of course not be determined using SAXS alone since this technique is a static average method and yields no information on fluctuations with time.

Once a diffraction pattern is obtained it is necessary to reference each ring such that in the case of a homogeneous one phase sample all rings are accounted for as arising from one liquid crystalline phase or from two phases in the case of coexistence. Often Bragg peaks are difficult to detect due to the variation of the form factor of the phase being studied and these must not be mistaken for systematic absences. To index a diffraction pattern
obtained from the different symmetry systems and determine which of the liquid crystalline phases it is, the following equations must be utilised.

Table 2.8.1 Variation of Q-value ratios and Bravais-Miller Indices for some common lyotropic liquid crystalline phases

<table>
<thead>
<tr>
<th>Liquid Crystalline Phase</th>
<th>Q-value Ratios(^a)</th>
<th>Bravais-Miller Indices</th>
</tr>
</thead>
<tbody>
<tr>
<td>Micellar</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Hexagonal</td>
<td>(1: \sqrt{3}: \sqrt{4}: \sqrt{7}: \sqrt{9}: \sqrt{12}...)</td>
<td>1010: 1120: 2020: 2130: 3030: 2240...</td>
</tr>
<tr>
<td>Cubic Q(^{212}) (P(4_3)(32))</td>
<td>(\sqrt{2}: \sqrt{3}: \sqrt{5}: \sqrt{6}: \sqrt{8}: \sqrt{9}: \sqrt{10}...)</td>
<td>110: 111: 210: 211: 220: 300: 310...</td>
</tr>
<tr>
<td>Cubic Q(^{223}) (Pm(3n))</td>
<td>(\sqrt{2}: \sqrt{4}: \sqrt{5}: \sqrt{6}: \sqrt{8}: \sqrt{10}: \sqrt{12}...)</td>
<td>110: 200: 210: 211: 220: 310: 222...</td>
</tr>
<tr>
<td>Cubic Q(^{224}) (Pn(3m)) (Diamond IPMS)</td>
<td>(\sqrt{2}: \sqrt{3}: \sqrt{4}: \sqrt{6}: \sqrt{8}: \sqrt{9}: \sqrt{10}...)</td>
<td>110: 111: 200: 211: 220: 221: 310...</td>
</tr>
<tr>
<td>Cubic Q(^{227}) (F(d3m))</td>
<td>(\sqrt{3}: \sqrt{8}: \sqrt{11}: \sqrt{12}: \sqrt{16}: \sqrt{19}: \sqrt{24}...)</td>
<td>111: 220: 311: 222: 400: 331: 422...</td>
</tr>
<tr>
<td>Cubic Q(^{229}) (I(m3m)) (Primitive IPMS)</td>
<td>(\sqrt{2}: \sqrt{4}: \sqrt{6}: \sqrt{8}: \sqrt{10}: \sqrt{12}: \sqrt{14}...)</td>
<td>110: 200: 211: 220: 310: 222: 321...</td>
</tr>
<tr>
<td>Cubic Q(^{230}) (I(a3d)) (Gyroid IPMS)</td>
<td>(\sqrt{6}: \sqrt{8}: \sqrt{14}: \sqrt{16}: \sqrt{20}: \sqrt{22}: \sqrt{24}...)</td>
<td>211: 220: 321: 400: 420: 332: 422...</td>
</tr>
<tr>
<td>Lamellar</td>
<td>1: 2: 3: 4: 5: 6,...</td>
<td>001: 002: 003: 004: 005: 006...</td>
</tr>
</tbody>
</table>

\(a\) Note that the number of reflexions observed will be dependent upon among other things the type of camera used, collimation of the beam and stiffness of the phase.

For a hexagonal system the unit cell is parametrised as \(a = b \neq c\), \(\alpha = \beta = 90^\circ\), \(\gamma = 120^\circ\) and \(V = abc\sin\gamma\). The reciprocal cell is therefore \(a^* = b^* = 2/a\sqrt{3}, c^* = 1/c, \alpha^* = \beta^* = 90^\circ\) and \(\gamma^* = 60^\circ\). \(Q_{hkl}\) (= Q defined in equation 2.8.1) is related to \(h, k\) and \(l\) as follows

\[Q_{hkl}^2 = (h^2 + k^2 + hk) a^*^2 + l^2 c^*^2\]  
2.8.2

and \(d_{hkl}\) is calculated from

\[d_{hkl} = \frac{a\sqrt{3}}{\sqrt{4 (h^2 + k^2 + hk) c^2 + 3l^2 a^2}}\]  
2.8.3

The Bravais-Miller indice is then \(hkl\) where \(i = -(h + k)\).

Cubic systems are parametrised as \(a = b = c\), \(\alpha = \beta = \gamma = 90^\circ\) and \(V = a^3\). Hence the reciprocal cell is defined by \(a^* = b^* = c^* = 1/a, \alpha^* = \beta^* = \gamma^* = 90^\circ\), therefore
The lamellar phase is perhaps the easiest liquid crystalline phase to index with the Bravais-Miller indices represented by 00l.

Some of the Bravais-Miller indices for the most commonly observed Bragg peaks are given in table 2.8.1 for each of these phases. See also the International Tables for Crystallography [89] for further classifications of the more complex liquid crystalline phases formed.

A beautiful technique for the full analysis of diffraction patterns has been developed by Luzzati et al. based upon pattern recognition by judicious choice of the phases of reflexions, giving information on electron density maps via a sophisticated computer analysis [105]. Unfortunately, this method of analysis is not possible in this laboratory and only indexing was performed.

In the wide-angle region (where the camera used here is capable of measuring Q values in the range of \(-0.6\) to 3.1 Å\(^{-1}\) corresponding to \(d \sim 11\) to 2 Å), information is obtained at the inter-atomic length scale, including reflexions characteristic of the state of the hydrocarbon interior of the surfactant aggregates. If the hydrocarbon chains are disordered, a diffuse ring centred at \(Q = (4.5\ \text{Å})^{-1}\) is observed [86] which is characteristic of liquid hydrocarbons [106, 107]. Phases with liquid-like hydrocarbon interiors are symbolised by the subscript \(\alpha\). Although the short-range organisation in liquid crystalline phases is similar to that for liquid hydrocarbons, the hydrocarbon chains are not totally disoriented as they are on average perpendicular to the polar/non-polar interface due to the anchoring of the head groups. Liquid crystalline phases with fluid-like interiors in general show a trend of decreasing lipid bilayer thickness or cylinder diameter with increase in temperature [86].

Not all surfactant mesophases contain hydrocarbon interiors in a fluid-like state. This change from disordered to ordered hydrocarbon chain is detected at wide-angles by the replacement of the diffuse ring by a sharp ring or series of rings. The number and relationship of these rings is characteristic of the exact nature of the frozen chains and these different configurations are distinguished by the subscripts \(\beta, \beta', \gamma\) and \(\delta\). \(\beta\) indicates frozen chains which may or may not be interdigitated, packed in a hexagonal array. \(\beta'\), like \(\beta\), consists of frozen chains packed in a quasi-hexagonal array but here the chains are tilted with respect to the polar/non-polar interface by an angle \(\theta\). \(\gamma\) corresponds to a combination of frozen and fluid chains and the \(\delta\) conformation comprises frozen...
chains in a helical conformation packed in a cubic array. For all frozen chain configurations, the hydrocarbon chains have free rotation about their long axis. For a full description of these states see references [106-112].

From the locations of the Bragg peaks the unit cell dimensions can be calculated. The number of surfactant molecules per unit cell \( N_s \) can then be determined from the known composition of the mesophase:

\[
N_s = \frac{V \Phi N_A 10^{-24}}{M_s \bar{v}_s} \tag{2.8.6}
\]

where \( V \) is the volume of the unit cell (which may have units of Å, Å² or Å³ depending upon whether the cell is one-, two- or three-dimensional), \( N_A \) is Avogadro's number, \( M_s \) is the molecular weight of the surfactant, \( \bar{v}_s \) the specific volume of the surfactant \( (\text{cm}^3 \cdot \text{g}^{-1}) \) and \( \Phi \) the volume fraction of the two component mesophase of surfactant concentration \( c \) \( (\text{g/g}) \),

\[
\Phi = \left(1 + \frac{\bar{v}_w}{\bar{v}_s} \left(\frac{1}{c} - 1\right)\right)^{-1} \tag{2.8.7}
\]

where \( \bar{v}_w \) is the specific volume for water = 1.003, 1.002, 1.023 and 1.036 at 27, 50, 70 and 90 °C respectively [113]. Both \( \bar{v}_s \) and \( \bar{v}_w \) are assumed to be invariant with concentration.

It should be noted however that equation 2.8.6 assumes that the paraffinic chains are clustered together such that water is totally excluded, i.e. this region consists entirely of the hydrophobic segment of the surfactant molecules [86]. This assumption has been demonstrated for the case of micelles [114]. Hence the interface is defined as being the surface that separates the water from the paraffinic medium, which is covered by the polar head groups [115, 116].

The specific volume \( \bar{v}_s \) of a dry surfactant can be deduced from [117]:

\[
M_s \bar{v}_s = M_{pol} \bar{v}_{pol} + M_{par} \bar{v}_{par} \tag{2.8.8}
\]

where \( M_{pol} \) and \( M_{par} \) are the molecular weights and \( \bar{v}_{pol} \) and \( \bar{v}_{par} \) are the specific volumes of the polar head group and paraffinic chains respectively. The specific volume of the paraffinic chains is calculated from:

\[
M_{par} \bar{v}_{par} = n_{CH_3} M_{CH_3} \bar{v}_{CH_3} + n_{CH_2} M_{CH_2} \bar{v}_{CH_2} + n_{CH} M_{CH} \bar{v}_{CH} \tag{2.8.9}
\]

where \( n_{CH_3}, n_{CH_2} \) and \( n_{CH} \) are the number of methyl, methylene and methine groups in the paraffinic chain and \( \bar{v} \) \( (\text{cm}^3 \cdot \text{g}^{-1}) \) can be obtained from \( v \) \( (\text{molar, Å}^3) \) for which tables of data at varying temperatures are available [83, 84, 112, 118]. A summary of the values used in this work is given in table 2.8.2 for chains in the \( \alpha \) conformation. For chains in
conformations other than $\alpha$ i.e. $\beta$ or $\delta$ the values given in table 2.8.2 must be scaled according to the following ratios 0.945 and 0.930, respectively [112]. The value of $v_{pol}$ for the surfactant of unknown specific volume can be obtained by comparison with other surfactants of known measured specific volume with the same polar head group, by extracting $v_{pol}$ from equation 2.8.8 and using equation 2.8.9 to calculate the partial specific volume of the chain. When a surfactant of known specific volume is not available for comparison it is necessary to base all calculations on the specific volume of the paraffinic chains only. That is, $\Phi$ is replaced by $\Phi_{par}$ in equation 2.8.7

$$\Phi_{par} = \left(1 + \frac{v_w}{v_{par}} \left(\frac{1}{c_{par}} - 1\right)\right)^{-1}$$ 2.8.10

where $v_s$ has been replaced by $v_{par}$ and the concentration ($c$) is now given by $c_{par} = cM_{par}/M_s$, corresponding changes are also made in equation 2.8.6.

Table 2.8.2 Values for the partial specific volumes and volumes occupied by the chemical groups

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>Partial Specific Volume $v$ (cm$^3$·g$^{-1}$)</th>
<th>Volume per Chemical Group $v$ (Å$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>27</td>
<td>50</td>
</tr>
<tr>
<td>CH</td>
<td>0.95</td>
<td></td>
</tr>
<tr>
<td>CH$_2$</td>
<td>1.16</td>
<td>1.18</td>
</tr>
<tr>
<td>CH$_3$</td>
<td>2.18</td>
<td>2.29</td>
</tr>
</tbody>
</table>

It is generally assumed that the symmetry of the aggregates is higher than the symmetry of the array [86]. Hence, the aggregates of the hexagonal phase can be described as circular cylinders, and the bilayers of the lamellar phase are infinite and flat. Within this framework, the radius of the cylinders is $r_s = a \sqrt{3/2} \Phi / 2\pi$ in the hexagonal phase (in the case of reverse hexagonal phases $\Phi$ is replaced by $1 - \Phi$ in the above equation) and the thickness of the bilayer is $d_s = a\Phi$ in the lamellar phase, where $a$ is the unit cell length. The mean area per polar head on the interface is $A = 2\pi r_s/N_s$ for the hexagonal phase and $A = 2/N_s$ for the lamellar phase, where $N_s$ is the number of surfactant molecules per unit length of cylinders and per unit area of bilayers, respectively. Note that the volume is determined by $V = \sigma = \sqrt{3}a^2/2$ (Å$^2$) in the case of hexagonal liquid crystalline phases, $V = d (\AA)$ for lamellae and $V = a^3 (\AA^3)$ in the case of cubic phases. Again, as noted above, when the specific volume of the surfactant is not known or cannot be determined, these
calculations are based on the paraffinic chain. Hence by this convention the radius calculated for hexagonal phases is for the chains only and not for the whole cylinder, and the bilayer thickness does not include contributions from the head groups of the surfactants.

Unfortunately, for most cubic phases, unlike lamellar, hexagonal and some other more complex liquid crystalline phases (e.g. the tetragonal or rhombohedral phases), the number of peaks obtained in the diffraction pattern is too few to determine the space group of the cubic phase. In such cases it is only possible to give a number of possible geometries. Hence full analysis and description of the unit cell (i.e. location and shape of the aggregates) is not feasible.

2.9 POLYMERISATION

All polymerisations were performed using free radical initiation, where two techniques were employed; thermal initiation of an added initiator (α,α'-Azobis(isobutyronitrile), AIBN, (CH₃)₂C(CN)N=N(CN)C(CH₃)₂), a water insoluble initiator which becomes integrated into the hydrocarbon region of the surfactant liquid crystalline phases), or ultraviolet radiation leading to direct decomposition of the monomer (mechanistic details for free radical polymerisation are discussed in § 2.9.1). Samples polymerised via the first method were prepared by adding AIBN in a fixed mole ratio to the surfactant, whereas samples to be initiated by direct decomposition of the monomer had no added initiator. Samples were then made up to the correct compositions by adding the appropriate amount of solvent (water in the case of polymerisation in liquid crystalline media and chloroform for polymerisation in a non-aggregated state). Prior to sealing, the ampoules were degassed by the freeze-pump-thaw technique (to remove as much oxygen as possible which acts to inhibit the polymerisation) until a constant pressure was obtained through one complete cycle. They were then flame sealed while still under vacuum. Samples containing no added initiator were equilibrated in a manner identical to that explained in § 2.1, whereas those containing added AIBN were equilibrated by repeated centrifugation and agitation using a vibrator at room temperature to ensure that the extent of polymerisation prior to equilibration of the samples was minimised.

Thermal polymerisations were performed between 45 and 60 °C, depending upon the stability of the samples, in a thermostated water bath or oven. Both being capable of temperature control to ± 1 °C. Photochemical polymerisations were performed in a photochemical reaction chamber (built in-house, by Tim Sawkins) which is capable of housing fourteen samples at a time. The chamber contains sixteen broad band emission UV lamps (of type NEC - FL8BL) having a wavelength centred at 360 nm which are evenly distributed around a cylindrical chamber of diameter 20 cm. This wavelength was
chosen instead of the more conventional 254 nm used in photochemically initiated free radical polymerisations due to absorption of light of this wavelength by the ampoules used to house the samples. The samples were placed on a carousel which was capable of individually rotating each sample as well as the entire ensemble to ensure that all samples were evenly irradiated. Sample to lamp distance was approximately 3 cm. Polymerisations performed in this manner were conducted in a temperature controlled environment at \(30 \pm 1^\circ\text{C}\). Both thermal and photochemically initiated polymerisations were stopped by removal of the samples from the reaction environment followed by rapid cooling.

The polymerisation's progress was monitored as a function of time by preparing a number of samples all having the same composition and stopping the polymerisations at the desired times. The extent to which polymerisation took place was determined by performing proton NMR on the samples which had been previously freeze dried to remove all solvent. Using the integration values obtained from the NMR spectra, it is possible to determine a standard ratio for the number of protons incorporated into the polymerisable moiety, as compared with, protons which will not be effected by the polymerisation. Hence, for a partially polymerised sample the ratio evaluated will differ from the standard ratio, this difference determining the extent to which polymerisation has occurred.

### 2.9.1 Mechanism for free radical polymerisation

Monomeric polymerisation can be accomplished by several different mechanisms depending upon the nature of the functionality involved. These mechanisms fall into the general categories of chain-growth or step-growth polymerisation. Free radical polymerisation is classified as a chain-growth process and involves repeated addition of a monomer unit to an active centre through a single chain process. During polymerisation the active centre is retained with each subsequent addition of monomer. Initiation of the polymerisation can occur from direct decomposition of the monomer functionality or by way of an added agent (initiator) which is capable of forming free radicals. The methods used for initiation are comparable to those for simple gas-phase chain reactions. These include thermal initiation, photoinitiation using near ultraviolet light (3600 Å) or initiation by high-energy radiation including electrons, gamma rays, X-rays and slow neutrons.

The reactions which occur during initiation using high-energy radiation are varied and non-specific, resulting from gross damage to molecular structures due to large transfers of energy [119] and hence this may not be an ideal method for polymerisation of surfactant lyotropic liquid crystalline phases.
Thermal initiation is widely used for the generation of free radicals but it is not easy to control the rate at which free radicals are produced due to the heat capacity of the system. Nevertheless for convenience, it has been utilised in this study. An initiator chosen to be used for thermal initiation should have a first-order decomposition rate constant in the range of $10^{-5}$ to $10^{-6}$ sec$^{-1}$ at the required temperature.

Unlike thermal initiation, photoinitiated polymerisation can be controlled accurately, since the generation of free radicals will vary with the intensity of the initiating light.

Both methods can be used to initiate polymerisation directly, often though they involve an added initiator which decomposes more readily than the monomer involved in the polymerisation. It is possible when using photoinitiation to use temperatures which are low enough to ensure that the added initiator does not undergo thermal decomposition and hence the polymerisation can be easily controlled.

One of the most widely used initiators is AIBN which undergoes decomposition both thermally and photochemically. Its thermal decomposition in solution is first order and varies only slightly with change of solvent. It is not susceptible to attack by radicals hence induced decomposition and transfer reactions are unimportant and it has been shown to have an efficiency of approximately 60\% over a wide range of monomer concentration. Its decomposition via homolytic bond breakage can be schematically illustrated as follows:

\[
\begin{align*}
\text{CN} & \quad \text{CN} \\
(CH_3)_2-C-N=N-C(CH_3)_2 & \quad \rightarrow \quad (CH_3)_2-C-N=N + C(CH_3)_2 \\
& \quad \downarrow \quad \text{CN} \\
(CH_3)_2-C & \quad + \quad N_2
\end{align*}
\]

The free radical 2-cyano-2-propyl formed during the decomposition of AIBN is susceptible to reaction with oxygen to give the radical $(CH_3)_2C(CN)$-O-O-. This peroxy radical's reactivity is quite different to that of the original radical and will often inhibit polymerisation all together. Oxygen not only acts to inhibit initiation but may also affect the growth of the polymer chains by reacting with the radical chain to again as above produce a radical whose reactivity is greatly reduced from that of the original radical. Hence removal of oxygen is essential. It should also be noted that due to the removal of N$_2$ from one of the initially formed free radicals the product formed by recombination of the two $\cdot C(CN)(CH_3)_2$ free radicals produces an initiator which has a reduced initiating power compared with the original AIBN and hence will greatly affect the extent and rate
of polymerisation and in some cases stop the reaction from proceeding. Therefore, anything which increases the rate constant for recombination of these two free radicals will act to inhibit the polymerisation.

In a typical chain-growth polymerisation, generation of one free radical via the decomposition of an initiator may lead to the polymerisation of thousands of monomer molecules. The following mechanism can be suggested for the occurrence of polymerisation.

**Initiation**

\[ I \rightarrow 2R^- \]

where I is the added initiator which is a thermolabile compound and R is the free radical produced on decomposition. The initial decomposition of the initiator into free radicals is the rate determining step of the polymerisation. This free radical then reacts with a monomer molecule to produce a new free radical, which in general will be more stable.

\[ R^- + M \rightarrow R^-M^- \]

This free radical is now capable of attacking a second monomer molecule in a step termed propagation. In the case where initiation occurs via direct decomposition of the monomer there is just one initiation step followed by propagation.

**Propagation**

\[ R^-M^- + M \rightarrow R^-M^-_2 \]
\[ R^-M^-_2 + M \rightarrow R^-M^-_3 \]
...   
\[ R^-M^-_x + M \rightarrow R^-M^-_{x+1} \]

The radical reactivity is presumed to be independent of chain length and as such the rate constant for all propagation steps is \( k_p \). Hence an activated monomer molecule attacks a second monomer, links to it, maintaining an activated centre, this unit can then attack a second monomer molecule, this continues so that the process leads to the rapid growth of an individual polymer chain from each activated monomer. The chain continues to grow until a bimolecular reaction between a pair of chain radicals annihilates the active centres. Two processes by which this may occur are:

**Termination**

Combination

\[ R^-M^-_x + R^-M^-_y \rightarrow R^-M^-_{x+y} \]

rate constant \( k_{tc} \)

and disproportionation through transfer of a hydrogen atom

\[ R^-M^-_x + R^-M^-_y \rightarrow R^-M^-_x + R^-M^-_y \]

rate constant \( k_{td} \)

Since termination is a diffusion controlled process for most liquid phase polymerisations, anything that increases the viscosity of the medium will affect the rate of termination and
hence the molecular weight of the polymer. If the termination rate is decreased there is an overall increase in the polymerisation rate and the molecular weight. At high conversions it is possible that the polymerisation rate will be very low since, the system becomes glassy and the monomer can no longer add to the growing polymer chains.

Termination involving a reaction between a primary and chain radical can be neglected since the concentration of primary radicals will normally be very low due to their rapid reaction with monomer.

There are though other termination steps which may intervene, one of which is chain transfer, which may have a large affect on the polymerisation. In chain transfer a new chain is initiated at the expense of the one that is currently growing, that is the reactivity of a radical is transferred to another species. This new radical may or may not (as is the case of inhibition or retardation) be capable of continuing the chain reaction. Chain transfer can involve monomer, initiator, solvent, or an added chain transfer agent. Termination may also occur via reaction of the active radical with the walls of the vessel.

Hence the average polymer chain length will be long whenever the termination steps occur more slowly than those of propagation. Chain length is affected by the relative rates of chain propagation and termination which are dependent upon temperature in a complex way, it is found that in general molecular weight decreases with increase in temperature. It can also be effected by the addition of specific additives which react in such a way as to control the molecular weight obtained upon polymerisation.

During propagation it is possible to obtain polymers which are not linear, but have innumerable branches in them and this is a common occurrence in free radical polymerisation. Branching arises when the radical end of a growing chain abstracts a hydrogen atom from the middle of a chain to yield an internal radical site which is then capable of continuing the polymerisation. The most common type of branching is short-chain branching (figure 2.9.1.1), and this arises from intra-molecular hydrogen abstraction from a carbon four atoms away from the radical end of the chain.

Branching can also arise via inter-molecular hydrogen atom abstraction, where the radical end of one chain reacts with a section of another chain. This form of hydrogen atom abstraction is termed long-chain branching, figure 2.9.1.2.

If the polymerisation involves substituted alkenes each addition of a monomer molecule leads to the formation of a chiral centre. When all of one group are on the same side of the zigzag backbone the conformation is termed isotactic. If the groups regularly alternate on opposite sides of the backbone the polymer is said to be in the syndiotactic conformation and that conformation in which the groups are randomly oriented is termed atactic. Each of the three stereochemical forms have different properties. The most
common polymers formed in normal free radical polymerisations are highly branched and atactic.

\[
\begin{align*}
\text{Branch point} & \\
\text{Repeat} & \\
\text{Branched Polymer} & 
\end{align*}
\]

**Figure 2.9.1.1** Short-chain branching involving intra-molecular hydrogen atom abstraction.

\[
\begin{align*}
\text{Branch point} & \\
\text{Repeat} & \\
\text{Branched Polymer} & 
\end{align*}
\]

**Figure 2.9.1.2** Long-chain branching involving inter-molecular abstraction of a hydrogen atom.

Hence the characteristics of chain-growth polymerisation are that:

a) only growth reactions add repeating monomer molecules one at a time to the chain,
b) the monomer concentration decreases steadily throughout the reaction,
c) high polymer is formed immediately and the polymer molecular weight varies little throughout the rest of the reaction,
d) long reaction times serve to improve yields but have only a slight affect on the molecular weight of the polymer, and
e) the reaction mixture therefore contains only monomer, high polymer and a small amount of growing polymer chains.

For a non-cross-linked polymer (i.e. those polymers formed predominantly from normal free radical polymerisation) therefore, the most important forces are van der Waals forces, this is due primarily to the weak attractive interactions between transient dipoles in neighbouring polymer chains. These forces act over short distances only and as such they are stronger for linear polymers where the polymer chains can line up in a regular and close-packed array. Many polymers have regions (or crystallites) which are essentially crystalline, consisting of highly ordered portions in which the polymer chains are bound together by van der Waals forces. This crystallinity is greatly effected by the steric interactions of the substituent groups on the chains.

For the systems studied here the general polymerisation functional group can be represented as $\text{R''R'C=CH}_2$, where R' is either a hydrogen or methyl group and R'' is any other functionality. It is expected from this type of polymerisable moiety that the free radical produced would be $\text{R''R'C} - \text{CH}_2\text{P}$ where P is the original free radical, that is the primary free radical $\text{R''R'PC} - \text{CH}_2$ would not be produced since it is unstable in comparison to the secondary or tertiary free radical which is produced. Hence the following reaction occurs (where * indicates the presence of a chiral centre). As the size of R'' and R' increases the rate of polymerisation will decrease due to steric hindrance.

![Chemical Diagram](attachment:chemical_diagram.png)
APPENDIX

2.10 FLATTENED CAPILLARIES

The flattened capillaries used for preparing oriented liquid crystalline phases were made by placing Lindemann X-ray capillaries of 0.7 of 1.0 mm internal diameter in a capillary tube mould as shown in figure 2.10.1 which was then placed in a furnace preset to 600 °C using the mould mount shown in figure 2.10.2. Upon heating the capillaries collapse and conform to the groove depth producing flattened capillaries of various sizes.

---

Figure 2.10.1 Capillary tube mould. a) Projection of lower section viewed from above. b) Specifications of the grooves. c) Side view of upper section. Dimensions are in mm.
45 - ALLOW 0.15 CLEARANCE FROM WIDTH 'A' (SEE MOULD).

**Figure 2.10.2** Capillary tube mould mount. a) Viewed from above. b) Viewed from the side. All dimensions are in mm
2.11 REFERENCES


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Chapter 3

DODECYLTRIMETHYLAMMONIUM BROMIDE

3.1 INTRODUCTION

In order to determine the effect that addition of a polymerisable moiety has upon the self-assembly of the surfactant molecules studied here, it is necessary to compare the behaviour of the different polymerisable surfactants with that of a well defined non-polymerisable surfactant.

To this end, two surfactants were chosen to be the bases for the polymerisable surfactants studied in this work. The single-chain analogue chosen was dodecyltrimethylammonium bromide (DTAB, CH₃-(CH₂)₁₁-N⁺(CH₃)₃Br⁻), a C₁₂ quaternary ammonium surfactant. DTAB can be compared with allyldodecyldimethylammonium bromide (ADAB, CH₃-(CH₂)₁₁-N⁺(CH₃)₂(CH₂-CH=CH₂)Br⁻ - discussed in chapter 4) and dodecyldimethylammoniummethacrylate bromide (DDAM, CH₃-(CH₂)₁₁-N⁺(CH₃)₂(CH₂-CH₂-O-CO-C(CH₃)=CH₂)Br⁻ - discussed in chapter 7) where one of the methyl groups in the head group of DTAB has been replaced by either an allyl or an ethylmethacrylate polymerisable moiety, respectively. In both cases, the hydrophilicity of the head group has been increased due to the replacement of a small hydrophobic group (a methyl group) with a bulkier, more hydrophilic one. Comparison of DTAB with ω-undecenyltrimethylammonium bromide (ω-UTAB, CH₂=CH-(CH₂)₉-N⁺(CH₃)₃Br⁻ - discussed in chapter 5) is also possible since in this case the integrity of the head group is preserved and instead the nature of the hydrocarbon chain is altered such that a slightly more hydrophilic group is present at the end of the paraffinic chain. A direct comparison of DTAB with sodium 10-undecenoate (Na-10, CH₂=CH-(CH₂)₈-CO₂⁻Na⁺ - discussed in chapter 6) is more difficult to perform since here both the head group and the hydrocarbon region of the surfactant have been altered. But by using ω-
UTAB as an initial comparison (differing from Na-10 only in the nature of its head group), it is also possible to use DTAB as a non-polymerisable standard for Na-10. When considering each of these surfactants it should be noted that there will be specific counterion, chain length and polymerisable group effects which may be difficult to qualitatively determine.

Allyldidodecylmethylammonium bromide (ADDAB, (CH₃-(CH₂)₁₁-2-N⁺(CH₃)(CH₂-CH=CH₂)Br⁻ - discussed in chapter 4) is more comparable with the double-chained analogue of DTAB - didodecyldimethylammonium bromide (DDAB, (CH₃-(CH₂)₁₁-2-N⁺(CH₃)₂Br⁻). Since DDAB is applicable to ADDAB only, discussion of this surfactant is left until chapter 4.

In addition to using DTAB as a direct comparison for the polymerisable surfactants studied here it can also be compared with other non-polymerisable surfactants such as dodecyltrimethylammonium chloride (DTAC, CH₃-(CH₂)₁₁-N⁺(CH₃)₃Cl⁻) [1-8] and hexadecyltrimethylammonium bromide (CTAB, CH₃-(CH₂)₁₅-N⁺(CH₃)₃Br⁻) [6, 8-13] which have both been extensively studied in the past. From this comparison it is possible to estimate the effect that both a change in counterion and chain length have on the self-assembly of the surfactant molecules.

DTAB is a widely studied surfactant, with a considerable amount of work having been performed at low concentrations [5, 9-12, 14-21]. Little work though, has been done in the higher concentration region of the phase diagram [6, 22-24]. Hence in this chapter the self-assembling behaviour of DTAB with water at all concentrations between 20 and 130 °C will be discussed.

### 3.2 RESULTS

#### 3.2.1 Determination of the critical micelle concentration for DTAB

To establish the purity of the surfactant, surface tension measurements using the du Noüy ring method (see § 2.5 for experimental details) were obtained at 25 °C, results are shown in figure 3.2.1.1. The concentration at which initiation of surfactant aggregation occurs is termed the critical micelle concentration (cmc). For a plot of surface tension versus log of the surfactant concentration the cmc is the concentration at which there is a break in this curve, such that following the onset of micellisation the curve plateaus out. A polynomial of degree two was fitted to the data points prior to surfactant aggregation having a correlation coefficient of 0.999. Using this fit the cmc was determined to be equal to 1.35x10⁻² M. The surface excess concentration is calculated from the slope of the pre-micellisation curve close to the cmc using equation 2.5.20 (since DTAB is a cationic surfactant) and the area per polar head group at the
interface from equation 2.5.21. Hence, the surface excess concentration of DTAB is found to be $3.4 \pm 0.1 \times 10^{-6}$ mol.m$^{-2}$ and the area per polar head group is equal to $49 \pm 1$ Å$^2$.

To ascertain the accuracy of the electrical conductivity method for determining the concentration at which aggregation occurs, measurements were performed on a series of samples in the concentration range of 0.01 to 0.02 M at 25 °C, results are shown in figure 3.2.1.2. From this plot the cmc is determined to be $1.61 \times 10^{-2}$ M. Using the method described in § 2.4 where the aggregation number is evaluated via equation 2.4.15 (i.e. $n = 44$, when $M = 169, \rho = 0.80$ g.cm$^{-3}$ and $l = 15.42$ Å) the number of counterions that remain associated with their surfactant molecules upon micellisation ($m$) was calculated to be 29, hence, the percentage dissociation is 34.1 %. If instead the value of the aggregation number is taken to be equal to 55 as determined by Evans et al. using the fluorescence probe technique [12] $m$ is found to be 36 and the percentage dissociation is then 34.5 %. The more simplistic method of taking a direct ratio of the

**Figure 3.2.1.1** Surface tension of aqueous DTAB measured at 25 °C using the du Noüy ring method. Errors are indicated by the size of the data points.
slopes above and below the cmc gives the percentage dissociation as 34.3 %. The final method utilises the head group area determined form surface tension measurements giving an aggregation number of 61 and percentage dissociation of 34.4 %. Hence, the percentage dissociation as calculated by all of these methods is comparable and approximately 34 % of all bromide counterions dissociate upon micellisation.

![Graph](image)

Figure 3.2.1.2 Specific conductivity as a function of DTAB concentration at 25 °C (errors in the measurements are of the order of the data points).

Table 3.2.1.1 gives a comparison of the results determined from this work with those of other studies, showing that the cmc as determined here is similar to values determined by other researchers but that the calculated percentage dissociation is significantly higher.

Comparison with the C16 analogue, CTAB which has a cmc equal to ca. 9x10^{-4} M [9-13] demonstrates that increasing the length of the hydrocarbon chain has a tendency to lower the concentration at which aggregation is initiated. This is a general trend for saturated paraffinic chain surfactants [15] and it has also been shown that increasing the length of the hydrocarbon chain increases the average micellar aggregation number and
Table 3.2.1.1 cmc values and percentage dissociations for the DTAB/water system

<table>
<thead>
<tr>
<th>cmc(^a) (x10(^2))</th>
<th>Technique</th>
<th>Aggregation Number</th>
<th>Percentage Dissociation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.64 [14]</td>
<td>Refraction</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.5 [15]</td>
<td>Light Scattering</td>
<td>~ 50</td>
<td></td>
</tr>
<tr>
<td>1.58 [9]</td>
<td>Specific Conductivity</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.44 N [16]</td>
<td>Equivalent Conductivity</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.42 [17]</td>
<td>Equivalent Conductivity</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.40 [18]</td>
<td>Surface Tension</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.6 [10]</td>
<td>Conductivity</td>
<td></td>
<td>23</td>
</tr>
<tr>
<td>1.6 [5]</td>
<td>Photochemical Process</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.54 m [12]</td>
<td>Conductivity</td>
<td>55</td>
<td></td>
</tr>
<tr>
<td>1.45 [20]</td>
<td>Specific Conductivity(^b)</td>
<td>54 ± 5(^c)</td>
<td>26.3</td>
</tr>
<tr>
<td>1.46 [21]</td>
<td>Ultrasound Velocity</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.35</td>
<td>Surface Tension</td>
<td>61(^d)</td>
<td>34.4(^e)</td>
</tr>
<tr>
<td>1.61</td>
<td>Specific Conductivity</td>
<td>44(^f)</td>
<td>34.18(^g)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>55(^h)</td>
<td>34.5(^i)</td>
</tr>
</tbody>
</table>

\(^a\) Units are in moles/l (molarity, M) unless stated otherwise, N = normality (g/l) and m = molality (moles/kg).
\(^b\) Using a flow dilution conductivity cell.
\(^c\) Determined by fluorescence quenching.
\(^d\) Calculated from the head group area determined from surface tension measurements assuming 100 % packing of the surfactant molecules in the micelle.
\(^e\) Calculated using n = 61 from equation 2.4.24.
\(^f\) Calculated from equation 2.4.15.
\(^g\) Calculated using n = 44 from equation 2.4.24.
\(^h\) From Evans et al. [12].
\(^i\) Calculated using n = 55 from equation 2.4.24.
\(^j\) Calculated using the ratio of the slopes above and below the cmc from figure 3.2.1.1.

Shifts the Krafft discontinuity to higher temperatures [25]. In contrast the cmc determined for DTAC (ca. 2x10\(^{-2}\) M [2, 3, 5]) indicates that a change from the bromide to the chloride counterion shifts the cmc to slightly higher concentrations. Percentage dissociations are known to be larger for surfactants having chloride counterions rather than bromide ions. This may be attributed to the chloride ions having a larger radius of
hydration which inhibits the ion from being closely bound to the charged head groups hence promoting dissociation and that the equilibrium constant for complexation ($K_e$, $RX \rightleftharpoons R^+ + X^-$) is such that the equilibrium lies more to the right for the chloride ion than for the bromide ion.

3.2.2 DTAB self-assembly

Previous results for the phase progression in the DTAB/water system are scarce with the only two reported studies being performed by Luzzati et al. [22, 23] in the early 1960s and later by Blackmore and Tiddy [6]. The results reported by Luzzati et al. [22, 23] were for the structural parameters determined from a diffraction pattern for a sample in the cubic phase at ~ 70 °C and 82 wt% DTAB. The pattern was initially interpreted as arising from a face centred cubic lattice comprising a packing of discrete micellar aggregates. This was later shown to be incorrect [23, 26], since the observed small-angle X-ray scattering (SAXS) data was incommensurate with this type of lattice. The cubic phase was then assigned as the bicontinuous cubic phase $Q^{230}$ (Ia3d, type I) having a unit cell length of 76.9 Å. It was also stated, that both a hexagonal and a lamellar phase are also formed in this binary system.

Later in 1988 Blackmore and Tiddy [6] performed concentration gradients at various temperatures and determined that a hexagonal phase is formed below 15 °C. Above 33 °C a cubic phase forms, which precedes a lamellar phase forming at temperatures exceeding 59 °C. These results therefore confirm those obtained by Luzzati et al. [22, 23].

A more complete determination of the DTAB/water phase behaviour was therefore required. The results obtained here for this binary system are shown in figure 3.2.2.1. Three liquid crystalline phases form in the temperature range of 20 to 100 °C. At 20 °C a normal hexagonal phase ($H_\alpha$) forms between 56.0 and 73.3 wt% which precedes a region of coexistence between the hexagonal phase and varying forms of hydrated crystals (the number and extent of hydration was not fully investigated). No other liquid crystalline phases are observed to form until there is an elevation in temperature at which point a bicontinuous cubic phase ($Q_\alpha$ of type $Q^{230}$ - Ia3d - Gyroid infinite periodic minimal surface (IPMS) [23, 27-31], this assignment being determined from SAXS data, which will be discussed more fully later) is observed at 36.5 °C. At still higher temperatures (65.4 °C) and concentrations (89.7 wt%) a lamellar phase ($L_\alpha$) is formed.

Figures 3.2.2.2, 3.2.2.3 and 3.2.2.4 show the results obtained for concentration gradients performed at 25, 40 and 70 °C, respectively as observed using a crossed
polarising microscope. Figure 3.2.2.2 shows that only one liquid crystalline phase \( (H_\alpha) \)

is formed before hydrated crystals are observed, whereas, a concentration gradient performed

at 40 °C (figure 3.2.2.3) indicates that a cubic phase is formed between the hexagonal phase and hydrated DTAB crystals. At 70 °C (figure 3.2.2.4) both cubic and lamellar phases are observed prior to the formation of hydrated crystals.

Figure 3.2.2.1 Partial phase diagram of the binary DTAB/water system. \( L_1 \) : micellar solution, \( H_\alpha \) : normal hexagonal phase, \( Q_\alpha \) : bicontinuous cubic phase, type \( Q^{230} \) (Ia3d - Gyroid IPMS [23, 27-31]), \( L_\alpha \) : lamellar phase, and crystals : hydrated DTAB crystals. The horizontally shaded areas (showing tie lines) indicate a region where two liquid crystalline phases coexist and the diagonally shaded areas indicate coexistence between a liquid crystalline phase and hydrated crystals.

Figure 3.2.2.5 shows a typical optical texture of a sample within the DTAB hexagonal region (61.3 wt%, 25 °C) when viewed using crossed polarising filters. The texture is typical for normal hexagonal phases and is often termed the "fan texture" [32, 33] (note the similarity between this texture and the fan texture of Friedel [34] for smectic A thermotropic liquid crystalline phases). This texture is observed when the primary axes of the hexagonal cylinders lie parallel to the glass slide [35]. Each fan is comprised of at least two sets of brushes which lie at an angle between 10 and 15° to the directions of the polariser and analyser, indicating that the hexagonal phase in the DTAB/water system is non-uniaxial [36]. The brushes arise due to the presence of singularities in
Figure 3.2.2.2 Optical texture observed for a 25 °C concentration gradient for the DTAB/water system under crossed polarising light. Showing the formation of a hexagonal liquid crystalline phase prior to hydrated DTAB crystals, (magnification 440).

Figure 3.2.2.3 View of a 40 °C concentration gradient for the DTAB/water system under crossed polarising light, (magnification 440). From left to right hexagonal and cubic phases are formed in addition to hydrated DTAB crystals.
Figure 3.2.2.4 View of a 70 °C concentration gradient for the DTAB/water system under crossed polarising light, (magnification 440). From left to right micellar, hexagonal, cubic and lamellar phases are formed prior to hydrated DTAB crystals.

Figure 3.2.2.5 Fan texture of the DTAB hexagonal phase (crossed polarising filters, magnification 880). The cylinders lie parallel to the glass slide and the brushes correspond to line disclinations of strength $s = + 1/2$. The brushes lie at an angle of 10 to 15° to the polariser and analyser and the central ends of the brushes of one fan do not converge to the same point, (61.3 wt% DTAB sample at 25 °C).
the form of line disclinations of strength \( s = + 1/2 \) (see figure 1.2.1.3 a)). The strength, \( s \) is determined by the number of brushes divided by four and is positive if the brushes rotate in the same sense as the polariser and analyser and negative otherwise [35, 37-39]. Note that the central ends of the brushes within one fan do not converge to the same point indicating that the molecular cylinders have the shape of involutes of developable domains [35, 40, 41].

The presence of more than two sets of brushes within each fan can be explained by the occurrence of more than two closely associated line disclinations. That is, a third line disclination interacts with one of a pair of disclinations which are oriented such that their Burgers vectors have the opposite sense, where the third Burgers vector is at some angle to the first two, or simply displaced in space (see figure 3.2.2.6).

![Figure 3.2.2.6](image)

*Figure 3.2.2.6* Associated line disclinations of strength \( s = + 1/2 \). In this case the Burgers vectors are displaced by their position in space only, (i.e. they have the same sense) but the situation where they are rotated with respect to each other is also possible.

The splaying out of the brushes into fine dark lines (as seen in figure 3.2.2.5) is explained by a change in curvature of groups of hexagonal cylinders in their arrangement about the line disclination [42].

At higher surfactant concentrations (coincident with an elevation in temperature) a bicontinuous cubic phase is formed. The phase is extremely viscous and optically
isotropic which distinguishes it from both the hexagonal and lamellar phases bordering it and also the isotropic fluid phase which is of low viscosity.

Figure 3.2.2.7 shows the optical texture viewed for a sample of the DTAB lamellar phase using crossed polarising filters. The texture is termed "mosaic" and is a typical texture observed in lamellar phases [43-45]. Note that both positive (i.e. the radial direction is "slow") and negative spherulites (in the vein of Rosevear [32]) are present. A "pinwheel" can also be distinguished for some of the maltese crosses which is characteristic of negative spherulites and is observed only in lamellar phases.

The behaviour of each of these liquid crystalline phases (hexagonal, cubic and lamellar) in the temperature range of 20 to 100 °C is remarkably classic, at temperatures above this though, the behaviour is no longer of a classic nature.

Figures 3.2.2.8, 3.2.2.9 and 3.2.2.10 show the optical textures viewed using crossed polarising filters for a series of samples at temperatures above 100 °C in the high concentration regime of the phase diagram. Figure 3.2.2.8 shows the view for a 70.7 wt% DTAB sample at 120.3 °C, on initial formation of this texture. The sample originates from the hexagonal phase at room temperature and upon increasing the temperature undergoes a phase transition to a cubic and then lamellar phase. At still higher temperatures the lamellar phase coexists with an isotropic fluid which contains highly birefringent regions as seen in this figure. Increasing the temperature above 130 °C is not possible due to decomposition of the surfactant, hence a pure isotropic fluid was not observed. If the sample is held at this temperature for fifteen minutes the texture shown in figure 3.2.2.9 is observed, here the birefringent cusp regions have narrowed and a larger proportion of the remaining lamellar phase is situated in a stable triangle at the intersection of the three arms of the cusp. This triangular region is not the only geometrical shape observed and other shapes including squares and pentagons are also observed depending upon the number of intersecting arms.

The texture shown in figure 3.2.2.10 is observed at higher temperatures and here the various geometrical shapes that occur can be seen. At this temperature the fluid is moving very rapidly and the individual arms of the cusps are not confined to remain with one of the shapes observed, i.e. the shapes are continually changing depending upon the number of arms present at any one time.

It has also been observed that these strongly birefringent cusps occur in the low surfactant composition micellar phase region for extremely thin samples.

The regions of the phase diagram initially assigned by optical microscopy were established by determining the structures using SAXS. Diffraction patterns were obtained for powdered bulk samples in each of the liquid crystalline phases of the
Figure 3.2.2.7 Mosaic texture of the DTAB lamellar phase (crossed polarising filters, magnification 440). The layers comprising the phase lie parallel to the glass slide, (89.2 wt% DTAB sample at 95 °C).

Figure 3.2.2.8 Texture observed initially for a 70.7 wt% DTAB sample at 120.3 °C under crossed polarising light, magnification 440.
Figure 3.2.2.9  Texture observed after a period of fifteen minutes for the sample shown in figure 3.2.2.8 under crossed polarising light, magnification 880.

Figure 3.2.2.10  Texture observed initially for a 81.6 wt% DTAB sample at 125 °C under crossed polarising light, magnification 440.
DTAB/water system and were comprised of Debye-Scherer rings which were produced by all domains in the irradiated volume.

The DTAB micellar phase produced a diffraction pattern in the small-angle region comprised of one diffuse ring whose diameter increased with increasing concentration (table 3.2.2.1). The wide-angle scattering showed one diffuse ring located at $2\pi/4.5 = 1.4\ \text{Å}^{-1}$ indicating a liquid-like state for the hydrocarbon chains [24] (see § 2.8).

The diffraction pattern of the hexagonal phase of DTAB is characterised by five sharp rings at small-angles with spacings in the ratios of $1:\sqrt{3}:\sqrt{4}:\sqrt{7}:\sqrt{9}$, which is expected for parallel cylinders packed in a two-dimensional hexagonal array (table 3.2.2.1). As for the micellar phase, the hydrophobic interior of the hexagonal phase is in a liquid-like state.

The cubic phase formed in the DTAB/water system has been found to produce a diffraction pattern with Debye-Scherer rings in the ratios of $\sqrt{6}:\sqrt{8}:\sqrt{14}:\sqrt{16}$ (table 3.2.2.1). The diffraction pattern may be uniquely assigned as arising from the Ia3d space group (i.e. bicontinuous cubic phase $Q^{230}$ (type I) in the notation of Luzzati [23, 27-31]). This cubic phase has also been shown to be related to the Gyroid IPMS [46, 47]. Here the hydrocarbon chains were also found to be in a fluid-like state. Note that the unit cell length calculated for the DTAB cubic phase compares favourably with that obtained by Luzzati et al. [22, 23] and is observed at a similar sample composition and temperature.

The DTAB lamellar phase produces a diffraction pattern at small-angles comprised of three sharp rings in the ratios of $1:2:3$ characteristic of a layered structure. This phase is also found to have molten paraffinic chains.

From the locations of the Bragg peaks, the unit cell dimensions and head group areas for the different phases were determined as described in § 2.8. Table 3.2.2.1 gives the structural parameters obtained (noting that all parameters are determined using an assumed structure (see § 2.8)). All equations were calculated for $T = 27^\circ\text{C}$ unless stated otherwise and based on the specific volume of the hydrocarbon chain which was calculated as described in § 2.8 according to equation 2.8.9.

The results obtained here for the phase behaviour of the DTAB/water system, have been shown to corroborate and extend those obtained by Luzzati et al. [22, 23] and Blackmore and Tiddy [6]. Unfortunately no other results have been published on the phase behaviour above $100^\circ\text{C}$. 
<table>
<thead>
<tr>
<th>DTAB % (w/w)</th>
<th>Phase</th>
<th>Observed Q (Å⁻¹)</th>
<th>Unit Cell Length (Å)</th>
<th>Volume Fraction Φ</th>
<th>Paraffin Chain Thickness (dₚ) (Å)</th>
<th>Water and Head Group Thickness (dₘ) (Å)</th>
<th>Mean Area per Polar Head (Å²)</th>
<th>hkl</th>
</tr>
</thead>
<tbody>
<tr>
<td>35.8</td>
<td>L₁</td>
<td>0.147</td>
<td>—</td>
<td>0.23</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>43.3</td>
<td>L₁</td>
<td>0.158</td>
<td>—</td>
<td>0.28</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>56.0</td>
<td>Hₐ</td>
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a Temperature 41 °C
b Temperature 65 °C
c Temperature 92 °C
3.3 DISCUSSION

From both the optical microscopy and X-ray analysis of the DTAB/water system it was observed that DTAB follows the traditional phase progression predicted for a single-chain surfactant of intermediate chain length and head group area. That is, with increase in concentration the phase progression is one of micellar, hexagonal, cubic and lamellar phases followed by hydrated crystals [48, 49].

How though, is this phase behaviour explained in relation to that observed for a change in hydrocarbon chain length (CTAB) and counterion (DTAC)?

The phase diagram obtained by Balmbra [8] for the CTAB/water system shows that a hexagonal phase is formed at \(-32^\circ C\) and 25 wt\%, a cubic phase at \(-40^\circ C\) and 76 wt\% and a lamellar phase at \(-50^\circ C\) and 87.5 wt\%. Blackmore and Tiddy [6] (who performed concentration gradients only on this system), have observed in addition to the hexagonal, cubic and lamellar phases an intermediate phase which lies between the hexagonal and cubic phases. Here the phase progression is such that the hexagonal phase forms at \(29^\circ C\) and is followed by the formation of an intermediate phase which exists between the temperatures of 48 and 52 \(^\circ C\). A cubic phase at 50 \(^\circ C\) then precedes a lamellar phase which is observed to form at 53 \(^\circ C\). The very small range over which the intermediate phase is formed may account for it being missed in the phase diagram obtained by Balmbra [8].

Both of these studies, though, make no mention of the formation of the gel phase observed by Vincent and Skoulios [50] for this system. The phase was found to form at low temperatures, between -5 and 20 \(^\circ C\) (a temperature region which is often not studied in liquid crystal work) and for water contents below 20 \%. The combination of these three studies leads to the phase progression of micellar, hexagonal, intermediate, cubic, gel and lamellar phases which are followed by the formation of hydrates of CTAB crystals, where the phases are formed at varying temperatures and compositions. This phase progression has also been shown to be typical for surfactants having hydrocarbon chains of this length [6].

By comparison of the DTAB and CTAB results it would appear that a change in the hydrocarbon chain length from a C\(_{12}\) to a C\(_{16}\) significantly alters the self-assembling behaviour of the surfactant. Based purely on an argument of the surfactant parameter [51-54] this is expected. A C\(_{16}\) single-chain surfactant has a different disorder/order transition, as a function of volume fraction and temperature, which affects both the length and volume of the chain differently as compared to a C\(_{12}\) single-chain surfactant. Since the nature of the paraffinic chain is a key determinant in surfactant self-assembly this manifests itself in the observed self-assembly of these surfactants. Hence, it may be concluded that lengthening the hydrocarbon chain promotes the formation of...
intermediate phases and also induces freezing of the paraffinic chains at higher surfactant concentrations. This conclusion was first drawn by Tiddy et al. [6] who contended that there is a definitive variation in the phase progression with change of hydrocarbon chain length. Note that the formation of intermediate phases and the occurrence of freezing of the paraffinic chains for a C_{16} cationic surfactant has also been observed in the hexadecyltrimethylammonium chloride (CTAC, CH_{3}-(CH_{2})_{15}-N+(CH_{3})_{3}Cl)/water system. In this system, two intermediate phases and a lamellar gel phase are observed, for surfactant concentrations of ~68 wt% CTAC and 30 °C, ~75 wt% CTAC and 35 °C and ~77 wt% CTAC and below 40 °C, respectively [7, 55] (see figure 6.2.3.10 for a reproduction of this phase diagram), this will be discussed further below in relation to a change in counterion.

The Krafft temperature and corresponding curve for the CTAB/water system is also observed to be displaced to higher temperatures in comparison to the DTAB/water system following the lower solubility found in general for longer chained surfactants. The trend of increasing insolubility with increasing paraffinic chain length has also been observed for saturated fatty acid soaps [25].

What effects then does a change in counterion induce?

The DTAC/water system is also found to differ from that of the DTAB/water system by the formation of a discrete cubic phase prior to the hexagonal phase (all subsequent phase behaviour being similar in the two systems). The formation of this additional phase can only be attributed to the change in counterion from a bromide to a chloride. The existence of a discrete cubic phase formed prior to formation of the hexagonal phase may be explained by the different effect that a bromide versus chloride counterion has on the growth of the micellar aggregates. It is known [56] that the chloride and bromide ions have different sizes in solution and that the average number of bound water molecules for the bromide ion is 1.5 and that for the chloride ion 2.0 [57]. Therefore, the hydrated chloride ion is larger than the hydrated bromide ion and as such the chloride ion is not as closely associated with the cationic head group of the surfactant and will not be as effective as the bromide counterion at neutralising the head group charge. That is, the complexation equilibrium lies further to the right for the chloride ion over the bromide ion (§ 3.2.1). This will then lead to a greater electrostatic repulsion between the head groups of the surfactants not only within the micellar aggregates but also between the surfactant aggregates themselves. Hence, the surfactant parameter (p) will be greater for the bromide counterion surfactant than for the corresponding chloride (i.e. v/al tends to 1/2 for bromide (cylinders) and to 1/3 for chloride (globules)). This difference in the extent of counterion binding for the two ions has been shown [58] to have an affect on the self-assembly of the surfactant molecules in the form of micellar elongation, where the bromide counterion is known to
promote micellar elongation. As the concentration is increased in the micellar region of
the phase diagram the number of micellar aggregates remains approximately constant
and hence there is an increase in the average aggregation number. This is
accommodated by the formation of rod-like micelles [51-53, 59, 60] which have a
reduced curvature (this then makes formation of a hexagonal phase from the micellar
phase more favourable). The chloride counterion does not induce such an elongation
and instead the size of the micellar aggregates remains approximately constant with the
number of aggregates increasing with increasing surfactant concentration. This
increase in the number of surfactant aggregates induces order upon the system. Hence,
the formation of a discrete cubic phase prior to the hexagonal phase in the DTAC/water
system is favoured. Note that the discrete cubic phase (Pm3n) consists of two types of
micellar aggregates neither of which are spherical in shape. Hence some distortion of
the micellar shape does occur for the chloride counterion with increase of surfactant
concentration but not to the same extent as seen for the bromide counterion.

The effect on the self-assembly of the surfactant induced by the introduction of the
chloride counterion is not restricted to the low concentration regime of the phase
diagram. Comparison of the CTAB and CTAC phase diagrams shows that the extent
and life-time of the gel phase in the CTAC/water system is much larger than that
observed in the CTAB/water system. It has been shown [20] that the more strongly
hydrated the counterion the greater the stiffness of the chains and the stronger the
repulsive interactions between the head groups of the surfactant (this effect is
particularly enhanced for double-chain surfactants). That is, the freezing or melting of
the paraffinic chains (the disorder/order transition) is related in a complex way to the
energy required to hydrate or dehydrate the polar head group and associated
counterions which in turn is related to the electrostatics of the ions (i.e. the counterions
interaction with the surrounding water medium). Hence, in the case of anionic
counterions the effect is enhanced as the degree of hydration is increased.

This change in hydrated ion size has also been studied for cationic ions (Na⁺ and K⁺)
for simple 1:1 electrolytes [61]. This study has shown that there is a considerable
change in the density profile/surface charge for the ion near the "neutral" surface with a
change in size of the ion and that this influences the structuring near the surface.
Hence, assuming that the same behaviour will be observed for anionic ions this can
then be used to explain the increased stability in the gel and intermediate regions found
in the CTAC/water system compared with the CTAB/water system.

The behaviour at high temperatures observed in the DTAB/water system could not be
studied fully due to the experimental difficulties encountered working at this
temperature. A more thorough study needs to be performed where it is possible to
control the temperature to ± 0.1 °C for both the optical microscopy (ensuring that

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samples remain sealed - i.e. there is no leakage) and X-ray diffraction so as to ascertain the nature of the phase transitions occurring above 100 °C. No mention of any unusual behaviour above 100 °C was reported for the DTAC/water system.

3.4 CONCLUSIONS

The DTAB/water phase behaviour presented here completes the series of four quaternary ammonium surfactants : DTAB, DTAC, CTAB and CTAC. From these results it appears that changes in the nature of the surfactant (such as a change in the counterion or chain length) have a severe affect on the subsequent self-assembly in water. But while some general conclusions can be made about the changes which will be induced by altering the characteristics of a surfactant they are not as yet possible to fully predict.
3.5 REFERENCES


Chapter 4

ALLYLDODECYLDIMETHYLAMMONIUM BROMIDE
AND
ALLYLDIDODECYLMETHYLAMMONIUM BROMIDE

4.1 INTRODUCTION

One of the simplest and most widely studied polymerisable moieties is the allyl group, which is based on a single carbon-carbon double bond (R-CH2-CH=CH2). Due to this simplicity, the allyl group has been incorporated into the head group of a single- and a double-chain quaternary ammonium surfactant, yielding allyldodecyldimethylammonium bromide (ADAB, CH3-(CH2)11-N+(CH3)2(CH2-CH=CH2)Br-) and allyldidodecyldimethylammonium bromide (ADDAB, (CH3-(CH2)11)2-N+(CH3)(CH2-CH=CH2)Br-).

A single allyl polymerisable moiety was chosen, despite being known for its resistance to polymerisation (i.e. it is difficult to initiate and termination reactions are often favoured over propagation during polymerisation), since this group is the smallest polymerisable moiety which is able to be used. That is, incorporation of this polymerisable moiety induces the minimal modification to the nature of the surfactant while still being capable of overcoming the electrostatic repulsion between the two head groups for the polymerisation to be performed. Addition of a second allyl polymerisable group (which increases the rate and extent to which polymerisation occurs) has been shown to undergo an intra- and inter-molecular polymerisation to form a six membered ring [1]. Therefore, while this may lead to a slight increase in the stability of the liquid crystalline phases upon
polymerisation (if the underlying geometry is maintained throughout the polymerisation) it also induces a significant perturbation to the monomeric surfactant in comparison with the non-polymerisable analogue. The difference between the nature of the head group in the monomer versus the polymer will also be enlarged. Hence, a single allyl polymerisable moiety only was incorporated into the head group region of the quaternary ammonium surfactants.

Addition of a polymerisable moiety into the head group of a surfactant will have an affect upon the surfactant's self-assembling properties. In the case of the allyl group, there will be an increase in the number of degrees of freedom for the head group of the surfactants. This will lead to surfactant molecules having different head group configurations and hence in affect the surfactant volume and head group area will fluctuate to a larger extent between the molecules, than in a non-polymerisable analogue. This increased flexibility will therefore, alter the inherent rigidity of the surfactant, which is important, since this affects the surfactant's self-assembly. The allyl group will also increase the overall hydrophilicity of the head group due to the presence of the carbon-carbon double bond. Therefore, by direct comparison with analogous non-polymerisable surfactants (dodecyltrimethylammonium bromide (DTAB, CH₃-(CH₂)₁₁-N⁺(CH₃)₃Br⁻) in the case of ADAB and didodecyldimethylammonium bromide (DDAB, (CH₃-(CH₂)₁₁)₂-N⁺(CH₃)₂Br⁻) in the case of ADDAB, where the allyl group has replaced the small hydrophobic methyl group in both surfactants) information on the exact effect that this addition will have upon surfactant self-assembly can be obtained and used to predict the behaviour of new surfactants which contain, this polymerisable moiety.

Not only is it possible to determine the effect of the polymerisable moiety upon self-assembly but since, ADAB and ADDAB are single- and double-chained analogues of each other, comparison of the self-assembling behaviour of the two surfactants can be used to determine the effect of addition of a second hydrocarbon chain.

Therefore, in conjunction with preparing polymers from liquid crystalline phases having defined molecular geometry in one-, two- or three-dimensions, information on the influence of particular changes to the characteristics and subsequent self-assembly of the surfactant may be obtained.

Both ADAB [2-4] and ADDAB [5-8] polymerisable surfactants have been studied previously and polymerised at low concentrations in both isotropic solution (i.e. below the critical micelle (cmc) or critical vesicle concentration (cvc), respectively) and in their aggregated state as micelles or vesicles. Both γ irradiation and thermal initiation using an added initiator were utilised, with the two methods giving conflicting results. The work performed here is, therefore, an extension of these studies, including the full phase behaviour of the surfactants and their polymerisation.
4.2 RESULTS

4.2.1 Physical characterisation of monomeric ADAB and ADDAB

Figures 4.2.1.1 and 4.2.1.2 show the Fourier transform infrared (FTIR) spectra for ADAB and ADDAB, respectively, made up as nujol mulls between NaCl plates. Both spectra show peaks characteristic of the allyl polymerisable moiety: the carbon-hydrogen bond stretching mode at 3015.6 cm\(^{-1}\) and 3003.7 cm\(^{-1}\), where the carbon atom is that involved in the carbon-carbon double bond and the carbon-carbon double bond stretch at 1467.1 cm\(^{-1}\) and 1465.4 cm\(^{-1}\), respectively for ADAB and ADDAB. The fingerprint region of the spectra shows peaks characteristic of the hydrocarbon chains and nitrogen-carbon bonds. Polymerisation may be readily detected by the disappearance of the peaks due to the allyl group during the polymerisation.

The proton and carbon 13 NMR spectra for ADAB and ADDAB (in CDCl\(_3\) using tetramethylsilane (TMS) as an added reference) are shown in figures 4.2.1.3 and 4.2.1.4, respectively. Assignment of the various peaks was based upon integration values and empirical additively rules concerning chemical shifts of substituted alkanes [9, 10]. In the proton NMR spectrum (figure 4.2.1.3 a)) for ADAB the allylic protons appear as a doublet of doublets centred at 5.75 \(\delta\) (CH\(_2\)=CH) and as a multiplet at 5.96 \(\delta\) (CH\(_2\)=CH). The carbon 13 NMR spectrum (figure 4.2.1.3 b)) shows that the two allylic carbons appear at 124.44 \(\delta\) (C=CH\(_2\)) and 129.96 \(\delta\) (CH=CH\(_2\)). Correspondingly, the allylic protons in ADDAB appear as a doublet of doublets at 5.7 \(\delta\) (CH\(_2\)=CH) and a multiplet at 5.9 \(\delta\) (CH\(_2\)=CH, figure 4.2.1.4 a)) and the allylic carbons at 124.60 \(\delta\) (C=CH\(_2\)) and 130.26 \(\delta\) (CH=CH\(_2\), figure 4.2.1.4 b)). See § 2.1 for a complete spectral analysis. Upon polymerisation these peaks will diminish in intensity and eventually disappear once polymerisation is complete, hence, proton NMR spectroscopy was employed as a means of following the rate of polymerisation. The extent to which polymerisation had occurred was determined by comparing the integral values for the vinylic protons to those values for protons which were not effected by the polymerisations. Carbon 13 spectroscopy may also be used to provide information on the types of linkages arising due to polymerisation [11-14].

4.2.2 Determination of the critical micelle concentration for ADAB

Figure 4.2.2.1 shows the curve obtained from surface tension measurements performed on aqueous ADAB solutions at 25 °C using the du Noüy ring method (see § 2.5 for experimental details). Aggregation of the surfactant molecules, is detected by the change in slope and subsequent plateau of the experimental curve, giving a direct measurement of the surfactant's cmc. For the ADAB/water system a polynomial of degree three, having a
correlation coefficient equal to 0.997, was an adequate fit to the data points obtained prior to the concentration at which aggregation occurred, using this fit the cmc was determined to be equal to $1.08 \times 10^{-2}$ M. The surface excess concentration was calculated from the slope of the pre-micellisation curve close to the cmc using equation 2.5.20 (since ADAB is a cationic surfactant) and the area per polar head group at the interface from equation 2.5.21. Hence, for the ADAB/water system the surface excess concentration of ADAB is $2.9 \pm 0.1 \times 10^{-6}$ mol.m$^{-2}$ and the area per polar head group is equal to $58 \pm 1$ Å$^2$.

![Figure 4.2.1.1 Fourier transform infrared spectrum of monomeric ADAB.](image1)

![Figure 4.2.1.2 Fourier transform infrared spectrum of monomeric ADDAB.](image2)
Figure 4.2.1.3 a) Proton and b) Carbon 13 NMR spectrum for monomeric ADAB in CDC$_3$ using TMS as an added reference.
Figure 4.2.1.4  a) Proton and b) Carbon 13 NMR spectrum for monomeric ADDAB in CDCl₃ using TMS as an added reference.
The electrical conductivity curve obtained for ADAB in water at 25 °C is shown in figure 4.2.2.2. The curve shows a distinct break at a concentration of 1.20x10^{-2} M ADAB corresponding to the initiation of surfactant aggregation, in good agreement with the value obtained from surface tension measurements. Determination of the percentage dissociation of the bromide counterion (β) was obtained using three different methods (see § 2.4). Firstly, using the ratio of the slopes of the two linear regions of the curve gave a value of β of 27.2 %. If instead equation 2.4.24 is employed with n = 44 as calculated from equation 2.4.15 (where \( M = 169, \rho = 0.80 \text{ g cm}^{-3} \) and \( l = 15.42 \text{ Å} \)) \( \beta \) is determined to be 27.3 %. The third method utilises the area per head group calculated from the surface tension measurements described above from which a value of n equal to 52 was determined, using this value, the percentage dissociation was found to be equal to 26.9 %. Again as was shown in the DTAB/water system the different methods used in calculating a value for the percentage dissociation give comparable results.

*Figure 4.2.2.1* Surface tension of the ADAB/water system, measured by the du Noüy ring method at 25 °C. Errors in the measurements are indicated by the size of the data points.
The values determined for the cmc of ADAB using specific conductivity and surface tension measurements compare favourably with the value obtained by Paleos et al. [2] (cmc(ADAB) = 1.25x10^{-2} M, at 25 °C) using electrical conductivity measurements only.

Both conductivity and surface pressure-area isotherm measurements were performed for ADDAB to determine the surfactant's cvc and head group area. Conductivity measurements were irreproducible due to inaccuracy in the determined concentration and loss of surfactant via adsorption to vessel walls. This is a consequence of the very low concentration at which vesicles are first formed in the ADDAB/water system (∼10^{-6} M). Surface pressure-area isotherm measurements also proved to be unsuccessful since the monolayer was found to not collapse due to ADDAB being too water soluble. Hence, the cvc and head group area at low concentrations of ADDAB could not be determined by these techniques.
4.2.3 Self-assembly of ADAB

The self-assembling behaviour for the ADAB/water system determined from this study is shown, by way of a schematic diagram, in figure 4.2.3.1.

After formation of a micellar phase ($L_1$, which exists as a one phase region up to 47.5 wt% ADAB) the system undergoes a first order phase transition yielding a normal hexagonal phase ($H_\alpha$) existing over a wide temperature and concentration range (48.8 to 83.4 wt% ADAB). When a composition of 83.4 wt% ADAB is reached a cubic phase ($Q_\alpha$) forms. No two phase region was observed between the hexagonal and cubic phases indicating that the transition is either weakly first order or second order. The cubic phase is then transformed into a normal lamellar phase ($L_\alpha$) following a first order phase transition.

**Figure 4.2.3.1** Partial binary phase diagram of the ADAB/water system. $L_1$: micellar solution, $H_\alpha$: hexagonal phase, $Q_\alpha$: bicontinuous cubic phase (type $Q^{230}$, Ia3d or Gyroid IPMS), $L_\alpha$: lamellar phase, Isotropic fluid: random packing of surfactant aggregates, and crystals: hydrated ADAB crystals. Horizontally shaded areas (showing tie lines) indicate regions where two liquid crystalline phases coexist, diagonally shaded areas indicate regions where a liquid crystalline phase coexists with hydrated crystals of ADAB and dashed lines indicate either a weakly first order or second order phase transition.
transition yielding a pure $L_\alpha$ phase at 94.1 wt% ADAB. As the temperature is increased the lamellar phase melts to give an isotropic fluid whose structure is unknown but which is most probably a highly concentrated reverse micellar phase. At higher compositions the $L_\alpha$ phase coexists with hydrated ADAB crystals (the extent and number of these crystalline hydrates were not investigated).

Figure 4.2.3.2 shows the birefringent and isotropic bands observed during a concentration gradient performed at 30 °C when viewed under crossed polarising filters indicating the formation of the hexagonal, cubic and lamellar phases with increasing ADAB concentration.

The texture shown in figure 4.2.3.3 is one typically found to form by the hexagonal phase of the ADAB/water system and is observed from both concentration gradients and bulk samples. The texture is similar to that observed for the hexagonal phase of the DTAB/water system (figure 3.2.2.5) where the cylinders lie parallel to the glass slide. Note that, in the ADAB/water system the phase is less highly oriented and that the curvature of the cylindrical aggregates varies discontinuously about the line disclination of order $s = +1/2$, as is evidenced by the splaying out of the brushes of the fan. The hexagonal phase is extremely stable to changes in composition and temperature and is very viscous. In comparison the cubic phase was observed to melt to an isotropic fluid at 62.8 °C and the compositional range over which it was observed was also thus reduced compared with the hexagonal phase.

A typical "mosaic" texture [15-18] observed for the ADAB lamellar liquid crystalline phase from both bulk samples and concentration gradients is shown in figure 4.2.3.4, this may be compared directly with the texture formed by the DTAB lamellar phase (figure 3.2.2.7), indicating that both phases have a similar surfactant geometry and orientation.

The phase behaviour observed in the ADAB/water system was confirmed using small angle X-ray scattering (SAXS). Diffraction patterns were obtained for powdered bulk samples in each of the mesophases of the ADAB/water system and were comprised of Debye-Scherer rings which were produced by all domains in the irradiated volume.

Samples within the micellar region of the ADAB/water system produced one diffuse ring at small-angles upon irradiation with X-rays (table 4.2.3.1) and one diffuse ring ($Q = 1.4 \text{ Å}^{-1}$) at wide-angles indicative of fluid-like chains, these diffraction patterns being typical for randomly distributed micellar aggregates [19].

Diffraction patterns obtained in the small-angle region for the hexagonal liquid crystalline phase of ADAB consisted of from three to five Debye-Scherer rings which were in the ratio of $1:\sqrt{3}:\sqrt{4}:\sqrt{7}:\sqrt{9}$ (table 4.2.3.1) as expected for parallel cylinders packed in a two-
Figure 4.2.3.2 30 °C concentration gradient of the ADAB/water system viewed under polarised light, magnification 440. The variable birefringent bands show the hexagonal, cubic and lamellar phases (left to right).

Figure 4.2.3.3 Optical texture observed for the ADAB hexagonal phase (75.7 wt% ADAB, 30 °C, crossed polarising filters, magnification 440). Cylinders lie parallel to the glass slide and the brushes correspond to line disclinations of strength s = + 1/2. Note that the brushes of the fans are splayed corresponding to discontinuous curvature of the hexagonal cylinders about the line disclinations.
Table 4.2.3.1 Structural parameters determined for the ADAB/water mesophases at $T = 27 \degree C$

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a Temperature 8 °C.
Figure 4.2.3.4  Mosaic texture of the ADAB lamellar phase (crossed polarising filters, magnification 440). The layers comprising the phase lie parallel to the glass slide, (95.1 wt% ADAB sample at 45 °C).

dimensional hexagonal array. As for the micellar phase, the paraffinic chains were found to be fluid-like [19].

The ADAB cubic phase is characterised by up to four sharp rings at small-angles with spacings in the ratios of \(\sqrt{6}:\sqrt{8}:\sqrt{14}:\sqrt{16}\) as expected for a bicontinuous cubic phase of type Ia3d (type I, space group 230 also known as the Gyroid infinite periodic minimal surface (IPMS) [20-26]). The wide-angle scattering was also found to show one diffuse ring indicating a liquid-like state for the paraffinic chains.

The diffraction pattern for the lamellar phase of ADAB is comprised at small-angles by four sharp rings having Q values in the ratios of 1:2:3:4, this pattern being characteristic of a one-dimensional layered structure; again the paraffinic chains were found to be fluid.

Structural parameters for the different liquid crystalline phases formed in the ADAB/water system are given in table 4.2.3.1. All calculations were determined for \(T = 27 \, ^\circ\text{C}\) unless otherwise stated. The specific volume of the hydrocarbon chains was used in all calculations and was determined as described in § 2.8 according to equation 2.8.9.

From calculations of the head group area in the various ADAB mesophases it is seen that, as the concentration of the surfactant increases the amount of water taken up by the head
groups of the surfactant as water of hydration decreases as does the electrostatic interactions between the head groups. This leads to a subsequent decrease in the head group area, as expected.

Evidence for the bicontinuity of the cubic phase found in this system was obtained using water self-diffusion proton NMR spectroscopy (performed at Physical Chemistry 1, University of Lund, Sweden, see § 2.2 for experimental details). From the SAXS results the water plus head group thickness in the ADAB cubic phase is of the order of 13 Å, this layer will include, of course, bound and unbound counterions, hydrated and non-hydrated head groups and free water. The water self-diffusion coefficient as measured in the ADAB cubic phase should be significantly reduced from that in water and this is indeed found to be true. Results for an 88.0 wt% ADAB sample are shown in figure 4.2.3.5. The diffusion coefficient for the water is calculated to be $1.53 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$, from equation 2.2.3. The self-diffusion coefficient for water in water at 25 °C has been determined by Mills [27] to be $2.299 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$. This value will be reduced once the water is impeded whether by obstruction or hydration effects. Hence, as the concentration of the surfactant is increased the water self-diffusion coefficient will be concomitantly reduced. Therefore, although in a bicontinuous cubic phase the water channels are continuous, the water self-diffusion coefficient will be considerably reduced from the value determined for water in water, particularly for cubic phases formed at high surfactant composition as is the case in the ADAB/water system. It has been determined that the ratio of $D_{\text{obs}}$ versus $D_{\text{D}_{2}O}$ for the discrete and bicontinuous cubic phases in the octaethyleneglycol mono n-dodecyl ether (C$_{12}$EO$_{8}$, CH$_{3}$-(CH$_{2}$)$_{11}$-(O-CH$_{2}$-CH$_{2}$)$_{8}$OH)/heavy water system (at approximately 35 and 70 wt% C$_{12}$EO$_{8}$, Pm3n and Ia3d, respectively) at 25 °C are 0.50 and 0.15, respectively [28]. Similarly, in the monoolein/heavy water system the ratio for the bicontinuous cubic phase (type Ia3d) of composition 75 wt% monoolein at 25 °C is ca. 0.2 [29]. Hence, the value obtained here (for the Ia3d ADAB cubic phase (88 wt% ADAB)) of 0.07 compares favourably with those obtained for other similar bicontinuous cubic phases and is significantly reduced as compared with a discrete cubic phase (Pm3n).

### 4.2.4 Self-assembly of ADDAB

A consequence of ADDAB having two hydrocarbon chains is that the geometries which it is able to adopt are restricted. Here, the surfactant parameter v/αl [30-32] is approximately equal to one and the surfactant should, therefore, spontaneously form mesophases built using bilayers as the fundamental building blocks. This tendency for the surfactant to form bilayer structures means that the probability of formation of a hexagonal or cubic phase in the binary ADDAB/water system is greatly reduced and indeed these liquid crystalline phases are not formed in this system.
Figure 4.2.3.5 Water self-diffusion proton NMR studies of an 88.0 wt% cubic phase sample of ADAB, errors are indicated by the size of the data points.

Figure 4.2.4.1. shows the partial phase diagram for the binary system of ADDAB in water as determined in this study. Two liquid crystalline phases only are formed between 20 and 100 °C, both consisting of bilayers as their fundamental building blocks. At concentrations below 3.2 wt% ADDAB an isotropic fluid (L) is formed which due to the double-chained nature of the surfactant is most probably comprised of vesicles. As the concentration is increased the vesicular phase is found to coexist with a birefringent phase consisting of bilayers intercalated with large water regions (Lx). This birefringent phase exists as a single phase between 8.8 and 42.7 wt% ADDAB. At ADDAB compositions above 76.1 wt% a normal lamellar phase is formed (planar bilayers intercalated with water, L_α) which melts to give an isotropic fluid at 57.8 °C. Between 42.7 and 76.1 wt% ADDAB the two lamellar phases coexist. It should be noted that the density of these phases differ markedly, with L_χ being denser than both L and L_α.
Evidence for the coexistence of two distinct lamellar phases was obtained by performing deuterium quadrupolar NMR studies upon samples prepared with deuterated water (see § 2.2 for experimental details). Note that changing the solvent from $\text{H}_2\text{O}$ to $\text{D}_2\text{O}$ may have an effect on the phase boundaries of the different liquid crystalline phases observed in the ADDAB/water system but the observed phase progression should not be altered (i.e. both the $L_\chi$ and $L_\alpha$ phases should still be formed and transform via a first order phase transition).

Figure 4.2.4.2 shows the spectra obtained for some characteristic regions of the phase diagram shown in Figure 4.2.4.1. Full splitting results are shown in Figure 4.2.4.3. From these results it is indicated that a first order phase transition between the $L_\chi$ and $L_\alpha$ phases occurs.
Figure 4.2.4.2 D$_2$O deuterium quadrupole NMR spectra for the binary ADDAB/D$_2$O system at 25 °C. a) 35.0 wt% ADDAB (one phase, L$_\chi$), b) 60.2 wt% ADDAB (two phase region, L$_\chi$ + L$_\alpha$), c) 75.6 wt% ADDAB (two phase region, L$_\chi$ + L$_\alpha$), d) 89.3 wt% ADDAB (one phase, L$_\alpha$).

In addition to showing that there is a first order phase transition between the L$_\chi$ and L$_\alpha$ phases, information on the underlying global geometry is also able to be obtained. The value of the measured quadrupole splitting is dependent upon the interaction of the phase with the applied magnetic field. This overall interaction is comprised of three individual components that are due to [33]:

- the average orientation of the surfactant mesophase,
- the variation of the orientation of the D$_2$O molecules at the interface, and
- the variation of the orientation of the surfactant molecules in the aggregate (i.e. the curvature of the interface).

For a powder sample the first contribution is a constant and the second variation is averaged out. Hence, the quadrupole splitting within a given surfactant/D$_2$O system is determined by the extent of curvature of the surfactant aggregates [33]. For example, the normal hexagonal phase has a quadrupole splitting of approximately a factor two less than
the corresponding lamellar phase splitting which is a direct consequence of the curvature inherent in the surfactant aggregates of the hexagonal phase as compared with the planar bilayers of the lamellar phase [34]. Therefore, in the case of the \( L_\chi \) and \( L_\alpha \) phases of the ADDAB/D\(_2\)O system where the quadrupole splitting of the \( L_\alpha \) phase is approximately a factor three greater than in the \( L_\chi \) phase (in the two phase region, see figure 4.2.4.3) this indicates that the \( L_\chi \) phase has a high degree of curvature and cannot be described as consisting of planar bilayers. Note that the measured value of approximately 1750 Hz for the \( L_\alpha \) phase is comparable with that of other planar bilayer lamellar phases [35].

![Graph](image)

*Figure 4.2.4.3* \( D_2O \) deuterium quadrupolar NMR splitting for the ADDAB/D\(_2\)O system at 25 °C, errors are indicated by the size of the data points.

Figure 4.2.4.4 shows the optical textures observed during a 30 °C concentration gradient. This photograph shows that an isotropic phase is initially formed which then transforms into a birefringent phase at higher surfactant compositions producing a texture which is atypical for normal lamellar phases (\( L_\alpha \)) consisting of planar bilayers. How this texture correlates to the underlying geometry of the surfactant molecules will be explained in § 4.3.2. It should be noted though that as the concentration of surfactant increases (from left to right in the figure) the texture initially one of maltese crosses (which are spherical
on average) superimposed with one to three dark concentric circles becomes comprised of elongated crosses which finally become completely drawn out. Since this texture has been produced during a concentration gradient, where the molecules are easily oriented by the constrictions imposed on them by the glass slide and cover slip during formation of the liquid crystalline phases, more information is usually able to be obtained from the optical textures produced under these conditions than from a texture observed from a bulk sample, where orientational ordering has not been imposed during the growth of the phase. This supposition is supported by the optical texture shown in figure 4.2.4.5 under crossed polarising filters for a 25.3 wt% ADDAB sample (L_X phase). Here the information observed for this phase in figure 4.2.4.4 is almost completely lost with only one or two individual maltese crosses being evident though it is still possible to discern the superimposed concentric dark bands. Again, the texture is not typical of a normal planar bilayer lamellar phase. This diluted lamellar phase is also found to be of low viscosity and is highly coloured/iridescent when bulk samples are viewed through crossed polarising sheets, indicating that there may be some microcrystalline order which is comparable to the wavelength of light.

Figure 4.2.4.4 30 °C concentration gradient of the ADDAB/water system viewed under crossed polarised light, magnification 440. The variation in the texture observed with increase in concentration (left to right) shows the formation of the lower ADDAB composition lamellar phase (L_y). Note the maltese crosses which are superimposed with dark concentric circles.
In contrast, the texture shown in figure 4.2.4.6 for a bulk sample in the L_α phase of the ADDAB/water system (85.3 wt%, 35 °C) is a typical mosaic texture often observed for normal lamellar phases consisting of planar bilayers intercalated with water with both positive and negative units [15] being apparent (compare with the texture observed for the L_α phase of ADAB, figure 4.2.3.4).

Hence, from the optical microscopy and D_2O deuterium quadrupole NMR results the lamellar phase formed at low ADDAB concentrations (L_x) does not consist of planar bilayers intercalated with water where the low concentration lamellar phase is a mere dilution of the highly concentrated phase (the relationship between these two phases will be discussed in § 4.3.2).

As further evidence for the existence of two distinct birefringent phases whose fundamental building blocks are bilayers, SAXS measurements were performed to determine the structures of the phases. Samples in both birefringent phases gave diffraction patterns comprised of Debye-Scherer rings which were produced by all domains in the irradiated volume.

The ADDAB low concentration lamellar phase (L_x) is characterised by a series of sharp rings at small-angles with Q values in the ratios of 1:2:3:4:5:6. Similarly in the high composition lamellar phase (L_α) the small-angle diffraction pattern consists of Bragg peaks in the ratios of 1:2:3:4. Despite both lamellar phases giving rise to diffraction patterns consistent with normal planar bilayers (i.e. Bragg peaks in the ratio of 1:2:3...), calculation of the head group area of the two phases assuming infinite flat bilayers (which is the major assumption made for calculation of head group areas of a lamellar phase, see § 2.8) shows that the head group area actually increases during the phase transition from L_x to L_α. An increase in head group area with increase in surfactant concentration leading to a phase transition is unlikely [19] hence, the lower composition lamellar phase cannot be comprised of infinite planar bilayers which is consistent with the results obtained from both optical microscopy and D_2O deuterium quadrupole NMR. A full interpretation of these results will be given in § 4.3.2. Table 4.2.4.1 gives the structural parameters calculated for the two lamellar liquid crystalline phases formed in the ADDAB/water system. All calculations were determined for T = 27 °C, the specific volume of the hydrocarbon chains was used in all calculations and was determined as described in § 2.8 according to equation 2.8.9.

4.2.5 Polymerisation of monomeric ADAB and ADDAB

Attempts to polymerise both ADAB and ADDAB in an isotropic state, in order to characterise the polymers self-assembly and compare it with that observed for the
Figure 4.2.4.5 Texture observed for a bulk sample of the ADDAB low ADDAB composition lamellar phase ($L_y$, 25.3 wt% ADAB, 30 °C, crossed polarising filters, magnification 440). Note the individual maltese crosses which are visible and the superimposed dark concentric circles.

Figure 4.2.4.6 Mosaic texture of the ADDAB normal lamellar phase ($L_{oo}$, crossed polarising filters, magnification 440). The layers comprising the phase lie parallel to the glass slide, (85.3 wt% ADAB sample at 35 °C).
Table 4.2.4.1 Structural parameters for the ADDAB/water system at 27 °C

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a Calculated assuming infinite flat bilayers.

monomeric form, were unsuccessful using both thermal initiation via AIBN (10 mol% to surfactant) and photochemical irradiation (where the surfactant was dissolved in chloroform at a concentration of 0.25 M). Exposure times ranged from one day to two weeks. ADDAB was found to polymerise to less than 5 % whereas, although, ADAB polymerised to approximately 30 % it was also found to decompose during the polymerisation (solutions became bright yellow and NMR analysis showed that the integrity of approximately 5 % of the surfactant was not maintained during the polymerisation). Attempted purification of polymeric ADAB was unsuccessful and unfortunately no further work could be performed on the polymeric forms of ADAB or ADDAB.
4.2.6 Polymerisation of liquid crystalline phases

The two different lamellar phases (25 and 85 wt% ADDAB, $L_X$ and $L_a$, respectively) of the ADDAB/water system were polymerised in an attempt to maintain the underlying surfactant geometry upon polymerisation. Unfortunately as for the isotropic polymerisation of ADDAB, polymerisation of the liquid crystalline phases formed by this surfactant was unsuccessful using both thermal and photochemical initiation over a time period of one day to four weeks. Hence, formation of the liquid crystalline phases had no influence over the polymerisation in this case (i.e. there was no enhancement of the extent of polymerisation due to favourable alignment of the surfactant molecules imposed by the liquid crystalline phase geometry).

In the ADAB/water system five regions from the phase diagram were chosen for polymerisation, corresponding to the dilute and concentrated regions of the micellar phase (5 and 40 wt% ADAB), the hexagonal phase (65 wt% ADAB), the cubic phase (88 wt% ADAB) and the lamellar phase (95 wt% ADAB). Ampoules for polymerisation were prepared as described in § 2.9. Thermal initiation was activated at 50 °C due to the cubic and lamellar phases melting at approximately 60 °C. No problems due to the surfactant self-initiating during equilibration of the liquid crystalline phases was experienced.

Table 4.2.6.1 shows the percentage conversions for the five regions of the ADAB/water phase diagram activated by thermal initiation of added AIBN (10 mol% to surfactant). The corresponding results for photochemical initiation are given in table 4.2.6.2.

These results indicate that, polymerisation which has been activated either thermally via an added initiator or photochemically, give almost identical results, i.e. there is no influence by the type of initiation on the extent to which polymerisation occurs. There is also no trend of increasing polymerisation with time for either forms of initiation. Table 4.2.6.3 gives the calculated median and mean for the polymerisations in the different liquid crystalline phases. All samples polymerise to approximately 30 % which is comparable with the results obtained for polymerisation in an isotropic state in chloroform. Therefore, as well as the type of initiation having no influence on the extent of polymerisation, the packing of the surfactant molecules does not change the yield of the polymer formed. It should be noted, that the higher ADAB composition phases were found to decompose during polymerisation when activated thermally (solutions became bright yellow or orange and NMR analysis showed that the integrity of approximately 5 % of the surfactant was not maintained during the polymerisation).

To determine if the underlying surfactant geometry was maintained during the polymerisation, SAXS experiments were performed on the samples after polymerisation had occurred. All samples studied were initiated photochemically, due to the decomposition of the samples during thermal initiation and were exposed for a period of two days.
Table 4.2.6.1 Percentage conversions for the five regions from the ADAB/water phase diagram polymerised thermally

<table>
<thead>
<tr>
<th>Time (days)</th>
<th>Low Weight</th>
<th>High Weight</th>
<th>Hexagonal</th>
<th>Cubic Phase</th>
<th>Lamellar Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Percent Micellar Solution</td>
<td>Percent Micellar Solution</td>
<td>Phase</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.25</td>
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<td>—</td>
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<tr>
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<td>37.2</td>
<td>39.4</td>
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<tr>
<td>31</td>
<td>24.2</td>
<td>25.2</td>
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</tr>
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</table>

Table 4.2.6.2 Percentage conversions for the five regions of the ADAB/water phase diagram polymerised photochemically

<table>
<thead>
<tr>
<th>Time (days)</th>
<th>Low Weight</th>
<th>High Weight</th>
<th>Hexagonal</th>
<th>Cubic Phase</th>
<th>Lamellar Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Percent Micellar Solution</td>
<td>Percent Micellar Solution</td>
<td>Phase</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.25</td>
<td>—</td>
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<td>—</td>
<td>33.5</td>
<td>32.6</td>
</tr>
<tr>
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<td>30.0</td>
<td>27.1</td>
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<tr>
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</tr>
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<td>22.7</td>
<td>33.6</td>
<td>27.3</td>
<td>—</td>
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<tr>
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<td>—</td>
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</tr>
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</tr>
<tr>
<td>16</td>
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<td>35.5</td>
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<td>—</td>
</tr>
<tr>
<td>19</td>
<td>29.6</td>
<td>31.4</td>
<td>28.7</td>
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Table 4.2.6.3  Statistics of the extent of polymerisation for the five ADAB liquid crystalline phases

<table>
<thead>
<tr>
<th></th>
<th>Low Weight Percent Micellar Solution</th>
<th>High Weight Percent Micellar Solution</th>
<th>Hexagonal Phase</th>
<th>Cubic Phase</th>
<th>Lamellar Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal Initiation</td>
<td>median 24.6</td>
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<td>23.1</td>
<td>30.8</td>
<td>28.9</td>
</tr>
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<td>mean 24.2</td>
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<td>22.6</td>
<td>29.1</td>
<td>27.8</td>
</tr>
<tr>
<td></td>
<td>standard deviation 4.0</td>
<td>3.6</td>
<td>3.1</td>
<td>6.4</td>
<td>6.8</td>
</tr>
<tr>
<td>Photochemical Initiation</td>
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<td>33.6</td>
<td>29.1</td>
<td>27.8</td>
</tr>
<tr>
<td></td>
<td>mean 28.4</td>
<td>29.0</td>
<td>31.9</td>
<td>29.1</td>
<td>29.2</td>
</tr>
<tr>
<td></td>
<td>standard deviation 4.7</td>
<td>4.4</td>
<td>3.7</td>
<td>2.5</td>
<td>3.4</td>
</tr>
</tbody>
</table>

Samples in the concentrated micellar region were found to produce diffraction patterns having one diffuse ring only at both small- and wide-angles. Comparison with the diffraction pattern obtained for a monomeric sample (table 4.2.3.1) shows that there is little difference between the average distance between the micellar aggregates in the partially polymerised and non-polymerised systems. Hence, formation of the ADAB polymer had little affect on the characteristics of the micellar solution.

In contrast the hexagonal, cubic and lamellar phases all showed in conjunction with the sharp Bragg peaks attributable to non-polymerised ADAB, retaining the original monomeric surfactant geometry, two inner diffuse rings. Calculation of structural parameters for what is assumed to be a structure now comprised of a non-polymerised surfactant matrix interwoven with polymer chains is given in table 4.2.6.4, all equations were calculated for $T = 27 \, ^\circ C$. Unit cell lengths and head group areas for the different phases were calculated assuming that the non-polymerised surfactant forming the hexagonal, cubic or lamellar matrix retains the original ratio of surfactant to water during the polymerisation. Comparison of the calculated values for the partially polymerised systems (table 4.2.6.4) with the monomeric values (table 4.2.3.1) shows that the presence of the interwoven polymer chains throughout the monomeric matrix has not disturbed significantly the packing of the surfactant molecules. Indeed, it has been
determined that both the cubic and lamellar phases have an increased stability of approximately 20 °C due to the presence of the interwoven polymer chains and that the textures observed for the birefringent phases are comparable to those observed when no polymer was present. Figures 4.2.6.1 and 4.2.6.2 show the optical textures for the partially polymerised hexagonal and lamellar phases, respectively. These figures can be compared with the optical textures observed for the non-polymerised phases (figures 4.2.3.3 and 4.2.3.4). Hence, although the polymer has not been fully incorporated into the monomeric matrix (i.e. the surfactant molecules have not maintained their original geometry) polymerisation has increased the stability of the phases significantly.

Table 4.2.6.4 Structural parameters for the polymeric liquid crystalline phases of ADAB at $T = 27 \degree$C

<table>
<thead>
<tr>
<th>ADAB (w/w)</th>
<th>Phase</th>
<th>Observed Q</th>
<th>Unit Cell Length (Å)</th>
<th>Volume Fraction</th>
<th>Paraffin Chain Thickness ($d_p$)</th>
<th>Water and Head Group Thickness ($d_w$)</th>
<th>Mean Area per Polar Head (Å$^2$)</th>
<th>hkl</th>
</tr>
</thead>
<tbody>
<tr>
<td>40.0</td>
<td>L$_1$</td>
<td>0.153</td>
<td>—</td>
<td>0.24</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td></td>
</tr>
<tr>
<td>63.1</td>
<td>H$_{\alpha}$</td>
<td>0.069$^a$</td>
<td>0.120$^a$</td>
<td>0.178</td>
<td>0.307</td>
<td>0.355</td>
<td>40.8$^b$</td>
<td>0.37$^b$</td>
</tr>
<tr>
<td>90.0</td>
<td>Q$_{\alpha}$ (1a3d)</td>
<td>0.074$^a$</td>
<td>0.130$^a$</td>
<td>0.203</td>
<td>0.234</td>
<td>0.312</td>
<td>75.7</td>
<td>0.51</td>
</tr>
<tr>
<td>95.0</td>
<td>L$_{\alpha}$</td>
<td>0.081$^a$</td>
<td>0.142$^a$</td>
<td>0.213</td>
<td>0.425</td>
<td>0.635</td>
<td>29.5$^c$</td>
<td>0.54$^c$</td>
</tr>
</tbody>
</table>

a  Diffuse inner rings due to interwoven polymer chains.
b  Calculated assuming that the remaining monomeric surfactant forming the hexagonal phase is still at a composition of 63.1 wt%.
c  Calculated assuming that the remaining monomeric surfactant forming the lamellar phase is still at a composition of 95.0 wt%.
Figure 4.2.6.1 Optical texture observed for the partially polymerised ADAB hexagonal phase (63.1 wt% ADAB, 30 °C, crossed polarising filters, magnification 440). Note that the sample is more highly disordered and that the intense colouration is due to an increased thickness of the sample, (compare with figure 4.2.3.3).

Figure 4.2.6.2 Mosaic texture of the partially polymerised ADAB lamellar phase (crossed polarising filters, magnification 440). The layers comprising the phase lie parallel to the glass slide, (95.0 wt% ADAB sample at 25 °C, compare with figure 4.2.3.4).
4.3 DISCUSSION

4.3.1 ADAB

Incorporation of the allyl polymerisable moiety into a single-chain quaternary ammonium surfactant has been found to have a considerable effect upon the surfactant's self-assembling behaviour.

From the electrical conductivity and surface tension measurements performed on ADAB (§ 4.2.2) and its non-polymerisable analogue DTAB (see § 3.2.1) it can be shown that addition of the allyl group changes the interactions between the surfactant molecules. Such that, both the concentration at which aggregation begins and the extent of dissociation of the bromide counterion are decreased slightly. That is, the interactions between the surfactant molecules are more favourable due to the presence of the allyl group, which also induces a slight reduction in the overall charge of the micellar aggregates (i.e. the allyl group, in effect reduces the electrostatic interactions between the head groups of the amphiphiles which is important since this interaction is one of the dominant interactions to be overcome during polymerisation).

Not only is the aggregation at low concentrations affected by this change in the nature of the surfactant but indeed its self-assembly over all surfactant compositions is altered. Comparison of the phase diagrams for the ADAB/water system (figure 4.2.3.1) and the DTAB/water system (figure 3.2.2.1) shows that the presence of the allyl group induces an increase in the solubility of the surfactant in water but a corresponding decrease in the stability of the concentrated liquid crystalline phases formed. Note that the concentrated phases are now accessible at room temperature, which therefore increases their availability for other applications. Although the phase progression for the two surfactants with increasing concentration is identical there are in fact striking differences between them. The first, most obvious difference are the regions in the diagram where the different phases are formed. A pure hexagonal phase is not observed until 56.0 wt% DTAB whereas in the ADAB system it is found to form at 48.8 wt%. This shift to lower compositions may be induced by the increased bromide counterion binding. The bromide counterion is known [36] to promote elongation of the micellar aggregates and hence, even a slight decrease in the extent of dissociation could lead to sufficient elongation such that, the hexagonal phase is stable at lower surfactant compositions.

The cubic phase formed from the hexagonal phase via a first order phase transition in the DTAB/water system is formed via either a weakly first order or a second order phase transition in the ADAB/water system and is formed at lower temperatures. This significant change can only be attributed to the presence of the allyl polymerisable group, which changes the overall rigidity, hydrophilicility and charge of the head group. These naturally affect both the head group area and the length and flexibility of the hydrocarbon
chain, since, both of these parameters are strongly influenced by the extent of hydration and counterion binding. Hence, even a seemingly small change to the nature of the surfactant by way of replacing a methyl group with an allyl group alters the balance of the interactions between amphiphiles significantly.

Why is the extent to which polymerisation occurs in both isotropic and self-assembled forms so low?

It has been shown [1, 37-42] that polymerisation of unsaturated non-amphiphilic quaternary ammonium compounds is extremely difficult and that thermal polymerisation in aqueous solution using water soluble initiators is not possible for monomers containing only one allyl group.

Results obtained here show that, it is possible to polymerise a quaternary ammonium surfactant containing one allyl group either in chloroform (where the surfactant is not self-assembled but does have a preferential alignment) or in water in a self-assembled state, where the extent of polymerisation in all cases is approximately 30%. Hence, addition of a hydrocarbon chain introducing an amphiphilic nature into the compound and the ability for the molecules to align preferentially leading to more favourable interactions between the molecules enables polymerisation to occur. Although, the extent of polymerisation is still very low due to the intrinsic resistance to polymerisation of the allyl group and also its placement near the charged center of the surfactant which introduces an electrostatic interaction, inhibiting polymerisation. It was found that increasing the length of the reaction time did not increase the extent of polymerisation, therefore, polymerisation is very rapid and reaches a plateau almost immediately.

The reason for the low conversion must therefore be a consequence of:

a) the rate constant for formation of a free radical from the allyl monomer being slow and/or the activation barrier being very high (note that this is now also influenced by the nearness of the electrostatic centre),

b) recombination to form the original carbon-carbon double bond prior to propagation is favourable (i.e. the time required for reformation of the original carbon-carbon double bond is not sufficient for a second carbon-carbon double bond to be found in the correct orientation for propagation to occur), and

c) the rate constants for the termination reactions are faster than those for the propagation steps (see § 2.9.1).

Therefore, the molecular weight of these polymers is expected to be low, this has indeed been found; molecular weights of the polymers formed using either thermal or photochemical initiation from self-assembled or isotropic states were less than 8000 as determined from dialysis experiments.
Paleos et al. [2-4] have shown, that polymerisation of ADAB both above and below its cmc using thermal initiation (added AIBN) and γ irradiation gave conflicting results. It was stated that by using γ irradiation polymerisation was effective within 48 hours (with the extent of polymerisation increasing with time) at a dose rate of 2300 rad.min⁻¹. Polymerisation of an isotropic solution by γ irradiation lead to complete decomposition of the surfactant whereas in the micellar state no decomposition occurred and molecular weight determinations showed that the average polymer chain contained approximately thirty monomer units (which is comparable with the micellar aggregation number at low surfactant concentrations), compared with a maximum of twenty as determined here for all self-assembled and isotropic forms. In contrast, polymerisations via thermal initiation gave irreproducible results and were abandoned [2-4]. These results are incommensurate with both the results obtained here and those observed in the study by Butler et al. [1, 37-42]. Also the large increase in the extent to which polymerisation occurs when γ irradiation is used was not explained - a brief trial, performed here, using γ irradiation on micellar solutions of ADAB showed that decomposition occurred to a large degree and no polymerisation was detected.

From this study, polymerisation of the liquid crystalline phases of the ADAB/water system were found to neither phase separate nor undergo a phase transformation during polymerisation. The unpolymerised monomer retained its original geometry with slight variations to the repeat distance and head group areas due to accommodation of the interwoven polymer. This polymer was incorporated throughout the monomer matrix and its presence lead to an increase in the stability of the liquid crystalline phases.

4.3.2 ADDAB

Addition of a second chain to the surfactant alters drastically the preferred geometrical packing of the surfactant molecules from one where the system forms highly curved interfaces (as observed in the ADAB/water system where micellar, hexagonal and cubic phases are formed) to that of almost planar interfaces. This preferential packing is mirrored in the determined phase diagram where the only self-assembled aggregates found to form in the ADDAB/water system are built using bilayers as their fundamental units.

What exactly is the progression in the geometric packing of the surfactant molecules with increase in surfactant concentration in the ADDAB/water system?

From the experimental results (§ 4.2.4) the two lamellar phases observed in the ADDAB/water system cannot be related in the sense that the low composition lamellar phase (L-χ) is a mere dilution of the high composition lamellar phase (L-α). Hence,
although the more concentrated phase shows all the characteristics of being a "normal" lamellar phase where the bilayers are assumed to be parallel, infinite and flat a different global surfactant packing must be assigned to the low composition phase although both phases locally are comprised of bilayers of surfactant intercalated with water.

Bellare et al. [43] have simulated the polarised microscope images produced for a series of surfactant geometries. In one simulation a lamellar type phase having a high degree of curvature (i.e. a structure resembling a multi-walled vesicular type phase or so called "onion" phase) is generated where the number of bilayers comprising the structure is altered. The computed images of these generated structures range from the traditional maltese cross to maltese crosses superimposed with concentric dark bands (these being observed when the spacing between the layers is smaller than twice the discretisation spacing of the computer program). Hence, in the case of a real system the number of dark bands superimposed on the maltese crosses relates indirectly to the number of bilayers in the multi-walled aggregates as long as the spacing between the bilayers is neither too long nor too short. Therefore, from figure 4.2.4.4 it may be deduced that the surfactant aggregates formed are probably a construction of multi-layered bilayers with a high degree of curvature. It is not possible to determine the number of bilayers in each aggregate from the observed texture since, the dark bands do not directly correspond to the bilayers (the length scale being of the order of $10^3$ times different between the observed texture and the underlying surfactant geometry).

This idea of the $L_\chi$ phase being comprised of highly curved surfactant aggregates based on surfactant bilayers is supported by the results obtained from D$_2$O deuterium quadrupole NMR and SAXS experiments.

The phase progression for the ADDAB/water system below 57.8 °C is postulated to involve initially, the formation of a normal vesicular phase (L) at very low surfactant concentrations, where the vesicles are comprised of a single bilayer and are on average spherical. As the concentration is increased the vesicles remain spherical but begin to be the composite of more than one bilayer i.e. "nesting" occurs [44]. This spherical nesting cannot continue indefinitely and eventually the spherical shape of the onion begins to distort and the average aggregation number increases giving a pure one phase region ($L_\chi$). This phase therefore consists of a multi-walled elongated structure similar to a multi-walled ribbon structure, where the ribbons here are based on bilayers and not on a solid surfactant packing as in the usual case. Hence, the local structure of the phase is indeed bilayers intercalated with large quantities of water but globally the bilayers are not infinite and flat. That is, the phase is a completely separate and unique thermodynamic liquid crystalline phase and can, therefore, coexist with a second normal lamellar phase ($L_\alpha$), which is formed at higher compositions. The viscosities of the two phases is also found to be very different, the first being of extremely low viscosity whereas the high
composition lamellar phase is very viscous. At temperatures above 57.8 °C the normal lamellar phase is no longer stable and an isotropic fluid is formed.

The coexistence of two essentially lamellar phases in double-chain surfactant/water systems has been previously observed by a number of groups [45-51] and theoretically predicted by Wennerström [52, 53] and Jönsson and Perrson [54]. One of the systems in which the formation of two lamellar phases has been observed is the non-polymerisable analogue of ADDAB, DDAB. The observance of two distinct lamellar phases which coexist in this system was first reported by Fontell et al. [46] and then later by Warr et al. [47] before a more complete phase diagram was published by Zemb et al. [51] in 1993. This diagram is reproduced in figure 4.3.2.1.

Figure 4.3.2.1 Partial phase diagram of the binary DDAB/water system, courtesy of Zemb et al. [51]. \( L_\alpha' \): collapsed lamellar phase with a periodicity of 32 Å including the thin water layer (6 Å), \( L_\alpha \): swollen lamellar phase which can be diluted with water up to 3% DDAB content. \( P_c \) is the critical point. The two phase region between the lamellar and the isotropic phase present at higher temperatures is too narrow to be determined experimentally (following Zemb et al. [51] figure 1).

Comparison of the two phase diagrams for the ADDAB/water system (figure 4.2.4.1) and the DDAB/water system (figure 4.3.2.1) reveals again as in the case of ADAB versus DTAB both similarities and differences, which can be attributed to the presence of the
allyl group. The major difference between these two phase diagrams is the presence of a critical point in the DDAB/water system above which a one phase lamellar region is observed (i.e. a lamellar phase which is continuous with increase in surfactant concentration). Whereas below the critical point two distinct lamellar phases are observed to exist and there is a region where a discontinuous transformation between the two occurs (i.e. the two phases coexist). At higher temperatures an isotropic phase is observed to form. From reported electron micrographs [51, 55, 56] the two distinct lamellar phases appear to have a global surfactant geometry which are very similar to those found in the ADDAB/water system. That is, the low composition phase is not comprised of parallel infinite flat bilayers unlike the high composition phase but instead the bilayers have a curvature associated with them forming multi-walled structures. Therefore, at temperatures below the critical point the free energy curve has two local minima allowing these two phases to coexist. As the temperature is increased the free energy curve no longer allows for the formation of two distinct phases and a continuous transformation is observed with the multi-walled aggregates of the low composition lamellar phase ($L_\alpha$ in figure 4.3.2.1, $L_\chi$ in the ADDAB/water system, figure 4.2.4.1) continuously transforming with increase in composition to finally be consistent with parallel infinite flat bilayers. Therefore, X-ray analysis both above and below the critical point should show a continuous and discontinuous variation (as was observed in the ADDAB/water system) in all determined surfactant parameters as the concentration of DDAB is increased respectively.

This critical point phenomenon though, is not observed in the ADDAB/water system and in comparing the two diagrams it can be imagined that the ADDAB/water phase diagram may be obtained from the DDAB/water phase diagram by shifting the formation of the isotropic phase to lower temperatures, that is, in effect reducing the stability of the high composition lamellar phase ($L_\alpha'$ in figure 4.3.2.1, $L_\alpha$ in the ADDAB/water system, figure 4.2.4.1).

This behaviour of reduction of the stability of the high composition liquid crystalline phase to changes in temperature upon addition of the allyl group to the head group of a surfactant was also observed in the ADAB/water system as compared with the DTAB/water system. Hence, the increased flexibility introduced into the head group of the surfactants upon replacement of a methyl with an allyl group leads to a decrease in the stability of the phases to changes in temperature. Therefore, a one phase continuous transition with increasing surfactant concentration is never observed in the ADDAB/water system due to this change in the intrinsic rigidity moduli of the surfactant.

Addition of the allyl polymerisable group into both single- and double- chain surfactants has been shown to induce similar changes in the observed self-assembly of the surfactant. That is, although the general phase behaviour for the surfactants is maintained (i.e. both
the single- and double-chain surfactants show phase behaviour which is comparable with
that of non-polymerisable surfactants of the same class) the allyl group has the effect of
producing subtle changes in the interactions between the surfactant molecules, such that,
the aggregates formed behave differently to changes in composition and temperature than
those observed when the group is not present.

The viscosities of the phases formed are also found to be affected by the presence of the
allyl group and in general there is a decrease in the viscosity of the phases.

Comparison of the ADAB/water phase behaviour and the ADDAB/water phase behaviour
shows that the change in the surfactant parameter on addition of the second hydrocarbon
chain exerts a significant influence on the self-assembly of the surfactants. For the
single-chain surfactant, liquid crystalline phases having a high interfacial curvature are
expected to form, whereas the double-chained surfactant should form bilayer structures
having much lower interfacial curvature, which is as observed in the two systems.

Why is polymerisation in the double-chained surfactant not possible whereas the single­
chain analogue has been shown to polymerise to approximately 30 % in both isotropic
and self-assembled forms?

Any discrepancy between these two surfactants must be due to the presence of the second
hydrocarbon chain in ADDAB. It has been shown [57, 58] that the second paraffinic
chain in double-chain surfactants adopts the conformation where the first two or three
carbon atoms lie parallel to the hydrophilic/hydrophobic interface. This conformation will
lead to an increased steric interaction between the surfactant molecules. This will be
accommodated by an increased separation between the surfactant molecules and head
group area in the liquid crystalline phases formed, as observed (see table 4.2.4.1). This
increased steric hindrance will, therefore, be important during the polymerisation since
this interaction is localised in the area where polymerisation will occur (see § 2.9.1). The
increase in the distance between two allyl groups caused by the configuration adopted by
the second chain will decrease the rate constant for the propagation steps giving the free
radical (which has already in the case of ADAB been shown to be difficult to generate) an
increased time for reformation of the original carbon-carbon double bond. This is in
addition to the increased hindrance to propagation of polymerisation caused by the added
steric interaction. Hence, in the case of the single allyl group where initiation is difficult
and termination is faster than propagation this increased interaction is sufficient to stop
polymerisation occurring other than to an extent of approximately 5 %.

Babilis et al. [5, 6, 8], have reported that polymerisation of ADDAB in its vesicular form
by γ irradiation is possible to 100 % in approximately five hours at a dose rate of 1850
rad.min⁻¹. Again as was the case for ADAB (§ 4.3.1) γ irradiation was found to be more
efficient than catalytic polymerisation induced by AIBN. Precipitation was shown to
occur during polymerisation which the authors have attributed to probable destruction of the surfactant monomer. It was also stated that ADDAB which follows the same polymerisation mechanism as ADAB was found to polymerise more readily than the single-chain surfactant which was stated to be due to favourable placements of the monomers in the vesicles. This is in conflict with the results obtained here, which show that polymerisation did not occur. The reasons for the differences in the results obtained for \( \gamma \) irradiation where polymerisation to 100% is observed versus thermal and photochemical initiation where polymerisation does not occur are presently unknown.

4.4 CONCLUSIONS

It has been shown that replacement of a methyl group in the head group region of a single- and a double-chain quaternary ammonium surfactant by an allyl polymerisable group changes the hydrophilicity and rigidity of the head group. It also introduces changes in the electrostatic interactions between the surfactant molecules, the solubility of the surfactant in water (making the high composition liquid crystalline phase more readily accessible) and the stability of the phases formed.

Polymerisation of the allyl group in this position of the surfactant was difficult to induce and did not occur in the double-chain surfactant. Where polymerisation did occur the liquid crystalline phases for the ADAB/water system were found to neither phase separate nor undergo a phase transformation during polymerisation. The unpolymerised monomer retained its original geometry with slight variations to the repeat distance and head group areas due to accommodation of the interwoven polymer, which is incorporated throughout the monomer matrix and leads to an increase in the stability of the liquid crystalline phases.

Hence incorporation of the allyl polymerisable moiety into the head group of a single-chain quaternary ammonium surfactant and subsequent polymerisation increased the accessibility of the high composition liquid crystalline phases and also their stability to changes in temperature.
4.5 REFERENCES

5.1 INTRODUCTION

Altering the position of the allyl polymerisable moiety from the head group of a quaternary ammonium surfactant (as is the case for allyldodecyldimethylammonium bromide (ADAB, CH$_3$-(CH$_2$)$_{11}$-N$^+$ (CH$_3$)$_2$(CH$_2$-CH=CH$_2$)Br), chapter 4) to the end of the hydrocarbon chain yields ω-undecenyltrimethylammonium bromide (ω-UTAB, CH$_2$=CH-(CH$_2$)$_9$-N$^+$ (CH$_3$)$_3$Br). This surfactant, therefore, has an identical head group to dodecyltrimethylammonium bromide (DTAB, CH$_3$-(CH$_2$)$_{11}$-N$^+$ (CH$_3$)$_3$Br, chapter 3) differing only in the nature of the hydrocarbon tail. Note that in comparing these surfactants the hydrocarbon chain of ω-UTAB is equivalent to a C$_{10}$ hydrocarbon chain only and not a C$_{12}$, due to the presence of the double bond which has been shown to be equivalent to reducing the chain length by approximately one CH$_2$ group [1]. The presence of the allyl polymerisable moiety has two consequences. Firstly due to the increased hydrophilicity of the group (as compared with a methyl group) the hydrophobicity of the paraffinic tail is decreased and secondly the length of the chain is effectively reduced. These effects should therefore manifest themselves in the subsequent self-assembly of the surfactant molecules.

It was observed from the self-assembly of ADAB (§ 4.2.3) that the presence of the allyl moiety in the head group of the surfactant not only increased the solubility of the surfactant, but also reduced the stability of the liquid crystalline phases formed to increases in temperature. The inclusion of the allyl group at the tail of the paraffinic chain should not introduce such a perturbation. Although, the hydrophilic nature of the allyl moiety will lead to an increased stability of the individual surfactant molecules in aqueous
solution (i.e. the onset of surfactant aggregation should be shifted to higher surfactant concentrations). Once the surfactant molecules have aggregated the subsequent phase progression should not be dominated by the presence of the polymerisable moiety (since this will on average be confined to the hydrophobic core) unlike the ADAB/water self-assembly. That is, the ω-UTAB phase diagram should more closely resemble that of DTAB rather than ADAB.

In addition to the change in position of the allyl moiety affecting the surfactant's self-assembly, a change in the rate and extent and ease of polymerisation both before and after self-assembly should be observed. By placing the allyl group at the end of the hydrocarbon chain both the electrostatic and steric interactions experienced when the allyl group was incorporated in the head group (see chapter 4) will be significantly reduced. Therefore polymerisations, at least in the non-self-assembled form should be facilitated. Moving the site at which polymerisation occurs away from the interfacial area also increases the likelihood of retention of the underlying surfactant geometry. That is, when polymerisation is initiated at a location isolated from the region where the effects of several competing interactions are concentrated (e.g. electrostatic forces, interfacial tension, hydration forces, molecular packing constraints and film curvature and rigidity) the likelihood of any perturbations to these interactions caused by the onset of polymerisation is markedly reduced as compared with when polymerisation occurs within this region. The increased mobility experienced by the polymerisable moiety in this position may though, disrupt the orientation of the carbon-carbon double bonds (crucial for polymerisation) such that, any free radical formed may be lost before it is able to propagate the polymerisation.

Hence, by altering the position of the polymerisable group both the self-assembly and subsequent polymerisation of the surfactant monomers will be affected.

5.2 RESULTS

5.2.1 Physical characterisation of monomeric ω-UTAB

Figure 5.2.1.1 a) shows the proton NMR spectrum of ω-UTAB in CDCl₃ using tetramethylsilane (TMS) as an added reference. The carbon-carbon double bond is detected by the presence of a doublet of doublets centred at 4.96 δ (terminal CH₂=C protons) and a multiplet centred at 5.80 δ (CH₂=CH- proton). The corresponding carbon spectrum is shown in figure 5.2.1.1 b) again indicating the presence of the carbon-carbon double bond through the peaks at 113.95 and 138.83 δ (see § 2.1 for complete spectral analyses). Both of these forms of one-dimensional NMR can be used to follow polymerisation via the carbon-carbon double bond. The simplest approach is via the
Figure 5.2.1.1  a) Proton and b) Carbon 13 NMR spectrum for monomeric \( \omega \)-UTAB in CDCl\(_3\) using TMS as an added reference.
variation in the ratios of the integration peaks obtained from proton NMR for the carbon-carbon double bond protons referenced to the methyl protons attached to the nitrogen atom, these being largely unaffected by the polymerisation. The ratio obtained from a pure monomeric sample acts as the reference, an increase in this ratio being due to a reduction in the number of carbon-carbon double bonds present in the sample.

The Fourier transform infrared spectrum (FTIR) of monomeric $\omega$-UTAB made up as a nujol mull between NaCl plates is shown in figure 5.2.1.2. Peaks at 1638.0 cm$^{-1}$ and 3017.2 cm$^{-1}$ are characteristic of the stretching modes of the carbon-carbon double bond ($\text{C}=$ and H-C= stretch, respectively). The extent of polymerisation may also be determined from FTIR by the variation of the area under the carbon-carbon double bond peaks.

![Fourier transform infrared spectrum of monomeric $\omega$-UTAB.](image)

**Figure 5.2.1.2 Fourier transform infrared spectrum of monomeric $\omega$-UTAB.**

### 5.2.2 Determination of the critical micelle concentration for $\omega$-UTAB

The surface tension measurements of $\omega$-UTAB for concentrations between $4 \times 10^{-3}$ and 0.15 M obtained by the du Noüy tensiometry method (see § 2.5 for experimental details) at 25 °C are shown in figure 5.2.2.1. The break in the experimental data points gives an indication of the concentration at which surfactant aggregation is initiated (i.e. the critical micelle concentration (cmc)). The pre-micellisation data points were fitted with a second order polynomial (correlation coefficient = 1.000) and the cmc was calculated to be $5.38 \times 10^{-2}$ M. Following the arguments outlined in § 2.5 the excess concentration of $\omega$-
UTAB at the interface was determined to be $3.5 \pm 0.1 \times 10^{-6}$ mol.m$^{-2}$ (from equation 2.5.20) and the area per polar head group is equal to $47 \pm 1$ Å (equation 2.5.21).

Figure 5.2.2.1 Surface tension/concentration curve for the $\omega$-UTAB/water system, measured by the du Noüy ring method at 25 °C. Errors are indicated by the size of the data points.

Figure 5.2.2.2 shows the corresponding electrical conductivity measurements. Again, the initiation of surfactant aggregation is evidenced by the break in the electrical conductivity/$\omega$-UTAB concentration curve. The cmc was found to occur at $5.71 \times 10^{-2}$ M $\omega$-UTAB using linear fits for the data points both before and after the onset of surfactant aggregation. The percentage dissociation ($\beta$) of the bromide counterions calculated from the ratio of the slopes of these linear fits is $32.9\%$. $\beta$ may also be determined following the method detailed in § 2.4. Tabor and Underwood [2] have measured the average aggregation number ($n$) of the $\omega$-UTAB micelles, at the cmc, to be 31 (from light scattering measurements). Using this value of $n$, $\beta$ is calculated to be $33.3\%$. If instead an estimation of the aggregation number is used to calculate the percentage dissociation a value of $34.1\%$ is obtained (where $n$ equals 44 using the area per polar head group as 47
Å determined from surface tension measurements). Therefore, the average percentage
dissociation of the bromide counterions upon micellisation is approximately 33.5 %.

The cmc of ω-UTAB (5.3x10^{-2} M) as determined by Tabor and Underwood [2] is
comparable to those values obtained here (note that, no method of determination was
given in this reference).

![Figure 5.2.2.2 Electrical conductivity of ω-UTAB in water at 25 °C. Errors
are indicated by the size of the data points.]

5.2.3 Monomeric self-assembly

For the binary ω-UTAB/water system, three liquid crystalline phases are formed at
temperatures between 20 and 100 °C. A hexagonal phase (H_α) forms at 20 °C between
63.2 and 77.4 % by weight. A cubic phase (Q_α) forms at 83.7 wt% ω-UTAB but is not
observed until temperatures in excess of 49.5 °C are achieved. The final liquid crystalline
phase observed, the lamellar phase (L_α), forms at 66.5 °C and 86.6 % by weight of ω-
UTAB. The partial phase diagram for this system, as determined here, is shown
schematically in figure 5.2.3.1.
Results from concentration gradients performed at various temperatures indicate that no phases other than the hexagonal, cubic and lamellar are formed in the temperature range of 20 to 100 °C, and that hydrated ω-UTAB crystals are present at all temperatures.

Figures 5.2.3.2, 5.2.3.3 and 5.2.3.4 show the optical textures formed during concentration gradients by the various phases when viewed with crossed polarising filters at 30, 55 and 70 °C, respectively. The 30 °C concentration gradient shows the formation of a micellar and hexagonal phase only prior to hydrated ω-UTAB crystals (figure 5.2.3.2). The 55 °C concentration gradient in contrast shows that a cubic phase is also stable under these conditions (where the formation is detected by the black band between the hexagonal texture and the hydrated ω-UTAB crystals, figure 5.2.3.3). At a temperature of 70 °C the lamellar liquid crystalline phase is also observed by its characteristic optical texture (formed between the cubic phase and hydrated ω-UTAB crystals, figure 5.2.3.4).
Figure 5.2.3.2 Optical texture observed for a 30 °C concentration gradient for the ω-UTAB/water system under crossed polarising light. From left to right the bands are due to the presence of an isotropic micellar solution and the birefringent hexagonal phase which is formed prior to hydrated ω-UTAB crystals, (magnification 440).

Figure 5.2.3.3 View of a 55 °C concentration gradient for the ω-UTAB/water system under crossed polarising light. Note the addition of the isotropic band due to the cubic phase prior to the formation of hydrated crystals, (magnification 175).
Figures 5.2.3.5 and 5.2.3.6 show typical optical textures observed through crossed polarising filters for samples within the $\omega$-UTAB hexagonal region of the phase diagram. Figure 5.2.3.5 is an example of the fan texture as explained in chapter 3 (§ 3.2.2). This photograph shows the presence of line disclinations of order $s = +1/2$ which may be paired such that, the two disclinations coincide (i.e. two sets of brushes met at a single point) or are influenced by one another but displaced in space. The disclinations may also remain unpaired. The brushes of the line disclinations lie at an angle of between 5 and 10°, indicating that the hexagonal phase is non-uniaxial. The brushes rotate in the same sense as the polariser and analyser which indicates a positive disclination order. Edge dislocations in the underlying surfactant geometry are also apparent by the sharp black boundaries between the fans.

In contrast, figure 5.2.3.6 shows an example of a highly coloured hexagonal texture (where the intense colouration is due to the increased thickness of the sample, now of the order of 100 µm). Again, the line disclinations and edge dislocations produce characteristic textures due to their interactions with plane polarised light. In this photograph the splaying out of the dark brushes due to discontinuous curvature of the hexagonal cylinders about the line disclinations is more pronounced than in the preceding

Figure 5.2.3.4 View of a 70 °C concentration gradient for the $\omega$-UTAB/water system under crossed polarising light. Here the texture due to the lamellar phase is also seen, (magnification 440).
As the temperature increases the hexagonal phase is found to melt at 98 °C and the transition between the two isotropic fluid phases (L₁ and L₁'') becomes continuous.

The stability of the cubic phase (Q₉) formed in the ω-UTAB/water system is restricted in both temperature and composition forming only above temperatures of 49.5 °C and melting at 90.8 °C.

The optical texture observed for a sample in the ω-UTAB lamellar phase when viewed through crossed polarising filters is shown in figure 5.2.3.7. The texture yields little information on the underlying surfactant geometry, in that few clear features are apparent, though it is possible to discern some maltese crosses within the general sandstone background. This texture is normally termed "mosaic" [3-6] (§ 3.2.2). Due to the insolubility of the surfactant at high concentrations the lamellar, like the cubic phase is not observed until the temperature has been raised, but the phase remains stable up to 100 °C. The lamellar phase has also been observed to have a large temperature hysteresis. On decreasing the temperature from the pure lamellar phase the transition temperature is found to be lowered by approximately 40 °C as compared to when the temperature is increased. Therefore, in this temperature range a supercooled lamellar state exists which is metastable. Both the cubic and hexagonal phases are not observed with decreasing temperature from the lamellar phase.

Assignments of the regions in the phase diagram were established by determination of the structures with small-angle X-ray scattering (SAXS). Diffraction patterns were obtained for powdered bulk samples in the micellar, hexagonal, cubic and lamellar phases and were comprised of Debye-Scherer rings which were produced by all domains in the irradiated volume.

Samples within the L₁ isotropic fluid phase produced diffraction patterns at small- and wide-angles comprised of one diffuse ring only [7].

The diffraction pattern of the bulk hexagonal phase of ω-UTAB at small-angles consists of five sharp rings in the ratios of $1:3:4:7:9$ as expected for parallel cylinders packed in a two-dimensional array (table 5.2.3.1). The wide-angle scattering showed one diffuse ring located at $2\pi/4.5 = 1.4$ Å⁻¹ indicating a liquid-like state for the paraffinic chains [7].

The ω-UTAB cubic phase is characterised by five sharp rings at small-angles with $Q$ values in the ratios of $\sqrt{6}:\sqrt{8}:\sqrt{14}:\sqrt{16}:\sqrt{20}$. These ratios being characteristic of one cubic phase only, the $Q^{230}$ (Ia3d) which is assumed here to be bicontinuous as has been shown in other systems [8-12]. This phase has been observed experimentally to be either of
Figure 5.2.3.5  Fan texture of the ω-UTAB hexagonal phase (crossed polarising filters, magnification 440). The cylinders lie parallel to the glass slide and the brushes correspond to line disclination of strength $s = + \frac{1}{2}$. The brushes lie at an angle of between 5 to 10° to the polariser and analyser. Edge dislocations between individual fans are indicated by sharp dark lines, (60.0 wt% ω-UTAB sample at 25 °C).

Figure 5.2.3.6  Fan texture of the ω-UTAB hexagonal phase (crossed polarising filters, magnification 175). The brushes correspond to line disclinations of strength $s = + \frac{1}{2}$, with the splaying out of the brushes indicating variations in the curvature of groups of cylinders about the line disclination, (72.7 wt% ω-UTAB sample at 25 °C).
Table 5.2.3.1 Structural parameters for the surfactant aggregates formed in the $\omega$-UTAB/water system at $T = 27\, ^{\circ}\text{C}$

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<td>90.0&lt;sup&gt;b&lt;/sup&gt;</td>
<td>Lα</td>
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<td>0.89</td>
<td>23.4</td>
<td>2.9</td>
<td>38.1</td>
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</table>

<sup>a</sup> temperature = 70 °C
<sup>b</sup> temperature = 90 °C
type I or of type II (§ 1.1) but due to the placement of the phase in the self-assembly progression of ω-UTAB it is most likely to be of type I. This phase has also been ascribed to the Gyroid infinite periodic minimal surface (IPMS) having genus per conventional cubic unit cell = 5 [13-18]. The presence of one diffuse ring only at wide-angles being indicative of liquid-like paraffinic chains.

Samples in the lamellar liquid crystalline phase of ω-UTAB produced diffraction patterns at small-angles comprised of two sharp rings only, in the ratio of 1:2 as expected for parallel planar bilayers [7]. This phase was also determined to have molten hydrocarbon chains.

The structural parameters for the self-assembled states observed in the ω-UTAB/water system were determined as described in § 2.8 (table 5.2.3.1). The specific volume of ω-UTAB was calculated using equation 2.8.8, since the specific volume of the polar head group is known [19] and the specific volume of the paraffinic chains may be determined using equation 2.8.9. Note that all parameters are calculated by using assumed structures (§ 2.8). All equations were calculated for T = 27 °C unless stated otherwise.

Figure 5.2.3.7 Mosaic texture of the ω-UTAB lamellar phase (crossed polarising filters, magnification 440). The layers comprising the phase lie parallel to the glass slide, (87.2 wt% ω-UTAB sample at 83.8 °C).
5.2.4 Polymeric $\omega$-UTAB

Polymerisation of the monomeric form of $\omega$-UTAB in chloroform (in which the surfactant does not self-assemble) using both photochemical (direct decomposition of the monomer) and thermal (via decomposition of added AIBN) initiation has been investigated. Results indicate that polymers obtained from either method were similar.

By studying the self-assembly of polymeric $\omega$-UTAB it is possible to determine if there are overlapping regions between the polymeric and monomeric phase behaviour. Any overlap which does occur increases the likelihood (i.e. there is an increased probability) that polymerisation of the monomeric liquid crystalline phases within this overlap region will lead to a retention of the underlying surfactant geometry upon polymerisation.

Polymeric $\omega$-UTAB was prepared by thermal initiation (10 mol% to surfactant) in a 0.25 M chloroform solution. The reaction mixture was maintained at 60 °C for seven days after which the polymerisation had preceded to approximately 80%. Increasing the reaction time did not increase the extent of polymerisation significantly. The so formed polymer had a molecular weight cut off of approximately 8000 (i.e. ~ thirty monomer units per polymer chain as determined by dialysis). Pure polymer was obtained by removal of the monomer and oligomer units using Sephadex G-15, a size exclusion gel filtration packing material, having a molecular weight cut off of 1500.

The proton and carbon 13 NMR spectra of polymeric $\omega$-UTAB in CDCl$_3$ using TMS as an added reference are shown in figure 5.2.4.1 a) and b). These spectra have been analysed for the polymeric configuration shown in the figures only and that of other polymer linkages have not been considered. That is, instead of linkages ..., head-to-tail, head-to-tail,... the linkage may be ..., head-to-head, head-to-head,... ; ..., tail-to-tail, tail-to-tail,... or combinations of these (note that here head and tail indicate the penultimate and terminal carbon atoms of the carbon-carbon double bond, respectively).

Other possibilities include configurations due to hydrogen abstraction producing linkages elsewhere in the chain (see § 2.9 for the different types of hydrogen abstraction processes possible during free radical polymerisation). From analysis of the spectra the head-to-tail, head-to-tail configuration comprises approximately 80% of the conformations formed during polymerisation. It should be noted that the peaks associated with the carbon-carbon double bond are no longer present, with the associated protons of carbons shifted either up or down field from their original position (compare with the spectra obtained for monomeric $\omega$-UTAB, figure 5.2.1.1 a) and b)).

Unfortunately, polymeric $\omega$-UTAB is extremely hygroscopic and a full phase diagram was not obtained. Concentration gradients only were performed in the temperature range 20 to 100 °C where new samples were used for each new temperature.
Figure 5.2.4.1  a) Proton and b) Carbon 13 NMR spectrum for polymeric ω-UTAB in CDCl₃ using TMS as an added reference.
Figures 5.2.4.2, 5.2.4.3 and 5.2.4.4 show the optical textures observed under crossed polarisers for concentration gradients at 25, 60 and 70 °C, respectively. Comparison with the phase behaviour of monomeric ω-UTAB shows that the solubility of the surfactant has been significantly increased upon polymerisation allowing access to both cubic and lamellar phases at 20 °C (i.e. the overall stability of these phases has been increased). Due to the polymers hygroscopic nature no pure hydrated polymer crystals were observed, coexisting with the lamellar liquid crystalline phase only. Figure 5.2.4.2 shows the phase progression observed during a 25 °C concentration gradient, showing the formation of a micellar (L1), hexagonal (Hα), cubic (Qα, assigned due to the extremely high viscosity of the phase as compared with the micellar isotropic phase) and lamellar (Lα) phases, the latter coexisting with hydrated polymeric ω-UTAB crystals. As the temperature is increased the lamellar phase exists as a pure phase above 30 °C. Figure 5.2.4.3 shows the variable birefringent bands observed during a 60 °C concentration gradient showing the presence of pure hexagonal, cubic and lamellar phases. At higher temperatures the polymeric phase behaviour mirrors that of the monomeric self-assembly.

Figure 5.2.4.2 Optical texture observed for a 25 °C concentration gradient for the polymeric ω-UTAB/water system under crossed polarising light. From left to right micellar, hexagonal, cubic and lamellar phases which coexists with hydrated ω-UTAB polymer crystals are observed to form, (magnification 440).
Figure 5.2.4.3 View of a 60 °C concentration gradient for the polymeric ω-UTAB/water system under crossed polarising light. Hydrated polymeric ω-UTAB crystals are no longer observed, (magnification 440).

Figure 5.2.4.4 View of a 70 °C concentration gradient for the polymeric ω-UTAB/water system under crossed polarising light. The cubic phase now coexisting with an isotropic fluid (L1°), (magnification 440).
At 70 °C the cubic phase begins to melt forming a second fluid isotropic phase (L₁', figure 5.2.4.4) and is completely melted by 75 °C (which is approximately 15 °C lower than was observed in the monomeric phase progression). The L₁, Hₐ, L₁' and Lα phases persist up to 95 °C where the hexagonal phase melts and there is a continuous transition between the two isotropic fluid phases. Hence, the monomeric and polymeric forms of ω-UTAB have been observed to self-assemble in water with a similar phase progression.

It should be noted that although the monomeric ω-UTAB/water system is a binary (or pseudo ternary system, where the counterions comprise the third phase) the polymeric ω-UTAB/water system is a multicomponent system due to the polydispersity of the polymer units. This will also be the case for polymerisation of lyotropic liquid crystalline phases due to the polymerisation reaction in the two being identical.

Due to the significant similarity of the monomeric and polymeric ω-UTAB/water phase progressions and the high conversion of monomer to polymer during isotropic polymerisation in chloroform the probability that the underlying surfactant geometry in the liquid crystalline phase will be retained upon polymerisation is increased.

5.2.5 Polymerisation of liquid crystalline phases

Unfortunately, due to the inaccessibility of the cubic and lamellar phases at room temperature these phases were not able to be polymerised. For a phase to be polymerisable it must be accessible at low temperatures, since for thermally activated samples, equilibration must take place at low temperatures to ensure that polymerisation does not commence prior to obtaining a fully equilibrated state. Hence, in the case of ω-UTAB the equilibrated state at high surfactant compositions (which are required for the formation of the cubic and lamellar phases) is the hexagonal phase plus hydrated ω-UTAB crystals. Therefore a minimum of one or two phase transitions (in the case of the cubic and lamellar phases, respectively) must be undergone to achieve the required state. As an increase in temperature is required for these transitions to be accomplished, the AIBN will be activated and polymerisation initiated before the true equilibrium state at this temperature is obtained. In the case of photochemical initiation (where no added initiator is required) the chamber used in this work is not capable of attaining temperatures in excess of 30 °C. Hence, these phases would be accessible if it was possible to equilibrate the samples at higher temperatures and then photochemically initiate the polymerisation at this equilibration temperature.

The hexagonal and micellar regions of the ω-UTAB/water system were therefore the only regions studied. Polymerisation samples were prepared, by the freeze-thaw-pump
method as described in § 2.9, for 5 (dilute micellar phase), 40 (concentrated micellar phase) and 70 (hexagonal phase) wt% ω-UTAB. The surfactant was not observed to self-initiate during equilibration.

Table 5.2.5.1 shows the percentage conversions for the three regions of the ω-UTAB/water system activated by thermal initiation of added AIBN (10 mol% to surfactant) at 60 °C or photochemically. Note that an error of approximately ± 5% can be expected in these values due to inaccuracies in the measured integration values.

**Table 5.2.5.1 Percentage conversions for the three regions of the ω-UTAB/water phase diagram polymerised either thermally or photochemically**

<table>
<thead>
<tr>
<th>Type of Initiation</th>
<th>Time (days)</th>
<th>Dilute Micellar Phase</th>
<th>Concentrated Micellar Phase</th>
<th>Hexagonal Phase</th>
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</thead>
<tbody>
<tr>
<td><strong>Thermal Initiation</strong></td>
<td></td>
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<tr>
<td>0.17</td>
<td>26.6</td>
<td>24.5</td>
<td></td>
<td>39.6</td>
</tr>
<tr>
<td>0.25</td>
<td>30.7</td>
<td>23.6</td>
<td>24.4</td>
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<tr>
<td>0.5</td>
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<td>28.4</td>
<td></td>
<td>34.0</td>
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<tr>
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<tr>
<td>0.75</td>
<td>30.7</td>
<td>—</td>
<td>35.0</td>
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<tr>
<td>1.0</td>
<td>—</td>
<td>28.4</td>
<td></td>
<td>43.7</td>
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<td>1.33</td>
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<td>2.0</td>
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<tr>
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<td><strong>Photochemical Initiation</strong></td>
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</tr>
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<td>32.2</td>
<td>34.2</td>
<td>—</td>
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<tr>
<td>0.5</td>
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<td>17.1</td>
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<td>22.0</td>
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<tr>
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<td>40.6</td>
<td>19.4</td>
<td>17.3</td>
<td>30.1</td>
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<td>23.1</td>
<td>19.4</td>
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<td>2.0</td>
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<td>4.0</td>
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<tr>
<td>6.0</td>
<td>26.8</td>
<td>16.7</td>
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<td>19.6</td>
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<tr>
<td>8.0</td>
<td>35.9</td>
<td>25.9</td>
<td></td>
<td>27.5</td>
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<tr>
<td>10.0</td>
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<td>33.6</td>
<td>14.9</td>
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<td>31.1</td>
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Whether initiated thermally or photochemically, similar results were obtained for all samples. The major discrepancies occurred for the concentrated micellar solutions where
the extent of polymerisation via photochemical initiation was considerably lower than that observed for thermal initiation, which also appears to have an activation time of approximately two days before the extent of polymerisation plateaus out. This was not observed for any of the other regions. The reason for this difference in the two methods of initiation for this region of the phase diagram is unknown.

The calculated mean and median for the polymerisations in the different regions are given in table 5.2.5.2, which indicate that polymerisation via thermal initiation is on average more successful. It should be noted that the extent of polymerisation is reduced significantly as compared with polymerisation of ω-UTAB in an isotropic state (which was found to polymerise to approximately 80%). Hence, the extent of polymerisation is reduced upon surfactant self-assembly.

<table>
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<th>Table 5.2.5.2 Statistics of the extent of polymerisation for the three ω-UTAB liquid crystalline phases</th>
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<td>Percent Micellar Solution</td>
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<td><strong>Thermal Initiation</strong></td>
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<td></td>
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<tr>
<td><strong>Photochemical Initiation</strong></td>
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</table>

To determine the effect that polymerisation has had on the underlying surfactant geometry, samples in each region were exposed for five days at 60 °C (using 10 mol% AIBN as initiator). Both micellar solutions were found to remain optically isotropic upon polymerisation and while the molecular weight of the polymer was found to be less than 8000 (i.e. less than thirty monomer units) which is comparable to the molecular weight of the monomeric micellar aggregates (at least in the dilute micellar phase region, as determined by Tabor and Underwood [2]) this does not ensure intra-micellar polymerisation (i.e. formation of a "polymerised micelle" see § 5.3).
The partially polymerised hexagonal phase was also found to produce optical textures similar to those observed for a pure monomeric hexagonal phase (see figure 5.2.5.1). Here, edge dislocations and line disclination of order $s = + 1/2$ are still observed and the brushes of the fan remain splayed due to variations in the curvature of groups of cylinders. The hexagonal phase begins to melt at approximately $80 \degree C$ entering a two phase region with an isotropic fluid before the transition is complete at $\sim 85 \degree C$. Hence, the stability of the phase has not been significantly increased nor decreased due to the presence of polymer.

Although the optical microscopy results indicate that the polymer has been incorporated into the monomeric surfactant matrix it was necessary to determine if the polymer had been fully incorporated into this matrix without disturbing the surfactant molecules. This would then be in contrast with the case of ADAB, where the polymer, although having become an integral part of the liquid crystalline phase, has not been formed by the
retention of the monomeric surfactant geometry. Hence, SAXS experiments were performed on the partially polymerised samples.

Diffraction patterns obtained at small- and wide-angles for samples in the concentrated micellar region consisted of one diffuse ring only. Comparison with the diffraction pattern for a monomeric sample (table 5.2.3.1) indicates that the average distance between the aggregates in the partially and non-polymerised systems is very similar, which suggests that the nature of the micellar solution is largely undisturbed by the presence of polymer.

Likewise the partially polymerised hexagonal phase produced a diffraction pattern at small-angles comprised of three sharp Bragg peaks in the ratios of 1:\(\sqrt{3}:\sqrt{4}\). No other peaks were detected, giving evidence that the underlying monomeric surfactant geometry is indeed maintained upon polymerisation. The chains were found to be in a fluid-like state by the presence of one diffuse ring at wide-angles.

Table 5.2.5.3 gives the structural parameters calculated assuming that the composition remains unchanged upon polymerisation (i.e. the phase is retained and no phase separation or transition has occurred). The specific volume of the surfactant is also assumed to remain constant upon polymerisation. All equations were calculated for \(T = 27\,^{\circ}\,C\). Comparison with the structural parameters determined for the monomeric hexagonal phase shows that using these assumptions the head group area, unit cell length and surfactant length are practically unchanged upon polymerisation (compare with table 5.2.3.1). Hence, the original liquid crystalline phase geometry is undisturbed upon partial polymerisation with the original stability of the phase also being maintained.

\[\begin{array}{|c|c|c|c|c|c|c|c|}
\hline
\omega\text{-UTAB} & \text{Phase} & \text{Observed} & \text{Unit Cell} & \text{Surfactant} & \text{Water} & \text{Mean Area} & \text{hkl} \\
\% & & Q \quad (\text{Å}^{-1}) & \text{Length (Å)} & \text{Aggregate} & \text{Thickness (Å)} & \text{Thickness per Polar} & \\
\text{(w/w)} & & & & \text{Thickness (} & & \text{Head (Å)} & \text{Head (Å)} \\
\hline
40.8 & L_1 & 0.175 & — & 0.39 & — & — & — \\
67.7 & H_\alpha & 0.203 & 35.7 & 0.66 & 30.5 & 5.2 & 57.6 \\
& & 0.352 & & & & & \\
& & 0.405 & & & & & \\
\hline
\end{array}\]
5.3 DISCUSSION

The position of the allyl polymerisable moiety has been shown to be crucial in determining the self-assembling properties of the surfactant and the extent to which polymerisation occurs either in an isotropic state or self-assembled form.

By comparing the concentration at which aggregation is initiated, the extent of dissociation of the bromide counterion, the excess surfactant concentration at the interface and the area per polar head group for \( \omega\)-UTAB, ADAB and DTAB, an indication of the effect that incorporation of the allyl polymerisable group into the tail of the paraffinic chain can be obtained. The measured cmc for \( \omega\)-UTAB, ADAB and DTAB (5.5 ± 0.2x10^{-2} M, 1.1 ± 0.1x10^{-2} M, 1.5 ± 0.2x10^{-2} M, respectively) indicates that by reducing the difference between the hydrophobic and hydrophilic regions of the surfactant the concentration at which surfactant aggregation is initiated is shifted to higher values. For all other measured parameters in the dilute concentration regime (i.e. close to the cmc) \( \omega\)-UTAB closely mirrors DTAB as it is expected since the two surfactants have the same head group. Whereas the solution behaviour of ADAB is significantly affected by the presence of the allyl moiety in its head group.

These results are carried over into the concentrated region of the phase diagram, where the phase progression of \( \omega\)-UTAB with increasing surfactant concentration resembles that of DTAB. Therefore, the presence of the carbon-carbon double bond at the end of the hydrocarbon chain does not significantly alter the balance of interactions between the surfactant molecules. The differences which do arise (i.e. decreased solubility at high surfactant concentrations and reduced phase stability) may be explained by an increase in the rigidity and an effective decrease in the length of the hydrocarbon chain. That is, by incorporating a carbon-carbon double bond into the tail of a hydrocarbon chain a subsequent restriction in the freedom of the paraffinic tail as compared with unsaturated hydrocarbon chains is introduced. This restriction in freedom promotes chain ordering which increases the temperature at which the order/disorder transition occurs, thereby, shifting the Krafft curve to higher temperatures. Note that this is the reverse to what is observed for saturated and unsaturated surfactants when the unsaturation is confined to the beginning or middle of the hydrocarbon chain [20].

The decrease in stability of the liquid crystalline phases formed by \( \omega\)-UTAB in comparison to DTAB may also be explained by the presence of the carbon-carbon double bond where the effective chain length is now approximately equivalent to a C_{10} hydrocarbon chain. Reduction in the chain length has been shown to affect both the type of liquid crystalline phases formed and also their stability with changes in temperature and composition. In general the stability of the phases is decreased as the effective hydrocarbon chain length is decreased. Hence, the presence of a carbon-carbon double
bond at the end of the hydrocarbon chain in a quaternary ammonium surfactant reduces the temperature and compositional ranges over which the liquid crystalline phases are formed.

By polymerising the monomeric surfactant prior to aggregation it has been shown (§5.2.4) that this reduced stability may be reversed. By covalently bonding the paraffinic tails forming low molecular polymers (which still have high degrees of freedom due to their low molecular weights and therefore lack of entanglement), the number of degrees of freedom of the surfactant have been increased sufficiently to allow both the cubic and lamellar phases to be stable at significantly reduced temperatures. Hence, the higher surfactant composition liquid crystalline phases have been stabilised by the polymerisation prior to self-assembly and the two phases are now accessible at room temperature.

The extent of polymerisation was enhanced by placement of the allyl group at the end of the hydrocarbon chain. Polymerisation occurred to approximately 80% as compared with 30% for ADAB under identical conditions. No decomposition of the surfactant was found to occur for ω-UTAB. By isolating the polymerisation site from the area where competing interactions are concentrated (e.g. electrostatic forces, interfacial tension, hydration forces, molecular packing constraints, film curvature and rigidity) the extent of polymerisation is increased since the molecule is able to accommodate the new covalent linkage without altering the head group interactions significantly.

Hence, placement of the polymerisable group at the end of the hydrocarbon chain increases the probability that polymerisation will occur to a high yield but decreases the accessibility of the liquid crystalline phase by reducing their overall stability.

Polymerisation of the lower concentration ω-UTAB mesophases indicates that the integrity of the mesophase is not altered upon partial polymerisation. It must be noted though that it is unlikely that polymerisation of these phases has involved intra-aggregate polymerisation alone. In the case of polymerisation in micellar solutions the rate of micellar dissolution is much faster than the rate of polymerisation. Therefore at low concentrations the micelles will have broken up before polymerisation of the aggregate is feasible. While this rate will decrease with increasing surfactant concentration the average length of a polymer chain is not altered (all polymer chains are comprised of a maximum of approximately thirty monomer units) whereas, the average aggregation number of the surfactant aggregates increases with increasing concentration. Hence, the mechanism for polymerisation must involve growth of the polymer chains within a surfactant aggregate, in free solution or in a subsidiary aggregate differing from that in which it originated. That is, the polymer chains must either terminate within the original aggregate and then diffuse as a single entity moving freely within the aggregate and into and out of aggregates or a growing polymer chain, which is lost from its original
aggregate, continues to grow and then terminates outside of the aggregates or becomes incorporated into another aggregate where it is finally terminated. Note that, either a growing or dead polymer chain may also act as seeds for the formation of a new aggregate.

Hence, the mechanism for polymerisation is very complex, but from this it can be ascertained that two things are crucial for intra-aggregate polymerisation only to occur. The rate of polymerisation must be shorter than the lifetime of the aggregates and the molecular weight of the growing polymer chain must be able to be controlled such that it is neither too low nor too high. That is, if the growing polymer chain continues to grow such that its molecular weight is greater than that of the aggregate it will begin to consume additional aggregates prior to termination, therefore destroying the phase. But if it is smaller than the molecular weight of the aggregate the surfactant aggregates will not be rigidified. Unfortunately, molecular weight is extremely difficult to control and in general polymerisable moieties with fast reaction rates form polymers with high molecular weights and those with slow reaction rates form polymer chains having low molecular weights.

A further problem was encountered during the polymerisation of a terminal paraffinic chain allyl group, the extent of polymerisation was reduced substantially upon surfactant self-assembly. Whereas, when the polymerisable group was contained within the head group the extent of polymerisation was equivalent in both self-assembled and isotropic forms. The reduced extent of polymerisation is due therefore, to the mobility of the paraffinic tails. Such that unlike in the case of polymerisation in the head groups, where the head groups are confined to the surface of the aggregates and therefore ideally oriented for polymerisation, the paraffinic tails are generally uniformly distributed throughout the surfactant aggregate being found at the core, at the interface and at all allowed positions in between [21-31]. Therefore, once a free radical is formed it may not be able to find a second polymerisable group or suitably abstractable proton which are oriented appropriately before it is lost. For example, in the case of thermal initiation using AIBN, the free radicals are formed but are unable to react in a time less than the time for recombination. But the recombined form is no longer an active initiator (due to loss of N₂, § 2.9) hence the added initiator may be destroyed without polymerisation occurring. That is, the surfactant aggregate acts as a cage inhibiting polymerisation. If a polymer chain is initiated it too may not be able to find an appropriately oriented carbon-carbon double bond and will be terminated by another growing chain or a free radical initiator or lost via diffusion from the aggregate or the original carbon-carbon double bond will be reformed.

Therefore, due to the lack of order of the hydrocarbon core of the surfactant aggregates and the confinement within the core for a time greater than that required for recombination
of the free radicals the extent of polymerisation is reduced. The disruption to the interactions between the surfactant molecules and therefore the surfactant geometry is markedly reduced from that when polymerisation occurs in the head group region and as such the original average surfactant orientation is maintained upon polymerisation.

5.4 CONCLUSIONS

Placement of an allyl polymerisable group at the end of the hydrocarbon chain of a quaternary ammonium surfactant introduces an increased rigidity into the paraffinic chains reducing both the solubility of the surfactant at high concentrations and stability of the liquid crystalline phases formed.

Polymerisation in this position is facilitated in comparison to when the polymerisable moiety is contained within the head group region of the surfactant. This is primarily due to the isolation of the allyl group from the region where the interactions between the surfactant molecules is concentrated with formation of the polymer not disrupting significantly these interactions which control the surfactant's self-assembly. Because of this the polymerised form of $\omega$-UTAB self-assembles such that the liquid crystalline phases formed have an increased stability towards changes in temperature.

Polymerisation of the mesophases formed by this surfactant with water is such that the original underlying surfactant geometry is maintained. The extent of polymerisation in the surfactant's self-assembled form is reduced in comparison to polymerisation in an isotropic solution due to the surfactant aggregates acting as a cage inhibiting polymerisation.
5.5 REFERENCES

SODIUM 10-UNDECENOATE

6.1 INTRODUCTION

Sodium 10-undecenoate (Na-10, CH$_2$=CH-(CH$_2$)$_8$-CO$_2$Na$^+$), like ω-undecenyltrimethylammonium bromide (ω-UTAB, CH$_2$=CH-(CH$_2$)$_9$-N$^+$(CH$_3$)$_3$Br$^-$, chapter 5), contains the allyl polymerisable moiety at the end of the hydrocarbon chain. The change in the nature of the head group from a quaternary ammonium to a carboxylate should alter dramatically the self-assembly observed for the Na-10/water system compared with that observed in the previous systems. Unlike the previous surfactants it is difficult to make a direct comparison between Na-10 and dodecyltrimethylammonium bromide (DTAB, CH$_3$-(CH$_2$)$_{11}$-N$^+$(CH$_3$)$_3$Br$^-$, chapter 3) due to both the nature of the head group and the hydrocarbon chain having been altered. Nevertheless by comparing the physico-chemical behaviour of ω-UTAB and Na-10, it should be possible to determine the affect that the trimethylammonium bromide and sodium carboxylate head groups have on controlling the self-assembly of surfactant molecules and their polymerisation. Any observed difference in the two surfactants can only be attributed to changes in the interactions between the head groups and chain flexibility.

It has been shown that the introduction of the allyl polymerisable group into the tail of the hydrocarbon chain itself does not significantly disturb the phase progression with changes in temperature and composition (ω-UTAB, chapter 5). Introduction of this group does, however, reduce both the solubility of the surfactant and the stability of the liquid crystalline phases. That is, the presence of a carbon-carbon double bond at the end of the hydrocarbon chain increases the rigidity of the chains. (Note that this is in contrast with the case where the double bond is incorporated into the beginning or middle of the chain where the flexibility of the chain is increased and the overall solubility of the
surfactant is also increased [1]). This increased rigidity is expected to be magnified in the Na-10/water system since the effective chain length has been reduced still further as compared with o-UTAB. The influence of the allyl polymerisable moiety is therefore more dominant in this surfactant and the chain length is now more closely approximated by a C₈ or C₉ hydrocarbon chain, since the presence of a double bond is equivalent to reducing the chain length by approximately one CH₂ group [2]. Therefore, as the concentration of Na-10 is increased it is likely that an order/disorder transformation will be observed. This is indeed what happens and a transition between a normal hexagonal phase (H₂) and a lamellar gel phase occurs, with both the long- and short-range (that of the paraffinic chains) order being effected during the transition. Transitions involving a change in both the long- and short-range order parameters are of great interest, as they are often encountered in lipidic systems [3-5].

Despite a substantial amount of information having been gathered on the equilibrium properties of mesophases, details of the mechanism of the structural transformations remain scant. Some thirty years ago a good understanding was established [6-10] concerning structures that do not undergo a topology change through a phase transition. These transitions involve firstly a change in the short-range order, as in the transformation of two lamellar phases, one with frozen chains (the so-called lamellar gel) and the other with paraffinic chains in a liquid-like state (Lα) [8-12]. Secondly, the long-range order is affected during the transition (as well as a phase symmetry change). A satisfying and consistent description was obtained for the case where a slight modification of the shape of the aggregates is implicated. This was well described by Luzzati and collaborators who showed for instance how circular cylinders of the two-dimensional hexagonal phase (H₂) become anisotropic ribbons of the deformed hexagonal (two-dimensional monoclinic or rectangular phase) [6]. In the case where a topological change is involved in the structural transformation, the mechanism is less understood. Only recently have studies dealt with this problem, and most reported observations are as a function of temperature [13-15], rather than as a function of composition [16, 17]. Epitaxial relations occurring at the transition have been evidenced [13, 15, 16, 18], indicating that two adjacent mesophases are strongly related; that is the new phase grows with a fixed orientation relative to the former one. Furthermore, dense reticular planes of the new structure develop from the dense planes of the former one [13, 15, 16, 18]. For instance, in non-ionic surfactant/water systems, clear relations were established between the dense planes of the two-dimensional hexagonal packing of cylinders (planes (10)), those of the three-dimensional bicontinuous cubic structure Ia₃d (planes (211)), and the planes of the one-dimensional layered stack of the lamellar mesophase [13, 15]. Hence, as an extension to these studies, the Na-10/water system enables the study of a transition involving both a change in the short- and long-range order with composition.
In addition, the affect of a solid wall on this transformation is investigated. It has been known for nearly a century that solid surfaces have an orienting action on liquid crystals [19, 20]. Textures, seen by means of optical microscopy are characteristic of the phase they represent [21-24] but also depend upon the nature of the substrate. The orientation or anchoring direction taken by such anisotropic materials at the surface of a substrate depends upon a set of competing parameters [25-27]. Anisotropic interactions between the liquid crystal molecules and the molecules of the solid are a major contribution in the orientation process, where the symmetry of the surface and several nonsuperficial layers of the substrate may play an important role [28]. In lyotropic liquid crystals, a classical example is the build-up of homeotropic lamellar mesophases, where the layers of the stack lie parallel to the flat surfaces of the walls. The nature of the first layer built is mainly governed by electric interactions between the substrate and the surfactant molecules. If this interaction is favourable, the adsorbed layer will be hydrophobic, (the polar heads are adsorbed onto the solid [29]), otherwise a thin water layer will remain between the substrate and the alternate stack of bilayers/water layers of the lamellar mesophase [30]. The terraced nature of the substrate surface, or more generally its roughness, may drastically change the anchoring directions [31]. If some of the parameters determining the structure of the substrate or liquid crystal are changed, anchoring transitions can occur, for example when the chemical potential of the system is varied [32, 33]. In addition, the history of the system plays an important role. Depending upon the way the contact between the two phases is made (for instance during the wetting of the substrate by the liquid crystal), the first selection of one anchoring direction may be switched to another one when an external change occurs (flow inducing shear [34] or an applied electric field in liquid crystal displays).

Complexity of these phenomena results in a variety of orientations: cylinders of the columnar phases in thermotropic liquid crystals, can orientate either in a planar or in a homeotropic configuration [35], the latter is generally not observed in the hexagonal phase of lyotropic systems. Indeed, it is often observed that the director of the mesophase (along the cylinders) is parallel to the walls [14, 15, 18, 35] and that the dense planes (10) are next to them [18]. Note that a mesophase does not necessarily orient itself with its most dense reticular planes along a solid wall, although this is common (see for example the cubic phase of the space group in the class Im3m, which orients with planes (111) along the walls [18]). The orientation of mesophases with complex structures seems to result from a compromise between the interactions of the substrate with the first closest plane of aggregates which will be built next to it, and the required structure of the mesophase which is to be preserved. Such observations have already been made; for instance anisotropic ribbons can lie with their flat parts tilted relative to solid flat walls [18].
As a consequence, growth of one phase from a former one in the presence of a solid wall is a result of epitaxial relations between the two structures, as well as with the substrate. It is shown here, that unusual growth can occur under certain conditions. In particular, bilayers of a lamellar gel liquid crystal can be grown perpendicular to flat walls, by slow evaporation of water from a normal hexagonal mesophase. This growth yields a spectacular texture, composed of interwoven spirals. This new texture arises due to a combination of, defects inherent in the system, anchoring, and nucleation effects [36-40]. The departure from the perfectly ideal crystallographic packing of the aggregates can take the form of twists, splays or bending of the aggregates [41] (see § 1.2.1). A detailed investigation of the nature of the defects is presented, enabling extraction of an estimate of the bending modulus for these phases.

As well as the observed effect on the self-assembly of Na-10 caused by the combination of the position of the allyl polymerisable moiety, the presence of a fatty acid soap head group and a shortened chain length, the subsequent polymerisation should also be effected. Hydrocarbon chains in a fluid-like state have a high degree of mobility [42-51] unlike the case when the chains are frozen, where they are presumed to be almost crystalline in their nature [8-11, 52-54]. Therefore, when the chains are in a fluid-like state polymerisation may retard their flexibility, whereas for frozen chains the number of degrees of freedom should be increased upon polymerisation. Hence, the nature of the paraffinic chains may have an effect upon the extent and ease of polymerisation of the liquid crystalline phases formed in the Na-10/water system and also on the degree of rearrangement which may occur during polymerisation.

Since Na-10 is the sodium salt of a fatty acid it is possible that in solution at low surfactant concentration several different forms of the surfactant will be present (i.e. the salt will undergo hydrolysis). These different forms consist of the parent fatty acid (undecenoic acid), the neutral soap and the charged carboxylate ion, due to dissociation of the sodium counterion. The presence of the parent fatty acid in the system will affect the initial aggregation of the surfactant and hence will be detectable by the methods used to determine the onset of aggregation of the surfactant, i.e. electrical conductivity and surface tension.

Many different transitions are observed during the self-assembly of Na-10 in water due to interactions between the carboxylate head groups and hydrocarbon chains. The phase behaviour displayed by Na-10 makes it an ideal surfactant to study in conjunction with the quaternary ammonium surfactants previously discussed as it extends the number of environments in which polymerisation takes place, thereby expanding the predictive power for polymerisation of liquid crystalline phases while retaining the underlying surfactant geometry.
6.2 RESULTS

6.2.1 Physical Characterisation of monomeric Na-10

Figure 6.2.1.1 shows the Fourier transform infrared (FTIR) spectrum of Na-10 made up as a nujol mull (NaCl plates). Characteristic peaks for the surfactant molecule appear at 3083.3 cm\(^{-1}\) corresponding to the carbon hydrogen stretch (where the carbon is that involved in the carbon-carbon double bond), the carbon-carbon double bond stretch gives rise to a peak at 1642.8 cm\(^{-1}\). Two peaks at 1560.0 cm\(^{-1}\) (the asymmetric carboxylate stretch) and 1462.5 cm\(^{-1}\) (the symmetric carboxylate stretch) show the presence of the carbonyl group. The carboxylate ion peaks are strong and very broad in comparison to the carbon-carbon double bond stretch peak which is of medium intensity and sharp. Upon polymerisation the two carbon-carbon double bond peaks will no longer be present in the spectrum. Percentage conversions can be determined by the ratio of the area under these peaks to the area under the carboxylate ion peaks.

The proton NMR spectrum of Na-10 in deuterated water using tetramethylsilane (TMS) as an added reference is shown in figure 6.2.1.2 a). This spectrum shows peaks characteristic of a carbon-carbon double bond. The vinyl protons appear as a doublet of doublets centred at 5.01 \(\delta\) (CH\(_2\)=CH-) and as a multiplet at 5.87 \(\delta\) (CH\(_2\)=CH\(-\). Figure 6.2.1.2 b) shows the corresponding carbon 13 spectrum, peaks at 113.8 and 139.7 \(\delta\) indicating the presence of the carbon-carbon double bond and the peak at 183.6 \(\delta\) is characteristic of a carbonyl group being present in the molecule which could not be
Figure 6.2.1.2  a) Proton and b) Carbon 13 NMR spectrum for monomeric Na-10 in D$_2$O using TMS as an added reference.
determined from the proton spectrum (see § 2.1 for a full analysis of these spectra). Polymerisation is monitored using proton NMR via reference of the peaks due to the carbon-carbon double bond protons with those unaffected by the polymerisation.

### 6.2.2 Determination of the critical micelle concentration for Na-10

The electrical conductivity curve for the Na-10/water system at 25 °C is shown in figure 6.2.2.1. Determination of the concentration at which Na-10 micellisation is initiated (i.e. the critical micelle concentration (cmc)) is not possible from this curve as there are no defined breaks. A consequence of the curve having a slowly changing slope is either that the system cannot be characterised by only free surfactant in water before the cmc and micelles plus free surfactant in water once the cmc is attained or that aggregation of the surfactant molecules is gradual with the aggregation number increasing with concentration. The first explanation (for the case of Na-10 where hydrolysis occurs in aqueous solution) is more likely to be the true situation. Hence other species must be present in solution which influence the aggregation of the surfactant.

The corresponding surface tension curve as measured by the du Noüy ring method at 25 °C is shown in figure 6.2.2.2. The surface tension curve shows three separate regions; two pseudo linear regions are observed before a plateau in the surface tension is reached. It is a mistake though to assume that this plateau is due to the solution undergoing aggregation to form micelles (yielding the true cmc) as is usually presumed in surface tension experiments. The observance of two almost linear regions prior to the plateau in the surface tension curve indicates the presence of auxiliary components in solution, which affect the solution behaviour and hence the concentration at which the surface tension plateaus out. The two breaks in the surface tension plot correspond to Na-10 concentrations of ca. 5x10⁻³ and 0.02 M. Note that the plateau observed here may be due to a solubility limit having been reached.

Conductivity and surface tension measurements (which involve the air/water interface) have been shown [55, 56] to be extremely sensitive to changes in the pH of the solution. Measurement of the surface tension of aqueous solutions of fatty acid soaps (which like all salts of weak acids undergo hydrolysis) will therefore be affected by the hydrolysis of the soap since the colloidal nature of the soap solutions is dependent upon the extent of hydrolysis [1, 57-67], which will also affect the conductivity of the solution. The pH of these solutions will therefore vary considerably with composition. Hence, determination of the cmc of fatty acid soaps using surface tension or conductivity methods is complicated. This will also be the case for other techniques if the change in the exact nature of the solution and the affect of changing solution pH is not taken into consideration.
Figure 6.2.2.1 Electrical conductivity of Na-10 in water measured at 25 °C. The two linear fits to the data show that for concentrations between ca. 0.07 and 0.15 M Na-10 (region indicated by the dotted lines) the conductivity is changing gradually with concentration and neither fit predicts the measured conductivity (i.e. there is no definitive break indicating the onset of micellisation). Errors are indicated by the size of the data points.

It has been shown [57] that the presence of a fixed amount of Na-OH suppresses hydrolysis of the soap enabling well defined cmc values to be obtained from both conductivity and surface tension experiments.

Another way of determining the solution behaviour of fatty acid soaps (and hence their cmc) at low concentrations is to monitor the solutions pH with increase in soap concentration. Solutions which do not undergo hydrolysis will, in agreement with the Debye-Hückel limiting law for uni-univalent electrolytes give a slope of + 1/2 in the pH
versus log [soap] curve indicating that the soap behaves as the salt of a strong base and a weak acid. As the concentration is increased though marked deviations from ideal behaviour are often observed indicating that another process is occurring which is becoming increasingly important in determining the solution behaviour. In the case of a fatty acid soap this process is hydrolysis, as already indicated from the surface tension and conductivity measurements.

![Graph showing surface tension vs. log [Na-10]](image)

Figure 6.2.2.2 Surface tension of Na-10 in water measured at 25 °C using the du Noüy ring method. Two breaks occur in the curve corresponding to Na-10 concentrations of ca. 5x10^{-3} and 0.02 M. Errors are indicated by the size of the data points.

Upon hydrolysis the parent fatty acid (HZ, where Z is the carboxylate ion) is formed which is able to exist as either free acid or as an acid soap (MHZ_{2}, where M is the counterion). The configuration of this acid soap dimer is assumed to be one in which the head groups are at opposite ends of the dimer and there is considerable overlap of the hydrocarbon chains [61, 62]. Note that this configuration is more stable and therefore forms in preference to the configuration where both head groups are located at the same end of the dimer due to head group repulsion and thermal effects. Hence, in solution it is assumed that hydrolysis of fatty acid soaps may be explained by the precipitation of only
three solid phases, each having well defined composition; HZ, MHZ₂ and MZ (neutral soap). It should be noted that the term solid phase does not indicate the formation of a solid which will precipitate from solution under the conditions employed here but rather that this neutral species will separate out under appropriate experimental conditions (e.g. on decreasing temperature to reach the solubility limit). Any one of these three solid phases may be precipitated first on increasing the soap composition and at higher concentrations two solid phases may coexist (note that the combination HZ and MZ is unstable with respect to MHZ₂) [66].

It has been proposed [66] that the nature of the species present in solution may be determined from the slope of the pH versus log [soap] curve and in this way the solution behaviour in the dilute concentration regime may be explained for fatty acid soaps in aqueous solution.

Figure 6.2.2.3 shows the pH versus log[Na-1O] curve obtained at 25 °C. The curve shows four unique regions. At low concentrations (below ca. 0.02 M, corresponding to the second break observed in the surface tension curve) Na-10 acts as an electrolyte yielding the predicted slope of +1/2. Deviations from this slope in this concentration region may be due to the influence of carbon dioxide or small deviations from the exact soap concentration. Note that the largest deviations occur for concentrations of Na-10 below approximately 5x10⁻³ M which corresponds to the first break observed in the Na-10 surface tension curve. As the concentration of Na-10 is increased above 0.02 M the slope tends to +1, which is characteristic of the presence of HZ in solution. A gradual transition to a slope of +3 occurs at higher compositions indicative of MHZ₂ being present in solution. Note that this concentration range, over which the largest variation in the solution pH is observed, corresponds to the region in the Na-10 conductivity curve where the conductivity deviates from linearity (i.e. Na-10 concentrations between ca. 0.07 and 0.15 M). Therefore in this concentration range the conductivity of the solution will be most strongly influenced by the large increase in the solution pH. At higher concentrations the curve begins to flatten out, indicating the presence of MZ and finally becomes slightly negative, which suggests micelle formation [66]. (See Lucassen [66] for a full account of hydrolysis in soap solutions as monitored by the pH of the solution.) Hence, for the Na-10/water system the cmc may be determined from the maximum in the pH versus log[Na-10] curve and is ca. 0.4 M. Therefore the equilibrium processes occurring on increase in Na-10 concentration are

\[ H_2O \rightleftharpoons H_2O \quad NaZ \rightleftharpoons NaZ \rightleftharpoons NaZ \]

where the first process to occur is dissociation of the neutral soap producing the carboxylate ion, this then reacts with water to form the parent fatty acid. Further reaction with neutral soap yields the acid soap dimer. As the concentration of Na-10 is increased
the predominant species in solution becomes the neutral soap which finally begins to aggregate to form micelles at the critical micelle concentration.

Figure 6.2.2.3 Solution pH of aqueous Na-10 measured at 25 °C. A slope of + 1/2 indicates that no precipitate is present and the solution acts as a dilute electrolyte solution. At higher concentrations the solid phase HZ is present which is characterised by a slope of + 1. Formation of MHZ$_2$ manifests itself as a change of slope to + 3. According to Lucassen [66] the cmc is detected by the occurrence of a slightly negative slope. The dotted lines indicate the concentration range shown in the Na-10 conductivity curve (figure 6.2.2.1). Errors in the experimental data points are indicated by the size of the points.
Hence the pH versus log[Na-10] curve confirms that in the Na-10/water system at low surfactant concentrations Na-10 undergoes considerable hydrolysis which dominates the solution behaviour.

The results obtained here for the dilute concentration regime of the Na-10/water system contrast with those obtained by several other groups [2, 68-71]. The cmc for Na-10 has been reported to be either ca. 0.04 mol.kg\(^{-1}\) [68, 69] or ca. 0.12 mol.kg\(^{-1}\) [2, 70, 71] as determined by specific conductivity, fluorescence quenching and vapour pressure osmometry. The first reported cmc (0.04 mol.kg\(^{-1}\)) measured by Larrabee Jr et al. [68] from specific conductivity was later reported as being due to premicellisation of the Na-10 surfactant molecules and that the true cmc was ca. 0.12 mol.kg\(^{-1}\), it was also stated that hydrolysis accounted for an error of less than 0.1 % [2]. But Paleos et al. [69] also obtained a value for the cmc to be approximately 0.04 mol.kg\(^{-1}\) using fluorescence quenching. Each of the three techniques (conductivity, surface tension and pH) used here have indicated though that hydrolysis is an important contribution to the solution behaviour of Na-10 in the dilute concentration regime and cannot be ignored when determining the cmc for Na-10.

### 6.2.3 Monomeric self-assembly

For the binary system Na-10 in water, only two liquid crystalline phases are formed between 0 and 100 °C. A normal hexagonal phase (H\(_{\alpha}\), two-dimensional structure of hexagonal symmetry with liquid-like chains) forms between 42.6 % and 55.5 % by weight and a lamellar gel phase (L\(_{\delta}\), layered structure with frozen chains in a helical conformation) between 69.8 % and 80.8 % at 25 °C. Between 55.5 and 69.8 % the two phases coexist. The partial phase diagram for this system as determined in this study is shown in figure 6.2.3.1.

Figure 6.2.3.2 shows a typical optical texture observed through crossed polarising filters of a sample within the Na-10 hexagonal phase region of the phase diagram. This texture, is comparable to that observed in the DTAB/water hexagonal phase and is a classic example of the sometimes called fan texture [21, 22], by virtue of its similarity with the well-known SmA fan texture of G. Friedel [72]. The texture is common to samples prepared by concentration gradients and those obtained from the bulk. The observance of the fan texture has been shown to arise when the director of the cylinders is aligned parallel to the wall [35]. Each fan is composed of two pairs of brushes. These brushes are not coincident with the directions of the polariser and analyser but rather lie at an angle of between 15 and 20° (indicating a non-uniaxial hexagonal phase, similar to the case found in tilted columnar phases of thermotropic liquid crystalline phases (C\(_{\alpha}\)Q) [73]). They do however rotate along with rotations of the polariser and analyser in the same.
sense. The topological nature of the singularity (line defect of strength, s) which is responsible for the formation of the brushes has been studied previously [35, 74-76]. The strength, s, is equal to the number of brushes divided by four and is positive if the brushes rotate in the same sense as the polariser and analyser and negative otherwise. Hence, line disclinations of strength \( s = \pm \frac{1}{2} \) are responsible for the brushes observed in figure 6.2.3.2, these disclinations are paired for all thicknesses used [35]. Note that the central ends of the two brushes of one fan have been observed not to converge to the same point indicating that the molecular cylinders have the shape of involutes to developable domains [35, 77, 78].

![Schematic binary phase diagram of the Na-10/water system.](image)

**Figure 6.2.3.1** Schematic binary phase diagram of the Na-10/water system. \( L_1 \): micellar solution, \( H_\alpha \): normal hexagonal phase, \( L_\delta \): lamellar gel phase with frozen hydrocarbon chains in a helical conformation perpendicular to the plane of the bilayers, and \( A \): hydrated Na-10 crystals. The horizontally shaded area indicates a region where two liquid crystalline phases coexist (tie lines) and the diagonally shaded area where \( L_\delta \) coexists with hydrated crystals of Na-10.
Figure 6.2.3.2 Fan texture of the Na-10 hexagonal phase (crossed polarising filters, magnification 440). The cylinders lie parallel to the glass slide and the brushes correspond to line disclinations of strength $s = +1/2$. The brushes do not lie coincident to the polariser and analyser but make an angle of between 15 and 20°. Note that even under this low magnification the central ends of the two brushes of one fan are seen not to converge to the same point.

As water is allowed to evaporate from the hexagonal phase on a glass slide the texture obtained after one or two days, is shown in figure 6.2.3.3 a) (viewed under crossed polarisers) and b) (viewed under plane polarised light). Although the texture resembles the smectic fan, it is not composed of classic focal conic domains [72] with layers parallel to the glass slide. The texture is forced to form by the presence of the disclinations inherent in the hexagonal phase. The layers remain parallel and at equal distances (except in the fractures), but do not have the shape of Dupin cyclides. They rather have the shape of cylinders whose cross-sections are evolutes of circles. As far as it is known, this striking texture has not been previously reported for lyotropic systems. It corresponds to the development of a new phase as evidenced by the occurrence of a boundary and an enhanced opacity of the new band. However the line disclinations within the hexagonal phase are maintained through the phase transition; note also that the angle of the brushes with respect to the polariser and analyser remains constant throughout the transition (15 to 20°). Further evidence for the phase change was obtained from small angle X-ray scattering (SAXS) which will be discussed later. X-ray measurements performed on this new phase showed that it consists of bilayers of surfactant molecules with frozen hydrophobic chains indicative of a lamellar gel phase.
Figure 6.2.3.3 Spiral texture for the Na-10 lamellar gel phase formed by slow evaporation of water from the hexagonal phase when grown on a flat surface (magnification 440). Note the brushes do not lie coincident to the polariser and analyser, maintaining the same angle observed in the hexagonal phase. The texture is viewed under a) crossed and b) plane polarised light.
Figures 6.2.3.4 a) and 6.2.3.5 show enlargements of the spiral texture when viewed under crossed polars and plane polarised light, respectively. The interwoven spirals which are observed in both cases indicate that their origin is physical and not due to an interference mechanism, whereas the brushes are no longer evident under plane polarised light. More than one spiral may originate from the same core of the line disclination \( s = + \frac{1}{2} \). When more than one spiral does originate from a single core these spirals have the same period (the distance measured between two consecutive arms of the same spiral along their common normal). Therefore these spirals are involutes of circles [79]. Furthermore, because they can be formally superimposed on one another (i.e. if the spirals were to have the same origin they would be indistinguishable) they are evolutes of the same circle (§ 6.3.3). On the other hand spirals originating from different cores have no relationship. The periodicity is different for spirals originating from different cores and totally independent of the distance between the cores. Nevertheless, spirals can only be formed in the presence of paired line disclinations, where the second core influences the growth originating from the first. If the two cores are sufficiently separated, spirals no longer form, instead striations are observed (figure 6.2.3.6) which is a consequence of the density of the cores being too low. Formation of spirals was monitored as a function of time. As the water evaporates it is observed that the number of turns increases and the spirals grow larger, i.e. outwards. The helicity of the spirals is statistically random throughout the texture.

The spiral texture can be obtained only by evaporation of water from the hexagonal phase. Indeed when a sample of the bulk lamellar gel phase is viewed through crossed polarising filters the resulting texture, figure 6.2.3.7, contrasts strikingly to the texture seen in figure 6.2.3.3, this feature will be discussed later (§ 6.3.3).

The nature of the substrate is also a determinant in the formation of the spiral texture. Attempts to form a uniform spiral texture on a piece of mylar or mica were unsuccessful. Mylar cannot be used because concentration gradients cannot be successfully performed due to its hydrophobicity. The texture shown in figure 6.2.3.8 is that obtained for a micellar solution on mica after slow evaporation of water to form first the hexagonal and then the lamellar gel phase. This texture which consists of long striations is characteristic for a mica surface and it resembles closely the texture seen on glass when the cores are no longer paired (figure 6.2.3.6). Mica is molecularly smooth upon cleaving and the absence of a uniform spiral texture on this substrate may be due to the absence of large nucleation sites on mica, in contrast to the glass surface.

Remarkably the spiral texture can be grown on a glass slide with no cover slip, if the concentration gradient is performed in a close to saturated water vapour atmosphere. This implies that the formation of such a texture is related to an anchoring process on a simple substrate and not induced by a confinement problem. Note that usually a free
Figure 6.2.3.4 Details of the domains in the Na-10 spiral texture (magnification 1760). Note the occurrence of multiple fractures originating from the same core and different periodicities for the interwoven spirals (the periodicity of all spirals originating from one core is ca. 1.1 μm and those from the second core ca. 0.9 μm). a) Crossed polarising filters. b) Circularly polarised light; the core radius (r_c) is estimated to be 0.2 and 0.16 μm, respectively. Note the presence of single core striations in conjunction with the spirals, which arise when the cores are no longer paired.
surface can induce features other than anchoring; for instance Grandjean terraces [38].

Similar features have been found in other binary surfactant/water systems. A concentration gradient performed at 25 °C for hexadecyltrimethylammonium chloride (CTAC, CH₃-(CH₂)₁₅-N⁺(CH₃)₃Cl⁻) gave initially a hexagonal phase (figure 6.2.3.9), as expected (binary phase diagram shown in figure 6.2.3.10) which was followed by the formation of the spiral texture (figure 6.2.3.11). As in the case of the Na-10 hexagonal phase, the hexagonal phase formed in the CTAC/water system is non-uniaxial with the brushes of the fan texture lying at an angle of between 5 and 10° relative to the polariser and analyser. This angle is conserved during the transition from the hexagonal to the lamellar gel phase. The texture tends to that of concentric circles rather than spirals when all four brushes converge almost to a single point. This is true for both CTAC and Na-10 systems. The stability of the spiral texture for CTAC is generally much reduced compared with Na-10. This relative instability is reflected in the more rapid crystallisation of pure CTAC from the gel phase which takes only a couple of days as compared with months in the Na-10 case. Again, there is little in common between the bulk lamellar gel texture (figure 6.2.3.12) and the texture of the lamellar gel phase grown on the glass slide (figure 6.2.3.11).

CTAC is an ideal system to study because it is believed that formation of the spiral texture arising from the gel phase grown on a flat glass surface, requires a direct phase transition between the hexagonal and gel phases. At higher temperatures CTAC no longer has a first order phase transition and the spiral texture should not be observed. Indeed, at 56 °C no spiral texture could be prepared by the concentration gradient method, as expected due to the formation of a cubic phase in agreement with the observations of Henriksson et al. ([80], figure 6.2.3.10). However, the spiral texture was still observed at any temperature prior to the formation of the cubic phase. In addition no intermediate phase was observed in contradiction to the reported phase diagram ([80], figure 6.2.3.10).

To further illustrate the requirement of a first order hexagonal-lamellar gel phase transition, sodium tetradecanoate (C₁₄Na, CH₃-(CH₂)₁₂-CO₂Na⁺) was investigated. The spiral texture is observed over a narrow temperature range only (55 - 67 °C), in agreement with the reported phase diagram [1, 81, 82]. The rarity of this texture arises from the fact that the majority of binary surfactant/water system have intervening phases between the hexagonal and lamellar gel phases and so do not undergo a direct phase transition between these two phases. This could explain the fact of why this texture has not been previously reported. Some characteristic examples were chosen to illustrate this statement.
Figure 6.2.3.5 Na-10 spiral texture viewed under plane polarised light (magnification 1760).

Figure 6.2.3.6 Single core striations formed, on glass for the Na-10 spiral texture when the cores are no longer paired (crossed polarising filters, magnification 440).
Three polyalkyl(ethylene oxide) surfactants were chosen as characteristic of non-ionic systems. According to Mitchell et al. [83], a bicontinuous cubic phase is located between the hexagonal and the lamellar phases for hexaethyleneglycol mono n-dodecyl ether (C₁₂EO₆, CH₃-(CH₂)₁₁-(O-CH₂-CH₂)₆-OH), octaethyleneglycol mono n-dodecyl ether (C₁₂EO₈, CH₃-(CH₂)₁₁-(O-CH₂-CH₂)₈-OH) and octaethyleneglycol mono n-hexadecyl ether (C₁₆EO₈, CH₃-(CH₂)₁₅-(O-CH₂-CH₂)₈-OH). In addition the two latter form a micelle close packed cubic at high water content. Concentration gradients performed on these surfactants at varying temperatures gave no evidence for the formation of a spiral texture.

Anionic surfactants can have different head groups and hydrocarbon chain character, and hence it is difficult to predict their phase behaviour. Sodium dodecyl sulfate (SDS, CH₃-(CH₂)₁₁-SO₄-Na⁺), a single-chained surfactant with a sulfate head group and a sodium counterion exhibits six liquid crystalline phases; a hexagonal, a two-dimensional monoclinic, a rhombohedral, a bicontinuous cubic, a tetragonal and a lamellar phase [16, 18, 84-86]. Sodium di(2-ethylhexyl) sulfosuccinate (AOT, CH₃-(CH₂)₃-CH(CH₂-CH₃)-CH₂-O-CO-CH₂-CH(SO₃-Na⁺)-CO₂-CH₂-CH(CH₂CH₃)-(CH₂)₃-CH₃), a branched double-chain surfactant with a sulfonate head group and sodium counterion forms a lamellar, a cubic and a reversed hexagonal phase [87, 88]. Potassium oleate (KO, CH₃-(CH₂)₇-CH=CH-(CH₂)₇-CO₂-K⁺) is a fatty acid with a potassium counterion and a double bond in the middle of the hydrocarbon chain. Unlike SDS and AOT, KO does not form a cubic phase but instead two intermediate phases between the hexagonal and lamellar, the rectangular and the complex hexagonal phase [1, 89-92]. For the three anionic systems studied there was no evidence for formation of a spiral texture.

Dodecyltrimethylammonium chloride (DTAC, CH₃-(CH₂)₁₁-N⁺(CH₃)₃Cl⁻) and hexadecyltrimethylammonium bromide (CTAB, CH₃-(CH₂)₁₅-N⁺(CH₃)₃Br⁻) were chosen to represent the class of cationic surfactants, because of their different chain lengths and counterions. DTAC forms a micelle packed cubic, hexagonal, bicontinuous cubic and lamellar phases [93], whereas CTAB has the same phase progression without the micelle packed cubic [94, 95]. These two surfactants, like all those above, have no first order phase transition between a hexagonal and a lamellar gel phase and a spiral texture was not observed.

Assignments of the regions in the phase diagram were established by determination of the structures with SAXS. Diffraction patterns were obtained for powdered bulk samples in the hexagonal and lamellar gel phases for Na-10. In addition, the reciprocal space of oriented samples in the lamellar gel phase (which gives rise to the spiral texture) of Na-10 and CTAC was fully determined. Samples for X-ray analysis were prepared as described in § 2.8.
Figure 6.2.3.7 Mosaic texture obtained from the Na-10 bulk lamellar gel phase (crossed polarising filters, magnification 440), where the layers are parallel to the glass slide.

Figure 6.2.3.8 Striations obtained for the oriented lamellar gel phase of Na-10 grown by slow evaporation of water from the hexagonal phase on mica (crossed polarising filters, magnification 440).
Figure 6.2.3.10  Hexadecyltrimethylammonium chloride and $^2$H$_2$O binary phase diagram (courtesy of Henriksson et al. [80]). $L_1$: micellar solution, $H_\alpha$: normal hexagonal phase, $L_\alpha$: lamellar phase, gel: lamellar gel phase of type $L_\beta$ or $L_\beta'$, $Q_\alpha$: bicontinuous cubic phase, Int$_1$ and Int$_2$ are intermediate phases, and Crystals: hydrated CTAC crystals. The horizontally shaded area (indicating tie lines) is a region of coexistence between two liquid crystalline phases and the diagonally shaded area one where the gel phase coexists with hydrated CTAC crystals.

For bulk samples, the diffractions patterns come out as Debye-Scherer rings produced by all domains in the irradiated volume. The Na-10 hexagonal phase is characterised by four sharp rings at small-angles with spacing in the ratios $1: \sqrt{3}: \sqrt{4}: \sqrt{7}$ as expected for parallel cylinders packed in a two-dimensional hexagonal array (table 6.2.3.1). The wide-angle scattering shows one diffuse ring located at $2\pi/4.5 = 1.4 \text{ Å}^{-1}$ indicating a liquid-like state for the paraffinic chains [3].

The diffraction pattern of the bulk lamellar gel phase of Na-10 is comprised at small-angles by three sharp rings in the ratio $1:2:3$ characteristic of a layered structure and a diffuse central ring located at $0.118 \text{ Å}^{-1}$ (for a 75.0 wt% sample) (table 6.2.3.1). This diffuse scattering reflects the existence of correlations over a range of 53.1 Å. The wide-angle pattern is characterised by a set of two sharp reflexions at $Q_1 = 1.337 \text{ Å}^{-1}$ (strong)
Figure 6.2.3.9  Fan texture of the CTAC hexagonal phase (crossed polarising filters, magnification 440). The brushes do not lie coincident to the polariser and analyser but make an angle of between 5 and 10°. Note that even under this low magnification the central ends of the two brushes of one fan are seen not to converge to the same point.

Figure 6.2.3.11  CTAC spiral texture for the gel phase grown on a flat surface (crossed polarising filters, magnification 440). Note the brushes do not lie coincident to the polariser and analyser, maintaining the same angle observed in the hexagonal phase.
and at $\sqrt{2}Q_1$ (weak), and two diffuse rings at $Q_0 = 0.945 \text{ Å}^{-1}$ and at $2Q_0$, all positions are independent of concentration. The sharpness of the reflexions, whose ratio, relative to $Q_0$, is $(1:\sqrt{2}:\sqrt{4}:\sqrt{5})$, has been analysed by Tardieu et al. [11]. The diffuse rings are ascribed to the polar groups organised according to a two-dimensional square lattice of edge equal to $2\pi/Q_0 = 6.7 \text{ Å}$. The sharp reflexions correspond to stiff chains organised with rotational disorder in another two-dimensional square lattice where the diagonal is the side of the polar group lattice ($Q_1 = \sqrt{2}Q_0$). The hydrocarbon chains are perpendicular to the plane of the lamellae and in a helical conformation (Lβ) [11]. X-ray diffraction experiments performed on a sample of the Na-10 system which produced the spiral texture between two capillaries and the equivalent texture of long striations on mica gave diffraction data, both at small- and wide-angles, identical to that of the bulk gel phase. It follows that the crystallographic structure associated with all the textures (figures 6.2.3.3-6.2.3.8) is the same and hence corresponds to the same thermodynamic lamellar gel phase. The same conclusion has been reached for the structure associated with the spiral texture obtained in CTAC, where the lamellar gel is of the type Lβ or Lβ′ (see § 1.1 and 2.8).

In order to determine fully the reciprocal space of the lamellar gel phase, oriented samples were used. Figure 6.2.3.13 shows a film obtained with the incident X-ray beam perpendicular to the mica windows of the cell. Three Bragg spots are detected along the vertical, indicating that the layers have grown parallel to the equatorial plane. These spots appear with a crescent shape due to a slight mosaicity of the sample. The former diffuse ring of the powdered sample now lies along the same axis as the Bragg spots. Rotating the sample along the vertical axis does not change this pattern which indicates a full symmetry of revolution along the normal to the layers. No other scattering has been detected in other geometries of the sample relative to the incident beam.

Table 6.2.3.1 gives the structural parameters obtained for the Na-10/water mesophases. All equations were calculated for $T = 27 ^\circ \text{C}$. The specific volume was calculated as described in § 2.8 using known values for the specific volume of the sodium carboxylate group as determined from the specific volume values for sodium tetradecanoate and sodium dodecanoate. The specific volume of the paraffinic chains was determined from equation 2.8.9.

In the lamellar gel the bilayer thickness (table 6.2.3.1) is consistent with frozen hydrocarbon chains in the helical configuration of 3.4 monomers (the CH$_2$ groups) per turn [96]. A bilayer consisting of chains in an all-trans conformation which are not interdigitated would have a thickness of $2 \times 11.6 \text{ Å} = 23.2 \text{ Å}$ according to Tanford's equation [97] (the effect of the presence of a double bond at the end of the hydrocarbon chain of Na-10 is equivalent to reducing the chain length by approximately one CH$_2$ group). The observed contraction of this thickness is consistent with the ratio of 1.145
Figure 6.2.3.12  Mosaic texture obtained from the CTAC bulk gel phase (crossed polarising filters, magnification 440), where the layers are parallel to the glass slide.

Figure 6.2.3.13  X-ray scattering pattern of the Na-10 lamellar gel phase oriented by slow evaporation of water from the hexagonal phase. The incident beam is perpendicular to the mica windows of the cell (inset); the Bragg diffraction spots located on the vertical axis indicate that the layers have grown perpendicular to the walls (periodicity 28.7 Å). Note the diffuse scattering spot located along the vertical (Q = 0.118 Å⁻¹).
**Table 6.2.3.1 Structural parameters for Na-10/water mesophases at 27 °C**

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* Diffuse ring.

a) Very weak.

b) Structural parameters calculated with Φ = 0.66 as if the Hₓ phase were extending up to 69.8%.

[11] between this extended form and the helix configuration for the chains in the L₅ phase. The cross-sectional area per chain can be calculated from the wide-angle spacing by assuming a two-dimensional square chain packing which for Q₁ = 2π/4.7 Å⁻¹ corresponds to A_c = 22.1 Å².

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Polymerisation of the monomeric form of Na-10 was not possible due to the insolubility of this surfactant in most solvents. Hence, the parent fatty acid (undecenoic acid) of Na-10 was polymerised in a chloroform solution (0.25 M) via thermal initiation of added AIBN (10 mol% to surfactant). The reaction mixture was maintained at 60 °C for seven days after which the polymerisation had preceded to approximately 80 %. Increasing the reaction time did not increase the extent of polymerisation significantly. The corresponding sodium salt polymer (i.e. polymeric Na-10) was obtained by reacting the acid polymer with an equimolar aqueous solution of Na-OH. The resulting precipitate was washed with ethanol, dissolved in water and then freeze dried. Pure polymeric Na-10 was obtained by removal of the monomer and oligomer units using Sephadex G-15 (see chapter 5). It must be noted that this method of preparation produces polymers which are polydisperse and therefore the polymeric Na-10/water system cannot be regarded strictly as a binary system.

The proton and carbon 13 NMR spectra of polymeric Na-10 in D₂O using TMS as an added reference are shown in figure 6.2.4.1 a) and b). These spectra have been analysed for the polymeric configuration shown in the figures only. From analysis of the spectra the head-to-tail, head-to-tail configuration comprises approximately 80 % of the conformations formed during polymerisation. It should be noted that the peaks associated with the carbon-carbon double bond are no longer present, with the associated protons or carbons shifted either up or down field from their original position (compare with the spectra obtained for monomeric Na-10, figure 6.2.1.2 a) and b)).

In contrast to the phase behaviour of the monomeric form of Na-10 in water, polymeric Na-10 forms only one liquid crystalline phase between 20 and 100 °C. A lamellar phase forms between 60.5 and 69.7 wt% of polymeric Na-10 at 20 °C. At concentrations below 45.4 wt% a micellar phase forms. Between 45.4 and 60.5 wt% the two phases coexist. Figure 6.2.4.2 shows the partial phase diagram for the polymeric Na-10/water system.

The polymeric Na-10 lamellar phase displays several different optical textures when viewed through crossed polarising filters. Figure 6.2.4.3 shows a typical "mosaic" texture which contrasts with the "oily streak" texture shown in figure 6.2.4.4. Both textures are typical of those commonly observed for lamellar liquid crystalline phases and characteristic of a homeotropic orientation (i.e. the orientation in which the optic axis is normal to the plane of the preparation) [21, 22, 98-100].

Figure 6.2.4.5 shows a third optical texture also commonly observed in the polymeric Na-10 lamellar phase. Here both positive (where the radial direction is "slow") and negative (where the radial direction is "fast") spherulites (in the vein of Rosevear [21])
Figure 6.2.4.1  a) Proton and b) Carbon 13 NMR spectrum for polymeric Na-10 in D$_2$O using TMS as an added reference.
Figure 6.2.4.2 Partial phase diagram for the polymeric Na-10/water system. $L_1$: micellar solution, Lam: lamellar phase, and crystals: hydrated polymer crystals. The horizontally shaded area indicates a region of coexistence between the micellar and lamellar phases (where the lines indicate tie lines between the two phases). The diagonally shaded area indicates coexistence between the lamellar phase and hydrated polymer crystals.

are apparent. The positive and negative spherulites are determined by considering the extinction cross as if it were a uniaxial interference figure, hence positive corresponds to a radial and negative to a tangential vibration direction for the component of higher refractive index. The positive spherulites are characterised by extinction arms which are narrowest at the center of the cross whereas the negative spherulites are broadest at the intersection. Each positive spherulite constitutes a focal domain viewed normal to its elliptical base. From this figure it may be seen that while the positive spherulites (observed due to the presence of line defects of strength $s = \pm 1$ in the sample) are such that the extinction cross formed by the brushes remains oriented perpendicular to each other upon rotation of the polariser and analyser. This is not the case for the negative
spherulites, where the plus shape of the spherulite is distorted upon rotation. This distortion is due to the arms of the negative spherulite being at different levels. That is, the negative spherulite results from the vertices of the adjacent positive spherulites which are alternatively on the top and bottom surfaces of the preparation [21]. This texture is, therefore also characteristic of a lamellar liquid crystalline phase (since negative spherulites are not observed for other phases), but has not previously been reported in lyotropic systems. It should be noted that while both positive and negative spherulites are often observed in optical textures formed by lamellar liquid crystalline phases (both being apparent in the oily streak texture shown in figure 6.2.4.4) the uniform matrix formed by alternative positive and negative spherulites shown here has not been previously observed such that both $s = +1$ and $s = -1$ line disclinations are randomly distributed throughout the sample at a single focus point. A similar texture, without these

![Figure 6.2.4.3 Mosaic texture observed for the polymeric Na-10 lamellar phase (crossed polarising filters, magnification 440), where the layers of the phase are parallel to the glass slide, (68.7 wt%, 86.7 °C).](image-url)
Figure 6.2.4.4 Oily streak texture obtained for the polymeric Na-10 lamellar phase (crossed polarising filters, magnification 440), where the layers are parallel to the glass slide, (68.7 wt%, 75.5 °C).

Figure 6.2.4.5 Optical texture observed for the lamellar phase of polymeric Na-10 (crossed polarising filters, magnification 880). Note the presence of both positive and negative spherulites and the "pin wheel" effect displayed by the negative as compared with the positive spherulites which maintain a perfect cross at their core on rotation of the polariser and analyser, (60.7 wt%, 25 °C).
features, has been observed in a thermotropic smectic liquid crystal [101] and lamellar
lyotropic liquid crystalline phases of some lipid/water systems [102] which have been
described as forming due to the presence of a network of parabolic focal conics. This
network can be used to explain some of the features observed in the texture produced by
the polymeric Na-10 lamellar phase but does not describe the texture fully. Formation of
this texture may therefore, in addition to the parabolic focal conic network, be due to
unusual anchoring of the bilayers to the substrate and/or the orientations adopted by the
bilayers of the phase due to the presence of polydisperse polymer.

All three optical textures of the polymeric Na-10 lamellar phase were observed for both
bulk samples and concentration gradients performed at various temperatures.

The structure of this phase was established by SAXS. The diffraction pattern of the
polymeric Na-10 lamellar phase is characterised by up to three sharp rings in the ratios of
1:2:3 as expected for parallel planes and one diffuse ring at wide-angles (Q = 1.4 Å⁻¹)
indicative of liquid-like chains. No other rings were observed. Calculation of the unit
cell length from the primary Bragg reflexion yields a repeat distance of the order of 35 Å.
This value is consistent with that obtained for the Na-10 lamellar gel phase (table 6.2.3.1)
such that the hydrocarbon chains are no longer in a frozen state and helical conformation
(i.e. the expansion of the unit cell length is consistent with the ratio of 1.145 determined
by Tardieu et al. [11]). Head group areas are also consistent with a bilayer structure.
Calculated structural parameters are given in table 6.2.4.1 and were determined assuming
that the specific volume of polymeric Na-10 is the same as that for monomeric Na-10
when the chains are in the alpha configuration. This assumption should not introduce
significant errors into the calculated structural parameters. All equations were calculated
for T = 27 °C, and based on an assumed structure (see § 2.8).

Comparison of the monomeric and polymeric Na-10/water systems shows that, in the
concentrated region few similarities occur between the two. This indicates that the nature
of the hydrocarbon chain plays a critical role in determining the self-assembly of these
systems. This lack of overlapping regions between the two systems suggests that
polymerisation of the liquid crystalline phases of Na-10 may not involve retention of the
underlying surfactant mesophase. This is particularly true in the case of the lamellar gel
phase where the nature of the paraffinic chains differs from that in the other regions of the
phase diagram. Here, not only is the carbon-carbon double bond lost upon polymerisation, but it is likely that the helical conformation of the paraffinic chains is not
maintained either. The hexagonal and micellar phases should not be influenced to the
same extent and hence a different behaviour should be observed for these two phases as
compared with the lamellar gel phase upon polymerisation.
Table 6.2.4.1 Structural parameters calculated for the lamellar phase of polymeric Na-10 at 27 °C

| Polymeric Na-10 % (w/w) | Phase | Observed Unit Cell Volume Surfactant Aggregate Water Mean Area hkl | | |
|-------------------------|-------|---------------------------------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|
|                         |       | Q | Length (a) | Fraction Aggregate Thickness (d_s) | Thickness (d_w) | Per Polar Head (A) | |
|                         |       | (Å⁻¹) | (Å) | | (Å) | | |
| 54.2                    | L₁ +  | 0.132 | 32.1 | 0.41 | 17.9 | 14.2 | 31.6 | 001  |
| Lam                    |       | 0.196 | 0.390 | 0.56 | 0.58 | 18.9 | 13.7 | 29.9 | 001  |
|                         | Lam   | 0.188 | 0.385 | 32.5 | 0.58 | 18.9 | 13.7 | 27.0 | 001  |
|                         | Lam   | 0.186 | 0.370 | 33.4 | 0.63 | 20.9 | 12.5 | 001  |
|                         | Lam   | 0.193 | 0.580 | 33.9 | 0.64 | 21.7 | 12.2 | 001  |

6.2.5 Polymerisation of liquid crystalline phases

Four regions in the Na-10/water system were chosen as being representative for polymerisation in the assembled forms of Na-10: the dilute and concentrated regions of the micellar phase (5 and 30 wt% Na-10), the hexagonal phase (50 wt% Na-10) and the lamellar gel phase (75 wt% Na-10). The surfactant was not observed to self-initiate during equilibration. All samples were prepared as described in § 2.9.

Table 6.2.5.1 shows the percentage conversions for the four regions of the Na-10/water system activated by thermal initiation of added AIBN (10 mol% to surfactant) at 60 °C or by photochemical initiation. Note that an error of approximately ± 5% can be expected in these values due to inaccuracies in the measured integration values obtained from proton NMR.

Both types of initiation were found to yield similar results. Thermal initiation of the dilute micellar solution though appears to involve a gradual increase in the rate of polymerisation with time. A plateau was reached after approximately two or three days. This initial increase was not observed for any of the other compositions (initiated either thermally of photochemically) which reached their final conversion rapidly.
Table 6.2.5.1 Percentage conversions for the four regions of the Na-10/water phase diagram polymerised either thermally or photochemically

<table>
<thead>
<tr>
<th>Type of Initiation</th>
<th>Time (days)</th>
<th>Dilute Micellar Phase</th>
<th>Concentrated Micellar Phase</th>
<th>Hexagonal Phase</th>
<th>Lamellar Gel Phase</th>
</tr>
</thead>
<tbody>
<tr>
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</tr>
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<td>32.3</td>
<td>20.8</td>
<td>13.0</td>
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<tr>
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<td>18.0</td>
<td>28.0</td>
<td>23.4</td>
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<tr>
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<td>—</td>
<td>16.8</td>
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<tr>
<td>4.0</td>
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<td>14.6</td>
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<tr>
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<td></td>
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<td>11.9</td>
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<tr>
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<td>15.5</td>
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</table>

Table 6.2.5.2 presents the calculated mean and median for the polymerisation in the different regions. Results indicate that, for all Na-10 compositions, polymerisation via thermal initiation is more successful. Polymerisation in the liquid crystalline phases of Na-10 is dramatically reduced as compared with that in isotropic solution which was found to polymerise to approximately 80%. That is self-assembly of the Na-10 monomer acts to inhibit polymerisation of the surfactant.

Final samples were polymerised via thermal initiation (10 mol% AIBN to surfactant) at 60 °C for a period of two days. Both the micellar and hexagonal phases remained visibly unchanged, whereas the lamellar gel phase underwent a phase transition upon polymerisation.
Table 6.2.5.2 Statistics of the extent of polymerisation for the four Na-10 liquid crystalline phases

<table>
<thead>
<tr>
<th></th>
<th>Low Weight Percent Micellar Solution</th>
<th>High Weight Percent Micellar Solution</th>
<th>Hexagonal Phase</th>
<th>Lamellar Gel Phase</th>
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<td>Thermal Initiation</td>
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<td></td>
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<tr>
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<td>23.2</td>
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<td>mean</td>
<td>26.7</td>
<td>21.7</td>
<td>25.8</td>
<td>19.1</td>
</tr>
<tr>
<td>standard deviation</td>
<td>15.2</td>
<td>10.9</td>
<td>14.4</td>
<td>3.5</td>
</tr>
<tr>
<td>Photochemical Initiation</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>median</td>
<td>23.3</td>
<td>19.0</td>
<td>13.3</td>
<td>11.9</td>
</tr>
<tr>
<td>mean</td>
<td>23.6</td>
<td>20.0</td>
<td>13.2</td>
<td>12.1</td>
</tr>
<tr>
<td>standard deviation</td>
<td>8.6</td>
<td>8.7</td>
<td>3.5</td>
<td>4.4</td>
</tr>
</tbody>
</table>

The partially polymerised micellar solutions (25.8 and 21.3 percent conversion, respectively) when viewed under crossed polarising filters were optically isotropic. The molecular weight of both samples was determined to be less than 8000 (corresponding to approximately forty monomer units) via dialysis. Although this could indicate intra-micellar polymerisation, it is unlikely as the molecular weight of polymeric Na-10 was also found to be less than 8000. This suggests that free radical initiation of the allyl polymerisable moiety in this position does not result in large molecular weight polymers. This is directly comparable with the results obtained for ω-UTAB where the molecular weight of the polymers synthesised from both isotropic and self-assembled states were also below 8000. It should be noted that while the aggregation number of the micelles may be less than forty at low surfactant concentrations it is likely to increase dramatically with an increase in concentration (see § 1.1). This is due to elongation of the aggregates as evidenced by the formation of a hexagonal phase subsequent to the micellar phase. That is, in the dilute region of the micellar phase a single polymer chain may constitute a micellar aggregate but this is unlikely in the more highly concentrated regions where the polymer will be only one component of the aggregate.

The optical texture observed for the partially polymerised Na-10 hexagonal phase (15.7 percent conversion) is shown in figure 6.2.5.1. Although the texture differs from that observed for the pure monomeric hexagonal phase (figure 6.2.3.2), it is typical for lyotropic hexagonal phases. The colouration is due to the increased thickness of the sample (~ 125 μm) as compared with the monomeric samples and the texture indicates a greater disorder in the underlying phase. Several edge dislocation can be distinguished.
and striations, as analysed by Rogers and Winsor [23], are also evident. Note that these striations are caused by different surfactant geometries and defects than those discussed in § 6.2.3 which were associated with the lamellar gel phase. The hexagonal phase is found to be stable to 100 °C. Hence the stability of the partially polymerised phase is comparable with that of the pure monomeric hexagonal phase.

![Optical texture observed for the partially polymerised Na-10 hexagonal phase (crossed polarising filters, magnification 440). Note the presence of edge dislocations and striations, (49.3 wt% Na-10, 98.3 °C).](image)

The lamellar gel phase (20.7 percent conversion) unlike the other samples undergoes a phase transition and separation upon polymerisation. Figures 6.2.5.2 and 6.2.5.3 show the presence of three phases in a given sample. Upon polymerisation the original lamellar gel phase transforms yielding a hexagonal phase, a lamellar phase and hydrated crystals. Figure 6.2.5.2 shows the textures due to the lamellar gel and hexagonal phases and figure 6.2.5.3 that of the lamellar phase.

All four components remain present on increasing the temperature to 100 °C. It was not possible to physically separate any of these four components so as to analyse each separately and determine which phases are comprised of polymeric Na-10. A plausible explanation, however, can be based on the phase diagrams of the pure monomeric and polymeric forms of Na-10 (figure 6.2.3.1 and 6.2.4.2, respectively). Polymerisation of the lamellar gel phase induces a phase transition to a lamellar phase. Specifically the paraffinic chains which were originally frozen and in a helical conformation become more
Figure 6.2.5.2 Optical textures observed for the hexagonal and lamellar gel phases of the partially polymerised Na-10 lamellar gel phase (crossed polarising filters, magnification 440).

Figure 6.2.5.3 Lamellar texture observed in a sample of the partially polymerised Na-10 lamellar gel phase (crossed polarising filters, magnification 440).
liquid-like and are no longer in the helical conformation. From the polymeric phase diagram, at a polymeric Na-10 composition of approximately 75 % by weight the lamellar phase coexists with hydrated polymer crystals. This therefore may explain the presence of the lamellar phase and hydrated crystals in the partially polymerised lamellar gel phase. A consequence of this phase separation of the polymerised form of Na-10 is that the remaining unpolymerised sample has an overall composition less than 75 wt% Na-10. From the monomeric phase diagram, this would push the system into the two phase region between the hexagonal and lamellar gel phases. Hence the presence of all four components may be explained if it is assumed that the hexagonal and lamellar gel phases contain no polymerised Na-10 and that the polymerised form yields a lamellar phase and hydrated polymer crystals.

To substantiate the findings of the optical microscopy investigations (i.e. that the micellar and hexagonal phases remain unchanged and that the lamellar gel phase phase separates upon polymerisation) SAXS experiments were performed on the partially polymerised samples.

The concentrated partially polymerised micellar phase produced a diffraction pattern at small- and wide-angles consisting of one diffuse ring only. The average distance between the aggregates (table 6.2.5.3) is comparable to that observed for the pure monomeric micellar phase (table 6.2.3.1). This indicates that the nature of the micellar solution remains largely unperturbed upon polymerisation.

Similarly, the diffraction pattern at small-angles for the partially polymerised hexagonal phase consisted of four sharp Bragg peaks in the ratios of 1: √3 : √4 : √7. No other peaks were observed. At wide-angles only one diffuse ring was present at Q = 1.4 Å⁻¹ indicating liquid-like chains [3]. These results in conjunction with those from optical microscopy indicate that upon partial polymerisation the underlying geometry of the surfactant molecules is maintained in the original hexagonal phase. Calculation of the structural parameters for this resultant phase show that there is a contraction in the unit cell length and an increase in the head group area (table 6.2.5.3). This is expected due to an increased confinement of the surfactant molecules due to the presence of polymer.

The diffraction pattern at small-angles obtained for the partially polymerised lamellar gel phase was very complicated, consisting of several Debye-Scherer rings. Using the information obtained from optical microscopy, the pattern was able to be indexed as follows. The presence of the hexagonal phase was evidenced by four sharp rings in the ratios of 1: √3 : √4 : √7. The lamellar phase gave two sharp rings in a ratio of 1:2 and the lamellar gel produced four sharp Bragg peaks having ratios of 1:2:3:4 and a diffuse central ring located as 0.117 Å⁻¹ (table 6.2.5.3). This diffuse scattering reflects the existence of correlations over a range of 53.7 Å. At wide-angles a diffuse ring at Q = 1.4 Å⁻¹ was detected which was attributed to the hexagonal and lamellar phases. In
conjunction with this ring two sharp reflexions at \( Q_1 = 1.31 \text{ Å}^{-1} \) (strong) and at \( \sqrt{2}Q_1 \) (weak) and two diffuse rings at \( Q_0 = 0.92 \text{ Å}^{-1} \) and at \( 2Q_0 \) were observed and were due to the presence of the lamellar gel phase (compare with § 6.2.3).

Table 6.2.5.3 gives a summary of these results. The structural parameters for the different phases arising from the lamellar gel phase could not be determined since the volume fraction for each phase was uncertain. The calculated unit cell lengths for each phase do though correspond reasonably well to those determined for the pure monomeric phases. The structural parameters for the hexagonal phase were calculated assuming that the composition remains unchanged upon polymerisation (i.e. the phase is retained and no phase separation or transition has occurred). The specific volume of the surfactant was also assumed to vary little upon polymerisation. All equations were calculated for \( T = 27 \, ^\circ\text{C} \).

These results indicate therefore that the micellar and hexagonal phases remain largely undisturbed upon partial polymerisation with the only changes being manifested as a slight change in the calculated structural parameters. In contrast the lamellar gel phase undergoes a phase transition and separation upon polymerisation.

### 6.3 DISCUSSION

#### 6.3.1 Critical micelle concentration

The change from a quaternary ammonium head group to a fatty acid soap has been shown to have a significant affect on the solution behaviour of the surfactant in the dilute concentration regime. Na-10 undergoes hydrolysis in this region which promotes the formation of the parent acid and acid soap dimers prior to micellisation. The formation of the parent fatty acid and dimers is used to explain the results obtained from measurements of the solutions conductivity, surface tension and pH. The formation of acid dimers has also been used to explain deviations in the measured physical parameters of aqueous solutions of monoalkyl sulfates \([62, 64, 103, 104]\). The creation of the acid soap dimers sufficiently stabilises the surfactant in aqueous solution such that the initiation of surfactant aggregation to form micelles is shifted to higher surfactant concentrations. It should be noted that the effective chain length of Na-10 is equivalent to a \( C_8 \) or \( C_9 \) hydrocarbon chain only which will therefore, also act to shift the cmc to higher concentrations of Na-10. Since it has been shown that in general decreasing the length of the hydrocarbon chain increases the concentration at which aggregation is initiated \([105]\). Therefore, the combination of a fatty acid head group and a shortened paraffinic chain can be used to explain the high cmc observed for Na-10 in aqueous solution. Comparison with the equivalent non-polymerisable fatty acid soaps sodium octanoate and sodium
decanoate (the C7 and C9 equivalents) which have cmcs at 25 °C of ca. 0.35 and 0.1 M, respectively [65] shows that this combination does indeed push the cmc to higher concentrations. Note that these values have been determined from conductivity measurements which were corrected for hydrolysis [106]. The presence of the terminal double bond, as in the case of ω-UTAB also acts to further increase the concentration at which aggregation occurs as compared with the non-polymerisable analogue.

Table 6.2.5.3 Structural parameters for the partially polymerised surfactant mesophases of Na-10 at 27 °C

<table>
<thead>
<tr>
<th>Na-10 % (w/w)</th>
<th>Phase</th>
<th>Observed Q</th>
<th>Unit Cell Length (Å)</th>
<th>Volume Fraction (φ)</th>
<th>Surfactant Aggregate Thickness (dₜ)</th>
<th>Water Thickness (dₚ)</th>
<th>Mean Area per Polar Head (Å²)</th>
<th>hkl</th>
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<td>44.1</td>
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</tr>
</tbody>
</table>

* Diffuse inner ring.

1) The correct weight percentage for each of these phases is unknown due to phase separation. Hence, the structural parameters for these phases could not be evaluated.

6.3.2 Structural transformation and epitaxial relation

The phase behaviour observed for the monomeric Na-10/water system does not resemble that observed for any of the quaternary ammonium systems discussed in previous chapters. The balance of interactions has been severely altered by replacement of the
quaternary ammonium head group and the shortening of the hydrocarbon chain. This combination produces a rare phase transformation and a new optical texture.

To describe the structures and to understand the physical reasons for the phase changes (in this case from a normal hexagonal phase to a lamellar gel phase), a precise picture of the shapes and the packing of the aggregates must be obtained, since the geometry of self-assembly is directly controlled by the intermolecular forces [107-110]. In principle this information can be extracted from the relative intensities of the diffraction lines for the observed patterns [6, 111-113], often though due to the complexity in the aggregate form factors these intensities are difficult to analyse [114]. Furthermore, the exploitation of the limited number of reflexions gives only an average structure, which reflects the nature and symmetry of the long-range order displayed by the mesophase. The real structure may depart from this mean picture, when diffuse scattering occurs due to various types of fluctuations of lower symmetry extending over a short-range.

To ease the task of structure determination, chemical constraints pertaining to the nature of the molecules and their geometry can be introduced to produce a choice of possible structures which have the correct symmetry [6]. The main constraint is the segregation of water from the hydrocarbon chains of the amphiphilic molecules. Using this well accepted assumption, which is demonstrated in several different cases [6, 8-10, 12, 46, 114, 115], the relative volumes of the aggregates and inter-aggregate water are obtained (table 6.2.3.1) from the known composition of the mesophase. Note that, as the water content decreases, the area per polar head at the water-surfactant interface never increases, even when phase boundaries are crossed, in agreement with the work of Luzzati and collaborators [6].

The above procedure has enabled analysis of the so-called lamellar gel phase for Na-10 in water. The one-dimensional periodic structure is an alternate stack of water layers separated by bilayers, where the hydrocarbon chains are perpendicular to the plane of the lamellae and in a helical conformation (L₅) [11]. The paraffinic chains maintain rotational motion along the long axis of the molecule [116] and lateral motion in the plane of the bilayer is believed to be slow [117, 118].

In the normal hexagonal phase H₆, the aggregates of amphiphilic molecules, whose paraffinic chains are in a liquid-like state, are generally described as indefinite cylinders of circular cross section. As these sections have symmetries higher than six, this description is compatible with the p6m symmetry of the lattice. For systems of surfactant in water (i.e. binary systems or mixtures of different amphiphilic molecules in the absence of any alkanes which can swell the interior of the aggregates), the radius of such cylinders must be smaller or at maximum equal to the length of an extended surfactant molecule (as there is no water within the hydrophobic region of the aggregates, see § 1.1). Therefore when the surfactant concentration increases, the aggregates grow and the
The hexagonal phase is preserved as long as the section of the cylinders does not become larger than this critical width, otherwise a phase transition usually occurs. This is exactly what occurs for Na-10 in water (see table 6.2.3.1). However, in certain lyotropic liquid crystals \[18, 119, 120\], it has been observed that the hexagonal mesophase can remain stable and the $p6m$ symmetry of the lattice preserved, even though its aggregates accommodate a higher number of surfactant molecules than expected.

Indeed, as the $p6m$ symmetry of the lattice imposes at least a six-fold symmetry on the distribution of any section, the growth of the cylinders can grow in several different ways. They may either keep their circular shape (isotropic growth), or deform with an anisotropic cross-section having a symmetry lower than six (in such a case the $p6m$ symmetry is preserved presumably through an orientational disorder of the section of the aggregates along their long axis, in addition to fast rearrangement of the aggregates performing a $2\pi$ rotation). Also, it is of course possible that within the hexagonal phase the aggregates undergo shape fluctuations on a short time scale which is difficult to detect as conventional scattering methods cannot distinguish between static and dynamic phenomena. The isotropic growth is usually not observed in a binary surfactant/water system, since it implies a large cost in free energy due to the formation of voids in the core of the cylinders. An anisotropic growth implies an inhomogeneity of the interfacial curvature, induced by a modulation of the mean area per chain at the interface of the aggregates. This is facilitated in the presence of a mixture of amphiphilic molecules giving rise to an inhomogeneous distribution along the interface: this has indeed been observed for ternary systems \[119, 120\]. For a binary system comprised of ionic amphiphilic molecules where all paraffinic chains are in a liquid-like state, modulation of the interface is still possible, as the degree of dissociation of the counterion may vary along the curved and flat areas of the interface. This has already been observed for SDS in water, in the vicinity of the hexagonal/monoclinic (i.e. deformed hexagonal) two-dimensional phase transformation \[16, 18, 86\].

The results for Na-10 in water suggest a similar phenomenon inducing the transition H$_{a}$/L$_{b}$, but in this case the transformation is likely to be driven by a change in the state of the paraffinic chains. As the water content is decreased, a larger number of the surfactant chains progressively become frozen. This induces inhomogeneities into the interior of the cylinders, and hence modulation of the interfacial curvature which will build up flat areas, precursors to the formation of the bilayers of the lamellar gel phase (a mixture of chains in different configurational states within the same aggregate is quite reasonable: see for instance L$_{\alpha\beta}$ and P$_{\alpha\beta}$ \[12\]). The hexagonal phase approaches the lamellar structure through layering. Apparently though, the growth of the bilayers, coplanar with the hexagonal packing of the rods cannot be carried out along the (10) planes; instead they are built up in perpendicular planes (see figure 6.2.3.13, where the cylinders of the H$_{a}$ mesophase initially parallel to the walls have become bilayers perpendicular to the
walls). The structural transformation between the H\textsubscript{c} and L\textsubscript{0} phases can be understood if instead of using the primitive unit cell (a = b, \(\gamma = 120^\circ\)) of the hexagonal structure one uses the associated centred rectangular one (a' = a, b' = \(\sqrt{3}a\)). The flat regions of the aggregates tend to align along the long side of the rectangular unit cell. This allows the opposing surfaces to maintain a sufficient separation, otherwise the edges of the anisotropic aggregates would come in too close a proximity, giving a configuration which presumably costs more in free energy due to a larger inter-aggregate repulsion (electrostatics and hydration forces). The converse process shows up on the other side of the transition. The layered structure of the L\textsubscript{0} phase is riddled with defects whose correlations resemble the diffraction pattern of the hexagonal H\textsubscript{c} phase. Indeed, this interpretation is supported by the occurrence of the diffuse scattering observed in the X-ray patterns of the L\textsubscript{0} phase. The location of this diffuse scattering in the reciprocal space (figure 6.2.3.13) corresponds to correlations between objects in planes whose period matches the repetition 59.8 Å (= 2\(\pi/0.105\)) of the rectangular unit cell associated to a hexagonal structure that would have existed at the same surfactant concentration (69.8 %) if the phase transition had not taken place (see table 6.2.3.1). Note that in such a case the cylinders would have a cross section too large (50.9 Å diameter) and they would lie too close to one another (8.9 Å separation). Therefore, it is argued that the ordering of the rods of the hexagonal phase still show up as heterophase fluctuations in the lamellar gel phase.

It is actually not surprising that some simple relations between the two phases (topological connections) must appear to ease the process that takes place, since the transition from a lamellar gel structure into a hexagonal one involves not only a large topological transformation from a one- to a two-dimensional lattice, but also simultaneous conformational changes of the paraffinic chains. Because both long-range and short-range order are affected through the transformation, such relations obviate the need for large molecular rearrangements which might be energetically expensive or kinetically quite slow, the latter being in contradiction with the kinetic observations of similar transformations [121]. Observations here, show that the normal hexagonal/lamellar gel phase transition involves relatively small changes in the positions of the surfactant and water molecules, as the layers are built in a stack which is coplanar with the hexagonal packing, which is in agreement with other experimental observations [122]. This is also in agreement with Caffrey's model [121] for the mechanism of the transformation between a lamellar structure and an inverted hexagonal liquid crystal for lipidic systems. This is despite the fact that the results obtained here contradict his prediction of an epitaxial relation between the two structures. As for Na-10 in water it is observed that the bilayers do not grow along the reticular planes (10) of the H\textsubscript{c} structure, but actually along the less dense planes which are perpendicular to the latter. As discussed above, this feature seems to be governed by the rearrangement of aggregates at the transition. The dominant inter-aggregate interaction is repulsive (electrical double layer, excluded
volume, and hydration force) and the associated contribution to the free energy of the system is minimised by reorganisation of the amphiphilic molecules into a smaller number of larger aggregates. Consequently, modifications of the intra-aggregate properties (short-range order/disorder transition due to changes in paraffinic chain conformations within the aggregates) appear to be presumably at the origin of changes of inter-aggregate properties (hydration forces and electrostatics due to surface charge modifications) inducing this phase transformation.

Note that alternative theoretical models have been invoked to explain the transformation from a hexagonal (normal or inverted structure) into a lamellar phase [109, 110, 123-125], and that different experimental situations can arise. In most of the cases, the system manages to cross from a situation with homogeneously curved interfaces (cylinders) to another one with zero curvature (bilayers), by building up intermediate phases. This process occurs through the production of structures with heterogeneous curvature or with negative Gaussian curvature (saddle-splay geometry). In the transformation discussed above, no stable intermediates have been observed, presumably due to the influence of the disorder/order transition at short-range precluding the formation of stable aggregates. However, it does not rule out the possibility of having short-lived meta-stable intermediates as proposed by Siegel [123-125].

6.3.3 Spiral texture

In addition to the information obtained from X-ray, the optical texture produced by the oriented lamellar gel phase is striking and gives a large amount of information about the nature of the defect which produces it.

It is known that configurations without strain and twist deformation in a mesomorphic phase made of long thin rods are characterised by the existence of physical planes perpendicular to the rods, enveloping a developable surface [77, 78]. Simple types of developable domains are the ones in which the developable surface is a circular cylinder (or hemi-cylinder) of radius $r_0$ [77, 78]. The pattern of the rods is the same in any orthogonal section of the cylinder. The rods are curved in involutes of the circular section of that cylinder. Such a configuration is one of a disclination line of strength $s = +1$ ($s = +1/2$ in the case of a hemi-cylinder) where the core radius $r_c > r_0$. The optical observations in the hexagonal phase (figure 6.2.3.2) are in agreement with those of Oswald and Kléman [35]. The surfactant rods lie in planes parallel to the wall, and the stable disclinations are wedge lines of strength $s = +1/2$ perpendicular to the walls.

The spiral texture of the lamellar gel structure can be analysed in a similar way, as analogies can be made for configurations of layers akin to those of rods from which they
have grown by a slow evaporation of water. Those layers, that have no elastic energy except for bending deformation are indeed evolutes of circles. This is evidenced from a number of experimentally observed facts:

Fractures arising from the core of a line wedge disclination of strength \( s = + 1/2 \) lead to the formation of the spirals or striations (figure 6.3.3.1). This is supported by the affect of polarised light on the spirals or striations. Since the spirals remain when viewed under both plane (figures 6.2.3.3 b) and 6.2.3.5), crossed (figures 6.2.3.3 a) and 6.2.3.4 a)) and circularly (figure 6.2.3.4 b)) polarised light their origin must be a physical one and not due to the interference of the light with the underlying structure. Using this conclusion the periodicity of the spirals is directly proportional to the size of the developable domain (here a hemi-cylinder), since the spirals are evolutes of circles. In some instances more than one fracture of the core occurs and the multiple fractures must be superimposable because they are produced from the same domain (slight fluctuations may occur due to the non perfect symmetry of revolution). This is indeed what is observed. Hence measurement of the spirals periodicity (\( p \)) can be used to calculate the radius (\( r_0 \)) of the hemi-cylinder : \( r_0 = p/2\pi \). Kléman [77, 78] and Oswald and Kléman [35] have demonstrated that the core radius (\( r_C \)) is related to \( r_0 \). For wedge lines of strength \( s = + 1/2 \):

\[
 r_0 = r_c \sqrt{\frac{\gamma_0}{\gamma_2} \left( \frac{1}{2} + \frac{1}{\pi} \right) + \left( 1 - \frac{1}{\pi} \right)} \]

6.3.3.1

where \( \gamma_0 \) (always a constant positive) and \( \gamma_2 \) are terms of surface energy due to the anchoring of the aggregates to the core, obeying the conditions, \( \gamma_2 < 0 \) with \( 0.61 < -\gamma_0/\gamma_2 < 0.83 \). From the core radius the elastic constant corresponding to the bending term (\( K_3 \)) [41] can be extracted:

\[
 r_c = \frac{K_3}{8 \left[ \frac{\gamma_2}{2} + \gamma_0 \left( \frac{1}{2} + \frac{1}{\pi} \right) \right]} \]

6.3.3.2

It was found that the periodicity of the spirals varied considerably for different regions of the texture and that it was completely independent of the distance between the centres of the cores. Spirals arising from separate cores were found to be non-superimposable due to the different size of the core from which they originated. The radius of the domain (\( r_0 \)) ranges from 500 to 3000 Å (deduced from the spiral periodicity). For one given core the value of the ratio \( \gamma_0/\gamma_2 \) satisfies the required conditions for the stability of the wedge line defect of strength \( s = + 1/2 \) (see above). To illustrate this, results extracted from figure 6.2.3.4 b) gave for one core a periodicity of 1.1 \( \mu \)m, a value of \( r_0 = 0.17 \mu \)m, \( r_c = 0.2 \)
\[ \gamma_0/\gamma_2 = 0.657 \] corresponded values for the second core in the pair were 0.9 μm, 0.15 μm, 0.16 μm and 0.653, respectively. All this gave evidence that the cores are very large, hence being able to give rise to multiple fracture sites and that the defects influence the growth of a fracture arising from a second defect situated close to it, but otherwise are independent of one another. When the growth of a fracture is not influenced by the presence of a second core a spiral is not formed, instead the fracture perpetuates into long approximately parallel striations. The occurrence of these striations is dependent upon the density of cores which in turn is dependent upon the thickness of the sample.

\[ L \]

![Figure 6.3.3.1](image)

**Figure 6.3.3.1** Paired line wedge disclinations of strength \( s = + \ 1/2 \) perpendicular to the plane of the figure, the developable domains are hemicylinders of radius \( r_0 \) inherent in the oriented lamellar gel phase. The spirals represent not only the fractures arising from the cores of the defects \( (r_c) \) but also the geometrical arrangement of the layers oriented parallel to the line disclination. Although the figure represents both of these physical characteristics the associated scale is considerably different (repeat distance between adjacent layers about 30 Å compared to about 1 μm). \( p \) is the periodicity of the spiral arms and \( L \) is the distance between the cores.

Note that the number of layers between two arms of the same spiral should be \( p/d_0 \), where \( d_0 \) is the repeat distance in the lamellar gel phase and \( p \) is the distance between
these two arms, if a constraint of constant thickness is imposed (figure 6.3.3.1). There
is also a longitudinal relaxation, due to the mismatches between successive layers. These
mismatches are relaxed by dislocations with Burgers' vectors in the layer. This
constraint is probably due to the "free volume" offered by the fractures, although it
remains to be understood what the nature of the phase inside the fractures is.

The involutes which are observed in the lamellar gel phase are images of the shapes of the
columns in the hexagonal phase. This does not mean though, that they occupy the same
positions exactly. However, the variation should not be large (corresponding to a mere
relaxation, due to the change in water content) since the evolutes which emerge from the
same disclination are all equal. It is possible that the various types of evolutes one
observes, emerging from various disclinations, represent a real phenomenon, (i.e. the
disclination cores in the hexagonal phase are really already different from one another).
Such a possibility cannot be underestimated, and arises from the different possible
densities of impurities and/or different core models which are energetically degenerate.
The first possibility implies a model in which the core consists of perfect hexagonal
material (in this case the core energy comes from the surface [35]). Alternatively, the
second case involves a model where the interior of the core is in a completely different
state, for instance a disordered isotropic fluid. If the second model is correct, two core
radii and not a continuum would be present. Hence the core region is believed to be filled
either by disordered isotropic fluid or by the hexagonal mesophase, the latter case being
more probable since \( r_0 \) is macroscopic.

Calculation of the value of the bending elastic constant (\( K_3 \)) requires an estimate of the
surface energy term \( \gamma_2 \). This term is unknown for the configuration of layers anchored to
the wedge line disclination. However, because these curved layers are obtained by
growth from the rods of the hexagonal phase, it is likely that the value of \( \gamma_2 \) is of the
same order of magnitude for both structures. For hexagonal phases in lyotropic liquid
crystals the value of \( \gamma_2 \) (of the order of \(-5\times10^{-3}\) ergs.cm\(^{-2}\)) [126] was deduced by
assuming that the magnitude of \( K_3 \) has a classical value of the order of \(10^{-6}\) dyne. Recent
experimental work on thermotropic columnar buckling instabilities has shown, however,
that the value of \( K_3 \) might be as large as six orders of magnitude greater than the above
classical value [127-130], and consequently may affect the estimate of \( \gamma_2 \). Since a large
contribution to the unusual effective value for the bending elastic constant (\( K_3 \)), has been
proposed to be attributed to column entanglement and defects in the tubular structure
[131, 132] the value of \( \gamma_2 \) proposed by Oswald [126] is maintained. Hence with this
estimate and the measured value of the core radius, \( r_c \) (figure 6.2.3.4 b)), \( K_3 \) is in turn
calculated to be about \(2\times10^{-7}\) dyne. The elastic constant \( K_3 \) can be related to the bending
rigidity (\( k_c \)) of Helfrich [133] and Fogden et al. [134], as \( K_3/k_c \) scales [126] like \( d_s/a^2 \)
(where \( d_s \) is the surfactant aggregate thickness and \( a \) is the periodicity of the structure).
From this, it is determined that \( k_c \) is about \(10^{-13}\) ergs which shows that the layers of the
lamellar gel phase are reasonably flexible. This flexibility makes possible the formation of such a highly curved configuration as in the spiral texture. Note that, as the main inaccuracy is in the measurement of $r_c$, and as $\gamma_2$ is unknown, the actual value of $K_3$ ($k_c$) may differ from this estimate.

The texture observed for a sample of the bulk lamellar gel phase (figure 6.2.3.7) contrasts strikingly from that obtained for the oriented sample (figures 6.2.3.3 - 6.2.3.6 and 6.2.3.8). The perpendicular orientation of the lamellar sheets on the glass slide and the presence of the defect inherent in the hexagonal phase (a line disclination of strength $s = +1/2$) are not present in a sample prepared directly from the bulk lamellar gel phase. These two differences lead to the bulk lamellar gel phase having a mosaic optical texture which is characteristic [21, 22] of sheets lying parallel to the surface of the glass slide.

This spiral texture, although new to lyotropic liquid systems, has been observed in several other systems, but the origin seems to be different than what has been found to be the case in this study. In all the previous reports either the presence of chirality or a cholesteric nature in the molecular architecture, or the geometrical structuring of domes and valleys were invoked to explain the formation of the spiral or concentric circle texture. A point defect at the center of a nematic droplet [41] gives a texture not unlike that obtained for the situation where the pairs of brushes meet at a single point to give concentric circles. Cholesteric systems may also give rise to spiral textures [39, 75, 135-140] whose pitch is a function of the twist between convoluted smectic layers. A similar texture has been reported in a thin polyethylene film [141], when the film is cooled rapidly through its melting point. This texture is characterised by spherulites superimposed with concentric circles. Some crystals [142] have also been shown to behave similarly during their growth. If the crystals are of one chiral form, spirals of a distinct helicity only result. However, variable helicity is observed in racemic mixtures or non chiral crystals.

Contrary to the situation above, the formation of the spiral texture in lyotropic systems is a direct consequence of the retention of the defects in the hexagonal phase through the phase transition and not due to a peculiar conformation of the frozen paraffinic chains (observed for both all-trans and helical conformations). In the transition from a hexagonal to a lamellar phase the mobility of the surfactant molecules is normally sufficient to ensure a rearrangement of the paired line disclinations, in order to relieve stress in the lamellar phase. In the case of a transition from a hexagonal to a lamellar gel phase on a flat glass surface where the evaporation of water is slow this is apparently no longer true. In this case the disclination array in the hexagonal phase is unable to rearrange during the transition, and the direction and topology of the defects remain unchanged. The mobility of the surfactant molecules is important in the formation of this texture. If the surfactant molecules readily diffuse through the system the probability of
rearrangement of the defects during the transition is increased. In the lamellar gel (Lβ, Lβ or Lγ type) phase the mobility of the surfactant molecules in the bilayer is significantly reduced in comparison to that in the lamellar (Lα) phase [117, 118]. If the evaporation of the water is also restricted the disruption of the defects inherent in the hexagonal phase is minimised, little rearrangement occurs and the spiral texture may be formed. The slower the evaporation of water, the more well formed and complete is the transition from the hexagonal texture to the spiral texture. The spirals observed in the experiment have a variable number of turns depending upon the duration of the growth. In certain cases there is a complete transfer of the hexagonal texture to the spiral texture and then no texture due to the bulk gel phase is evident.

Clearly then, anything that increases the mobility of the surfactant molecules will diminish the likelihood of formation of the spiral texture. The presence of any intervening phase between the hexagonal and lamellar gel phases seems to preclude the formation of the spiral texture. This was observed for all other surfactant systems studied that did not have a direct phase transition between a hexagonal and a lamellar gel phase. Presumably, in these cases the hexagonal disclination network is not retained in the intervening phase.

The absence of chirality in these systems does not rule out the possibility of a spiral growth geometry under the mechanism proposed by Pomeau [142], despite the growth of the spirals observed here is outwards rather than his contrary prediction of inwards growth. The surface irregularities of the glass slide can act in the same way as impurities in the system.

The absence of a spiral texture in bulk phases suggests that the preferential alignment of the cylinders in the hexagonal phase along the walls is a prerequisite for the formation of this beautiful texture, because the line disclinations must lie normal to the wall.

Essentially, the lamellar gel phase samples prepared on glass slides by evaporation of an anchored hexagonal phase are suspended in an unfavourable orientation, which would not be found under more usual conditions. It is not surprising then that this texture has not been widely observed.

The phase progression displayed by the Na-10/water system is difficult to compare with that observed for the systems previously discussed. Some similarities can though be drawn between Na-10 and ω-UTAB. Both surfactants have been shown to have an increased intrinsic rigidity of the paraffinic chains which acts to decrease the solubility of the surfactant and promote ordering of the chains upon aggregation. This preference to form more highly ordered systems being substantially enhanced in the Na-10/water system. Any further correlation is not possible since the introduction of the fatty acid head group cannot be isolated from the consequential reduction in the paraffinic chain.
length and hence the greater dominance of the terminal carbon-carbon double bond. But it is apparent that this combination affects significantly the surfactants solution behaviour and will also have important contributions to the observed behaviour upon polymerisation.

6.3.4 Polymerisation

Polymerisation of Na-10 prior to self-assembly was achieved to a similar extent as was the case for ω-UTAB (§ 5.2.4). This indicates that the nature of the head group has little affect on the polymerisation mechanism when the carbon-carbon double bond is sufficiently isolated from it. Hence it may be assumed that the polymerisation of Na-10 is attained in an identical manner to that of ω-UTAB and that the so-formed polymers will vary only in their different head groups and paraffinic chain lengths. It has been shown (see § 6.2.4) that polymerisation prior to self-assembly precludes the formation of both the hexagonal and lamellar gel phases which were formed in the Na-10/water system. In contrast, the polymeric form of ω-UTAB has a similar phase progression to that observed for the monomer differing only in the temperatures and compositions at which the different mesophases are formed. This difference in the behaviour of the two polymeric forms must therefore be explained by the change in head groups of the original surfactants. The average head group area of the trimethylammonium bromide group is considerably larger than that of the sodium carboxylate, whereas the paraffinic chain backbone of the polymers will be almost identical. The intrinsic shape of the Na-10 polymer, in comparison to polymeric ω-UTAB will therefore be more commensurate with the formation of the bilayer structure of the lamellar phase rather than the more highly curved geometries required for formation of the hexagonal and cubic phases. This indicates that the micellar phase formed by polymeric Na-10 is most likely comprised of disk-shaped aggregates.

This explanation cannot though be used to explain why a hexagonal and lamellar gel phase are formed by the monomer and not by the polymeric form of Na-10. This difference, in contrast to the explanation given above is due to the change in the nature of the paraffinic chains. The lamellar gel phase is not able to be formed in the polymeric Na-10/water system since formation of the polymer precludes adoption of a helical configuration by the paraffinic chains. The alternative to this is therefore to form a lamellar phase. In contrast to this explanation, formation of the hexagonal phase by monomeric Na-10 may be due to the increased flexibility and mobility available to the paraffinic chains in the non-polymerised form. This increased freedom is such that curved geometries are able to be formed prior to the orienting effect of the shortened paraffinic chain and the terminal carbon-carbon double bond become dominate and induce a disorder/order transition yielding the lamellar gel phase.
From the monomeric and polymeric Na-10/water phase diagrams the precise nature of the paraffinic chains is therefore critical in determining the self-assembly of the amphiphiles. This is carried over into the polymerisation of the liquid crystalline phases of Na-10. The micellar and hexagonal phases, where the paraffinic chains are in a fluid-like state are found to respond towards polymerisation in an identical manner to the micellar and hexagonal phases of ω-UTAB (see § 5.2.5 and 5.3). Specifically, the integrity of the mesophases remains unaltered upon partial polymerisation, although it is unlikely that intra-aggregate polymerisation has occurred. Again, as was the case for polymerisation in the liquid crystalline phases of ω-UTAB, the extent of polymerisation was found to be significantly reduced as compared to polymerisation of an isotropic solution of Na-10. This may be explained by the high degree of mobility of the paraffinic chains and the surfactant aggregate acting as a cage inhibiting the polymerisation (see § 5.3 for a fuller explanation).

A considerable amount of work has been performed on polymerisation in the micellar and premicellar regions of the Na-10/water phase diagram [2, 68-71, 143-148]. Varying results have been indicated by these different groups. Paleos et al. [69] assuming a cmc of ca. 0.04 M polymerised "micelles" in aqueous 0.1 M solutions (which according to the results obtained here (§ 6.2.2) corresponds to the concentration range where the acid dimer predominates) obtaining intra-micellar polymers using γ irradiation. A similar result was reported by Sprague et al. [2, 68, 70, 143, 148] who also used γ irradiation but assumed a cmc of 0.12 mol.kg⁻¹ (samples were polymerised above and below the stated cmc but none were above 0.4 M - the cmc determined here, again, this concentration range is dominated by the presence of the acid dimer). Polymerised samples both above and below 0.12 mol.kg⁻¹ yielded similar results when subjected to fluorescence quenching, viscosity, conductivity and electron spin resonance experiments. Chu and Thomas [71] have also based their results on the conductivity measurements of Sprague et al. [2, 68, 70, 143, 148] (i.e. there is a change in the aggregation state at concentrations of approximately 0.04 and 0.12 mol.kg⁻¹) indicating that the molecular weight of the produced polymer was different in the region below 0.043 M and above 0.15 M due to an increase in the aggregation number of the micellar units. Polymerisation was performed either by γ irradiation or thermal initiation of added potassium persulphate (a water soluble initiator). Durairaj et al. [144-146] indicated that polymerisation occurred between 15 and 30 % conversion only (which is similar to the results obtained here) when solutions in excess of 0.4 M Na-10 were polymerised thermally using ammonium persulphate (a water soluble initiator) as the added initiator. Finally Shibasaki and Fukuda [147] showed that polymerisation via γ irradiation in a 10 wt% micellar solution was only polymerised to approximately 10 %.

Results obtained here indicate that polymerisation in the dilute and concentrated regions of the micellar phase produce polymers of approximately equivalent molecular weight
(see § 5.3 for an explanation) and that the extent of polymerisation was approximately 25%. Therefore, subsequent experiments performed on the polymers formed in the different regions of the micellar phase should give almost identical results irrespective of the original concentration of the micellar solution, this is as observed in the cases reported above. Note that in determining the cmc (which was often used to explain the behaviour observed upon polymerisation of micellar and isotropic solutions) none of these groups took into consideration the effect of hydrolysis on the solution behaviour.

Others [147, 149, 150] have also reported polymerisation in the hexagonal region of the Na-10/water system. Shibasaki and Fukuda [147], whose phase diagram determined by thermal analysis contrasts strikingly with that both obtained here and by Friberg et al. [149, 150] (who determined the phase boundaries of the hexagonal phase during their study of the polymerisation in the Na-10 hexagonal phase) indicated that polymerisation by γ irradiation in the Na-10 "hexagonal phase" occurred to a maximum of 30% conversion. It should be noted that the results obtained here and by Friberg et al. suggest that the region thought to be a hexagonal phase by Shibasaki and Fukuda is actually a concentrated micellar phase. These results, when this is taken into consideration, correlate well with the percentage conversion determined for the concentrated micellar phase in this study. No description of the state of the partially polymerised sample was given.

Friberg et al. [149, 150] have stated that polymerisation of the Na-10 hexagonal phase via thermal initiation of potassium persulphate is essentially complete in one day and is transformed into a lamellar phase. The resulting polymer was found to have a molecular weight of approximately 55000, corresponding to approximately 270 monomer units. Therefore, the results of Friberg et al. differ in comparison with those obtained in this study, where polymerisation occurred to approximately 30% only and no phase transition was observed to occur. At this stage, a reason for this difference is unknown.

Polymerisation of the lamellar gel phase, where the chains are frozen and in a helical arrangement does not maintain the integrity of the phase. This disruption to the underlying surfactant geometry is caused by a loss of order in the paraffinic chains upon polymerisation. Here, also the extent of polymerisation was reduced when compared with an isotropic solution. An explanation for this reduction cannot be given in a manner similar to that for the micellar and hexagonal phases where the high degree of mobility was used. Here instead, the highly ordered conformation adopted by the paraffinic chains is used, which increases the average distance between the carbon-carbon double bonds. This increased distance and the inherent rigidity of the chains of the lamellar gel phase restricts the carbon-carbon double bond from adopting the correct orientation for polymerisation to precede and the free radical is lost via recombination. Hence again the surfactant aggregate acts as a cage inhibiting polymerisation and here the extent of
polymerisation is reduced to an even lower value than in the phases where the chains are in a molten state.

Shibasaki and Fukuda [147] have also reported polymerisation in a Na-10 gel phase. Again the composition of this phase does not correlate with the composition of the lamellar gel phase determined here. Polymerisation occurred to approximately 20% and no analysis of the resulting sample was given.

Therefore as was observed in the self-assembly of Na-10 in the monomeric versus polymeric forms the nature of the paraffinic chain is critical in determining the behaviour of the system.

6.4 CONCLUSIONS

Placement of an allyl polymerisable moiety at the end of the hydrocarbon chain of a fatty acid soap (yielding Na-10) induces a first order transition between the normal hexagonal phase and the lamellar gel phase in the binary phase diagram. This transition is also observed in the CTAC and C_{14}Na/water systems. The spectacular spiral texture obtained for the lamellar gel phase yields information about the defects inherent in the liquid crystalline phase. Its formation requires several factors to be fulfilled:

a) the presence of a direct phase transition between a hexagonal and a lamellar gel phase,
b) the slow evaporation of water during phase formation of the lamellar gel,
c) surface irregularities of the substrate and,
d) the retention of the paired line wedge disclinations of strength $s = +1/2$ inherent in the hexagonal phase from which the lamellar gel phase is grown.

All of these conditions must be met simultaneously if a spiral texture is to be observed.

Analysis of the aggregate configuration has enabled determination of the radius of the developable domain, estimates of the core radius (which appears to be reasonably large $\approx 0.2 \ \mu m$), and hence the bending elastic constant. The growth of the lamellar gel structure is coplanar with the packing of cylinders of the hexagonal phase, with an unexpected build up of layers in planes perpendicular to the densest reticular planes (10) of the hexagonal structure. It appears that modifications of the intra-aggregate properties (short-range order/disorder transition due to changes in paraffinic chain conformations within the aggregates) are at the origin of changes to the inter-aggregate properties inducing this phase transformation.

In conjunction with the formation of the spiral texture, the position of the carbon-carbon double bond at the end of the paraffinic chain facilitates polymerisation in isotropic solution as compared with polymerisation in the head group region of a surfactant due to
isolation of the polymerisable moiety from the interfacial area. The so-formed polymer’s phase progression is found to be altered from that of the monomer due to a change in the nature of the paraffinic chains.

As well as this combination affecting the surfactant’s self-assembling behaviour at high surfactant compositions, the dilute region is also affected, due to hydrolysis. These influences act together to shift the cmc of Na-10 to a surfactant concentration which is in excess of the cmcs obtained for surfactants with a quaternary ammonium head group.

Polymerisation of the mesophases formed by Na-10 in water is such that the underlying surfactant geometry is maintained for phases with fluid-like hydrocarbon chains (i.e. the micellar and hexagonal phases) but induces a phase transition (due to disruption of the paraffinic chain order) for phases with frozen hydrocarbon chains.

Therefore, the exact nature of the paraffinic chains (either molten, frozen or bound in a polymer chain) is critical in determining the self-assembly of both the monomeric and polymeric forms of Na-10 and also in the polymerisation of the lyotropic liquid crystalline phases.
6.5 REFERENCES


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Chapter 7

DODECYLDIMETHYLAMMONIUM METHYL METHACRYLATE BROMIDE

7.1 INTRODUCTION

Incorporation of the ethylmethacrylate polymerisable moiety into the head group of a C_{12} single-chain quaternary ammonium surfactant yields dodecyltrimethylammoniumethylmethacrylate bromide (DDAM, CH_{3}-(CH_{2})_{11}-N+(CH_{3})_{2}(CH_{2}-CH_{2}-O-CO-C(CH_{3})=CH_{2})Br^{-}). This polymerisable surfactant differs from those introduced previously by the nature of its polymerisable moiety. Here, the polymerisable moiety used is much bulkier and is of a more hydrophilic nature than the allyl group, it is also more readily polymerised. This simple replacement of the allyl group with the ethylmethacrylate alters the characteristics of the surfactant considerably. Due to the size of the polymerisable moiety contained within the head group of DDAM, its behaviour may differ from that of typical single-chain quaternary ammonium surfactants. The length of the polymerisable group is equivalent to that of a hydrocarbon chain containing six carbon atoms. The presence of two hydrocarbon chains affects the partitioning between the hydrophobic and hydrophilic regions of the surfactant and hence its self-assembling properties. The flexibility of the ethylmethacrylate group is extremely high, being comparable to that of an unbranched C_{6} hydrocarbon chain, and will therefore alter the inherent rigidity of the surfactant. By reason of this flexibility and the presence of a carbonyl group (containing oxygen, an electron donating atom), it has been proposed [1] that the geometry shown in figure 7.1.1 is one of the possible configurations adopted by this surfactant. If this conformation is adopted, the ethylmethacrylate is replacing a position traditionally included as part of the head group of a single-chain surfactant. It will instead, occupy the environment which partitions the hydrophobic and hydrophilic sections of the surfactant being neither solely in one nor the other. Hence the addition of
the ethylmethacrylate group increases the number of degrees of freedom of the head group considerably and introduces a polydispersity into the calculated surfactant parameter. The geometries adopted by DDAM are therefore dissimilar from both those observed for double- (e.g. allyldidodecylmethy lammonium bromide, ADDAB, (CH$_3$-(CH$_2$)$_{11}$)-N$^+$-(CH$_3$)-CH$_2$-CH=CH$_2$Br$^-$, chapter 4) and single-chain surfactants (e.g. allyldodecyldimethylammonium bromide, ADAB, CH$_3$-(CH$_2$)$_{11}$-N$^+$-(CH$_3$)$_2$(CH$_2$-CH=CH$_2$)Br, chapter 4). Although DDAM exhibits properties which can be attributed to both of these types of surfactants it cannot be classified as either a single- nor a double-chain surfactant.

![DDAM structure](image)

**Figure 7.1.1** One of the proposed geometrical conformations adopted by the DDAM surfactant molecule in solution [1] (note that, the conformations adopted by DDAM are dependent upon the surfactants environment and will therefore, vary both with temperature and composition).

DDAM, therefore, is very distinctive in comparison to those surfactants previously discussed here. This difference may be categorised as follows. Firstly, the configuration that the surfactant adopts in solution, affects directly the surfactant's self-assembling behaviour as compared with those surfactants containing the allyl polymerisable moiety. Secondly, the ethylmethacrylate polymerisable group has an increased reactivity towards polymerisation over the allyl group. These two aspects of the surfactant were expected to influence the surfactants ability to retain its underlying geometry upon polymerisation and enable the surfactant to polymerise to a greater extent than has been found to occur in surfactants polymerised via the allyl moiety.

Due to the ability of this surfactant to polymerise to a high degree over a short time scale (minutes as compared with hours for the polymerisable surfactants based on the allyl moiety) it has been widely studied in the low concentration regime [1-8]. Polymerisation in dilute micellar solutions of allyl polymerisable surfactants has been shown to produce polymers having molecular weights which are similar to the aggregation numbers of the
micelles from which they were generated [9-18]. It is believed though [19, 20], that this is due to an imposition of the free radical polymerisation of the allyl group rather than the surfactant self-assembly imposing a restriction on the size of the polymer such that it conforms to the aggregation number of the micelle (see chapter 5, § 5.3). Varying opinions on whether this has been achieved in the DDAM/water system have been discussed by a number of groups [1-8]. But due to the increased reactivity of the ethylmethacrylate group towards polymerisation the molecular weight of the polymer chains produced are considerably larger than that of the aggregate in which they were initiated. Hence, the likelihood of obtaining a "polymerised micelle" in the dilute concentration region is reduced. This increased reactivity may though be advantageous in the higher composition liquid crystalline phases formed in the DDAM/water system.

7.2 RESULTS

Incorporation of the ethylmethacrylate functional group into the head group of the surfactant leads to DDAM polymerising readily, to the extent that the monomeric form of DDAM will polymerise on standing without any added initiators or any attempt to remove oxygen. Due to this rapid polymerisation care must be taken in storing the surfactant and it must be used within a week of preparation to ensure that contamination from polymeric DDAM is maintained to a minimum. The presence of any oligomer/polymer greatly affects the self-assembly, surface tension and conductivity of the surfactant, all of which may be used as indicators for the presence of polymeric DDAM.

7.2.1 Physical characterisation of monomeric DDAM

Figure 7.2.1.1 a) shows the proton NMR spectrum of DDAM in CDCl3 using tetramethylsilane (TMS) as an added reference. Peak assignment of the vinyl protons at 5.85 δ (proton trans to the methyl group) and 6.13 δ (proton cis to the methyl group) can be used to monitor the progression of the polymerisation with time, the methyl group attached to the carbon-carbon double bond (1.94 δ) is also monitored due to its shift up field upon polymerisation. Percentage conversions for the polymerisations as a function of time are evaluated by comparing the integral values obtained for the vinyl protons with those of other protons in the molecule which are not effected by the polymerisation (e.g. the methyl group at the end of the hydrocarbon chain (0.89 δ)). The corresponding carbon 13 spectrum (figure 7.2.1.1 b)) shows the presence of a carbon-carbon double bond by the well defined peaks at 126.69 and 134.55 δ. The occurrence of polymerisation is also followed by the shift of these peaks up field (see § 2.1 for a complete spectral analysis).
Figure 7.2.1.1  a) Proton and b) Carbon 13 NMR spectrum for monomeric DDAM in CDCl₃ using TMS as an added reference.
The Fourier transform infrared (FTIR) spectrum of DDAM made up as a nujol mull between NaCl plates is shown in figure 7.2.1.2. Characteristic peaks for the surfactant molecule appear at 3019.3 cm\(^{-1}\) due to the carbon-hydrogen bond stretching mode, where the carbon atom is that involved in the carbon-carbon double bond, the carbon-carbon double bond stretch appears at 1633.7 cm\(^{-1}\) and the carbon-oxygen double bond is observed at 1720.8 cm\(^{-1}\). Polymerisation may be detected using FTIR due to the disappearance of the carbon-carbon double bond peak at 1633.7 cm\(^{-1}\), and the shifting of the carbon-oxygen double bond peak due to loss of conjugation upon polymerisation.

![Figure 7.2.1.2 Fourier transform infrared spectrum of monomeric DDAM.](image)

### 7.2.2 Determination of the critical micelle concentration for DDAM

Figure 7.2.2.1 shows the curve obtained from surface tension measurements using the du Noüy ring method (see § 2.5 for experimental details). Aggregation of the surfactant molecules, manifests itself as a change in slope and subsequent plateau of the experimental curve, giving a direct measurement of the surfactant's critical micelle concentration (cmc). A polynomial of variable order can be used to fit a curve to the experimental data points obtained prior to the concentration at which aggregation occurs. For the DDAM/water system a polynomial of degree two gave an adequate fit to the data with a correlation coefficient equal to 0.990, using this fit the cmc was determined to be equal to 5.66\(\times10^{-3}\) M. The surface excess concentration is calculated fom the slope of...
the pre-micellisation curve close to the cmc using equation 2.5.20 (since DDAM is a cationic surfactant) and the area per polar head group at the interface from equation 2.5.21. Hence, for the DDAM/water system the surface excess concentration of DDAM is found to be 2.8 ± 0.1x10^{-6} mol.m^{-2} and the area per polar head group is equal to 58 ± 1 Å^2.

Small amounts of polymeric DDAM may be detected by the presence of a minimum in the surface tension curve and as the amount of polymer increases the solutions at higher concentrations become turbid.

![Surface tension curve for DDAM/water system](image.png)

Figure 7.2.2.1 Surface tension curve for the DDAM/water system measured at 25 °C using the du Noüy ring method. Errors are indicated by the size of the data points.

The electrical conductivity curve obtained for DDAM in water at 25 °C is shown in figure 7.2.2.2. The curve shows a distinct break at a concentration of 7.29x10^{-3} M DDAM corresponding to the initiation of surfactant aggregation. Evaluation of the percentage dissociation of the bromide counterion (β) was obtained using three different methods. Firstly, by taking the ratio of the slopes of the two linear regions of the curve, using this
method $\beta$ is equal to 28.9%. If instead equation 2.4.24 is utilised with a value of $n = 44$ calculated from equation 2.4.15 (where $M = 169, \rho = 0.80 \text{ g.cm}^{-3}$ and $l = 15.42 \text{ Å}$) $\beta$ is determined to be 29.5%. The third method uses the area per polar head group calculated from the surface tension measurements. From this the aggregation number is determined to be 51 and the percentage dissociation 29.4%. Again as for the previous surfactants the different methods used in calculating a value for $\beta$ are found to give comparable results.

![Graph](image)

**Figure 7.2.2.1** Specific conductivity of DDAM in water measured at 25 °C. Errors are indicated by the size of the data points.

The values determined for the cmc of DDAM using specific conductivity and surface tension measurements compare favourably with those obtained by Nagai *et al.* [2] (cmc(DDAM) $\sim 6 \times 10^{-3} \text{ M}$ using electrical conductivity and dye solubilisation measurements) but are considerably higher than the value obtained by Hamid and Sherrington [1] where the cmc was found to be in the range of 1.9 to $3.6 \times 10^{-3} \text{ M}$ depending upon the method used.
7.2.3 Monomeric self-assembly

The self-assembling behaviour of DDAM in water, as determined here, is shown in figure 7.2.3.1. DDAM forms three liquid crystalline phases at surfactant concentrations in excess of those where a micellar phase (L₁) is formed in the temperature range of 20 to 70 °C. At still higher concentrations hydrated DDAM crystals are also observed.

![Diagram](image)

Figure 7.2.3.1 Schematic diagram of the partial binary phase diagram determined for the DDAM/water system. L₁: micellar, H₆: normal hexagonal, Qₐ: bicontinuous cubic (type Ia₃d, Q^{230} or Gyroid IPMS), Lₐ: lamellar, and A: hydrated DDAM crystals. The horizontally shaded areas indicate regions where two liquid crystalline phases coexist (i.e. these lines indicate the tie lines between the two liquid crystalline phases). Diagonally shaded areas indicate regions where a liquid crystalline phase coexists with hydrated crystals of DDAM.

A normal hexagonal phase (H₆) forms at concentrations of DDAM between 69.6 and 73.8 wt%, this precedes a cubic phase (Qₐ) forming between 78.1 and 81.7 wt%, prior to the formation of a lamellar liquid crystalline phase (Lₐ) between 87.3 and 91.0 wt%. All phase transitions were observed to be first order. Each of the three liquid crystalline phases form at room temperature with the Krafft discontinuity remaining below room temperature until concentrations exceeding 91.0 wt% are reached.
Thermotropic studies on the pure monomeric surfactant showed that on decreasing the temperature below the melting point of the surfactant (87 - 89 °C) the texture obtained is that shown in figure 7.2.3.2 which is first formed at approximately 78 °C. If the temperature is subsequently increased again the texture does not disappear at the melting point of the surfactant but is found instead, to persist to varying temperatures. The reason for this observed persistence of the texture initially formed is due to the monomeric DDAM surfactant being thermally initiated at these moderate temperatures and the sample becoming contaminated by the presence of oligomer/polymer. It was also possible to determine the presence of the polymer and its continued formation at these temperatures due to the increased viscosity of the sample. If a sample of the monomeric surfactant is maintained at this temperature for a period of approximately fifteen minutes the sample is completely polymerised, forming a polymeric film which adheres to the surfaces of the slide and cover slip such that it is no longer possible to shear the sample (i.e. DDAM is able to thermally self-initiate in air).

The extent and rapidity of this polymerisation meant that all bulk DDAM samples were equilibrated at room temperature to reduce any polymer contamination.
The ease of formation of polymeric DDAM does however, cast some doubts on the reliability of the binary phase diagram reported in figure 7.2.3.1. Several attempts were made to determine DDAM's self-assembling behaviour accurately by using added inhibitors (4-methoxyphenol, hydroquinone and methylhydroquinone) but these were found to be unsuitable due to a) the inhibitor reacting with the surfactant to produce deep red solutions exhibiting no liquid crystalline phase formation and b) the inhibitor altering the phase progression (in one case the hexagonal phase was no longer observed). Addition of inhibitor to the reaction mixture during the synthesis of the surfactant was also found to be unsuccessful. The phase diagram shown in figure 7.2.3.1 is that obtained using no added polymerisation inhibitors, and as such may be inaccurate due to partial polymerisation (ampoules were observed to polymerise on standing over a period of time (anywhere from one day to a few weeks depending upon the concentration of the sample)). Equilibration at high concentrations was, therefore, difficult to perform while avoiding formation of polymer. The presence of polymer in a monomeric DDAM sample was easily detected by the subsequent self-assembling properties of the samples (i.e. samples at higher concentrations no longer showed the phase progression initially observed on dilution with water).

Concentration gradients performed at various temperatures revealed that no liquid crystalline phase formation was evident above 70 °C. Figure 7.2.3.3 shows a concentration gradient performed at 25 °C where the micellar, hexagonal, cubic and lamellar phases are formed.

A typical optical texture observed for a bulk sample within the hexagonal phase of the DDAM/water system under crossed polarising filters is shown in figure 7.2.3.4. The intense colouration is due to the thickness of the sample (~100 μm) and the texture is comparable to that of the fan texture observed in the DTAB/water system (figure 3.2.2.5) with the sample being less highly oriented. A similar texture to that for DTAB is observed in the DDAM/water system when the hexagonal phase is formed during a concentration gradient (i.e. the fan texture was observed to form with line disclinations of strength s = +1/2). The hexagonal phase is extremely unstable with temperature and does not occur above approximately 40 °C. The viscosity of this hexagonal phase in comparison with hexagonal phases formed in other systems studied here is also greatly reduced, which may be due to a shortening of the cylindrical aggregates having the consequence of an increased instability to changes in temperature.

The cubic phase which follows the hexagonal phase on increase in DDAM concentration is also found to have a reduced viscosity and an instability to increases in temperature, melting at approximately 45 °C.
Figure 7.2.3.3 Concentration gradient performed at 25 °C for the DDAM/water system (crossed polarising filters, magnification 440). From left to right micellar, hexagonal, cubic and lamellar phases are apparent.

Figure 7.2.3.4 Optical texture for a bulk sample in the hexagonal region of the DDAM/water system (71.4 wt%, 30 °C, crossed polarising filters, magnification 440).
Figure 7.2.3.5 shows the optical texture observed for a bulk sample of the lamellar phase observed in the DDAM/water system under crossed polarising filters. The texture is typical for lyotropic lamellar liquid crystalline phases [21, 22] and is usually described as consisting of "oily streaks". The texture has been well studied in relation to the underlying geometry of the surfactant molecules and defects present (see references [23-25]). The oily streak texture, contrasts strikingly, though, with the texture observed for the lamellar phase obtained during a concentration gradient as shown in figure 7.2.3.6. This texture is not one classically ascribed to being formed by a lamellar liquid crystalline phase and must, therefore, arise due to the presence of unusual orientational effects, anchoring and defects not normally found in lamellar liquid crystalline phases. (This is the case for the formation of the spiral texture in the lamellar gel phase of sodium 10-undecenoate (Na-10), see chapter 6). Unfortunately due to the instability of this surfactant towards polymerisation further detailed investigation into the formation of this texture was not possible.

Small-angle X-ray scattering (SAXS) was performed on the liquid crystalline phases observed by optical microscopy for the DDAM/water system. Several problems were encountered during these experiments. Due to the low flux of the X-ray's generated by the SAXS equipment available in this laboratory, long exposure times are necessary (times from twelve to sixty hours are often required to obtain a good diffraction pattern), but as stated previously samples allowed to stand are prone to polymerisation. This was often found to be the case, and the diffraction pattern obtained could not be indexed to one liquid crystalline phase only. If samples were run twice under identical conditions it was often found that the intensities of the observed Bragg peaks had altered (due to an increase in the amount of polymer present). When a diffraction pattern from a pure monomeric liquid crystalline phase was obtained in all cases only one Bragg peak was of reasonable intensity, where a second peak was observed the intensity was extremely low, making detection difficult (even when data collection was over a reasonable time period).

The results given in table 7.2.3.1 are those for what are believed to be pure samples for each of the liquid crystalline phases observed in the DDAM/water system. Diffraction patterns were obtained for powdered samples and were comprised of Debye-Scherer rings which were produced by all domains in the irradiated volume.

Samples within the DDAM micellar region produced one weak diffuse ring at small- and wide-angles \( (Q = 2\pi/4.5 = 1.4 \text{ Å}^{-1}) \), indicative of a random packing of surfactant aggregates [26, 27].

The hexagonal phase produced a small-angle diffraction pattern consisting of two rings with Q-values in the ratio of 1:\sqrt{3}, here the first ring was of medium intensity and the second was extremely weak. This pattern is suggestive of parallel cylinders packed in a
Figure 7.2.3.5 "Oily streaks" texture observed for the bulk DDAM lamellar phase. The layers comprising the phase lie parallel to the glass slide, crossed polarising filters, 89.8 wt% sample at 25 °C, magnification 440.

Figure 7.2.3.6 Optical texture obtained during formation of the lamellar phase in the DDAM/water system from a 30 °C concentration gradient (crossed polarising filters, magnification 440).
two-dimensional hexagonal array (table 7.2.3.1). The hydrocarbon chains were found to be in a liquid-like state producing one diffuse ring at wide-angles at $Q = 1.4 \text{Å}^{-1}$ similar to the chains in the micellar phase.

The DDAM cubic phase gave a diffraction pattern at small-angles comprised of two rings only (often only one weak ring was observed), as for the hexagonal liquid crystalline phase. Both rings were of low intensity, though the second was considerably less intense than the first. The rings were in a ratio of $\sqrt{6} : \sqrt{8}$ which is attributable to one space group only, despite only two rings being observed, the $Q^{230}$ ($Ia3d$). This cubic phase is assumed to be bicontinuous and of type I [28-32] and has been ascribed to the Gyroid infinite periodic minimal surface (IPMS) [9, 10, 12-15]. This phase was also found to have liquid-like paraffinic chains.

The lamellar liquid crystalline phase was observed to produce a diffraction pattern with only one ring at small-angles (this being the most difficult phase to equilibrate without any formation of polymer) and as such no conclusion as to the exact nature of the phase geometry can be drawn, but it is assumed to be comprised of parallel planar bilayers. This phase too was determined to be of the $\alpha$-type, viz. molten paraffin chains.

It was not possible to obtain a diffraction pattern for the thermotropic liquid crystalline phase formed by pure monomeric DDAM, as all samples were found to contain polymer due to the temperatures at which the phase was formed.
Table 7.2.3.1 gives the structure parameters for each of the liquid crystalline phases formed, all equations were calculated at 27 °C and the specific volume was taken to be equivalent to that for the hydrocarbon chains (see § 2.8).

### 7.2.4 Polymeric DDAM

The monomeric form of DDAM was polymerised as an isotropic solution, in order to compare the self-assembling behaviour of the polymer with that of the monomeric surfactant and observe any differences between surfactant aggregation before and after polymerisation. The polymeric form of DDAM was prepared by thermal initiation via added AIBN (5 mol% to surfactant) in a 0.25 M solution of the surfactant in chloroform, in which the surfactant was found to form an isotropic solution only i.e. no aggregation of the surfactant molecules was observed when chloroform was used as the solvent. The sample was reacted at 60 °C for one day after which time polymerisation was essentially complete, with the polymer remaining soluble throughout the polymerisation. Initiation was also invoked by direct initiation of the surfactant using ultraviolet light, both techniques producing similar results.

Figure 7.2.4.1 a) and b) show the proton and carbon 13 spectra obtained for polymeric DDAM. It should be noted that these spectra have been analysed for the polymeric configuration shown in the figures only (see chapter 5, for other types of possible linkages formed during polymerisation). Peaks corresponding to the carbon and hydrogen atoms previously observed in the presence of a carbon-carbon double bond are absent with the relevant peaks being shifted up or down field depending upon their new environment (e.g. the carbonyl carbon (p) is moved down field in the polymeric spectrum due to the carbon-oxygen double bond no longer being conjugated with the carbon-carbon double bond, compare with the monomeric DDAM spectra shown in figure 7.2.1.1 a) and b)).

Pure polymeric DDAM was found to be completely insoluble in water and no liquid crystalline phases were observed to form for all concentrations in the temperature range 20 to 100 °C. Hence the act of covalently bonding the surfactant molecules has either a) decreased the surfactant's solubility significantly, such that, liquid crystalline phases may still form at very high temperatures or pressures or b) altered the surfactant's amphiphilic nature to such a degree that the polymer can no longer be considered to have any surfactant characteristics (i.e. the polymer does not behave as a polysoap).

If instead a mixture of both monomeric and polymeric forms of DDAM were combined in varying ratios, a lamellar phase was observed to form, having unusual elasticity.
Figure 7.2.4.2  a) Proton and b) Carbon 13 NMR spectrum for polymeric DDAM in CDCl₃ using TMS as an added reference.
properties which varied with the ratio of the two components (this though was extremely
difficult to control due to the continued polymerisation of the monomeric surfactant).
Hence although pure polymeric DDAM is insoluble in water its solubility is increased
when combined with monomeric DDAM (the ratio of monomer to polymer for formation
of the lamellar liquid crystalline phase was of the order of 90:10).

7.2.5 Polymerisation of liquid crystalline phases

Due to the sensitivity of DDAM towards polymerisation it was not possible to study the
polymerisation of the liquid crystalline phases formed in the DDAM/water system and
only polymerisation of the micellar solutions was performed.

Ampoules for polymerisation were prepared as described in § 2.9. Unfortunately
polymerisation was initiated immediately following removal of oxygen via the freeze­
pump-thaw method, which meant that equilibration of the concentrated liquid crystalline
phases was not possible prior to commencement of polymerisation. Any attempt to form
the micellar phase first and then remove water in an attempt to induce equilibration of the
more highly concentrated phases involved removal of water under vacuum which again
induced polymerisation and hence could not be used as a method of preparation.

However, polymerisation in the micellar region was possible due to the ease of
equilibration of these solutions, but controlled initiation had to be started immediately
following sealing of the ampoule. Polymerisation was performed for both 5 and 40 wt%
surfactant concentrations in the micellar region of the DDAM/water system, using both
thermal and photochemical initiation. For all samples, (i.e. all exposure times) polymer
formation resulted in the precipitation of granular solid which remained dispersed at low
conversion but which settled out as the extent of polymerisation increased. Polymerisations were performed over the time scale of fifteen minutes to one day.

Figures 7.2.5.1 and 7.2.5.2 show the percentage conversions for 5 and 40 wt% DDAM
micellar solutions initiated photochemically. Both concentrations show a trend of
increasing polymerisation with time, with both being essentially 100 % polymerised after
approximately six hours.

Thermal initiation reached > 95 % conversion after the first fifteen minutes for both the 5
and 40 wt% micellar solutions. Indicating that the combination of an increase in
temperature (which has been observed to initiate polymerisation of DDAM in air) and the
presence of AIBN leads to a more efficient polymerisation.
Figure 7.2.5.1 Percentage conversion for a 5 wt% DDAM micellar phase, initiated photochemically. Errors are indicated by the size of the data points.

Figure 7.2.5.2 Percentage conversion for a 40 wt% DDAM micellar phase, initiated photochemically. Errors are indicated by the size of the data points.
The formation of a precipitate upon polymerisation of the micellar solutions indicates that intra-micellar polymerisation alone did not occur and hence a "polymerised micelle" was not obtained. This insolubility indicates that the molecular weight of the forming polymer chains was comparable to that of polymeric DDAM and therefore, greater than the aggregation number of the micellar aggregates.

These results suggest that polymerisation in the higher liquid crystalline phases (if possible) would have mirrored the results found in these two cases, i.e. formation of a completely insoluble polymer rendering retention or formation of liquid crystalline phases impossible.

7.3 DISCUSSION

The addition of the ethylmethacrylate polymerisable moiety has been shown to have a marked affect on the observed aggregation of the surfactant molecules in comparison to dodecyltrimethylammonium bromide (DTAB, CH₃-(CH₂)₁₁-N⁺(CH₃)₃Br⁻, chapter 3) and ADAB (chapter 4). Changing the nature of the polymerisable functionality from a small slightly hydrophilic group, as is the case for the allyl polymerisable moiety to a large group with significantly increased hydrophilicity and flexibility has the direct consequence of reducing the concentration at which aggregation is initiated by approximately a factor of two. The extent of dissociation of the bromide counterion is, though, found to be similar for the two surfactants, these results are mirrored when DDAM is compared with the non-polymerisable surfactant DTAB.

Both the area per polar head group and the surface excess concentration at the air/water interface as determined from surface tension measurements are found to be similar for both ADAB (see § 4.2.2) and DDAM, supporting the supposition that DDAM adopts the conformation shown in figure 7.1.1. It should be noted, that, although, determination of the area per polar head group and the surface excess concentration measurements support the argument for adoption of this configuration at the air/water interface (i.e. the interface at which surface tension is measured, see § 2.5), they cannot be used to infer that this configuration is maintained upon aggregation (where the interface is now liquid/liquid).

The phase diagrams obtained for these three surfactants (figures 3.2.2.1, 4.2.3.1 and 7.2.3.1 for DTAB, ADAB and DDAM, respectively) indicate that the liquid crystalline phases formed in the DDAM/water system have a much lower stability towards changes in temperature than the corresponding phases observed in the DTAB/water and ADAB/water systems. This lowering of the liquid crystalline phases stability must therefore, be a direct consequence of the presence of neither a purely hydrophilic nor hydrophobic side group i.e. the ethylmethacrylate polymerisable moiety.
Although the phase progression for the three surfactants is determined to be the same, the surfactant volume in the DDAM case is larger than that for DTAB and ADAB and its head group has a greater degree of flexibility. The steric interaction between the surfactant molecules is also increased and the C₁₂ hydrocarbon chain does not have the degree of orientational/translational freedom that is apparent in the other surfactants. The increased flexibility and the introduction of dual hydrophilic/hydrophobic characteristics into the head group due to the presence of the ethylmethacrylate group induces a fluctuating polar/apolar interface to the surfactant molecules. Hence, for a proportion of the surfactant molecules the hydrophilic/hydrophobic interface will be positioned further down the hydrocarbon chain with the interface fluctuating with time. That is, in effect these surfactant molecules can no longer be considered as possessing a C₁₂ paraffinic chain. This effective reduction in the length of the hydrocarbon chain and increase in the flexibility of the surfactant will increase the surfactant's solubility and reduce its ability to form stable liquid crystalline phases. The effect of reducing the length of the hydrocarbon chain is well known and in general self-assembling behaviour is not instigated below a chain length of approximately eight (this being a function of amphiphilicity). The effect of increasing the flexibility of the surfactant on self-assembly has been shown [33] in the case of non-ionic surfactants, where the head group contains large flexible ethylene oxide groups, which, like the ethylmethacrylate group have a dual hydrophilic/hydrophobic nature. Comparison of a series of C₁₂ ethylene oxides with sodium dodecyl sulfate (SDS, CH₃-(CH₂)₁₁-SO₄-Na⁺) [34] shows that the solubility of the non-ionic surfactants is increased and the variation of surfactant self-assembled phases is reduced (in general, more phases are observed to form as the number of ethylene oxide groups increases). Where self-assembly does occur, the thermal stability of the liquid crystalline phases is low. These results are, therefore, analogous to those found here for the self-assembly of DDAM as compared with DTAB, confirming the conclusion that the ethylmethacrylate introduces a large degree of freedom into the head group of the surfactant. The exact degree to which the ethylmethacrylate group influences the fluctuation of the position of the interface is impossible to determine experimentally and the position of the hydrophilic/hydrophobic interface is therefore, unknown. It can be assumed though, that a larger portion of the DDAM surfactant, as compared with DTAB and ADAB, will reside in the water region of the liquid crystalline phases.

Polymerisation in the micellar region of the DDAM/water system has been performed at concentrations directly following aggregation using a variety of initiators (polymerisation has also been performed in benzene, in which the surfactant has been shown to form inverse micelles, and other non-aggregating solvents) by several groups [1-8]. Results have shown that in water, polymerisation occurs rapidly and to a high degree for all initiators used (including AIBN) and that molecular weight determinations gave the
number of monomer units as greater than 20000 (the experimental limit for the methods used) in some cases. Conversions and molecular weights were also found to be high in non-aggregating solvents (including chloroform).

These results are analogous with those obtained during this study for the concentrated micellar region and support the claim that polymerisation in the micellar region of the DDAM/water system does not produce a "polymerised micelle" formed by intra-micellar polymerisation.

7.4 CONCLUSIONS

Despite the increase in DDAM's ability to polymerise, it was found, that the placement of the ethylmethacrylate polymerisable moiety into the head group of a quaternary ammonium surfactant did not result in the maintenance of the liquid crystalline phase geometry upon polymerisation.

The presence of the ethylmethacrylate group was found to reduce the stability of the liquid crystalline phases formed and was so susceptible to polymerisation that it made working with the surfactant extremely difficult.
7.5 REFERENCES


Chapter 8

PHASE TRANSITIONS IN A BINARY DENDRIMER/WATER SYSTEM

8.1 INTRODUCTION

It has been proposed that dendritic macromolecules (i.e. molecules having a three-dimensional branching or tree-like structure) closely resemble micelles, in that they also have a distinctive inside and outside. Dendritic macromolecules though, do not possess the dynamic structure of a micelle and hence, have been loosely termed "bound micelles" [1]. It is possible to synthesis dendrimers such that, they have approximately equal numbers of periphery groups as the aggregation number of a micelle with equivalent radii dimensions and head group areas. Peripheral groups may be functionalised such that they resemble the head groups of surfactants. For example, peripheral groups may be carboxylates with sodium counterions, as is the case for some fatty acid surfactants. Preliminary work using solvatochromic probes, has been performed showing that some dendritic macromolecules have similar solubilising properties to aqueous micelles, i.e. probes are solubilised in the interiors of the macromolecules [2, 3] supporting the idea of "bound micelles".

Due to their covalent nature and bound state, it is reasonable to guess that these macromolecules resemble the product obtained when surfactant molecules constrained in a micellar structure undergo intra-micellar polymerisation. Hence, the solution properties of these macromolecules may exhibit similar behaviour to those of polymerised globular micelles.

The framework of starburst or cascade dendrimers consists of a central atom or reactive core which is capable of acting as a branch point (i.e. a point where it is possible to anchor more than one other molecular segment such that the growth of the molecule...
will be truly three-dimensional) when subjected to suitable chemical reactions. The exact nature of this central reactive core may take several forms. The most commonly used cores in the synthesis of dendrimers contain a reactive nitrogen (NRH₂ or NH₃) or aromatic ring, where branching generally occurs via heteroatoms in conjunction with hydrocarbon chains but may be purely via hydrocarbon chain linkages.

Synthesis of dendritic polymers has been developed since the early 1980s by Tomalia et al. [1, 2, 4-7] and Newkome et al. [8-11] and more recently by Fréchet and Hawker [3, 12-15], Miller and Neenan [16-18] and others [19-21]. Two major techniques are utilised in the synthesis of these macromolecules a) divergent construction and b) convergent construction.

**Divergent construction**

Divergent construction first developed by Tomalia et al. [1, 2, 4-7] and Newkome et al. [8-11] may be explained as follows. An initial reactive core (I) undergoes reaction using suitable reagents such that a minimum of two new functional groups are anchored at the focal point of the central core. Incorporated into these newly attached segments of the molecule are further atoms or functional groups which are capable of acting as new branching points. These new branch points then undergo reaction yielding further branching points at the periphery. As each subsequent reaction is performed a number of concentric shells, termed "generations", are built up which are discernible by the extent of branching that has occurred. Hence, the molecule is built outwards from the initial reactive core in a three-dimensional manner. Such a construction is shown schematically in figure 8.1.1. Here an initial reactive core (I) capable of anchoring three further molecules is shown, each subsequent branching point is then only capable of attaching a further two functional groups.

![Figure 8.1.1 Divergent construction of a dendritic macromolecule. I is the initial reactive core.](image)

This is the case where growth proceeds directly from what will eventually be the central core of the dendrimer. It is also possible for these individual dendrons to be anchored with a number of other such dendrons to a central initiator core (I), if the original branching point of the dendron is capable of further attachment (as shown in figure...
Growth of a dendritic macromolecule via the divergent method may yield dendrimers which do not have perfect symmetry due to the difficulty of controlling each stage of growth. That is, as each generation is completed, further reaction may have occurred, causing a partial next generation to be grown. Also, some potential branching points may not have undergone reaction and as such there will be holes in the structure. Hence without careful control of the reaction conditions several defects may occur during the growth of the dendrimer when a divergent construction method is used. These defects may also lead to the dendritic macromolecules being polydisperse. The extent of this polydispersity is dependent upon both the chemical functionality undergoing reaction and on the final generation number and will generally increase with generation number.

**Convergent construction**

The convergent construction method which has only recently been developed by Fréchet and Hawker [3, 12-15] and independently by Miller and Neenan [16-18] differs from the divergent construction not only in the way that the dendrimer is built up, but also in the ease of control of the growth. In this method, two molecules containing reactive functional groups (X, these molecules will eventually be the terminal groups of the dendrimer with periphery groups, S) are reacted with a single molecule which contains a functional group (Y) such that, the molecule is capable of being anchored to a further molecule in a subsequent reaction. This functional group (Y) though is insensitive to the initial addition of the two molecules. The assembly, along with an identical segment is then attached to a further single molecule and the process is repeated until sufficient generations have been built up. This results in a wedge-like configuration and the final step involves attachment of a number of these wedge-like segments (dendrons) to a central core (I) which does not have the ability of anchoring to a further molecule.

This technique yields dendritic macromolecules which are highly symmetric and monodisperse due to the fine control possible during the build up of each generation. That is, there are no holes due to branching points being skipped and no initial growth of new generations, only complete generations are formed. Figure 8.1.2 shows a schematic diagram of the convergent construction method. The individual dendrons are shown as partial circles for ease of representation.

Using any of the above techniques for the growth of dendritic macromolecules, it is possible to synthesise a large variety of molecules which vary not only in their generation number and terminal functionality but which are also based on a wide number of branching functional groups [1-21]. These starburst or cascade dendritic
polymers differ substantially from the linear, branched or cross-linked polymers most commonly formed. Whereas, linear, branched or cross-linked polymers generally behave as random coils in solution, where the exact polymer configuration is dependent upon salt concentration, temperature and composition, and may change from linear stretched chains to coiled conformations, dendritic polymers are more restricted in the configurations that they are able to adopt. This restriction, stems from the presence of three distinct regions in the dendrimer architecture a) an interior core, b) interior layers comprised of generations of spacers which are radially anchored to the initiator core and c) an exterior or periphery.

Figure 8.1.2 Convergent construction of a dendritic macromolecule. a) Convergent growth of the wedge-like segments (dendrons) of the dendrimer. S designates functional groups which will eventually be the surface groups of the dendrimer, X is the initial reactive functional group and Y and Z are functional groups which are unreactive to X but are able to be chemically manipulated allowing further reactions to occur. b) Assembly of the final macromolecule (shown here for a central core capable of anchoring four dendrons). I is the initial reactive core.

The exact nature and number of conformations formed in dendritic polymers is dependent upon the generation number. It has been shown experimentally [3, 15], theoretically [22-24] and by way of molecular dynamics modelling [7, 11] that a transition in the dendrimer structure occurs during the progression from the third to the fourth generation in a dendrimer series. This transition in shape is from an extended or
starfish-like morphology to a globular or more congested structure and is due to the increased importance of steric requirements of the dendritic branches. This change to an overall more spherical shape continues as the generation number is increased. This has been confirmed by measurements of intrinsic viscosity as a function of generation number. The viscosity is seen to increase to a maximum and then decrease again for dendrimers of increasing generation number, with the maximum corresponding to a generation number of three to four [4, 15, 24]. In comparison the viscosity of random coil polymers increases almost linearly with increasing molecular weight. The appearance of a maximum in the intrinsic viscosity versus molecular weight or generation number curve for starburst macromolecules indicates that their shape should tend towards spherical as the generation number is increased [4, 15, 24]. It has been shown [4] that the Mark-Houwink shape factors (α, which are used to fit theoretical curves to the viscosity data) compare favourably with the formation of "soft" spherical structures as the generation number of the dendrimers is increased.

The packing of the branching arms of dendritic macromolecules and hence the overall shape of the dendrimers is still under debate, but two main theories are currently used to explain or fit experimental observations.

The first, formulated by de Gennes and Hervet [22] gives a picture of the dendrimers as being comprised of spacers which are elongated, extending radially from a central core, with each generation lying in its own concentric shell. As such the density is found to increase away from the central core and the majority of peripheral groups lie near the surface of the dendrimer throughout all stages of the growth. Thus the interior of the dendrimer is reasonably empty. Hence the growth of the dendrimer (assuming complete generation growth) is restricted by the available surface area per terminal group (i.e. space-filling on the surface) and the maximum generation number increases with spacer length. The dendrimers are expected to have some flexibility at low generations but become increasingly rigid with increase in generation number.

The second theory differs greatly from that of de Gennes and Hervet and was proposed by Lescanec and Muthukumar [23]. Here the terminal groups are not restricted to the surface of the dendrimer but rather penetrate the entire molecule. This yields highly folded branches and a density profile which is fairly uniform throughout the molecule for all stages of growth.

Neither of these growth theories have as yet been disproven by experimental results and there is still much debate as to which picture of the dendritic macromolecules is correct, though the model of de Gennes and Hervet is at present the most highly favoured.

The starburst dendritic macromolecule studied here ((K^+O_2C)_16-[G-4])_2-[C], contains thirty two carboxylate (K^+O_2C in the notation) periphery groups with potassium
counterions and has a diameter comparable to micelles formed by fatty acid surfactants, with a similar aggregation number. The generation four ([G-4] in the notation) starburst dendritic polymer was synthesised (by Dr Craig Hawker, IBM, Almaden, USA) using the convergent construction method described above. It is monodisperse and approximately spherical in shape. A two-dimensional schematic of the dendritic polymer is shown in figure 8.1.3.

Figure 8.1.3 Two-dimensional schematic of the generation four starburst dendritic macromolecule (\(\text{K}^+ \cdot \text{O}_2\text{C})_{16} \cdot \text{[G-4]}_2 \cdot [\text{C}]\).

The binary system of this polymer with water was investigated in order to determine its solution properties i.e. the formation of equivalent lyotropic liquid crystalline phases, or due to its spherical shape whether it could be used as a model for hard or soft sphere interactions in solution. At present it is presumed that these macromolecules behave as soft spheres. The pure polymer was also studied as a function of temperature, to detect the formation of any thermotropic liquid crystalline phases.
8.2 RESULTS

For the binary system \( (K^+O_2C)_{16}-[G-4])_2-[C] \) in water, there was no liquid crystalline phase formation at any concentration, in the temperature range of 25 to 100 °C, as evidenced by both optical microscopy and small-angle X-ray scattering (SAXS). Above a concentration of \( 10^{-4} \) M the polymer was no longer completely soluble in water. Instead, monocrystallites were formed in equilibrium with polymer in solution. As the concentration was increased a precipitate was no longer observed. The bulk solution appeared to be homogeneous, although two phases, with the only apparent change being an increase in the viscosity of the solution.

Bulk samples of the polymer were studied by SAXS but no reflexions were observed in the range of \( Q = 3 \) to \( 0.05 \) Å\(^{-1} \) (5 to 120 Å in real space).

Although a thorough study of the dendrimer/water system was not performed, initial investigations showed six distinct regions in the concentration profile based on changes in the viscosity and amount of particulate matter present in the sample. Figure 8.2.1 shows the schematic partial phase diagram for the \([G-4]/water\) system, as determined here. For concentrations of polymer below \( 10^{-4} \) M, solutions were clear with no visible particulate matter and appeared isotropic when viewed using the optical microscope. The pH of these solutions was measured to be approximately 10 on preparation. Concentrations above \( 10^{-4} \) M yielded solutions which were slightly turbid, with a visible precipitate (i.e. it was possible to separate the solution from the monocrystallites which had grown). Samples in this region, when viewed under a polarising microscope using plane polarised light, gave evidence of an isotropic solution (soluble polymer) in equilibrium with monocrystallites of the starburst polymer. The monocrystallites were large in size, polydisperse and distributed randomly throughout the sample. The field of view remained black when the sample was viewed using crossed polarisers, i.e. the previously visible crystals could no longer be seen.

As the concentration was increased the bulk solutions remained visibly turbid but particulate matter could no longer be observed by the naked eye. The corresponding image under an optical microscope is shown in figure 8.2.2 (20 wt% sample). Monocrystallites of varying size and shape are randomly distributed throughout the sample. Again the field of view was black when viewed under crossed polarisers.

At concentrations above approximately 40 wt%, bulk solutions appeared visibly homogeneous, that is, phase separation was no longer possible and the samples were not turbid in appearance. A slight increase in the viscosity of the solution was observed with an increase in concentration. Samples viewed using the optical microscope
showed a large increase in the number of monocrystallites present. These varied in size and colour as shown in figure 8.2.3 (70 wt% sample). The colouration has been explained previously by the fact that the directors of the single crystals are randomly oriented throughout the suspension [25]. Needle- and plate-like crystals are apparent, giving evidence of heterogeneous crystal growth.

![Phase diagram](image)

Figure 8.2.1 Partial phase diagram of the generation four dendrimer and water between 25 and 100 °C. The system moves from one phase of solubilised polymer through hetero (where some crystallites grow at the expense of others, i.e. each nucleation site is weighted differently) and then homogeneous (all nucleation sites produce crystallites which grow evenly, i.e. each site is weighted equally) nucleation.

As further polymer was added, a dramatic increase in viscosity was observed to the point where the solution no longer flowed, with the bulk solutions remaining homogeneous in appearance. Note the large number and more even distribution of monocrystallites present in a 75 wt% sample viewed under crossed polarising filters.
Figure 8.2.2 View of a 20 wt% polymer sample under plane polarised light at 25 °C, magnification 175. Note the presence of monocrystallites which are randomly distributed in size and shape.

Figure 8.2.3 View of a 70 wt% sample using crossed polarising filters at 25 °C, magnification 440. Monocrystallites vary in size, shape and colour and are formed via heterogeneous nucleation.
The large variation in size of the monocrystallites was also reduced at this higher concentration, but the colouration remained. At concentrations above 90 wt% of polymer only hydrated crystals were present.

For all concentrations little change was observed with increasing temperature in the range of 25 to 100 °C. Concentration gradients performed at varying temperatures mirrored the results obtained from bulk samples, showing both the change in viscosity and crystal formation.

A pure sample of the starburst polymer was monitored with increasing temperature to determine if any ordering of the polymer occurred on heating, yielding thermotropic liquid crystalline phases. As the temperature was increased the crystals began to slowly darken in colour, but there was no change in the shape of the crystals and all edges remained sharp. At approximately 160 °C the polymer began to decompose. The crystals continued to darken in colour eventually turning black but no molten state was achieved up to a temperature of 365 °C.

8.3 DISCUSSION

A preliminary phase study of the generation four starburst polymer \(((K^+O_2C)_{16}[G-4])_2[C]\) and water binary system has been presented and is shown schematically in figure 8.2.1. No liquid crystalline phase formation was observed. This may have been due to the conformational limitations associated with the spherical shape of the generation four starburst polymer macromolecule as suggested by Friberg et al. [5]. In the study performed by Friberg et al. a generation three ([G-3]) starburst polymer based on a polyethylene backbone was found to act as the polar solvent in a non-aqueous lyotropic lamellar liquid crystalline phase, in the [G-3]/octanoic acid binary system. Modelling showed that the generation three polymer was disc-shaped with the terminal amine pairs of the polymer taking opposite directions to the plane of the disc thereby enabling alignment and formation of a lamellar liquid crystal. In contrast, Friberg’s studies showed that the spherical shape of the corresponding generation four polymer and high degree of conformational freedom of the generation two polymer did not allow alignment to occur, and hence no lyotropic liquid crystalline phase formation was observed. These observations are in agreement with the experimental and theoretical studies discussed in § 8.1.

Although no liquid crystalline phases were formed for this system the polymer was expected to show properties characteristic of a spherical colloidal dispersion. Typically hard sphere colloids show transitions occurring at volume fractions of 0.494; freezing, 0.545; melting [26] and 0.64; glass transition [27]. These values have been confirmed...
experimentally in a system of polymethylmethacrylate (PMMA) spheres coated with a thin layer of poly-12-hydroxystearic acid, [28] which behave as model hard spheres.

Figure 8.2.4 View of a 75 wt% sample under crossed polarising filters at 25 °C, magnification 175. Monocrystallites present in this sample are more evenly distributed in size and shape and are formed via homogeneous crystal growth.

The binary starburst polymer/water system studied here does not show transitions at the above volume fractions and hence cannot be classified as a hard sphere system, which is expected following the arguments presented in § 8.1. The crystal growth observed here did not mirror that found by Pusey and van Megen [28], which showed that in the PMMA system, homogeneous nucleation was observed at low volume fractions which was superseded at higher volume fractions by heterogeneous nucleation. In contrast it appears that heterogeneous nucleation dominates in the starburst system at low concentrations followed by homogeneous nucleation at higher concentrations. Okubo [25] has observed a similar transition from hetero to homogeneous nucleation for monodisperse colloidal silica spheres (diameter ca. 110 nm) in deionised water. He also observed similar growth formations (the size of the crystallites was found to increase as the concentration of silica spheres decreased) and colour patterns.

As a consequence of these observations it is concluded that the starburst polymer spheres do indeed approximate soft spheres as had been previously presumed. The
polymer molecule is flexible giving rise to a deformable electrical double layer which may partially account for the soft sphere behaviour of the system.

The absence of any X-ray reflexions seems to indicate that the spacings are too large, or that the spheres are uncorrelated. Light scattering experiments should be a more appropriate method for studying the structural aspects of this system. These experiments were unable to be performed during the current study.

8.4 CONCLUSIONS

Preliminary investigations have shown that the generation four starburst polymer ((K+O2C)16-[G-4])2-[C] undergoes no lyotropic or thermotropic liquid crystalline phase formation. Instead the behaviour more closely resembles that of soft spheres, which undergo heterogeneous nucleation followed by homogeneous nucleation at higher concentrations. A full interpretation of the complete mechanism of crystallisation requires a better understanding of the aggregation and structure of the crystallites and hence further experimental work.
8.5 REFERENCES

Chapter 9

CONCLUSION

The focus of this thesis has been on elucidating the essential requirements for polymerisation of surfactant lyotropic liquid crystalline phases. The ultimate aim is to maximise the extent and rate of polymerisation, while minimising any changes to the underlying global surfactant geometry. That is, an optimal system will have no phase transitions or separations upon polymerisation.

The nature of the integral components constituting a surfactant molecule (i.e. the hydrophilic and hydrophobic entities), their influence on each other and the interactions between the surfactant molecules controls the surfactant's solution behaviour for all surfactant concentrations. These interactions also influence any subsequent reactions performed either when using the solution as the reaction environment or when it is part of the reaction media (as is the case for polymerisation of liquid crystalline phases).

It was necessary therefore to determine how changes to the surfactant molecule affect its self-assembly and polymerisation. To this effect one non-polymerisable and five polymerisable surfactants were studied each differing in some critical aspect of the surfactant structure. The systems studied were chosen so as to simplify the different interactions involved in both surfactant self-assembly and polymerisation in an attempt to magnify the effect that a single change to the surfactant architecture has. This was achieved by using polymerisable moieties and surfactant head groups which had been well studied, and looking at the binary phase behaviour of these surfactants with water only. Taking this final step ensures that the effects due to other components in solution for example added salts, co-surfactant or an oil (yielding a ternary or multicomponent system) do not swamp the observed solution behaviour.
The two polymerisable moieties investigated were the allyl group (CH$_2$-CH=CH$_2$) and the ethylmethacrylate group (CH$_2$-CH$_2$-O-CO-CH(CH$_3$)=CH$_2$). These two groups differ from each other by both their ease of polymerisation and in their ability to influence the self-assembly of the surfactant into which they are incorporated. Here the ethylmethacrylate was found to be more readily polymerised and to produces polymers of higher molecular weight. The allyl polymerisable moiety (due to its relative smallness) introduces fewer disruptions into the surfactant's self-assembly than the much bulkier and more hydrophilic ethylmethacrylate group which tends to dominate the solution characteristics of the surfactant.

In addition to altering the nature of the polymerisable moiety its position in the surfactant molecule also affects the surfactant's self-assembly, placement being in either the head group of the surfactant or at the end of the hydrocarbon chain.

The polymerisable moieties were incorporated into either a single- or double-chain quaternary ammonium surfactant or a single-chain fatty acid soap. By systematically altering the nature of the surfactant it was possible to determine not only which types of surfactants displayed suitable phase behaviour but also under which conditions polymerisation of the lyotropic liquid crystalline phases was most suitable.

Dodecyltrimethylammonium bromide (DTAB, CH$_3$-(CH$_2$)$_{11}$-N$^+$(CH$_3$)$_3$Br) was chosen as the non-polymerisable standard in this study. It is a C$_{12}$ single-chain surfactant based on a quaternary ammonium head group. Its determined phase behaviour in water (see chapter 3) is typical for medium chain length surfactants belonging to the cationic class of amphiphiles.

Replacement of a single methyl group in the head group region of DTAB by an allyl polymerisable group yields allyldodecyldimethylammonium bromide (ADAB, CH$_3$-(CH$_2$)$_{11}$-N$^+$(CH$_3$)$_2$(CH$_2$-CH=CH$_2$)Br). The double-chain analogue is allyldidodecylmethylammonium bromide (ADDAB, (CH$_3$-(CH$_2$)$_{11}$)$_2$-N$^+$(CH$_3$) (CH$_2$-CH=CH$_2$)Br, see chapter 4). Introduction of the allyl group changes both the hydrophilicity and rigidity of the head group. It also induces changes to the electrostatic interactions between the surfactant molecules and hence the solubility of the surfactant in water (making the higher composition liquid crystalline phase more accessible) and the stability of the phases formed.

Isotropic polymerisation of these two surfactants resulted in an extent of conversion of ca. 30 % for ADAB and in the case of ADDAB polymerisation did not precede at all. Polymerisation of the allyl group in the head group of the surfactant limits the extent of conversion due to the large electrostatic interactions between the head groups of the surfactant monomers which acts to inhibit the reaction. The increased steric interactions due to the presence of the second paraffinic chain in the case of ADDAB
are such that in combination with the electrostatic interactions polymerisation is completely inhibited.

These results were mirrored when polymerisation took place within the self-assembled forms of these surfactants. That is, polymerisation of the liquid crystalline phases of ADDAB were found not to polymerise and those of ADAB polymerised to ca. 30%.

Hence, in the case of the allyl polymerisable moiety contained within the head group of a surfactant self-assembly of the surfactant monomers, there was no effect on the extent or ease of polymerisation. Where polymerisation did occur, the liquid crystalline phases in the ADAB/water system neither phase separated nor underwent a phase transformation. The unpolymerised monomer retained its original geometry, with slight variations to the repeat distance and head group areas caused by the accommodation of interwoven polymer, which was incorporated throughout the monomer matrix. The presence of interwoven polymer lead to an increase in the stability of the liquid crystalline phases of ADAB.

Placement of the allyl polymerisable group at the end of the hydrocarbon chain of DTAB instead of its head group produces ω-undecenyltrimethylammonium bromide (ω-UTAB, CH2=CH-(CH2)9-N+(CH3)3Br, chapter 5). This introduction increases the rigidity of the paraffinic chains, reducing both the solubility of the surfactant at high concentrations and the stability of the liquid crystalline phases formed. This introduction has a reduced effect on the observed self-assembly as compared with placement of the allyl polymerisable moiety in the head group.

Polymerisation of ω-UTAB in isotropic solution is facilitated in comparison to ADAB and approximately 80% conversion is achieved. This increase in the extent of polymerisation is primarily due to isolation of the allyl group from the interactions between the head groups of the surfactant molecules. Formation of the polymer does not in this case disrupt significantly the interactions which control the surfactant's self-assembly. The observed self-assembly of the polymerised form of ω-UTAB is such that the liquid crystalline phases formed have an increased stability towards changes in temperature as compared with those formed by monomeric ω-UTAB.

Polymerisation of the mesophases formed in the ω-UTAB/water system proceeded to approximately 40% conversion only. This reduction in comparison to polymerisation in an isotropic solution is attributed to the large mobility of the paraffinic tail in the surfactants self-assembled form. Hence, a free radical once formed may not be able to find a second carbon-carbon double bond in the correct orientation within the time required for reformation of the original carbon-carbon bond, due to the aggregate acting as a cage inhibiting polymerisation. The partially polymerised liquid crystalline phases were found to have the same global geometry as the original non-polymerised phase.
Altering the position of the allyl polymerisable moiety therefore affects both the self-assembly of the surfactant and its polymerisation. But placement in both the head group and at the end of the hydrocarbon chain has been shown to be incompatible with full conversion and retention of the underlying surfactant geometry.

Changing the nature of the head group from a quaternary ammonium (as in the case of \(\omega\)-UTAB) to a fatty acid soap yields sodium 10-undecenoate (Na-10, \(\text{CH}_2=\text{CH}(\text{CH}_2)_9\text{CO}_2\text{Na}^+\), chapter 6). This change has been shown to have a large effect on the phase behaviour of the surfactant. Here, a first order transition between the normal hexagonal phase and the lamellar gel phase is induced (i.e. the shortened chain as compared with \(\omega\)-UTAB increases the dominance of the carbon-carbon double bond inducing a disorder/order transition). This transition in conjunction with a number of other conditions (see chapter 6) gives rise to the spectacular spiral texture obtained for the lamellar gel phase grown from the hexagonal phase.

The presence of the fatty acid head group does not affect polymerisation in isotropic solution compared to a quaternary ammonium head group (\(\omega\)-UTAB). The resulting polymer, due to a change in the nature of the hydrophobic region, displays a reduced phase progression compared to the monomeric form. Hence as the length of the hydrocarbon chain is decreased, the dominance of the polymerisable moiety over the surfactant self-assembly increases. Disruptions to the paraffinic chains (e.g. during polymerisation) will therefore be magnified resulting in a variation in the solution behaviour before and after polymerisation. Hence, there is a critical chain length below which the interactions between the surfactant paraffinic chains become increasingly important in determining the surfactant's behaviour in both the polymerised and non-polymerised forms.

These results were equally applicable to polymerisation of the liquid crystalline phases of Na-10. In the lamellar gel phase, where the nature of the chains is such that they are highly ordered, a phase transition occurs upon polymerisation. However, partial polymerisation of the hexagonal and micellar regions where the interactions between the paraffinic chains are not the dominant interactions and the chains are in a molten state, results in a retention of the underlying surfactant geometry. The extent of polymerisation, as was observed for \(\omega\)-UTAB, is much reduced in the self-assembled form due to the aggregate acting as a cage inhibiting polymerisation.

The exact nature of the paraffinic chains (either molten, frozen or bound in a polymer chain) is critical in determining the self-assembly of both the monomeric and polymeric forms of a surfactant and also in the polymerisation of its lyotropic liquid crystalline phases. From these results it appears that retention of the underlying surfactant geometry during polymerisation requires the chains to be in a molten state (if polymerisation takes place within the tail of the paraffinic chain), such that the inherent
rigidity of the chains is not the dominant influence in the self-assembly of the surfactant. Altering this dominance via polymerisation will induce a shift in the balance of interactions controlling surfactant self-assembly, inducing a phase transition.

The final polymerisable surfactant dodecyltrimethylammoniumethylmethacrylate bromide (DDAM, CH₃-(CH₂)₁₁-N+(CH₃)₂(CH₂-CH₂-O-CO-C(CH₃)=CH₂)Br, chapter 7) is formed by replacing a single methyl group in the head group of DTAB with the ethylmethacrylate polymerisable moiety. The presence of the ethylmethacrylate group significantly alters the amphiphilic nature of the surfactant, and the interactions between the surfactant molecules, which reduces the stability of the liquid crystalline phases.

Polymerisation in both isotropic solution and self-assembled forms was rapid and went to near-completion. The resultant polymer was completely insoluble in water. The molecular weight of the polymer chains was substantially increased as compared with those formed by the allyl polymerisable moiety. Therefore, not only is the nature of the polymerisable group and its position in the surfactant molecule important but also the length of the polymer chains which it forms. If the molecular weight of the polymer chains is greater than the aggregation number of the components comprising the surfactant mesophase a phase separation or transition will be induced.

From this series of surfactants it may be surmised that polymerisation of single-chained systems occurs more readily when the polymerisable moiety is placed at the end of the paraffinic chain, rather than in the head group of the surfactant, for isotropic polymerisations. This is due to reduced steric and electrostatic interactions. Once polymerisation occurs within the aggregated state of the surfactant though, the large mobility available to the tail (over the head group) and the cage-like effect of the surfactant aggregate decreases dramatically the extent to which polymerisation will occur. In contrast, the self-assembled form of the surfactant monomers had little or no effect on the extent or ease of polymerisation when the polymerisable group was contained within the head group of the surfactant.

Disruptions to the inherent rigidity of the paraffinic chains generally lead to a change of the surfactant's self-assembly behaviour. Hence anything that increases the extent of this disruption will decrease the probability of retention of the underlying surfactant geometry upon polymerisation.

Therefore, for successful polymerisation of surfactant lyotropic liquid crystalline phases, it seems necessary that the polymerisable moiety be located in the head group of the surfactant to reduce flexibility, be readily polymerised in an isotropic state (i.e. it polymerises quickly and to near completion) and form polymer chains having an easily controllable molecular weight. From the surfactants studied here neither the allyl nor
the ethylmethacrylate polymerisable moieties are appropriate choices for obtaining this goal. A more reasonable group to use should though be based on the allyl group rather than the ethylmethacrylate (since the phase behaviour of surfactants containing this group will be dominated by its presence).

While the conditions outlined above are a definite advantage they still do not ensure that polymerisation of the surfactants liquid crystalline phases with retention of the underlying geometry is possible. Self-assembly of the surfactant monomer may show that some of the phases are not accessible and also the resulting polymer may be insoluble in the monomeric solution or in water, resulting in precipitation or a phase transition/separation.

Once the correct polymerisable group and conditions have been established for binary surfactant/water systems, the next step is to try and completely rigidify the structure such that it may be hydrated or dehydrated without any changes to the structure occurring. This, however, is still in the future. A considerable amount of work is still required in order to fully understand these systems and produce a completely polymerised liquid crystalline phase with retention of the underlying surfactant geometry.