The work reported in this thesis concerns, not only the synthesis of mesoporous MCM-41 materials, but also their characterisation and analysis by a number of techniques. The methods used most frequently were small angle X-ray and neutron scattering. These procedures, especially when used in conjunction, are very powerful, giving much structural information in a critical size range. Other techniques used included gas adsorption isotherm analysis, quasielastic neutron scattering, X-ray and neutron diffraction, and transmission and scanning electron microscopy. The Langmuir trough was also used for some studies.

The most commonly used methods for characterising MCM-41 are X-ray diffraction, gas isotherms, transmission electron microscopy, and nmr. Of these methods, the first two give information about bulk properties of MCM-41 and identify long range characteristics. Gas adsorption isotherms are often used to estimate average pore volumes and characterise MCM-41 surface behaviour, while X-ray diffraction is usually used to provide confirmation that the MCM-41 phase has been synthesised or to observe structure evolution over time. Only a few workers have taken the diffraction work further with modelling. Small angle X-ray scattering is not often used. The first three commonly used techniques investigate the silica framework only. Transmission electron microscopy is generally used to show localised order, and to investigate pore dimensions by direct imaging. MCM-41 materials doped with boron have been developed to improve TEM imaging of this material. Some modelling of channel arrangement has been based on these images. This technique has also been extended to investigate channel structure by filling individual pores with platinum to allow direct imaging of the spatial behaviour of one channel.

The last technique, nmr, the only one which looks at molecular level interactions both within the silicate framework and between the silicate and the template, has been used
in several ways. $^{29}\text{Si}$ and $^{27}\text{Al}$ magic angle spinning (MAS) nmr allow observation of the degree of silicate polymerisation,$^{2,16,32}$ and $^{13}\text{C}$, $^{14}\text{N}$ and $^{1}\text{H}$ nmr have been employed to look at the surfactant behaviour during syntheses.$^{33}$ Solid state $^{13}\text{C}$ nmr has given additional structural information about surfactant molecules within silicate mesophases.$^{2,34}$ $^{1}\text{H}$ nmr has also been used to characterise molecules such as water residing in the MCM-41 channels.$^{35-37}$ This method has been developed to allow calculation of channel dimensions from such measurements.$^{38,39}$ MCM-41 materials doped with various transition metals have been investigated with electron paramagnetic resonance,$^{40-42}$ which also gives information on chemical interactions on a molecular scale.

Other techniques which have been used to characterise MCM-41 include IR$^{43}$ and FTIR, to investigate surface siloxyl groups,$^{44}$ and, when combined with temperature programmed ammonia desorption, to allow the number and strength of acid sites in Al substituted materials to be determined.$^{2,45}$ Temperature programmed desorption has also been applied to calculate pore volumes.$^{46}$ Thermogravimetric analysis has been used to investigate MCM-41 stability and silica/surfactant ratios in dried, unheated synthesis gels$^{47}$ and dried as-synthesised samples.$^{33}$ These showed that the MCM-41 samples contain around 50 wt% surfactant, and 10 wt% water, with the remaining mass being silica.$^{33}$ Various forms of catalytic testing have also been done.$^{45,48-50}$ Rheological studies of the surfactant template have been carried out.$^{51}$ High temperature calorimetry studies measured the enthalpy of MCM-41 relative to that of quartz, while a Raman study suggested the presence of 3-fold siloxane rings in the wall structure.$^{52}$ Some small angle neutron scattering work has also been reported by Firouzi et al.$^{47}$ who merely give one pattern and by Glinka et al.$^{53}$ who carried out a more detailed analysis, to investigate the formation mechanism of MCM-41. Scanning electron microscopy is becoming a more common characterisation technique, as templated materials with macroscale structure are developed.$^{54}$

Results of these characterisation techniques, where relevant, are discussed throughout this work, in the context of the experimental results reported.

### 3.1 Size

The choice of characterisation techniques for this work was largely governed by considerations of size. ‘Meso’ is a Greek prefix meaning ‘in between’, which is used to refer to objects in the size range 20-500 Å.$^{55}$ The interesting features of MCM-41 materials, the channels, are in the mesoscale size range. Structures in this size range can be awkward to access, being neither at an atomic nor a microscopic scale. The material, being mostly amorphous silica, has few X-ray diffraction peaks which are resolvable under normal, high angle X-ray diffraction conditions. The wide angle diffraction pattern shows only a broad feature at around 20-40° $\theta$ (for $\lambda = 1.8963(1)$ Å) in highly ordered MCM-41 samples, and a narrower distribution of 10-20° $\theta$ (for $\lambda = 1.0052(8)$ Å) in less well ordered samples. Such a distribution is characteristic of the distribution of Si-O bond lengths in amorphous silica.$^{56,57}$ At small angles, which may not be within the range of ordinary settings for conventional wide angle cameras,
up to five peaks may be seen. These diffraction patterns result from the hollow channel array which has a repeat distance of ca. 40 Å. This distance however, falls in the centre of the detection range for most small angle scattering cameras, making small angle diffraction and scattering an ideal technique for the study of MCM-41. Small angle scattering also had the advantage that sample preparation did not require any alteration of the sample state. Wet or dried samples could be investigated, and facilities were available for observation of in situ heating or shearing of the samples. The time necessary for a SAS pattern to be taken was short enough that successive shots allowed limited kinetic data to be obtained. Contrast variation techniques, used in small angle neutron scattering, also allowed some chemical information, in that size range, to be determined.

Small angle diffraction does not, however, allow determination of pore diameters without modelling. It gives only the distance between pore centres. Complementary analysis techniques are therefore needed. Gas adsorption techniques are useful in determining pore characteristics such as surface area and energies of adsorption in the mesoscale region. There is some debate over whether the assumptions made in the Kelvin equation (see section 3.4.1, equation 3.13 below) are legitimate for small mesopores, but pore volumes determined using this method are often reported in the literature. Quasielastic neutron scattering measurements on adsorption sites for various gases have also been used in this work to characterise pore wall structures. Atomic scale interactions were also investigated by studying the formation of silicate-surfactant films on the Langmuir trough.

Diffraction techniques do not give a good impression of the amount of amorphous material which co-exists with the ordered channel arrays. Transmission electron microscopy can provide information on thin, dried samples in the mesoscale size range and has been used in this work to give an indication of the overall order in the sample. Scanning electron microscopy covers a slightly larger size range (0.1 - 10 microns) and, although the channels in MCM-41 can not be detected using this technique, it allows direct observation of the crystallite morphology. All of the above techniques have been used in conjunction, in this work to investigate the formation and the structure of MCM-41.

### 3.2 Small Angle Scattering

Small angle scattering (SAS) was used in two ways - as a diffraction technique, since the Bragg peaks for the size range of interest happen to fall within the limits of the small angle region - but, also using the more traditional small angle scattering methods of fitting the fall off from the region of the straight-through X-ray beam, with the scattering function from particles of different shapes and densities. Diffraction techniques are discussed in greater detail in section 3.3 below. Quantities in bold type in the discussions which follow are defined to be vector quantities.
3.2.1 Small Angle Scattering Theory

A detailed treatment of the theory of SAS is readily available in many textbooks, so only a brief explanation of the background, relevant to the experiments discussed here will be given. Small angle scattering measures the elastic scattering of X-rays or neutrons, that is, when the radiation incident on a sample undergoes a change of direction, but not of energy. Such scattering is shown in Figure 3.1 where \( s \) and \( s_0 \) are unit vectors of the incident and scattered radiation respectively, both with wavelength, \( \lambda \).

\[ Q = \frac{2\pi}{\lambda} (s - s_0) \quad \text{where} \quad |Q| = Q = \frac{4\pi}{\lambda} \sin \theta \]  

(3.1)

For elastic scattering, the amplitude of the radiation scattered by an object differs only in phase from that of the incident radiation. Phase, \( \phi \) depends upon the position of the wave in space and is defined as \( 2\pi/\lambda \) times the difference between the optical path length of the wave and an arbitrary reference wave, \( r \). The path difference therefore is \( -r(s-s_0) \), and so the phase becomes \( \phi = (-2\pi/\lambda)r.(s-s_0) \). The scattering vector, \( Q \), is then defined to be:

\[ I(Q) = \Psi P(Q)S(Q) \]  

(3.2)

Figure 3.1 Scattering of incident radiation from a point object.

Interatomic distances are small on the size scale of the small angle scattering experiment, and so are not generally observed in SAS patterns. It is therefore more convenient to consider an assembly of individual scattering objects, for example micelles or particles. Such an object has a factor, \( P(Q) \) which describes interparticle scattering and a structure factor, \( S(Q) \) which describes intraparticle scattering, if it is assumed that there is no correlation between particle orientation and interparticle motion. The intensity of radiation scattered from \( N \) such objects in a volume, \( V \) is:
where $\Psi = N/V$, the number density of individual scattering particles in the sample. Each of these individual scatterers will interact with radiation depending on the constituent atoms of that sample. The interaction with X-rays will be dependent upon the number of electrons around each atom, and the interaction with neutrons upon the number of particles in the nuclei of the atoms making up the scattering material. This interaction is quantified in terms of a scattering length for each atom, which differs for X-rays and neutrons. Table 3.1 shows the X-ray and neutron scattering lengths for the elements of interest in this work. The scattering length density of the whole scattering particle is then defined as:

$$
\rho_n(r) = \frac{b_i d N_A}{M_w} \quad (3.3a)
$$

for neutrons

$$
\rho_x(r) = \frac{n d N_A b_x}{M_w} \quad (3.3b)
$$

for X-rays

where $d$ is the physical density of the material, $b_i$ is the neutron scattering length for a particular nucleus, $n$ is the number of electrons per molecular unit of scatterer, and $b_x$ is the scattering length per electron ($2.8 \times 10^{-13}$ cm). For both X-rays and neutrons, the scattering length has coherent and incoherent parts. The incoherent part, in the case of neutron scattering is related to neutron, and nuclear spin and is isotropic. It forms a constant background in the coherent SANS scattering patterns and is particularly significant for some nuclei, most importantly $^1$H (see Table 3.1). For X-rays, the incoherent scattering is small at small angles and so can usually be ignored.

<table>
<thead>
<tr>
<th>Atom</th>
<th>X-ray scattering length at $Q = 0$ / $10^{-14}$ m</th>
<th>Neutron scattering length / $10^{-14}$ m</th>
<th>Neutron coherent cross-section / $10^{-28}$ m$^2$</th>
<th>Neutron incoherent cross-section / $10^{-28}$ m$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^1$H</td>
<td>0.281</td>
<td>-0.37423</td>
<td>1.7599</td>
<td>79.91</td>
</tr>
<tr>
<td>$^2$D</td>
<td>0.281</td>
<td>0.6674</td>
<td>5.597</td>
<td>2.04</td>
</tr>
<tr>
<td>C</td>
<td>1.686</td>
<td>0.66484</td>
<td>5.554</td>
<td>0.001</td>
</tr>
<tr>
<td>N</td>
<td>1.967</td>
<td>0.936</td>
<td>11.01</td>
<td>0.49</td>
</tr>
<tr>
<td>O</td>
<td>2.249</td>
<td>0.5805</td>
<td>4.235</td>
<td>0.000</td>
</tr>
<tr>
<td>Na</td>
<td>3.092</td>
<td>0.363</td>
<td>1.66</td>
<td>1.62</td>
</tr>
<tr>
<td>Si</td>
<td>3.935</td>
<td>0.4149</td>
<td>0.015</td>
<td>2.163</td>
</tr>
<tr>
<td>S</td>
<td>4.497</td>
<td>0.2847</td>
<td>1.0186</td>
<td>0.007</td>
</tr>
<tr>
<td>K</td>
<td>5.340</td>
<td>0.371</td>
<td>1.73</td>
<td>0.25</td>
</tr>
<tr>
<td>Br</td>
<td>9.80</td>
<td>0.679</td>
<td>5.79</td>
<td>0.10</td>
</tr>
</tbody>
</table>

The intraparticle scattering factor, $S(Q)$ is equal to $\langle |F(Q)|^2 \rangle$, where $F(Q)$ is the Fourier transform of the particle density distribution shown in equation 3.4 below. That is, it is
the form factor directly related to the shape of the particle, and to the contrast $\Delta \rho$

between the scattering length density of the particle $\rho(r)$, and the surrounding medium, $\rho_s$. The use of contrast in neutron experiments is discussed further below.

$$F(Q) = \int \Delta \rho \exp(iQ \cdot r) d^3 r$$  \hspace{1cm} (3.4)

### 3.2.1.1 The Guinier Approximation

The Guinier approximation provides a method of extracting information from the very low Q parts of the scattering curve.\(^6^1\) It results from making an expansion of the exponential in equations 3.2 and 3.4 in a power series, with terms in $Q \cdot r$. For centrosymmetric particles, with a radius of gyration, $R_g$, and a uniform scattering length density, the term in $r$ vanishes, and for $Q \cdot R_g << 1$, the interparticle scattering factor $P(Q)$ becomes:

$$P(Q) = I(0) \exp\left(-\frac{Q^2 R_g^2}{3}\right)$$

where

$$R_g^2 = \frac{1}{\Delta \rho V} \int \rho^2 (\rho - \rho_s) d^3 r$$ \hspace{1cm} (3.5)

and $I(0) = (\Delta \rho V)^2$

$I(0)$ can therefore be determined by extrapolation from a ln(I) versus $Q^2$ plot, using only those points which obey the Guinier approximation, *ie*. those at Q values such that $Q \cdot R_g < 1$. Unfortunately, however, this approximation is not valid for the particles studied in this work. From other methods, described below, the MCM-41 particles have coherence lengths of the order of 1000 Å, even in the least ordered systems, and particle sizes which are larger still. The lowest Q value available was *ca.* 0.006 Å\(^{-1}\) which corresponds to a $d$-spacing of around 1000 Å. At this Q value however, the Guinier approximation is only valid for particles with a radius of gyration below 160 Å. An alternative method discussed in the next section was therefore used to analyse the SAS data.

### 3.2.1.2 Porod’s Law

Porod’s law\(^6^2\) is a power law describing the behaviour of I(Q) at higher Q than the Guinier region. It characterises the scattered intensity of a system where two scattering length densities are separated by a sharp boundary, and the length scale of curvature fluctuation in the boundary is large compared with $2\pi/Q$.

$$P(Q) = \frac{2\pi (\rho - \rho_s)^2 S}{Q^4}$$ \hspace{1cm} (3.6)

S is the total area of surface boundary. From equations 3.2 and 3.6, a plot of ln(I) versus ln(Q) will generate a curve where, at the largest Q values, all shapes of particle will give a cross-section which decreases as $Q^{-4}$. At lower values of Q there will be regions of nearly constant slope which have been interpreted variously as indicators of
particle shape,\textsuperscript{63} or as the fractal dimension of the object at low $Q$ and the fractal dimension of the surface structure at intermediate $Q$.\textsuperscript{64} Deviations from $Q^{-4}$, even at high $Q$ values, are often seen in practice, since the boundaries in question are not perfectly sharp and the scattering length densities within the phases contain local fluctuations.\textsuperscript{66-70} From equation 3.6, it can be seen that the intensity on any point of a scattering curve which obeys power law behaviour will be proportional to the square of the contrast, $\Delta \rho$. It is therefore possible, in systems which show power law scattering, to carry out contrast variation experiments as described in the next section.

### 3.2.1.3 Contrast Variation in Neutron Scattering

The intensity, $I(Q)$, of the scattering from a system is thus related to the square of the contrast, $\Delta \rho$. The contrast is the difference in scattering length density between the particle and the medium. In a system where particles with scattering length density, $\rho$, are suspended in aqueous solution with scattering length density, $\rho_s$ the contrast can be made to vary, by varying the composition of that solution. This is the basis of the contrast variation method frequently used in small angle neutron scattering.

The scattering length density for neutrons, $\rho_n$ is given by:

$$\rho_n = \frac{dN_A}{M_W} \sum b_i$$  \hspace{1cm} (3.3a)

where $\sum b_i$ is the summation of the scattering lengths of all nuclei in the scattering medium, $d$ is the density of the medium, $N_A$ is Avogadro’s number, and $M_W$ is the molecular weight of the scatterer. The variation of scattering length density with changes in isotopic composition leads to the ability to change the contrast of a solution without significantly varying other properties of the sample.

The contrast variation method of small angle neutron scattering often relies on the differences between the scattering length densities of $\text{H}_2\text{O}$ ($0.562 \times 10^{10}$ cm$^{-2}$) and $\text{D}_2\text{O}$ ($6.34 \times 10^{10}$ cm$^{-2}$).\textsuperscript{71} As these are of opposite sign, it is possible to create solutions having intermediate scattering length densities by mixing $\text{H}_2\text{O}$ and $\text{D}_2\text{O}$ in various proportions. Particles in a solution which have a uniform scattering length density which is the same as that of the surrounding solution will not contribute to the scattering in a SANS experiment and are said to be contrast matched (ie. $I(Q) = 0$). Figure 3.2, below, illustrates this concept. We measure the scattering from a series of samples containing fractions of $\text{H}_2\text{O}$ and $\text{D}_2\text{O}$, which bracket an unknown scattering length density for particles in a solution. The point of zero scattering, the contrast match or null point, for that sample can thus be determined, and therefore its scattering length density. From equation 3.5 or 3.6, above, it can be seen that a plot of $\sqrt{I}$ versus $[\text{D}_2\text{O}]$ will be linear, crossing the concentration axis at a $\text{D}_2\text{O}$ concentration corresponding to a scattering length density equal to the average scattering length density of the particles in solution.
20% D₂O in (D₂O+H₂O)

65% D₂O in (D₂O+H₂O)

90% D₂O in (D₂O+H₂O)

Figure 3.2 The concept of contrast matching. The concentration of D₂O in the solvent is given on the left, and the contrast relative to that of the suspended silica particles is shown on the right.

Table 3.2 Scattering length densities for all components used in the MCM-41 preparations studied.

<table>
<thead>
<tr>
<th>Material</th>
<th>Neutron Scattering Length Density / ×10¹⁰ cm⁻²</th>
</tr>
</thead>
<tbody>
<tr>
<td>CTAB</td>
<td>-0.244†</td>
</tr>
<tr>
<td>SiO₂</td>
<td>3.48⁷¹</td>
</tr>
<tr>
<td>H₂SO₄</td>
<td>2.101†</td>
</tr>
<tr>
<td>NaOH</td>
<td>1.826†</td>
</tr>
<tr>
<td>CH₃COOH</td>
<td>1.046†</td>
</tr>
<tr>
<td>H₂O</td>
<td>-0.562⁷¹</td>
</tr>
<tr>
<td>D₂O</td>
<td>6.34⁷¹</td>
</tr>
<tr>
<td>KBr</td>
<td>1.461†</td>
</tr>
</tbody>
</table>

Note: † calculated from the atomic scattering lengths⁷² and densities of the materials.⁷²

In the case of MCM-41 the surfactant template has quite a different scattering length density to the silica. The surfactant is mostly hydrogenous and so its scattering length density in the crystalline state is small and negative, -0.244×10¹⁰ cm⁻², while that of amorphous silica is 3.48×10¹⁰ cm⁻².⁷¹ This difference in contrast will mean that
different parts of the surfactant/silicate composite structure will be contrast matched at different concentrations of H$_2$O/D$_2$O. It is therefore possible to draw conclusions about the distribution of surfactant and silica in the composite particles. The scattering length densities for all components of the MCM-41 preparations are given in Table 3.2 for reference purposes.

### 3.2.2 Instrumentation and Sample Containment

The samples were characterised using the small angle X-ray scattering (SAXS) camera in the Research School of Chemistry at the Australian National University. The machine is made up of an Elliott GX-13 X-ray generator which creates Cu K$_\alpha_1$ and K$_\alpha_2$ X-rays by impinging electrons from a heated tungsten filament on a rotating copper anode. X-rays created pass through a Huxley-Holmes camera, 980 mm in length, and the scattered X-rays are sensed by a Gabriel detector. This is a linear position sensitive detector consisting of a gold plated wire under high potential in a P10 gas (90% argon, 10% methane) atmosphere. A schematic for the SAXS camera is shown in Figure 3.3.

![Schematic diagram of the small angle X-ray scattering camera at the Research School of Chemistry, ANU.](image)

The SAXS patterns presented in this work were taken using X-rays of wavelength 1.54 Å and are shown as plots of intensity against the momentum transfer, Q. All samples for X-ray pattern determination were run in Lindemann glass (lithium borate) X-ray capillary tubes. Dry powder samples were run in 0.7 mm or 1.0 mm diameter capillaries and wet gel samples were generally run in 1.5 mm capillaries owing to the difficulties involved in filling smaller capillaries with the stiff gel. Samples for in situ heating experiments, despite being wet synthesis gels, were run in 1.0 mm capillaries. All capillaries were sealed with Torr-Seal™ high vacuum glue. The sample was not usually in contact with the seal. In situ heating experiments on the SAXS camera were carried out using the capillary heater designed and built by Trevor Dowling at the RSC. The coiled Nichrome resistance heater was used in the range of 70-100°C to heat nitrogen gas and controlled at the set temperature by an Omega CN76000 temperature controller to an accuracy of ±1.0°C although as much as 30 minutes was required to reach the set temperature. The heated gas was blown down the length of the capillary, with pressure controlled by a gas rotameter.
The small angle neutron scattering experiments were carried out on the LOQ small angle scattering instrument at ISIS at the Rutherford Appleton Laboratory, UK; on the SAD instrument at IPNS, at Argonne National Laboratory, Chicago, USA; and on the NG3SANS instrument at the CNRF, NIST, Washington, USA. LOQ and SAD are both time-of-flight instruments on pulsed spallation neutron sources. At these spallation sources, neutrons are generated by the impact of protons on a tantalum or uranium target producing a pulse of neutrons. The time-of-flight between the neutron generation at the target and the arrival of each neutron at a detector is measured, and from this the neutron velocity and thus wavelength may be calculated. Rotating blade “choppers” and frame overlap mirrors shape each pulse, preventing fast neutrons from the next pulse, or slow neutrons from the previous pulse interfering with those of the current pulse. The interaction of the neutrons with the sample gives a scattering pattern measured in counts versus time-of-flight which is then converted to momentum transfer, Q. A schematic of LOQ is shown in Figure 3.4.

**Figure 3.4** Schematic of the LOQ time-of-flight small angle neutron scattering machine at ISIS, RAL, UK, used with permission.

The NIST small angle scattering machine, NG3SANS is on a reactor source which generates a continuous neutron beam. In this machine a particular wavelength (6 Å for the experiments reported here) is selected by a monochromating crystal. The scattering pattern is determined as a function of counts at a particular angle, for neutrons of that energy only. Both reactor and spallation sources use a moderator to control the energy spectrum of the neutrons, reducing the energy of “hot” neutrons by passing them through a liquid methane filled area, prior to entry into the neutron guides for each machine. Figure 3.5 shows a schematic of the NIST, NG3SANS machine. The samples were contained in flat quartz cells, 1 mm sample thickness, sealed with teflon stoppers. All static SANS measurements were performed at 25°C.
Measurements of the MCM-41 synthesis gels under shear were also made at ISIS on the LOQ instrument, and at NIST on the NG3SANS instrument. In both cases a quartz shear cell in a Couette geometry was used. The gap between the inner (static) cylinder and the outer (rotating) cylinder was 0.5 mm in both cases. The shear cells were run at temperatures between 25 and 40°C, by using a water bath to pump thermostatted water through the inner cylinder, excepting in the region of the neutron window.

Shear rates used varied from one revolution per minute (0.02 s⁻¹) up to 10 000 s⁻¹ on the LOQ shear cell and from 78 to 3112 s⁻¹ on the NIST shear cell. Figure 3.6 shows a
photograph of the LOQ shear cell. Solutions used in the shear cell contained 89.7 wt% D$_2$O, to give the greatest available contrast (it is not possible to achieve a higher concentration of D$_2$O in a MCM-41 synthesis gel, as the sodium silicate solution contains a significant amount of H$_2$O).

### 3.3 Synchrotron X-ray Powder Diffraction

Powder diffraction was carried out using both neutrons and X-rays. The theory is the same for both so it is discussed only once. However, as the purpose of the two experiments were very different, the instrumentation and sample containment are discussed separately.

#### 3.3.1 Powder Diffraction Theory

Again, a more detailed account of X-ray diffraction may be found in many textbooks. A brief overview relevant to the work discussed in this thesis is given here. X-ray diffraction is dependent upon the fact that X-rays have a wavelength comparable to that of the regular atomic spacing in crystals. Diffraction arises from interference between X-rays scattered by being passed through a solid containing regular arrays of atoms. Where the X-rays waves are scattered so that their amplitudes are in phase, the intensity is enhanced, where the amplitudes are out of phase they cancel. The waves are in phase and undergo constructive interference when the path-length difference (AB+BC in Figure 3.7) is an integral number of wavelengths.

\[
n\lambda = 2d \sin \theta \quad (3.7)
\]

![Figure 3.7 Bragg diffraction from a series of planes.](image)

This is also expressed in the Bragg equation below, where $\lambda$ is the wavelength of the X-rays.

In a crystal, a set of crystallographic planes hkl can be defined as the set of parallel equidistant planes, one of which passes through the origin, and the next nearest makes intercepts of a/h, b/k, and c/l on the three crystallographic axes. a, b, and c are the dimensions of the smallest repeat unit of the crystal (the unit cell). hkl are called the Miller indices. The spacing between diffracting planes is called the $d$-spacing. In a hexagonal system such as MCM-41 it is a measure of the centre-to-centre distance ($2/\sqrt{3}$
times the \( d \)-spacing for a hexagonal system) between the hexagonally arranged channels in the MCM-41 matrix.

In powder diffraction, the sample is made up of many randomly oriented microcrystallites and so all reflections, from every possible orientation of the crystal, will be present in the diffraction pattern. For a system with two dimensional hexagonal symmetry, such as MCM-41 (although the diffraction in this case is from layers of ordered channels rather than atoms) the unit cell dimensions \( a \), \( b \) are equal, and one of the cell angles is equal to 90° while the other angle is 120°. The angles at which the \( hkl \) planes diffract is given by:

\[
\frac{1}{d^2} = \frac{4}{3} \left| \frac{h^2 + hk + k^2}{a^2} \right| (3.8)
\]

In MCM-41 there is no repeat unit in the \( c \) axis and so only reflections from the \( hkl \) planes, in two dimensions, are seen.

X-ray peaks although usually most intense at the Bragg angles, are not delta functions. Broadening of the peak is caused by several factors; instrumental resolutions, crystal imperfections, small crystal size and overall sample size. Since most of these factors are roughly constant in MCM-41 patterns, and the resolution functions of the X-ray machines used are known to be much smaller than the peak widths, the peak widths can be used to obtain an estimate of the crystal size. The Scherrer equation\(^{82}\) predicts:

\[
B(2\theta) = \frac{0.94 \lambda}{L \cos \theta} (3.9)
\]

where \( B(2\theta) \) is the full width in radians subtended by the half maximum intensity width of the powder pattern peak, \( \lambda \) is the wavelength of the radiation, \( L \) is the edge dimension of the crystal (assuming cubic crystals) and \( \theta \) is half the scattering angle. Although this equation was derived for cubic crystals, it gives quite a good approximation, if for each \( hkl \) reflection, the value of \( L \) is interpreted as an average crystal dimension perpendicular to the reflecting planes.\(^{82}\)

### 3.3.2 Instrumentation and Sample Containment

MCM-41 samples mounted in 1.0 mm diameter Lindemann tubes were examined by X-ray diffraction on the Australian National Beamline Facility at the Photon Factory synchrotron, Tsukuba, Japan. The “Big Diff” instrument on Beamline 20a is a powder diffractometer equipped with image plate detection\(^3\) (Figure 3.8). In this diagram, synchrotron radiation enters from the left, is monochromated in the circular apparatus in the centre of the figure and passed through to the diffractometer, the large circular drum on the right. The diagram also shows a number of beamstops and slit controllers. Samples are housed in the large (ca. 2.5 m diameter) stainless steel cylinder which is evacuable. Image plates are mounted 1 m away from the sample, on the circumference of the cylinder. After exposure, the image plates are removed from the cylinder,
scanned and digitally converted into intensity versus angle data. The wavelength of the synchrotron radiation is tuneable so that it can be optimised for collection of data at specific lattice spacing ranges. The samples required exposures of ca. 5 minutes at $\lambda = 1.8963(1) \, \text{Å}$ (one pattern, taken earlier, used $\lambda = 1.54 \, \text{Å}$).

Figure 3.8 Schematic of the layout of the Australian National Beamline Facility on Beamline 20a at Tsukuba, Japan, used with permission.

3.4 Gas Adsorption Isotherms

The interaction of gases with MCM-41 is of interest for several reasons. Firstly, the characteristic MCM-41 nitrogen adsorption isotherm$^{3,11,39}$ and high surface areas$^{1}$ were used to confirm synthesis of this material. Secondly, methane and hydrogen isotherms were run to assist in the quasielastic neutron scattering gas adsorption studies, and finally, nitrogen and hydrogen isotherms were analysed to provide thermodynamic information on the MCM-41 surface. The theory described below is given in outline only. More detailed accounts may be found in Adamson,$^{85}$ and Gregg and Sing.$^{86}$

3.4.1 Adsorption Isotherm Theory

Adsorption of gases on solid surfaces can take place as physisorption, in which there is no change in the molecule adsorbed or the adsorbing surface beyond some physical re-arrangement of molecules, or as chemisorption in which a reaction significantly modifying the electronic properties of the surface and/or the adsorbate occurs. The two may be distinguished by the energy released during the adsorption, which is much larger for chemisorption. In this work, using unreactive gases, at low temperatures on a silica substrate, only physisorption was observed, and so the discussion which follows is limited to this type of adsorption.

Adsorption isotherms were initially categorised into five types by Brunauer,$^{87}$ which indicate different adsorption behaviours due to surface characteristics. These classifications have been adopted by IUPAC,$^{88}$ with the addition of one extra category. Figure 3.9 shows the five typical adsorption isotherms as plots of amount adsorbed in mmol g$^{-1}$ versus $P/P_0$ where $P$ is the pressure of the adsorbate and $P_0$ is the vapour pressure of the adsorbate at the temperature at which adsorption is occurring. Type I is a Langmuir type isotherm, having a monotonic approach to a limiting adsorption which
often corresponds to one monolayer. Type II corresponds to reversible, unrestricted monolayer-multilayer adsorption on a surface and is very common for physical adsorption. The point where the almost linear middle portion of the isotherm begins is called the “B” point and is often taken to indicate the stage at which monolayer coverage is complete and multilayer adsorption about to begin. Type III is rare and occurs in cases where the heat of adsorption is equal to, or less than, the heat of liquefaction of the adsorbate. Types IV and V are examples of capillary condensation phenomena indicating a porous solid. These isotherms level off before the saturation vapour pressure is reached and may show hysteresis. Nitrogen isotherms on MCM-41 are typical of Type IV isotherms and Type IV is typical of mesoporous adsorbents generally. The sharpness of the steps in Type VI isotherms depends upon the system and the temperature. They represent stepwise multilayer adsorption on a uniform non-porous surface and the step height represents the monolayer capacity for each adsorbed layer.

Figure 3.9  The six types of gas adsorption isotherm as categorised by Brunauer, and adopted by IUPAC.\textsuperscript{85,88}

The analysis of isotherms of Type II and IV, which are typical of multilayer adsorption, is accomplished by use of the BET equation. The derivation of this equation is based on a detailed balancing of forward and reverse adsorption rates and by assuming that the heat of adsorption is the same for all adsorbed layers, except the first one which may have some special value. The heat of adsorption for successive layers is assumed to be equal to the heat of condensation of the liquid adsorbate. The resulting equation is often written in the form:

\[
\frac{x}{n(1-x)} = \frac{1}{cn_m} + \frac{(c-1)x}{cn_m}
\]  (3.10)
where \( n \) is the amount adsorbed, \( n_m \) is the moles of gas per gram of solid adsorbed at the monolayer point (known as the monolayer capacity), \( x \) is the relative pressure, also written as \( P/P_0 \), and \( c \) is a constant related to the difference between the heat of adsorption for the first monolayers and that of all successive monolayers. \( n_m \) and \( c \) can be evaluated from the slope \((s)\) and intercept \((i)\) of the straight line best fitting a plot of \( x/n(1-x) \) versus \( x \). For MCM-41 materials, such BET plots are typically linear over the range \( 0.05 < P/P_0 < 0.3 \). At higher \( P/P_0 \) values, the capillary condensation requires different theory for analysis. One example is shown in Figure 3.10. From this \( n_m \) may be calculated using \( n_m = 1/(s+i) \). The surface area of the solid, \( S \), may then be calculated from \( S = n_m N A_m 10^{-20} \) where \( S \) is the specific surface area, \( N \) is Avogadro's number and \( A_m \) is the area of the adsorbate molecule. The values of \( A_m \) used in this work are 16.2 Å² for nitrogen, 10.3 Å² for hydrogen and 14.2 Å² for methane. For a system of hexagonally close-packed cylinders with an internal diameter between 28-35 Å and walls 10 Å thick, the limiting surface area can be calculated to be 990 - 880 m² g⁻¹ (neglecting external surface area). MCM-41 materials typically have specific surface areas of around 1000 m² g⁻¹, indicating that they are largely composed of such channels, although there is some contribution from the external surface area of the particles in real systems.

![Figure 3.10 BET plot for nitrogen adsorption on acetic acid titrated MCM-41 at 77 K, showing the curve (crosses) over the whole pressure range for the isotherm. The fitted part of the data is indicated by a solid line.](Image)
From adsorption data taken over several temperatures, the isosteric heat of adsorption, \( q^{st} \) can be calculated from equation 3.11:

\[
q^{st} = RT^2 \left| \frac{\partial \ln x}{\partial T} \right|_{\theta} \tag{3.11}
\]

In this equation, \( R \) is the gas constant, \( T \) is temperature and \( \theta \) is the fraction of the surface covered (i.e. \( \theta = n/n_m \)). If the isotherms are recorded over a small temperature range, a plot of \( \ln x \) versus \( T \) for a particular \( n \) may appear linear. It may therefore be assumed that \( q^{st} \) is independent of temperature over small temperature ranges, so that equation 3.11 may be integrated to give:

\[
q^{st} = \frac{RT \ln P_2}{T_2 - T_1} \left| \frac{P_2}{P_1} \right|_n \tag{3.12}
\]

where \( P_1 \) and \( P_2 \) are the equilibrium pressures at temperatures \( T_1 \) and \( T_2 \) respectively. Values of \( q^{st} \) may be calculated from isotherms measured at only two temperatures provided the temperature range is small enough to justify the assumption that \( q^{st} \) is independent of temperature. For values of \( \theta \) above a monolayer, values of \( q^{st} \) close to that of the enthalpy of vaporisation of the adsorbate indicate that physisorption only is taking place. Much higher values would indicate chemisorption. For less than monolayer coverages, variation in the value of \( q^{st} \) at different coverages may distinguish between a homogeneous and heterogeneous surface. Plots of \( q^{st} \) versus \( \theta \) can give information about adsorption sites, surface heterogeneity and adsorbate interactions.

In porous systems with Type IV isotherms, the sharp rise in the isotherm around \( P/P_0 = 0.4 \) is due to capillary condensation in the pores. If the adsorbent is represented as a bundle of various-sized capillaries, the pore radius distribution may be calculated from the desorption branch of the isotherm, using the Kelvin equation for cylindrical pores open at one end:

\[
\ln(x) = \left| \frac{-2 \gamma V_1}{RT} \left( \frac{1}{r^k} \right) \cos \phi \right| \tag{3.13}
\]

In this equation, \( r^k \) is the radius of the capillary from which liquid begins to evaporate at the relative pressure, \( x \), \( \gamma \) is the surface tension, \( V_1 \) is the molar volume of the liquid adsorbate and \( \phi \) is the contact angle between the liquid and the capillary wall (usually taken to be zero, so that \( \cos(\phi) = 1 \)). The Kelvin radius is the radius of the capillary plus the thickness, \( t \), of the adsorbed layer remaining on the pore wall after desorption. That is, the actual radius of the capillary is \( r = r^k - t \). The thickness, \( t \), is taken to be \( t = (n/n_m)\sigma \) where \( n \) is the amount adsorbed at relative pressure \( P/P_0 \), \( n_m \) is the monolayer capacity, and \( \sigma \) is the effective thickness for each layer (3.45 Å for N\(_2\) at 77 K).
Comparison plots between an unknown material and a non-porous material with similar surface characteristics can show the existence of micropores in the unknown.\textsuperscript{93} Adsorption values in normalised units (mmol m\textsuperscript{-2}) at the same P/P\textsubscript{0} value for the unknown are plotted against those for the non-porous substrate, with a non-zero intercept on the unknown adsorption axis indicating the presence of micropores. The method is merely a comparison between the shapes of the two isotherms - if they are identical over the entire pressure range measured the plot will be merely a straight line passing through the origin. The slope of the line is equal to the ratio of the surface area for the two adsorbents. Adsorption data for MCM-41 were compared to the standard nitrogen isotherm at 77 K for hydroxylated silica.\textsuperscript{86} A comparison plot for a sulphuric acid titrated sample (X3.6) is shown in Figure 3.11.

![Figure 3.11](image)

**Figure 3.11** Comparison plot for adsorption data from nitrogen at 77 K adsorbed on a sulphuric acid titrated MCM-41 sample. The intercept on the y-axis is at -2.4829 mmol m\textsuperscript{-2}. The circles are the experimental data, while the line is the fit to the linear region.

### 3.4.2 Instrumentation and Sample Preparation

Gas adsorption isotherm data were measured with a Sartorius microbalance at 77 K. The calcined samples had been heated \textit{in situ} to ca 250\textdegree C under a vacuum of better than 10\textsuperscript{-4} torr for at least 12 hours before isotherms were measured. Both sample and counterweight were held at 77 K to avoid differences in buoyancy due to the density of nitrogen gas, as this had been found to be a significant problem for the very low surface area uncalcined samples. A schematic of the adsorption apparatus is shown in Figure 3.12. To ensure equilibrium adsorption, the pressure above the sample and its mass were monitored at 10 second intervals after each gas admission using an analogue to digital card in an IBM compatible computer and the results continuously displayed. Further gas was admitted to the system after the rise in pressure levelled out for each previous admission.
3.5 Quasielastic & Inelastic Neutron Scattering

Quasielastic neutron scattering (QENS) and inelastic neutron scattering are used here to gain information on the motions of molecules of hydrogen and methane adsorbed into MCM-41 over various temperature ranges. This allows conclusions to be drawn concerning the structure and motion of these molecules as adsorbates. But also, since these molecules are so well characterised as pure materials, they can be used as probes to investigate the properties of the MCM-41 framework.

3.5.1 Theory

A brief overview of some of the theory behind quasielastic and inelastic neutron scattering is given here. A much more detailed account can be found in many textbooks. Thermal neutrons have energies comparable to molecular energy levels and wavelengths which are of the order of interatomic spacings in solid phases. This makes them a good probe of molecular dynamics.

Inelastic scattering occurs when the scattered neutron undergoes an exchange of energy and momentum with the sample, which causes both the direction and magnitude of the
neutron's wavevector to change. QENS refers to inelastic scattering in which the energy change is small, and originates from interactions with nuclei diffusing or reorientating over time scales of $10^{-10}$-$10^{-12}$ s. The energy transfer involved can be up to 1 meV (8.06 cm$^{-1}$) and results in a broadening of the narrow elastic line associated with neutrons which are scattered with no energy transfer. The term "inelastic scattering" is usually used to refer to higher energy transfers, up to 1 eV and higher, resulting from interactions with molecular vibrations, crystal lattice phonons, and electronic excitations.

Inelastic neutron scattering has both coherent and incoherent components. In coherent scattering, from the 'average' crystal, the neutron wave interacts with the whole sample as a unit so that scattered waves from different nuclei interfere. Coherent scattering therefore gives information on the relative spacings between atoms, and inelastic coherent scattering thus gives information on collective motions of atoms, such as vibrations in a crystal lattice. In incoherent scattering, from the variations within the crystal, (often isotropic) the neutron wave interacts independently with each nucleus in the sample so that scattered waves from different nuclei do not interfere. Rather, intensities from waves scattered from each nucleus are additive. This means that incoherent scattering may be from the same atom, at different positions and different times. This results in Doppler broadening of the incident energy distribution from which information about atomic diffusion and the range and type of motion may be deduced.

The QENS and inelastic scattering measurements reported in this work are of inelastic incoherent scattering, and measure $S_{\text{inc}}(Q,\omega)$, where $S$ is the incoherent, inelastic scattering function, $Q$ is the momentum transfer (as defined in section 3.2 above) and $\omega$ is the energy transfer (see equation 3.14 below). Hydrogen has a large incoherent cross-section compared to both the coherent and incoherent cross-sections of other elements (see Table 3.1, the cross-section, $\sigma = 4\pi b^2$ where $b$ is the scattering length). Thus QENS and inelastic scattering are used here as a probe of the hydrogen motions in the methane molecules, and of dihydrogen interactions with the MCM-41 pore walls.

For inelastic scattering from molecules with internal degrees of freedom (which are assumed to be decoupled from the translational degrees of freedom), the scattering cross-section results from a sum of the scattering function for each internal energy level, over all of the internal excitations of the molecule. Often the molecule may be treated as a rigid body, but for sufficiently high energy transfers, vibrational modes will also be excited. The inelastic scattering seen in the measurements of gas adsorbed on MCM-41 shows a broad continuum of intensity to the highest energy transfers measured. Such continuous spectra arise from the nature of the molecular form factors and from translational recoil in the scattering collision which broadens the rotational transitions as well as the vibrational modes which may also start to become excited at the highest energy transfers. In the hydrogen data, peaks are also seen at energies which correspond to the $J = 0 \rightarrow 1$ rotational transitions (see Chapter 5). The energies of the rotational levels for hydrogen are given by $E_{\text{rot}} = J(J+1)B$ where $B = 7.35$ meV.
In a quasielastic experiment, \( S_{\text{inc}}(Q, \omega) \) can be separated into a purely elastic component, \( S_{\text{inc}}^{\text{el}}(Q, \infty) \delta(\omega) \) superimposed upon the quasielastic component \( S_{\text{inc}}^{\text{q}}(Q, \omega) \).

\[
S_{\text{inc}}(Q, \omega) = S_{\text{inc}}^{\text{el}}(Q, 0) \delta(\omega) + S_{\text{inc}}^{\text{q}}(Q, \omega) \quad (3.15)
\]

The quasielastic component is the time Fourier transform of a time dependent term and which therefore possesses a non-vanishing broadening that gives information on the characteristic times of the nuclear motion. The coefficient of the delta function is the space-Fourier transform of the final distribution of scattering nuclei averaged over all possible positions (since all positions are equivalent). It has the dimensions of a structure factor and is called the elastic incoherent structure factor (EISF). The EISF can be calculated experimentally from the ratio:

\[
\text{EISF} = \frac{I_{\text{el}}(Q)}{I_{\text{el}}(Q) + I_{\text{q}}(Q)} \quad (3.16)
\]

where \( I_{\text{el}} \) is the integrated intensity of the elastic part and \( I_{\text{q}} \) is the integrated intensity of the quasielastic part of the data. They are found by fitting the observed peak shapes to a delta function and a Lorentzian peak shape, which is assumed for the wider quasielastic contribution. The EISF is the fraction of total quasielastic intensity contained in the purely elastic peak.

Instrumental resolution therefore becomes important in these experiments. The finite resolution of real machines means that the delta function will not appear as an infinitely sharp line, but has an energy width characteristic of the instrument. This width determines the time scales over which motions are observable. Motions which are too rapid cause peak broadenings which are negligible in comparison to that of the instrumental resolution and so are not visible, whereas motions which are too slow cause considerable broadening which tends to a flat background underlying the spectra (see Figure 3.13). As broadening is a function of temperature, it is therefore possible to watch molecular motions being activated, as mobility increases with temperature.

*Figure 3.13* Components of a quasielastic scattering peak due to different types of motion occurring on different time scales within the same system.
Sinc\((Q, \omega)\) for quasielastic scattering is the result of single particle motions. Thus, by assuming that coupling between the various degrees of freedom can be ignored, it can be written as the convolution of the lattice motions, rotational motions and vibrational motions for a molecular solid, or translational, rotational and vibrational motions for a liquid. That is:

\[
S_{inc}(Q, \omega) = S_{inc}^T(Q, \omega) \otimes S_{inc}^R(Q, \omega) \otimes S_{inc}^V(Q, \omega)
\]  

(3.17)

where the superscripts T, R, and V correspond to contributions from translational, rotational and vibrational components respectively. In the quasielastic region, vibrations contribute only through a Debye-Waller factor, \(\exp(-\langle u^2 \rangle Q^2)\) where \(\langle u^2 \rangle\) is the mean square amplitude for the vibrational motion, however they are also visible as peaks in the higher energy inelastic scattering regime.

Rotational motions have been described by a number of different models ranging from isotropic rotational diffusion for molecules with no preferred orientation in space, to jump diffusion through any number of possible sites on a circle or sphere. For isotropic rotational diffusion, the incoherent structure factor is:

\[
S_{inc}^R = \frac{1}{\pi} \sum_{m=1}^{\infty} (2m+1) j_m^2(QR) \frac{m(m+1)D_R}{[m(m+1)D_R]^2 + \omega^2}
\]

(3.18)

where \(D_R\) is the isotropic rotational diffusion constant, \(R\) is the radius of the sphere, \(j_m(x)\) is the spherical Bessel function of order \(m\). This type of motion produces broadening of the quasielastic Lorentzian widths which are oscillatory in \(Q\) and therefore bounded. Dihydrogen in the solid state is a prime example of free rotation. The isotropic rotational diffusion model has also been used to model the motion of methane in the zeolites ZSM-5\(^{104}\) and NaY.\(^{105}\) In solid methane, tunnelling of the methane hydrogens between sites on the surface of a sphere is observed as discrete peaks on either side of the quasielastic peak.\(^{100,106}\) These tunnelling peaks were not observed in the methane adsorbed on MCM-41 investigated in this work.

Translational motions, modelled as continuous diffusion via a random walk give a scattering law:

\[
S_{inc}^T(Q, \omega) = \frac{1}{\pi} \frac{DQ^2}{\omega^2 + (DQ^2)^2}
\]

(3.19)

where \(D\) is the translational diffusion constant \(D = \langle l^2 \rangle / 6 \tau\) in which \(l\) is the step length taken in time \(\tau\). The energy spectrum of the scattered neutrons is a Lorentzian, with a half width at half maximum which increases with the momentum transfer according to a \(DQ^2\) law. This allows a direct determination of the diffusion constant at small \(Q\) values and small energy transfers. That is, under conditions of weak interparticle interactions where the continuous stochastic motion description is obeyed, which is also the limit for jump translational diffusion models.
### 3.5.2 Instrumentation and Sample Preparation

Prior to the neutron scattering experiments involving methane adsorption, the MCM-41 sample was outgassed at 250°C with pumping to $10^{-5}$ torr for about 12 hours. It was then heated for three hours at 350°C at $10^{-5}$ torr, before being transferred into the aluminium sample container under an atmosphere of pure helium. This was then mounted in a displex cryostat capable of reaching 15 K. A few measurements were also made in a cryostat at 1.5 K. The sample, from an ordinary MCM-41 preparation, weighed 0.725 g. It was filled with methane at 760 torr, sample temperature 140 K, that is, well above the condensation temperature of liquid methane and 6.68 mmol g$^{-1}$ of methane was taken up.

Prior to any hydrogen adsorption experiments, the material was outgassed under a pressure of $10^{-4}$ torr at 350°C for two days, to remove any residual water in the mesopores. A small quantity of residual hydroxyl groups arising from incomplete siloxyl condensations in the synthesis remain as the only hydrogenous material in the substrate. To remove these the calcined MCM-41 material, prepared using an acid-titrated synthesis, was soaked in D$_2$O to exchange the hydrogen for deuterium. Although the experiment involved doping this deuterium exchanged material with hydrogen gas, further exchange of the deuterium was unlikely because the low temperature experimental conditions and lack of catalytic material ensured stability of the dihydrogen molecules both to spin conversion (so that spin equilibrium was never reached) and exchange. The sample, weighing 1.10(5) g, was transferred to an aluminium sample can mounted in a cryostat capable of reaching 1.5 K. Hydrogen gas was admitted to the sample in volumetrically determined amounts, with an accuracy of ca. 2% in volumes, and 2 torr in pressure, which is 0.2% of the highest pressures used.

The quasielastic neutron scattering spectrometer, QENS, at the Intense Pulsed Neutron Source, Argonne National Laboratory was used for the inelastic neutron scattering experiments. This time-of-flight spectrometer has an energy resolution of about 0.08 meV, and possesses counter banks at scattering angles of 40, 90, and 130°. A schematic of this type of instrument is shown in Figure 3.14.

![Schematic of a typical time-of-flight neutron spectrometer.](image)

In the methane experiment there were clear changes in the elastic scattering intensity and the momentum transfer (Q) dependence of the quasielastic broadening with
temperature between 15 and 180 K. Quasielastic neutron scattering experiments on the outgassed MCM-41 at a number of temperatures, were also carried out to ensure that any inelastic scattering from the siloxyl groups was accounted for and also to define the elastic resolution function of the instrument. The resolution was found to be about 80 microelectron volts over a momentum transfer, Q, range of $0.3 < Q < 2.6 \text{ Å}^{-1}$. The resolution of the instrument did not allow clear observation of excitations below ca. 100 microelectron volts and no conclusions were made on the existence of tunnelling. Data from bulk methane were taken with the same apparatus in a subsequent experiment as a control.

In the hydrogen experiment, a series of spectra at 1.9 K were taken with hydrogen loadings of 0, 9.5, 12.1, 21.5, 34.5 and 40.3 mmol g$^{-1}$ on the MCM-41. At higher temperatures, spectra were obtained at 9.8 K (34.5 mmol g$^{-1}$), 13.3 K (37.7 mmol g$^{-1}$), 14.7 K (33.1, 40.3 mmol g$^{-1}$), and 21 K (23.1 mmol g$^{-1}$).

### 3.6 Neutron Powder Diffraction

The theory of neutron powder diffraction is identical to that of X-ray powder diffraction and has been discussed in detail in Section 3.3 above. The instrumentation and sample preparation for the neutron work is described below.

The neutron powder diffractometer HIPD$^{108}$ at the Intense Pulsed Neutron Source, Argonne National Laboratory with 30$^\circ$ and 90$^\circ$ scattering angle counter banks was used for the elastic neutron scattering experiments to discover the structure of hydrogen adsorbed in MCM-41. To optimise short wavevector diffraction results on this machine, resolution has been compromised to obtain high intensity at a given wavelength. The counter bank at 30$^\circ$ was at a comparatively low scattering angle for this type of instrument. Thus this diffractometer is capable of reaching to longer $d$-spacings than more conventional neutron powder diffractometers. Powder diffraction patterns were measured at 4.2 K, with good statistics since subtractions were necessary, at 0, 19.3, 27.2, 34.8 and 50.4 mmol g$^{-1}$. The latter sample was produced by loading to 50.4 mmol g$^{-1}$ at 21 K and cooling over 30 mins to 4.2 K. This enabled the excess, unadsorbed hydrogen to first liquefy, and then crystallise, producing a completely loaded sample with the excess as crystalline solid hydrogen. Although it depends on the temperature, full filling of the space within this sample of MCM-41, by hydrogen, was about 40 mmol g$^{-1}$.

A point about the diffraction concerns the use of H$_2$ rather than D$_2$. Apart from concerns about isotopic effects changing the system properties marginally, it would seem that the lack of incoherent background in D$_2$ would be a significant advantage. However the deuterium scattering length is virtually the same as that of silicon and oxygen at about 6 pm, while the proton is -3.8 pm. This large difference between H and Si or O potentially, and in fact does, produces large changes in contrast at different fillings, while D$_2$ filling would just tend to gradually obscure void scattering. This consideration favours H$_2$ over D$_2$. Ideally both experiments should be performed, but
neither is obviously preferable in a high-flux experiments such as this, where incoherent effects are more easily subtracted.

### 3.7 Langmuir Trough

The Langmuir trough is a convenient method for studying the behaviour of thin, usually monomolecular, films of molecules.\(^85,109,110\) In this work it is used primarily as a dilution method to investigate the limiting behaviour of silicate ions aggregating at a surfactant headgroup in two dimensions, without the additional complication of the three dimensional solution chemistry of micelle formation. It observes the silica-surfactant complex in a much simplified state, and it was hoped therefore to draw some conclusions concerning the formation of this likely MCM-41 precursor species.

#### 3.7.1 Theory

To form a monomolecular film of an insoluble surfactant on a liquid surface, it must generally be spread from a low concentration solution, where the solvent is one which will spread on the liquid surface, rather than forming a lens at the interface. The spreading solvent will carry the molecule of interest with it as it spreads, ensuring a relatively even distribution of the insoluble species. This solvent must also evaporate readily, leaving only the molecule of interest behind. Generally one liquid will spread on the surface of the other if it has a low surface tension compared to that of the liquid at the surface.\(^85\) Chloroform was chosen for these experiments since it spreads well on water (spreading coefficient 23 mN m\(^{-1}\) at 20°C),\(^110\) evaporates readily and dissolves the quaternary ammonium surfactants used in the study.

The quantities measured in a Langmuir trough experiment are the amount of the material per unit area - a known quantity calculated from the amount of solution spread, and the trough area - and the film pressure (\(\Pi\), in mN m\(^{-1}\)). The film pressure is defined as the difference between the surface tension of the clean surface and that of the film-covered surface.\(^85\) In this work the film pressure was measured by the Wilhelmy plate method,\(^85,109\) with the plate being made of 10.0 mm wide filter paper (Whatman’s Chr 1) to ensure a zero-contact angle between the plate and the meniscus, once the plate is wetted.\(^111\) The change in force acting on the plate as the film is compressed is measured by an electronic microbalance and recorded digitally. Since only the change in force is measured, the length of the filter paper plate is unimportant, as it is constant. The width of the plate is assumed to be negligible.\(^111\) This method is sensitive to temperature changes and so the trough must be thermostatted to ensure these do not cause errors in the measured \(\Pi\). Measurements on the films are therefore expressed as \(\Pi\)-A plots where A may be the real area occupied by the film on the trough or expressed as area per molecule in the film.

Various types of monolayer give different types of \(\Pi\)-A curves which are described as gaseous, liquid or solid films.\(^85\) Examples of the isotherm expected from each are shown in Figure 3.15. Gaseous films are those where the area per molecule is large compared with the actual molecular areas, so that it obeys the equation of state of a two
dimensional perfect gas. These films can be expanded indefinitely without phase change. Solid films are those of low compressibility with almost linear $\Pi$-$A$ plots. They are quite rigid and appear to consist of close-packed molecules, but may become liquid-like upon expansion. Liquid films are of two types, liquid expanded and liquid condensed. Both show some degree of cooperative interaction and the $\Pi$-$A$ plots extrapolate to zero pressure at large areas per molecule. Liquid expanded films have higher compressibility than solid films and may show a first-order transition to gaseous films at low pressure, and, upon compression, a point of reasonably sharp change to a film of much higher compressibility, called an intermediate film. Liquid expanded films are typical of long chain compounds having highly polar groups such as amides and alcohols. Further compression of an intermediate film results in a liquid condensed film, with linear $\Pi$-$A$ behaviour but relatively low compressibility. Such films have been described as films with close-packed heads which are re-arranged upon compression or as semi-solid films where the water between polar headgroups is squeezed out until a solid film is obtained. Limiting areas per molecule in these films are found by fitting a straight line to the solid-like part of the curve and extrapolating it down to the area axis.

Figure 3.15 Isotherms typical of each type of monomolecular film, and suggested molecular conformations for each. The polar headgroup is indicated as a circle.

Solutions of soluble surfactants may also be studied on the Langmuir trough. In this case the surfactant is dissolved in the sub-phase and a proportion of the dissolved molecules assemble at the air-water interface.\textsuperscript{112} This film, which forms due to the favourable free energy of freeing the surfactant hydrocarbon chains from the water phase, is called the surface excess. It is defined as the difference between the number of moles of surfactant in the surface region and in the bulk solution.\textsuperscript{85} Isotherms from the surface excess were measured in the same way as isotherms from a monomolecular film, however the actual surface excess present was not evaluated in this work. Much work has previously been carried out on the structure of the surface excess of CTAB under a range of experimental conditions.\textsuperscript{113-115}
3.7.2 Instrumentation and Sample Preparation

The Langmuir trough used in this work was a NIMA 601A Langmuir trough with a surface area of 600 cm² (20 cm wide by 30 cm long) and thermostatted to 20±1°C. A Wilhelmy plate for surface pressure measurement was used for these measurements, with a clean paper plate used for each compression experiment. Isotherms were typically run in a continuous compression mode at compression rates of 20-100 cm² min⁻¹ to a fixed pressure or area, and then run on a constant area or constant pressure mode while following the film behaviour over time. Care with solvent purity and general cleanliness was necessary to exclude even low levels of impurities. The spreading solvent, chloroform was distilled in glass to remove traces of grease and all glassware was cleaned with an ionic detergent and rinsed with large quantities of fresh, Millepore filtered water, with a resistivity of 1.8×10⁵ Ω m.

Prior to film spreading, a similar volume of solvent to that which would be used to spread the film was spread on the water surface and compressed to ensure no isotherm from impurities had formed. The surfactant (C₁₈H₃₇)₂N(CH₃)₂ Br, synthesised by Dr Tim Senden was used as received. It was chosen since it has a similar headgroup to that of CTAB, and is insoluble in water so that it would form a monolayer film when spread on the water surface. The solutions spread typically had a concentration of 0.996 mg ml⁻¹. Sodium silicate solution was either used as received or diluted with fresh Millepore water immediately before use. It was injected under the Langmuir trough barriers on the side away from the film, and allowed to diffuse towards the compressed surfactant film. This will cause a slight change in the pH of the substrate, which may also affect the film behaviour. Given the relative volumes of the substrate and the added sodium silicate solution, any change will, however, be small. Studies of CTAB surface excess in solutions below the critical micelle concentration (0.8-0.9 mM)¹¹⁶,¹¹⁷ and its behaviour in the presence of silicate solutions were also investigated using these methods.

3.8 Electron Microscopy

Scanning electron microscopy (SEM) was performed using a JEOL JSM6400 microscope, a Cambridge S360 microscope or a Hitachi S4500 field emission scanning electron microscope (FESEM). Samples were prepared by depositing the wet gel or, in the case of the calcined materials, either as a slurry in water onto a SEM stub and allowing it to dry in a desiccator before gold coating or by brushing small amounts of powder onto conductive silver tape before coating. Transmission electron microscopy was carried out on a JEOL 120 CX microscope. The samples were prepared by crushing under methanol and dispersed on a holey carbon film mounted on a copper grid. Both of these methods were used to image the MCM-41 powders. The scanning electron micrographs included in this thesis were taken by Dr Julieanne Dougherty and Dr John Thompson, and the transmission electron micrographs by Dr Ray Withers, all from the RSC.
3.9 References


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