Chapter 4

Isotropic phases in DDAB ternary systems

This chapter provides experimental evidence for the assertion that geometry can be a central determining factor in surfactant behaviour. For the carefully chosen model systems studied here, everything does indeed behave as predicted in the previous chapter. As a result of the mutual insolubility of the components and the lack of cosurfactant, the assumptions underlying those models are satisfied. The data presented here from X-ray and neutron scattering experiments are complemented by previous electrical conductivity and NMR self-diffusion measurements and the whole edifice relies on the study of phase diagrams as an essential basis.

4.1 Review of previous work

Ternary systems of the double-chained cationic surfactant didodecyldimethylammonium bromide (abbreviated to DDAB, with chemical formula \((C_{12}H_{25})_2(CH_3)_2NBr\)) were studied extensively between 1983 and 1986 by Evans, Ninham and coworkers [6,26,101,17,27,40,46]. They studied the isotropic \(L_2\) phases (water-in-oil microemulsions) formed in ternary mixtures of DDAB, water and the alkanes cyclohexane, hexane, hexene, octane, decane, dodecane and tetradecane. They also studied the effects of mixing oils and of adding a single-chained surfactant or a long-chained alcohol as cosurfactant. A brief summary of their findings, essentially as set out in Chen et al. [27] is as follows.

(i) The surfactant is virtually insoluble in both water and oil between 25°C and 80°C. So it all resides at the oil-water interface. This is in contrast to many other surfactants, and is an essential condition for testing the theories of Chapter 3.

(ii) The ternary phase diagrams for DDAB, water and a number of different oils are shown in Figure 4.1. All have a large isotropic liquid phase \(L_2\) which can,
in all cases except tetracane, be diluted to the oil corner. For tetracane the single-phase region is an isolated island in the middle of the three-component triangle. For the shorter-chained oils, the positions of these pendant drops shows a strong dependance on the chain length of the oil. With shorter oils, less water is required for the formation of this phase than for longer oils.

(iii) In all cases these phases conduct electricity at low water content, including even cyclohexane at less than 2% water by weight. In a system with such low solubility of the surfactant in water and oil this implies the existence of long connected water pathways through bulk oil. For all the oils except tetracane, dilution with water causes a decrease in electrical conductivity, with eventual passage to a non-conducting state through a percolation-like transition. This transition appears to take place for each surfactant at what is essentially a fixed water/surfactant ratio, this ratio increasing with increasing length of the oil. For tetracane the behaviour is qualitatively different with high conductivity throughout. For the most strongly penetrating oils, cyclohexane and hexene, there is an initial increase in conductivity before the percolation.

(iv) NMR self-diffusion coefficients [17] for oil and surfactant are almost constant across the single-phase region, with the surfactant diffusion rate always extremely low. For the oil, the diffusion coefficients are consistently about half those of bulk oil at the same temperature. For water on the other hand, the behaviour mirrors the conductivity results: on dilution from the low-water boundary to the conductivity percolation line, the diffusion coefficient drops by a factor of between 10 and 20. Further NMR measurements have been made by Fontell et al. [46], concentrating in detail on the system DDAB/dodecane/water, with similar findings. For tetracane, the situation is again different, with both the oil and the water diffusion rates remaining high throughout the single-phase region. For tetracane the water diffusion rate is consistently higher than even the highest rates for the other systems, suggestive of a qualitatively different structure.

(v) Raising the temperature, even to 80°C, has relatively little effect on these systems. In general the extent of the single-phase region increases somewhat with increasing temperature, and the sharpness of the percolation threshold is reduced [27].

These are indeed ideal systems to model. They are rare in that they form microemulsions over such large ranges of composition and without the need for cosurfactant or salt. Their relative temperature independence and the mutual insolubility of the components make them an ideal proving ground for the geometric approach to surfactant microstructure. If it is to work anywhere it should work here. Further, these systems are ideal from the point of view of X-ray scattering, since the bromide ions give excellent contrast. The large step in electronic density between the polar and nonpolar regions improves the validity of the two-media approximation.
Figure 4.1: Isothermal phase diagrams for DDAB/alkane/water systems at 20°C, reproduced from Fontell & Jansson [47]. A more complete tetradecane phase diagram is shown in Figure 4.12.
On the basis of the experimental evidence summarised above, the authors concluded that for the oils up to and including dodecane, the isotropic phase had a highly connected structure of water cylinders in oil, the connectivity of which decreased with water dilution at constant curvature until there were only isolated spheres left [27]. This qualitative idea has been made quantitative in the DOC cylinders model described in Chapter 3. It is shown here on the basis of small-angle X-ray scattering results that this reasoning stands up to quantitative analysis. That model is applied to samples along both oil- and water-dilution paths in the $L_2$ phases of the systems DDAB/cyclohexane/water and DDAB/dodecane/water. Each of these systems is satisfactorily explained by the model with only small variation of the effective surfactant packing parameter $v/a\ell$.

As mentioned above, tetradecane shows markedly different behaviour. The higher conductivity and the absence of the anti-percolation suggest major topological differences in the structure. As a result of the inability of the longer oil to penetrate and swell the surfactant chains, the interface is much flatter. The phase separation on oil dilution is also indicative of a qualitatively different situation. It is shown below that all this is satisfactorily explained by the DOC lamellar model, where the structure consists of a random water-swollen reverse bilayer in bulk oil.

### 4.2 Cyclohexane

Cyclohexane is the most strongly penetrating of all the oils mentioned above, and the $L_2$ phase region in the system DDAB/cyclohexane/water lies very close to the surfactant-oil axis of the phase diagram. Nine samples were prepared, lying along a single water dilution path. These span the full range of water contents within the $L_2$ phase, from 2% to 22% water by weight. The sample compositions are shown on the phase diagram in Figure 4.2; they and quantities derived from the compositions are listed in Table 4.1.

#### 4.2.1 Experimental procedure and results

Absolute scaled SAXS spectra were measured on the small-angle camera at Saclay, using pure water as a reference. Cu $K_\alpha$ radiation was used with semilinear collimation. The spectra were desmeared using the procedure described by Lake [77], improved by a triangular smoothing between iterations [138]. The $q$-range of the measurement is $0.015\text{Å}^{-1} < q < 0.55\text{Å}^{-1}$, giving a real-space resolution of approximately 10Å. Typical spectra are shown on both linear and logarithmic scale in Figure 4.3. Quantities derived from the measured spectra are listed in Table 4.2.

The values of the calculated and measured invariants in Tables 4.1 and 4.2 agree to better than 10% throughout, which implies that the two-media sharp-interface as-
Table 4.1: Quantities determined from composition for samples in the system DDAB/cyclohexane/water. $C_s$ is the surfactant concentration; $[W]/[S]$ the water to surfactant molar ratio; $\phi$ the polar (or internal) volume fraction; $\rho_1$ the electronic density of the polar region; and $Q^*$ the value for the invariant calculated from $\phi$, $\rho_1$ and the electronic density in the hydrocarbon tails which remains constant throughout at $\rho_2 = 0.267 \text{eÅ}^{-3}$.

<table>
<thead>
<tr>
<th>Sample</th>
<th>DDAB wt %</th>
<th>Oil wt %</th>
<th>Water wt %</th>
<th>$C_s$</th>
<th>$[W]/[S]$</th>
<th>$\phi$</th>
<th>$\rho_1$ eÅ$^{-3}$</th>
<th>$Q^*$ nm$^{-4}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyclo 1</td>
<td>41.3</td>
<td>57.1</td>
<td>1.6</td>
<td>0.76</td>
<td>0.97</td>
<td>6.8</td>
<td>0.464</td>
<td>3.84</td>
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<td>Cyclo 2</td>
<td>40.9</td>
<td>56.5</td>
<td>2.5</td>
<td>0.76</td>
<td>1.57</td>
<td>7.6</td>
<td>0.450</td>
<td>3.65</td>
</tr>
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<td>Cyclo 3</td>
<td>40.0</td>
<td>55.2</td>
<td>4.8</td>
<td>0.74</td>
<td>3.05</td>
<td>9.4</td>
<td>0.426</td>
<td>3.34</td>
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<tr>
<td>Cyclo 4</td>
<td>38.7</td>
<td>53.9</td>
<td>7.4</td>
<td>0.72</td>
<td>4.93</td>
<td>11.6</td>
<td>0.407</td>
<td>3.10</td>
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<td>52.3</td>
<td>10.3</td>
<td>0.70</td>
<td>7.10</td>
<td>13.9</td>
<td>0.393</td>
<td>2.94</td>
</tr>
<tr>
<td>Cyclo 6</td>
<td>36.7</td>
<td>50.5</td>
<td>12.8</td>
<td>0.69</td>
<td>8.96</td>
<td>16.0</td>
<td>0.384</td>
<td>2.87</td>
</tr>
<tr>
<td>Cyclo 7</td>
<td>34.1</td>
<td>50.0</td>
<td>15.9</td>
<td>0.64</td>
<td>11.9</td>
<td>18.4</td>
<td>0.375</td>
<td>2.71</td>
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<tr>
<td>Cyclo 8</td>
<td>34.1</td>
<td>47.3</td>
<td>18.6</td>
<td>0.65</td>
<td>14.0</td>
<td>20.9</td>
<td>0.370</td>
<td>2.72</td>
</tr>
<tr>
<td>Cyclo 9</td>
<td>32.7</td>
<td>45.7</td>
<td>21.6</td>
<td>0.62</td>
<td>17.0</td>
<td>23.5</td>
<td>0.365</td>
<td>2.68</td>
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</tbody>
</table>

Table 4.2: Quantities measured from X-ray spectra for samples in the system DDAB/cyclohexane/water. $D^*$ is the real-space peak position ($D^* = 2\pi/q_{\text{peak}}$); $l_c$ is the correlation length; $Q^*$ is the measured invariant as discussed in Chapter 2; $\Sigma$ is the internal surface determined from the Porod limit; and $\sigma$ is the headgroup area per molecule calculated from $\Sigma$ assuming that all surfactant lies at the interface. The uncertainty in $\Sigma$ and hence in $\sigma$ is of the order of 10%.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$D^*$ Å</th>
<th>$l_c$ Å</th>
<th>$Q^*$ nm$^{-4}$</th>
<th>$\Sigma$ Å$^2$/Å$^3$</th>
<th>$\sigma$ Å$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyclo 1</td>
<td>42</td>
<td>17</td>
<td>3.6</td>
<td>0.031</td>
<td>68</td>
</tr>
<tr>
<td>Cyclo 2</td>
<td>45</td>
<td>19</td>
<td>3.5</td>
<td>0.031</td>
<td>68</td>
</tr>
<tr>
<td>Cyclo 3</td>
<td>50</td>
<td>20</td>
<td>3.1</td>
<td>0.030</td>
<td>67</td>
</tr>
<tr>
<td>Cyclo 4</td>
<td>54</td>
<td>22</td>
<td>3.1</td>
<td>0.029</td>
<td>67</td>
</tr>
<tr>
<td>Cyclo 5</td>
<td>56</td>
<td>23</td>
<td>3.0</td>
<td>0.029</td>
<td>69</td>
</tr>
<tr>
<td>Cyclo 6</td>
<td>59</td>
<td>23</td>
<td>3.0</td>
<td>0.028</td>
<td>67</td>
</tr>
<tr>
<td>Cyclo 7</td>
<td>69</td>
<td>26</td>
<td>2.9</td>
<td>0.026</td>
<td>67</td>
</tr>
<tr>
<td>Cyclo 8</td>
<td>74</td>
<td>27</td>
<td>2.9</td>
<td>0.027</td>
<td>69</td>
</tr>
<tr>
<td>Cyclo 9</td>
<td>83</td>
<td>29</td>
<td>2.9</td>
<td>0.025</td>
<td>67</td>
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</tbody>
</table>
Figure 4.2: Partial phase diagram at room temperature for the system DDAB/cyclohexane/water. Compositions of samples used in SAXS are indicated; they correspond to a water dilution line at surfactant/oil ratio about 0.68 by weight. Although the first sample falls outside the indicated region, it was monophasic nonetheless: the true boundary lies between this sample and the surfactant/oil axis.
Figure 4.3: Typical SAXS spectra for the system DDAB/cyclohexane/water, (a) plotted on linear scale and (b) on logarithmic scale. Note the clear Porod law decrease on the logarithmic plot.
umption is a very good approximation in this system. The surfactant headgroup areas measured from the Porod limit are also remarkably constant at 68 Å² per molecule, although their accuracy can in practice be no better than 10%. It is important to note that there is no sharp change in the character of the scattering spectra as the percolation threshold is passed—while the conductivity changes dramatically, the structure seen by the scattering experiment evolves smoothly along the whole of the dilution line.

The value of \( a = 68 \text{ Å}^2 / \text{molecule} \) is consistent with that obtained from X-ray measurements on the water-rich lamellar phase in the binary surfactant/water system [46]. From the same measurements, one deduces an average surfactant chain length of a little more than half the bilayer thickness of 23 Å. For the calculations that follow, we stick for simplicity to a constant value of \( \ell = 12 \text{ Å} \). (This is admittedly somewhat unrealistic, but a more rigorous treatment of the tails will have to wait for the results of studies of chain packing in curved monolayers and bilayers [37].) The volume of the surfactant molecule has been measured at 784 Å³ and is assumed to remain constant throughout. These values are consistent\(^1\) with an unswollen value of \( v / a \ell \approx 0.85 \) [136].

\[\text{4.2.2 Comparison with models}\]

As is the case for all the DDAB/oil/water systems studied except tetradecane, the random filling models—Talmon-Prager and the cubic random cell—fail utterly. Both models predict an increase in conductivity with increasing water content, directly contrary to the behaviour observed. More than that, they predict rapid changes in the interfacial curvature, something which we must regard as highly unlikely in these systems.

Attempts to fit the measured scattering spectra for samples Cyclo 1 and Cyclo 9 to a model of hard (water-in-oil) spheres are shown in Figure 4.4. As set out in Section 3.1 the radius and density of the spheres are determined by \( \phi \) and \( \Sigma \). Full scattering spectra for hard spheres with no other interactions were calculated using the Hayter-Penfold RMSA procedure [52]. For sample Cyclo 9, this procedure gives an excellent fit to the data. As this sample is beyond the anti-percolation line, a structure of spheres makes sense. Such a conclusion is also supported by the oscillations observed in a Porod plot of \( q^4 I(q) \) against \( q \); minima at \( qR \approx 4.5 \) and 6.5 are in agreement with the radius \( R = 28 \text{ Å} \) determined from \( \phi \) and \( \Sigma \). For this sample, the spheres give a value of 1.5 for the effective surfactant packing parameter \( v / a \ell \). This is consistent with strong penetration of the oil into the surfactant tails, swelling their volume by a factor of between 1.5 and 2. At low water content, for sample Cyclo 1, the situation is entirely different. The oscillations in \( I(q) \) disappear, the solution conducts electricity, the peak position is in the wrong place and of the wrong intensity. Furthermore, an

\[\text{\(^1\)The } v \text{ in } v / a \ell \text{ is the volume of the tails plus any adsorbed oil, and excludes the hydrophilic part of the molecule.}\]
Figure 4.4: Measured X-ray scattering data (full curves) for samples Cyclo 1 (a) and Cyclo 9 (b), compared with calculated scattering curves for a model of identical hard spheres of water in bulk oil.
Table 4.3: Parameters resulting from a fit to the DOC cylinders model for the system DDAB/cyclo-hexane/water. $n$ is the density of cells in space, $Z$ is the co-ordination number and $R$ is the sphere radius (fixed at twice the cylinder radius $r$). $D^*$ is the predicted real-space peak position and $v/a\ell$ the effective surfactant packing parameter.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$n$ (10^{-5})</th>
<th>$R$ (Å)</th>
<th>$Z$</th>
<th>$D^*$ (Å)</th>
<th>$v/a\ell$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyclo 1</td>
<td>1.3</td>
<td>7.5</td>
<td>4.0</td>
<td>42</td>
<td>2.25</td>
</tr>
<tr>
<td>Cyclo 2</td>
<td>1.1 (2)</td>
<td>8.4</td>
<td>4.0</td>
<td>45</td>
<td>2.14</td>
</tr>
<tr>
<td>Cyclo 3</td>
<td>7.7 (2)</td>
<td>11</td>
<td>4.0</td>
<td>51</td>
<td>1.92</td>
</tr>
<tr>
<td>Cyclo 4</td>
<td>6.0 (2)</td>
<td>13</td>
<td>3.5</td>
<td>55</td>
<td>1.77</td>
</tr>
<tr>
<td>Cyclo 5</td>
<td>6.1 (2)</td>
<td>15</td>
<td>2.5</td>
<td>55</td>
<td>1.72</td>
</tr>
<tr>
<td>Cyclo 6</td>
<td>5.0 (2)</td>
<td>18</td>
<td>2.0</td>
<td>59</td>
<td>1.64</td>
</tr>
<tr>
<td>Cyclo 7</td>
<td>3.5 (2)</td>
<td>21</td>
<td>1.5</td>
<td>66</td>
<td>1.55</td>
</tr>
<tr>
<td>Cyclo 8</td>
<td>3.7 (2)</td>
<td>23</td>
<td>0.5</td>
<td>65</td>
<td>1.57</td>
</tr>
<tr>
<td>Cyclo 9</td>
<td>2.5 (2)</td>
<td>28</td>
<td>0.0</td>
<td>74</td>
<td>1.48</td>
</tr>
</tbody>
</table>

An attempt to fit with spheres gives a radius of 6.6Å and hence a very high value of 3.9 for $v/a\ell$.

Parameter values for a fit to the DOC cylinders model are given in Table 4.3. These values have been obtained by a combination of fixing $v/a\ell$ to the value determined from the fit to spheres at high water content, and fitting to $D^*$, since for the low water fractions found in this system it seems to be impossible to achieve a sensible structure without allowing some increase in $v/a\ell$. The values obtained are not unreasonable: in particular, $D^*$ is always correct to within 10% and $\phi$ and $\Sigma$ are fitted to at least the accuracy of the measurements. The surfactant parameter is calculated using the exact method of Section 3.5.

It is fair to ask where the increase in $v/a\ell$ comes from. The answer is that for sample Cyclo 1, with approximately one water molecule per surfactant molecule the headgroup area must be decreased somewhat. While this is not borne out by any noticeable decrease in the measured values of $\sigma$, it should be remembered that the uncertainty in these values is of the order of 10%. In addition it seems reasonable to suppose that in packing around this extremely curved interface, the surfactant is reducing its effective tail length. At such high curvatures each chain feels less pressure from its neighbours and so is not forced into such a stretched-out configuration. The extremely low water/surfactant ratio is also the explanation for the decrease in the conductivity observed for this system at very low water contents. At this point much of the polar region is taken up by the surfactant headgroups. Even without any binding effects, the mere narrowness of the cylinders reduces the mobility of the ions.

Figure 4.5 shows the results of calculation of full scattering curves for various models using the numerical procedure described in Section 2.2. The calculated curves are compared with the measured scattering for the sample Cyclo 1, at the water-poor edge.
Figure 4.5: Comparison of various theories with experiment for the low water-content sample Cyclo 1. The sample composition is given in Table 4.1. The measured experimental data (full curve) is reasonably well approximated by the DOC cylinders model (dashed-dotted curve); the cubic random cell (dotted curve) and hard spheres (dashed curve) models both fail.
of the single-phase region, with $\phi = 0.068$ and $\Sigma = 0.031\text{Å}^2/\text{Å}^3$. For the cubic random cell model, these values are obtained by setting the cube edge length $\xi = 12.3\text{Å}$. This model is clearly ideally suited to the calculation method used, as one can simply choose the cubic mesh size $T$ equal to $\xi$ or $\xi/2$ and the resulting calculation is exact, except for problems with averaging over too small an irradiated volume. (Too exact, as mentioned before: this model gives no peak without a slight variation in the cube size.) As can be seen, the shape of the calculated curve is completely wrong. The predicted peak position is at $q = 2\pi/\xi = 0.51\text{Å}^{-1}$, which is outside the $q$-range plotted and too large by a factor of over three. As discussed above, the model of hard spheres also fails. Calculation with the cube algorithm gives a curve with the peak in the same position but of slightly different shape to that of the Hayter-Penfold calculation given in Figure 4.4. The DOC cylinders curve was calculated using the parameters given in Table 4.3, and is clearly in better agreement with the experimental curve. In particular, the peak position is essentially correct. The "noise" in the CRC and DOC cylinders curves at small $q$ is statistical scatter caused by the small volume used in the calculation, as discussed in Section 2.2.3.

In conclusion, even at extremely low water contents, the DOC cylinders model gives a satisfactory account of the observed behaviour of the DDAB/cyclohexane/water system. The calculated scattering curve shows good agreement with the experiment. For the other samples, at high water content the predicted $D^*$ is in good agreement with that observed. At low water content where $v/a\ell$ cannot remain constant, a fit to $D^*$ gives a smooth increase in $v/a\ell$. The predicted connectivities give a percolation between samples Cyclo 7 and Cyclo 8, in agreement with conductivity measurements.

### 4.3 Dodecane

The DDAB/dodecane/water system has been studied in detail by Fontell et al. [46]. Compared with cyclohexane, the $L_2$ phase teardrop is swung a long way to the left, that is, towards the oil/water axis of the ternary phase diagram. As the larger dodecane molecule penetrates the surfactant tails less strongly than cyclohexane, we expect an effective surfactant parameter rather closer to 1, that is, a less strongly curved interface. The dodecane system would therefore be expected to form much larger structures than did the cyclohexane system. Nonetheless, the phase shares the important common feature of all these systems: it is conducting at lower water contents with an anti-percolation to a nonconducting solution at the left-hand edge.

An interesting feature of the phase diagram, shown in Figure 4.6 is the "nose" at the bottom of the $L_2$ phase. The NMR measurements show that the water self-diffusion constant shows no sign of decreasing with increasing water content along the bottom of the phase, in contrast to the strong decrease observed at higher oil contents. This suggests that there may be a qualitatively different behaviour in this part of the single-phase region, with a structure perhaps more like that in the tetradecane system.
Figure 4.6: Phase diagram for the system DDAB/dodecane/water, showing the compositions of samples used in the SAXS study. Note that sample Dod 1b is in the "nose" region, while Dod 1a and Dod 5b are near to the critical point.
Table 4.4: Compositions and measured quantities for samples in the system DDAB/dodecane/water. \( C_s \) is the surfactant concentration, \( \phi \) the polar volume fraction, \( D^* \) the real-space peak position, \( l_c \) the correlation length, \( \Sigma \) the internal surface determined from the Porod limit and \( \sigma \) the headgroup area per molecule. Uncertainty in the measured quantities is of the order of 10%.

<table>
<thead>
<tr>
<th>Sample</th>
<th>DDAB</th>
<th>Oil</th>
<th>Water</th>
<th>( C_s )</th>
<th>( \phi )</th>
<th>( D^* )</th>
<th>( l_c )</th>
<th>( \Sigma )</th>
<th>( \sigma )</th>
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<tbody>
<tr>
<td>Dod 1a</td>
<td>15.5</td>
<td>63.2</td>
<td>21.3</td>
<td>0.276</td>
<td>19.6</td>
<td>210</td>
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<td>68</td>
</tr>
<tr>
<td>Dod 2a</td>
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<td>60.0</td>
<td>25.0</td>
<td>0.270</td>
<td>22.7</td>
<td>230</td>
<td>51</td>
<td>0.0111</td>
<td>68</td>
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<tr>
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<td>29.2</td>
<td>0.288</td>
<td>26.6</td>
<td>225</td>
<td>52</td>
<td>0.0118</td>
<td>68</td>
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<tr>
<td>Dod 4a</td>
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<td>51.0</td>
<td>37.0</td>
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<td>33.2</td>
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<td>83</td>
<td>0.0091</td>
<td>68</td>
</tr>
<tr>
<td>Dod 5a</td>
<td>12.7</td>
<td>44.3</td>
<td>43.0</td>
<td>0.239</td>
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<td>320</td>
<td>79</td>
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<td>68</td>
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<tr>
<td>Dod 6a</td>
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<td>41.8</td>
<td>403</td>
<td>94</td>
<td>0.0083</td>
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</tr>
<tr>
<td>Dod 2b</td>
<td>24.3</td>
<td>23.4</td>
<td>52.3</td>
<td>0.49</td>
<td>52.2</td>
<td>150</td>
<td>0.025</td>
<td>85</td>
<td></td>
</tr>
<tr>
<td>Dod 3b</td>
<td>20.4</td>
<td>36.4</td>
<td>43.2</td>
<td>0.39</td>
<td>42.3</td>
<td>180</td>
<td>43</td>
<td>0.016</td>
<td>68</td>
</tr>
<tr>
<td>Dod 4b</td>
<td>16.4</td>
<td>49.0</td>
<td>34.6</td>
<td>0.31</td>
<td>32.0</td>
<td>217</td>
<td>55</td>
<td>0.013</td>
<td>74</td>
</tr>
<tr>
<td>Dod 5b</td>
<td>11.8</td>
<td>63.2</td>
<td>25.0</td>
<td>0.21</td>
<td>22.3</td>
<td>270</td>
<td>77</td>
<td>0.008</td>
<td>60</td>
</tr>
</tbody>
</table>

4.3.1 Experimental results

Compositions of samples prepared are shown on the phase diagram in Figure 4.6, and in Table 4.4, along with various quantities measured from the scattering experiments. Spectra were in the first instance measured on the same setup at Saclay as for cyclohexane. In cases for which the spacing was too large they were remeasured on the high-resolution camera D22 at the LURE synchrotron facility in Orsay. In particular, all of series b was measured at LURE, using a wavelength of \( \lambda = 1.22\text{Å} \). This allowed collection of data down to \( q = 0.003\text{Å}^{-1} \), or 2000Å in real space. As the D22 camera has point collimation, no desmearing was used for these runs. Calculated and measured values of the invariant \( Q^* \) are not shown: as for cyclohexane, excellent agreement was obtained. Measured values of the headgroup area remain uncannily constant at 68Å² for series a despite the expected uncertainty of 10%, although there is considerably more spread in the values for series b which were measured separately.

Spectra are shown in Figures 4.7 and 4.8. Note that series a is a water dilution path similar to that followed for cyclohexane, while series b is an oil dilution path. As for cyclohexane, there does not appear to be any sudden change in the character of the scattering curves as the percolation line is crossed. In this case conductivity measurements give this transition at a water-to-surfactant ratio of 2.5 [40]. The only cases in which the spectra look significantly different are at the two extremes of our oil dilution path, samples Dod 1b and Dod 5b. The first of these lies in the "nose" region, in which different behaviour was expected on the basis of the NMR results.
Figure 4.7: Measured SAXS spectra for the system DDAB/dodecane/water along a water dilution path (series a), plotted on (a) linear and (b) logarithmic scale. The Porod law behaviour is clearly visible. High water-content samples Dod 6a and Dod 7a show a small secondary peak in the log plot, possibly indicative of strong excluded volume effects.
Figure 4.8: Measured SAXS spectra for the system DDAB/dodecane/water along an oil dilution path (series b), plotted on linear scale (above) and in Porod representation $q^4I(q)$ vs $q$ (below). The strong scattering at extremely low angle in sample Dod 5b is the result of large fluctuations in the vicinity of the critical point. The qualitatively different shape of the Porod plot for sample Dod 1b, in the "nose" region suggests a different microstructure.
Figure 4.9: Comparison between the scattered intensity measured for sample Dod 5a and that calculated for a system of hard spheres of water radius 120Å and density $5.44 \times 10^{-8}\text{Å}^{-3}$ calculated using the Hayter-Penfold method.

The second, along with the nearby Dod 1a, is in the immediate vicinity of the critical point at which the L$_2$ phase separates into oil-rich and oil-poor parts. The resultant density fluctuations are the cause of the strong scattering at the lowest angles.

4.3.2 Comparison with models

As before, an attempt to fit the spectra with model of spherical reverse micelles is successful for samples at water contents higher than the percolation threshold. Figure 4.9 shows the results of such a fit for sample Dod 5a, which is near the measured percolation line. With our choice of $\ell = 12\text{Å}$ this gives a $v/\ell$ of 1.10, which is within the range expected. For sample Dod 7a, near the phase boundary, a similar fit gives the lower value of 1.06, which is thus a lower bound on the curvature of the surfactant monolayer. Predictions of the DOC cylinders model are given in Table 4.5. The apparent discrepancy between the successful fit to the spheres model for sample Dod 5a and the prediction of the DOC model that it has a co-ordination number
Table 4.5: Parameters resulting from a fit to the DOC cylinders model for the system DDAB/do-decane/water. \( n \) is the density of cells in space, \( Z \) the co-ordination number and \( R \) the sphere radius (fixed at twice the cylinder radius \( r \)). \( D^* \) is the predicted real-space peak position and \( v/\alpha l \) the effective packing parameter for the structure, assuming a tail length of \( l = 12\AA \).

<table>
<thead>
<tr>
<th>Sample</th>
<th>( n )</th>
<th>( R )</th>
<th>( Z )</th>
<th>( D^* )</th>
<th>( v/\alpha l )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \text{Å}^{-3} )</td>
<td>( \text{Å} )</td>
<td>( \text{Å} )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dod 1a</td>
<td>( 1.7 \times 10^{-7} )</td>
<td>54</td>
<td>3.5</td>
<td>179</td>
<td>1.20</td>
</tr>
<tr>
<td>Dod 2a</td>
<td>( 1.5 \times 10^{-7} )</td>
<td>62</td>
<td>3.0</td>
<td>189</td>
<td>1.17</td>
</tr>
<tr>
<td>Dod 3a</td>
<td>( 1.6 \times 10^{-7} )</td>
<td>67</td>
<td>2.5</td>
<td>186</td>
<td>1.16</td>
</tr>
<tr>
<td>Dod 4a</td>
<td>( 5.6 \times 10^{-8} )</td>
<td>107</td>
<td>1.5</td>
<td>262</td>
<td>1.11</td>
</tr>
<tr>
<td>Dod 5a</td>
<td>( 5.3 \times 10^{-8} )</td>
<td>118</td>
<td>1.0</td>
<td>266</td>
<td>1.10</td>
</tr>
<tr>
<td>Dod 6a</td>
<td>( 2.9 \times 10^{-8} )</td>
<td>149</td>
<td>0.5</td>
<td>326</td>
<td>1.08</td>
</tr>
<tr>
<td>Dod 7a</td>
<td>( 1.7 \times 10^{-8} )</td>
<td>193</td>
<td>0.0</td>
<td>391</td>
<td>1.06</td>
</tr>
<tr>
<td>Dod 3b</td>
<td>( 1.8 \times 10^{-7} )</td>
<td>75</td>
<td>3.5</td>
<td>178</td>
<td>1.14</td>
</tr>
<tr>
<td>Dod 4b</td>
<td>( 1.6 \times 10^{-7} )</td>
<td>73</td>
<td>4.0</td>
<td>198</td>
<td>1.14</td>
</tr>
<tr>
<td>Dod 5b</td>
<td>( 5.2 \times 10^{-8} )</td>
<td>86</td>
<td>3.5</td>
<td>268</td>
<td>1.13</td>
</tr>
</tbody>
</table>

\( Z \approx 1 \), is due simply to the fact that for such low connectivities, almost all of the internal volume lies within the interstitial spheres rather than within the connecting cylinders. As scattering counts the squares of the weights of different contributions to the electronic density, the resultant scattering curve is virtually indistinguishable from that for spheres alone.

It was impossible to fit samples Dod 1b and Dod 2b using the DOC cylinders model. To do so would require extremely high packing fractions for the hydrocarbon-coated water spheres—inter-sphere separations far less than the two extended chain lengths. In this situation, once the water network is very much larger than the interstices, it seems reasonable to assume that the description of the structure in terms of the morphology of the water network is no longer valid. Instead of packing the tails together in such a fashion, one expects that the structure will become distorted, with the normal bilayer formed between neighbouring water regions becoming the dominant structural unit. In this limit, the phase is better described as a disordered lamellar structure than as a disordered network of cylinders.

The parameter values in Table 4.5 are less certain than those for the cyclohexane system. This is because (i) at the relatively high packing fractions involved, the estimate used for the peak position \( D^* \approx n^{-\frac{1}{3}} \) is almost certainly inaccurate, as it is for dense systems of hard spheres, and (ii) the surfactant packing parameter \( v/\alpha l \) changes very slowly with the connectivity \( Z \) so that it is difficult to predict \( Z \) with any precision. As a result, neither of the two proposed schemes for choosing \( n, r \) and \( Z \), namely fitting to \( \phi, \Sigma \) and \( v/\alpha l \) or to \( \phi, \Sigma \) and \( D^* \), works very well. In fact it seems that the model is somewhat unstable: the parameter values obtained are rather sensitive to small uncertainties in the measured or estimated values of \( \phi \).
Figure 4.10: Comparison between measured (full curve) and calculated (dashed curve) SAXS spectra for sample Dod 1a. The calculated curve was generated using the DOC cylinders model and the algorithm of Section 2.2 with parameter values $n = 1.95 \times 10^{-7} \text{Å}^{-3}$, $R = 51 \text{Å}$, and $Z = 3.6$. The noise in the low-angle part of the calculated curve is an artefact of the method of calculation.
Figure 4.11: Comparison between measured (full curve) and calculated (dashed curve) SAXS spectra for sample Dod 3a. The calculated curve is for the DOC cylinders model with $n = 1.48 \times 10^{-7} \text{Å}^{-3}$, $R = 69\text{Å}$ and $Z = 2.2$. 
and $\Sigma$. Nonetheless, the predicted scattering curve, is not all that sensitive to these values. With only slightly different values for the model parameters (output of a different version of the fitting program), model scattering curves were calculated for samples Dod 1a and Dod 3a, using the cube method of Section 2.2. The results are shown in Figure 4.10 and 4.11 compared with the measured SAXS spectra, and show the reasonable semi-quantitative agreement. The model does not predict the strong rise in intensity at very small angle for sample Dod 1a. As already mentioned, this is a product of the fluctuations always found in the vicinity of a critical point. Such a critical phase separation can only be brought about by an attractive interaction, an effect which is obviously beyond the scope of this model.

### 4.4 Tetradecane

The system DDAB/tetradecane/water exhibits qualitatively different behaviour to the systems with shorter-chain alkanes and alkenes. It is here considered in more detail than the others, as there is little previous work published. The phase diagram has been studied in detail by Larché [79] from whose work Figure 4.12 is redrawn. At room temperature there is a large isotropic phase in the centre of the three-component triangle, which is referred to here as $L_e$. This solution does not show Bragg peaks and hence must have a disordered structure.

Unlike the $L_\alpha$ phases for the shorter oils, the $L_e$ phase cannot be diluted with tetradecane without separating into two phases. On dilution with water it separates into two phases with the water-rich lamellar phase $L_\beta^1$ in excess, rather than demixing to spill out water, which is the usual behaviour of such systems [70]. Toward the top of the phase diagram, the $L_e$ phase is in equilibrium with excess oil, whereas increase in surfactant concentration gives rise to equilibrium with the surfactant-rich lamellar phase $L_\alpha^2$. If one dilutes the $L_e$ phase with a binary surfactant/water mixture at constant surfactant to water ratio, a cubic phase is obtained. This transition is extremely temperature-sensitive [79]. As for the other oils, the cubic phase region is likely to be a reversed bilayer (water inside the film separating two bulk oil regions) lying on a periodic minimal surface with a cubic underlying lattice [64]. For other oils this region contains several structures with different topology [11,109].

In contrast to the systems with short chain alkanes or alkenes, the conductivity of the $L_e$ phase is always high, which means that the structure has to be water continuous throughout. There is no antipercolation. If oil penetration determines interfacial curvature as predicted by Chen et al. [27], then the surfactant parameter is expected to be close to one since tetradecane does not penetrate the surfactant tails. It is reasonable to expect a value between 0.95 and 1.05.

These observations suggest a qualitatively different picture to that of the systems with shorter-chain oils. As the tetradecane does not interpenetrate the surfactant tails, the interface is consequently much flatter. This conclusion is supported by
Figure 4.12: Phase diagram for the system DDAB/tetradecane/water, redrawn from the work of Larché [79]. Compositions of samples used in the X-ray and neutron scattering study are marked. The discrepancies are either a result of the different temperatures used or of the slight difference between H₂O and D₂O.
the observation that upon addition of strongly penetrating hexane, the tetracane system reverts to the behaviour of shorter-chain oils, with both a percolation threshold and the possibility of dilution to the oil corner. Addition of a single-chain surfactant has the same effect, while adding a long-chain alcohol to the dodecane system switches its behaviour to that of tetracane. All of this can be explained by a qualitative difference in behaviour between systems with $v/\alpha l \approx 1$ and $v/\alpha l$ much larger than 1.

Since there is no cosurfactant added and essentially no oil penetration, we cannot be satisfied with a model which requires ad hoc variation of the total interface per unit volume $\Sigma$ or the packing parameter $v/\alpha l$ with composition. As for the other systems, the relative lack of temperature dependence of the phase diagram and of the scattering—in this case, repeat scattering runs at 80°C show little difference in the results—suggests that the interface is rather stiff. In the language of the physicists, the splay bending modulus is high compared with the thermal energy: $k_c \gg kT$.

At first sight, no satisfactory explanation for the behaviour of this phase exists. It cannot be a dispersion of spherical droplets: water droplets in oil would not conduct and could be diluted to the oil corner; oil droplets in water could be diluted with water. Neither would give reasonable curvature. It also seems unlikely to be a DOC-cylinder structure like that used to model the microemulsion phases for the shorter-chain oils, because this structure can be diluted by oil, has a high interfacial curvature and displays a conductivity percolation. A DOC-lamellar or random bilayer structure, already proposed for other ternary systems [129], is not expected to exist over such a large composition range; it is usually found in ternary or quaternary systems only over a very narrow temperature and composition range close to a lamellar phase [20,107].

### 4.4.1 Experimental procedure and results

Compositions of the samples are indicated in Table 4.6, and also on the phase diagram in Figure 4.12. Measurements were made at 28°C; at that temperature all samples were monophasic. SAXS experiments were done on D22 at LURE and SANS on the first series only (all made with D$_2$O) at the PACE facility at Orphée (Saclay, France). Data reduction was made using standard methods, including absolute scaling by comparison with scattering of pure D$_2$O [138].

Spectra from along a typical water dilution line are shown in Figures 4.13 and 4.14. The real space peak position $D^*$ shifts with water content, increasing with water dilution. A well-defined Porod regime (see Figure 4.14) allows an unambiguous determination of $\Sigma$. The neutron and X-ray spectra are very similar, hence the assumption of constant bromide counter-ion concentration is valid within the experimental resolution of 12Å. This is contrary to the result obtained with SDS systems, in which details of the local electronic densities or scattering length density distributions are responsible for the peak shape and position [139]. Quantities calculated from the measured spectra are given in Table 4.7.
Table 4.6: Quantities determined from composition for the two series of samples in the system DDAB/tetradecane/water. \( C_s \) is the surfactant concentration, \([W]/[S]\) the water-to-surfactant molar ratio, \([O]/[S]\) the oil-to-surfactant ratio, \( \phi \) the polar volume fraction, and \( \Sigma \) the interfacial area per unit volume, assuming a headgroup area of 68 Å² per molecule.

<table>
<thead>
<tr>
<th>Sample</th>
<th>D₂O wt %</th>
<th>DDAB wt %</th>
<th>Oil wt %</th>
<th>( C_s ) M</th>
<th>([W]/[S])</th>
<th>([O]/[S])</th>
<th>( \phi ) %</th>
<th>( \Sigma ) Å²/Å³</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetra 1a</td>
<td>27.0</td>
<td>36.5</td>
<td>36.5</td>
<td>0.73</td>
<td>17.1</td>
<td>2.3</td>
<td>27.9</td>
<td>0.030</td>
</tr>
<tr>
<td>Tetra 2a</td>
<td>34.0</td>
<td>33.0</td>
<td>33.0</td>
<td>0.67</td>
<td>23.8</td>
<td>2.3</td>
<td>33.7</td>
<td>0.028</td>
</tr>
<tr>
<td>Tetra 3a</td>
<td>42.0</td>
<td>29.0</td>
<td>29.0</td>
<td>0.60</td>
<td>33.5</td>
<td>2.3</td>
<td>40.6</td>
<td>0.025</td>
</tr>
<tr>
<td>Tetra 4a</td>
<td>51.0</td>
<td>24.5</td>
<td>24.5</td>
<td>0.52</td>
<td>48.2</td>
<td>2.3</td>
<td>48.7</td>
<td>0.022</td>
</tr>
<tr>
<td>Tetra 5a</td>
<td>60.0</td>
<td>20.0</td>
<td>20.0</td>
<td>0.43</td>
<td>69.4</td>
<td>2.3</td>
<td>57.2</td>
<td>0.018</td>
</tr>
<tr>
<td>Tetra 1b</td>
<td>30.0</td>
<td>21.0</td>
<td>49.0</td>
<td>0.40</td>
<td>33.1</td>
<td>5.4</td>
<td>27.1</td>
<td>0.015</td>
</tr>
<tr>
<td>Tetra 2b</td>
<td>38.0</td>
<td>18.6</td>
<td>43.4</td>
<td>0.37</td>
<td>47.3</td>
<td>5.4</td>
<td>34.0</td>
<td>0.014</td>
</tr>
<tr>
<td>Tetra 3b</td>
<td>46.0</td>
<td>16.2</td>
<td>37.8</td>
<td>0.33</td>
<td>65.7</td>
<td>5.4</td>
<td>41.1</td>
<td>0.013</td>
</tr>
</tbody>
</table>

Table 4.7: Quantities measured from X-ray and neutron scattering experiments for the system DDAB/tetradecane/water. \( D^* \) is the real-space peak position, \( l_c \) is the correlation length and \( \Sigma \) is the internal surface.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( D^* ) Å</th>
<th>( l_c ) Å</th>
<th>( \Sigma ) Å²/Å³</th>
<th>( \sigma ) Å</th>
<th>( D^* ) Å</th>
<th>( \Sigma ) Å²/Å³</th>
<th>( \sigma ) Å²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetra 1a</td>
<td>84</td>
<td>25</td>
<td>0.031</td>
<td>71</td>
<td>80</td>
<td>0.031</td>
<td>71</td>
</tr>
<tr>
<td>Tetra 2a</td>
<td>97</td>
<td>31</td>
<td>0.027</td>
<td>67</td>
<td>100</td>
<td>0.029</td>
<td>72</td>
</tr>
<tr>
<td>Tetra 3a</td>
<td>120</td>
<td>37</td>
<td>0.029</td>
<td>80</td>
<td>114</td>
<td>0.027</td>
<td>75</td>
</tr>
<tr>
<td>Tetra 4a</td>
<td>160</td>
<td>45</td>
<td>0.024</td>
<td>77</td>
<td>150</td>
<td>0.023</td>
<td>74</td>
</tr>
<tr>
<td>Tetra 5a</td>
<td>190</td>
<td>53</td>
<td>0.023</td>
<td>89</td>
<td>190</td>
<td>0.019</td>
<td>74</td>
</tr>
</tbody>
</table>

| Tetra 1b | 157 | 0.017 | 71 |
| Tetra 2b | 190 | 0.015 | 67 |
| Tetra 3b | 250 | 0.014 | 70 |
Figure 4.13: Absolute scaled small-angle neutron and X-ray scattering spectra for the samples in dilution line a for the system DDAB/tetradecane/water (D$_2$O) at 28°C. The extreme similarity between the two sets of measured spectra confirms the hypothesis that the counterion distribution within the polar region is constant to the limit of experimental resolution ($\approx 12\text{Å}$).
Figure 4.14: Neutron scattering data for the system DDAB/tetradecane/water plotted on logarithmic scale, showing the extremely clear Porod law behaviour at large angles. Sample compositions are given in Table 4.6.

4.4.2 Comparison of models

The parameter values resulting from fitting a Teubner-Strey expression to the spectra are given in Table 4.8. The fits are very good indeed, but as usual one can infer little from these results, in particular nothing about the microstructure. Here we note that that ξ is of the same order of magnitude as $D^*$, which means that a Voronoï lattice is a reasonable choice for structural models.

One observes in Table 4.7 that the measured $l_c$ is considerably smaller than $D^*$, with the ratio about 3 for all samples. This is incompatible with the Talmon-Prager and CRC models, which predict $l_c \approx D^*$. As discussed in Chapter 3 this is a direct proof of the existence of local correlations. Peak positions for these models, also given in Table 4.8, are too low by a factor of roughly two as usual.

Peak positions for the oil-in-water and water-in-oil spherical droplet models were calculated using the standard Hayter-Penfold RMSA procedure [52], with the droplet charge set to zero and are shown in Table 4.9. It turns out that the peak positions obtained for a dispersion of water spheres in oil are in reasonable agreement with those measured, even with the radii imposed by the volume fractions and interfacial areas ($r = 3\phi/\Sigma$). The shapes of the full scattering curves are not perfect but are
Table 4.8: Fits of X-ray scattering data to the parametric expression of Teubner & Strey [126] and to the Talmon-Prager and cubic random cell models, for the system DDAB/tetradecane/water. For the Teubner-Strey expression, \( d \) is the spatial periodicity and \( \xi \) is the correlation distance; for TPR (the repulsive or "hard sphere" version of the Talmon-Prager model), and CRC to the cubic random cell model. \( D^* \) is the real-space peak position and \( v/\alpha \ell \) is the effective surfactant packing parameter.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Teubner-Strey</th>
<th>Talmon-Prager</th>
<th>Cubic random cell</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( d )</td>
<td>( \xi )</td>
<td>( D^* )</td>
</tr>
<tr>
<td>Tetra 1a</td>
<td>81</td>
<td>52</td>
<td>39</td>
</tr>
<tr>
<td>Tetra 2a</td>
<td>93</td>
<td>50</td>
<td>46</td>
</tr>
<tr>
<td>Tetra 3a</td>
<td>110</td>
<td>35</td>
<td>56</td>
</tr>
<tr>
<td>Tetra 4a</td>
<td>151</td>
<td>52</td>
<td>66</td>
</tr>
<tr>
<td>Tetra 5a</td>
<td>177</td>
<td>62</td>
<td>79</td>
</tr>
<tr>
<td>Tetra 1b</td>
<td>143</td>
<td>45</td>
<td>77</td>
</tr>
<tr>
<td>Tetra 2b</td>
<td>184</td>
<td>60</td>
<td>93</td>
</tr>
<tr>
<td>Tetra 3b</td>
<td>235</td>
<td>74</td>
<td>108</td>
</tr>
</tbody>
</table>

Table 4.9: Attempt to fit to spheres for the system DDAB/tetradecane/water. \( R \) is the sphere radius, \( D^* \) is the real-space peak position and \( v/\alpha \ell \) is the effective surfactant packing parameter.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Oil-in-water</th>
<th>Water-in-oil</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( R )</td>
<td>( D^* )</td>
</tr>
<tr>
<td>Tetra 1a</td>
<td>28</td>
<td>70</td>
</tr>
<tr>
<td>Tetra 2a</td>
<td>36</td>
<td>84</td>
</tr>
<tr>
<td>Tetra 3a</td>
<td>49</td>
<td>106</td>
</tr>
<tr>
<td>Tetra 4a</td>
<td>66</td>
<td>136</td>
</tr>
<tr>
<td>Tetra 5a</td>
<td>95</td>
<td>185</td>
</tr>
<tr>
<td>Tetra 1b</td>
<td>54</td>
<td>135</td>
</tr>
<tr>
<td>Tetra 2b</td>
<td>73</td>
<td>168</td>
</tr>
<tr>
<td>Tetra 3b</td>
<td>95</td>
<td>206</td>
</tr>
</tbody>
</table>

certainly no worse than some fits with the DOC cylinders model accepted in previous sections (Figures 4.15–4.17). However, the spherical microstructure requires an *ad hoc* variation of the surfactant parameter \( v/\alpha \ell \) from 1.13 to 1.5 with composition. Such a variation is highly improbable. Moreover, the phase equilibria and the conductivity data could not be explained by water-in-oil droplets. Oil-in-water droplets lead to peak positions inconsistent with those measured.

For the DOC models we adopt the procedure of seeking a fit of the three parameters to the measured or known \( \phi \), \( \Sigma \) and \( D^* \), rather than \( \phi \), \( \Sigma \) and \( v/\alpha \ell \). The surfactant parameter is thus an output of the calculation rather than an input. The oil-in-
Figure 4.15: Comparison between measured and calculated X-ray scattering spectra for sample Tetra 1a. The full curve is the normalised X-ray scattering, the dashed-dotted curve is the prediction of water spheres in oil and the dashed curve that of the DOC reversed lamellar model. The arrow indicates the peak position predicted by the cubic random cell model.

Figure 4.16: Comparison between measured and calculated X-ray scattering spectra for sample Tetra 3a. Legend as for Figure 4.15.
water version of the DOC cylinders model fails in much the same way as the model of oil droplets in water. Dismissal of the (more normal) water-in-oil DOC cylinder model is more difficult. Parameter values for this model are given in Table 4.10. This structure would explain the conductivity of the L_x phase, but not the nature of the phase transitions and equilibria. In the adjacent cubic phase and in both the lamellar phases the surfactant forms a bilayer and not a monolayer. Furthermore, the scattering can only be reconciled with a connected cylinder structure if one assumes an unlikely variation of the surfactant parameter. The proposed structure has a connectivity Z of about 5 throughout the stability range of the L_x phase. While this certainly gives the high conductivities observed, the packing constraint would have to be relaxed and v/αl allowed to vary by 20% for this to work. The resulting values are in many cases higher than those found for dodecane. The DOC-cylinder structure must therefore be rejected, even though it is compatible with the peak position.

This leaves the DOC lamellar model. This structure has already been found in other systems and is referred to as the L_3 or “sponge” phase by other authors. Since we are in the middle of the phase diagram, the DOC-lamellar structure could be a priori a reversed (water inside the bilayer) or a direct bilayer (oil inside). The calculations in Table 4.10 show that either structure is plausible. Both give reasonably good prediction of the peak position along with v/αl close to 1 and fairly constant. This is to be expected from Babinet’s principle: an exchange of polar and nonpolar regions does not change the scattering.
Table 4.10: Attempts to fit the DOC models to the system DDAB/tetradecane/water. For the DOC cylinders model (here as usual with water inside) $Z$ is the co-ordination number and $r$ is the cylinder radius. For the DOC lamellar model, $t$ is the oil or water half-thickness (the total bilayer thickness is $2t + 2\ell$) and $\psi$ is the pseudo volume fraction. $D^*$ is the predicted real-space peak position and $v/\ell$ the effective surfactant packing parameter.

<table>
<thead>
<tr>
<th>Sample</th>
<th>DOC w/o cylinders</th>
<th>DOC reverse lamellae</th>
<th>DOC direct lamellae</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$D^*$</td>
<td>$Z$</td>
<td>$r$</td>
</tr>
<tr>
<td></td>
<td>Å</td>
<td>Å</td>
<td>Å</td>
</tr>
<tr>
<td>Tetra 1a</td>
<td>84</td>
<td>4.5</td>
<td>28</td>
</tr>
<tr>
<td>Tetra 2a</td>
<td>96</td>
<td>4.5</td>
<td>36</td>
</tr>
<tr>
<td>Tetra 3a</td>
<td>118</td>
<td>5</td>
<td>47</td>
</tr>
<tr>
<td>Tetra 4a</td>
<td>143</td>
<td>5</td>
<td>62</td>
</tr>
<tr>
<td>Tetra 5a</td>
<td>184</td>
<td>5</td>
<td>86</td>
</tr>
<tr>
<td>Tetra 1b</td>
<td>156</td>
<td>3.5</td>
<td>55</td>
</tr>
<tr>
<td>Tetra 2b</td>
<td>190</td>
<td>4</td>
<td>71</td>
</tr>
<tr>
<td>Tetra 3b</td>
<td>229</td>
<td>5</td>
<td>91</td>
</tr>
</tbody>
</table>

However, since the neighbouring cubic phase is a reversed bilayer structure, we conclude that the L$_c$ phase must also be, the better to explain the extremely temperature-sensitive phase transition between them. This makes sense of the equilibria between the L$_c$ phase and the two lamellar phases. Such a structure would also explain why the phase cannot be diluted with water or oil, since unfolding or excessive swelling of this random lamellar structure would induce forbidden variations of $v/\ell$. Figures 4.15–4.17 show the results of approximate calculation of the full scattering curve as set out in Section 3.3. This gives reasonable agreement with the experiment, certainly better than that for the model of water spheres in oil.

It is possible to take this reasoning further and actually deduce the geometric limits on this structure from the positions of the phase boundaries. This is similar to the phase boundary calculation made for the DOC cylinders model. The left-hand phase boundary essentially lies along a line of constant surfactant/water ratio. This is equivalent to an upper limit on the water film thickness; this cannot be more than about 64Å (see Figure 4.18). Beyond this it seems that the structure is no longer stable and the dilute lamellar phase, with water thickness at least 70Å is in excess.

The right edge is approximately an upper limit on the surfactant concentration. This is directly linked to the cell size, and thus to the peak position $D^*$. In this part of the phase diagram, the size of the oil domains between the water bilayers becomes quite small. Once $D^*$ is less than about 80Å (Figure 4.18) the phase prefers to go into equilibrium with the concentrated lamellar phase, which has hydrocarbon thickness about 27Å, slightly less than two fully extended chain lengths. Larché [79] has noted that this equilibrium is extremely temperature-sensitive. This could be one of the first examples of an “unbinding” transition between highly charged concentrated
Figure 4.18: Measured boundaries of the Lₐ single-phase region in the system DDAB/tetradecane/water, compared to the limits imposed by various geometric constraints on the proposed DOC lamellar structure.
The top and bottom boundaries of this phase appear to be set by limits on the allowed curvature of the reverse bilayer. Dilution with oil has the effect of trying to flatten out the bilayer, which has negative Gaussian curvature (see Chapter 3). The limit appears to be roughly $\langle K \rangle t^2 < 10^{-2}$: in other words the principal curvature radii cannot be greater than about five times the total water thickness. A first effect of this appears to be a breaking of the symmetry between the two sides of the bilayer. While making $\psi$ different to $\frac{1}{2}$ at constant cell size changes the curvature in the wrong direction, at constant composition it has the compensatory effect of reducing the cell size and in fact keeps $\langle K \rangle$ negative, thereby maintaining the desired degree of "foldedness". The limit is reached when $\psi$ approaches 0.18, at which point $\langle K \rangle$ must change sign and no amount of change in the cell size will keep the surface sufficiently folded. Approximate phase boundaries deduced from geometric constraints on the DOC lamellar structure are shown compared to the experimental phase boundaries in Figure 4.18.

The calculations in Table 4.10 give values of the pseudo-volume fraction $\psi$ used to generate the structure (see Section 3.3) ranging between 0.25 and 0.5. This gives a bicontinuous structure, in agreement with the conductivity measurements, with a mean curvature which is not too far from zero. The total bilayer thickness $(2t + 2\ell)$ is generally of the order of $D^*/2$. The persistence length, the typical distance over which the bilayer normal remains roughly parallel to itself is also about $D^*/2$, as for all Voronoi models.

This model also gives some understanding of the slow increase of conductivity with water content. Along any water dilution line the bilayer thickness increases. The connectivity of the bilayer also increases as $\psi$ relaxes to its desired value of $\frac{1}{2}$.

### 4.4.3 Conclusions

In this system all the standard models run into problems when tested against the scattering data. The cubic random cell and Talmon-Prager models predict the peak in the wrong position unless local correlations are introduced. Droplets or DOC cylinder models require unlikely ad hoc variation of the surfactant parameter $v/a\ell$ with water content and cannot be reconciled with the phase diagram. Of the quantitative models, only the DOC-lamellar model, describing a random bilayer, is compatible with the observed scattering. We therefore conclude that the observed $L_x$ region is in fact a DOC-lamellar (or $L_3$) phase. This model is compatible not only with the scattering data but also with the conductivity measurements and the experimental phase diagram. It gives a simple explanation for the positions of the measured phase boundaries in terms of such geometric constraints on the structure as the bilayer thickness, the cell size and the film curvature.
For systems with lower bending constant $k_z$, such a microstructure is restricted to a very narrow channel near the edge of the lamellar phase. In this system it extends over a much broader range of composition, but still has in common with other L$_3$ phases the ability to be in equilibrium with excess oil and with lamellar phase [21]. This is not the first example of a more concentrated L$_3$ structure: such a phase was mapped out by Ekwall in the central region of the ternary sodium octanoate/octanoic acid/water system [36]. In that system, as in this one, the disordered lamellar structure exhibits a peak in scattering. In diluted L$_3$ structures on the other hand, where no spontaneous curvature restricts the swelling [107,50], the scattering can be divided into a low-$q$ part where $I(q)$ is approximately constant, followed at $q > 2\pi/D^*$, by a region in which $I(q) \sim q^{2}$, and finally a Porod region where $I(q) \sim q^{4}$. In the case studied here, the scattering is dominated by the interaction peak which merges into the Porod limit at high $q$.

### 4.5 Discussion

The results presented here show that microstructure is important and that interfacial curvature can be a determinant of behaviour. The spectra presented can all be fitted with the phenomenological expression of Teubner & Strey, but their explanation in terms of the geometric models used provides a far richer understanding of why these systems behave the way they do.

Experiments have also been made with octane and a mixture of hexane and tetradecane [8,9]. Those results are not presented here. In both cases there is similar agreement with the DOC cylinders model to that found for cyclohexane and dodecane. Not all details of the behaviour are predicted, but it is clear that the basic ideas are right: highly connected networks form at low water content and on dilution they become less and less connected, with only moderate change in the curvature, until the percolation is reached and there is nothing left but spheres. Any further dilution requires them to grow, which they cannot without the surface becoming too flat.

Two extensions of this work to related systems have been made. Firstly, in an attempt to discover the extent of validity of these theories when the solvent is changed, a study has been commenced of the phase diagram of the system DDAB/decanol/water. Preliminary conclusions are presented in Appendix A. A study has also been made of the related surfactant $(C_{10}H_{21})_2(CH_3)_2NBr$ (2C$_{10}$DAB) in which the tails have length ten rather than twelve. This surfactant is extremely hygroscopic, and forms structures with rather flat interfaces. The phase diagram of the ternary system 2C$_{10}$DAB/hexane/water contains two different isotropic liquid phases, one of which behaves like the DOC cylinders model. The other is probably well-described by the normal (oil in the bilayers) DOC lamellar model [129].