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Direct Liquid Crystal Templating of Mesoporous Silica

by

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A dissertation submitted in partial fulfilment of the requirements of the degree of Doctor of Philosophy at the University of Southampton

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The work described in this thesis is concerned with the development of ordered mesoporous silicas by direct templating from lyotropic liquid crystal phases of the surfactants Pluronic P123, Pluronic F127, CTAB and Brij 78. The factors affecting the regularity, morphology, pore diameter and wall thickness of the templated mesoporous silicas were examined by exploring the reaction composition space and plotting the structural properties on TMOS/surfactant/water ternary diagrams. The silicas were studied using the complementary techniques of small angle X-ray diffraction, transmission electron microscopy and N₂ adsorption isotherms.

Mesoporous silicas with hexagonal (H₃) pore morphologies templated from the H₃ phase of CTAB were prepared from fumed silica/CTAB/water/NaOH mixtures under hydrothermal conditions. The mesostructure showed very good long-range order and very narrow pore size distributions, with ~3.4 nm diameter pores and ~1.4 nm thick walls.

In addition, mesoporous silicas were prepared using a sol-gel route from TMOS/surfactant/0.5 M HCl(aq) mixtures at 45°C. The central regions of the ternary diagrams of these mixtures were explored. Using Pluronic P123, mesoporous silicas with hexagonal (H₃) pore morphologies were formed with pore diameters in the range of 5 - 10 nm. With Brij 78 and Pluronic F127, mesoporous silicas with 3d cubic pore morphologies were formed with pore diameters in the range of 2.9 - 4.5 nm and 4 - 10 nm for Brij 78 and Pluronic F127 respectively.

The mesoporous silicas produced via the sol-gel route had the most ordered structures with a TMOS:water molar ratio in the range of 1:5 to 1:7, leaving little water present after hydrolysis. For ordered silicas, the sum of the pore diameter and wall thickness is roughly constant, where the pore diameter decreases with increasing TMOS content and decreasing surfactant content there is commensurate increase in wall thickness.

Finally, 1,3,5 trimethyl benzene was used to swell the hydrophobic core of Pluronic P123 and F127 micelles, allowing the templating of mesoporous silica with pore diameters up to 14 nm.
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Table 6.8 BET surface areas, pore volumes, and pore diameter for silicas from Pluronic P123 with propanediol* Wall thickness was obtained by subtracting the pore size (ii) from the pore to pore distance (i).

Table 6.9 Peak positions and peak widths at half height for X-ray diffraction patterns obtained from calcined mesoporous silicas prepared from Pluronic P123 with butanediol.

Table 6.10 BET surface areas, pore volumes, and pore diameter for silicas from Pluronic P123 with butanediol.* Wall thickness was obtained by subtracting the pore size (ii) from the pore to pore distance (i).

Table 6.11 Peak positions and peak widths at half height for X-ray diffraction patterns obtained from calcined mesoporous silicas prepared from Pluronic P123 with 2,2 dimethoxy propane.

Table 6.12 BET surface areas, pore volumes, and pore diameter for silicas from Pluronic P123 with 2,2 dimethoxy propane* Wall thickness was obtained by subtracting the pore size (ii) from the pore to pore distance (i).

Table 6.13 Peak positions and peak widths at half height for X-ray diffraction patterns obtained from calcined mesoporous silicas prepared from Pluronic P123 with Brij 72.

Table 6.14 BET surface areas, pore volumes, and pore diameter for silicas from Pluronic P123 with Brij 72. * Wall thickness was obtained by subtracting the pore size (ii) from the pore to pore distance (i).

Table 6.15 Peak positions and peak widths at half height for X-ray diffraction patterns obtained from calcined mesoporous silicas prepared from Pluronic P123 with Brij 76.

Table 6.16 BET surface areas, pore volumes, and pore diameter for silicas from Pluronic P123 with Brij 76. * Wall thickness was obtained by subtracting the pore size (ii) from the pore to pore distance (i).

Table 6.17 Peak positions and peak widths at half height for X-ray diffraction patterns obtained from calcined mesoporous silicas prepared from Pluronic P123 with Brij 78.

Table 6.18 BET surface areas, pore volumes, and pore diameter for silicas from Pluronic P123 with Brij 78. * Wall thickness was obtained by subtracting the pore size (ii) from the pore to
pore distance (i).

Table 6.19 Peak positions and peak widths at half height for X-ray diffraction patterns obtained from calcined mesoporous silicas prepared from Pluronic P123 with Brij 78, 50wt% surfactant.

Table 6.20 BET surface areas, pore volumes, and pore diameter for silicas from Pluronic P123 with Brij 78, 50wt% surfactant.* Wall thickness was obtained by subtracting the pore size (ii) from the pore to pore distance (i).

Table 6.21 Peak positions and peak widths at half height for X-ray diffraction patterns obtained from calcined mesoporous silicas prepared from Pluronic F127 with 1,3,5 trimethyl benzene.

Table 6.22 BET surface areas, pore volumes, and pore diameter for silicas from Pluronic F127 with 1,3,5 trimethyl benzene.* Wall thickness was obtained by subtracting the pore size (ii) from the pore to pore distance (i), as calculated for a H$_2$ structure.

Table 6.23 Peak positions and peak widths at half height for X-ray diffraction patterns obtained from calcined mesoporous silicas prepared from Pluronic F127 with 1-decanol.

Table 6.24 BET surface areas, pore volumes, and pore diameter for silicas from Pluronic F127 with 1-decanol.* Wall thickness was obtained by subtracting the pore size (ii) from the pore to pore distance (i), as calculated for a H$_2$ structure.

Table 6.25 Peak positions and peak widths at half height for X-ray diffraction patterns obtained from calcined mesoporous silicas prepared from Pluronic F127 with Brij 72.

Table 6.26 BET surface areas, pore volumes, and pore diameter for silicas from Pluronic P123 with Brij 72. * Wall thickness was obtained by subtracting the pore size (ii) from the pore to pore distance (i), as calculated for a H$_2$ structure.

Table 6.27 Peak positions and peak widths at half height for X-ray diffraction patterns obtained from calcined mesoporous silicas prepared from Pluronic F127 with Brij 76.

Table 6.28 BET surface areas, pore volumes, and pore diameter for silicas from Pluronic P123 with Brij 76. * Wall thickness was obtained by subtracting the pore size (ii) from the pore to pore distance (i), as calculated for a H$_2$ structure.

Table 6.29 Peak positions and peak widths at half height for X-ray diffraction patterns obtained from calcined mesoporous silicas prepared from Pluronic F127 with Brij 78.

Table 6.30 BET surface areas, pore volumes, and pore diameter for silicas from Pluronic P123 with Brij 78. * Wall thickness was obtained by subtracting the pore size (ii) from the pore to pore distance (i), as calculated for a H$_2$ structure.
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Finally I would like to thank my parents David and Denise for their support, encouragement and proof reading.
Abbreviations

Brij registered trademark of ICI Americas Inc.
Pluronic registered trademark of BASF
EO one ethylene oxide unit $-\text{CH}_2\text{CH}_2\text{O}-$
PO one propylene oxide unit $-\text{CH}_2(\text{CH}_2)\text{CH}_2\text{O}-$
Brij 78 $\text{C}_{16}\text{EO}_n \ n\sim20$
Pluronic P123 $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$
Pluronic F127 $\text{EO}_{106}\text{PO}_{70}\text{EO}_{106}$
CTAB Cetyltrimethylammonium bromide
HCl hydrochloric acid
TEM transmission electron microscopy
SEM scanning electron microscopy
BET Brunauer-Emmett-Teller
PXRD Powder X-ray diffraction
$H_1$ hexagonal phase
$L_\alpha$ lamellar phase
$I_1$ micellar cubic phase
$V_1$ cubic phase
$L_1$ micellar solution
$L_2$ inverse micellar solution
cmc critical micelle concentration
Chapter 1

Introduction to Mesoporous Materials
Chapter I

Introduction to Mesoporous Materials

1.1 Introduction to Mesoporous Materials

1.1.1 Structure, nomenclature and composition

The field of ordered mesoporous materials (defined as pore diameters of 2.0 nm-50 nm by IUPAC\(^1\)) began in 1992 when researchers at Mobil (Beck and co-workers) synthesised a range of mesoporous silicate materials known as M41S\(^2\). The Mobil materials have highly ordered channel systems with narrow pore size distributions, which can be tailored between 2-10 nm, and very high surface areas, ca. 1000 m\(^2\) g\(^{-1}\). This was a significant increase in the range of pore sizes that could be synthesised; previously Zeolites had the largest pores in a highly ordered channel system, with the largest being 1.0-1.4 nm in diameter. Unlike Zeolites, the channel walls of M41S materials are made up of amorphous silica/aluminosilicate. This family of mesoporous silicates was synthesised from amorphous silica in the presence of the ionic surfactant CTAB under hydrothermal conditions. The M41S family consists of three structure types. The first of these, MCM-41 (Mobil Corporation Material 41), contains a hexagonal arrangement of channels. A second material, MCM-48, has a complex interconnecting 3-dimensional channel system. Finally, MCM-50 has a lamellar structure. Later, it was shown that similar structures could be prepared directly from liquid crystal phases, and these materials were labelled according to the liquid crystal phase from which they were formed (hexagonal (H\(_{1}\)), cubic (V\(_{1}\)) and lamellar (L\(_{\alpha}\))). Figure 1.1 shows the range of pore morphologies observed for such mesoporous materials.

![Figure 1.1 TEM images of mesoporous silicas. a) Hexagonal pore morphology (hexagonal array of cylindrical holes), b) Cubic pore morphology, one projection of the structure (complex interconnecting channel system with the Ia3d space group), c) Lamellar pore morphology (sheets of silica)\(^3\)](image-url)
A method for the synthesis of mesoporous silica with an H₁ structure templated using CTAB was in fact described in a 1971 US patent, but the authors did not realise what they had produced, describing it only as a low bulk density silica. Only in 1997 when F. Di Renzo noticed this patent and the silica was synthesised then fully characterised, that it was realised that it was an ordered mesoporous material with 3.2 nm diameter pores⁴. Partial exchange of silica for alumina, in M41S materials, results in a mesoporous aluminosilicate. In a similar manner, it is also possible to include transition metals in the framework of the walls. Ordered mesoporous materials are not only limited to silicas, but extend to a variety of other inorganic oxides and metals, see section 1.1.4.

### 1.1.2 Surfactants and Lyotropic Liquid Crystal Phases

The presence of a surfactant in the reaction mixture is the key to the production of the highly ordered channels structures found in the M41S family of mesoporous silicates and all other mesoporous materials. In order to understand the mechanisms by which these ordered structures are formed, it is necessary to understand how surfactants behave in aqueous solutions.

Surfactant molecules consist of a water soluble headgroup at one end of the molecule (hydrophilic component) attached to one or more water insoluble hydrocarbon chain (hydrophobic component). As these molecules display characteristics of both hydrophilic and hydrophobic molecules they are also known as amphiphiles (loving both kinds). The solubility of the hydrophilic headgroup arises from its polar or ionic nature whereas the hydrophobic tail is nonpolar and insoluble in water. Table 1.1 shows the structures of some common amphiphiles used to prepare mesoporous materials.

The most important commercial non-ionic surfactants are the polyoxyethylene (POE) compounds and polyoxyethylene-polyoxypropylene-polyoxyethylene block copolymer. POE surfactants consist of a long polyoxyethylene ((OCH₂CH₂)ₙ) chain capped with a hydroxyl group at one end which forms the hydrophilic headgroup, and a hydrocarbon chain attached at the other end which forms the hydrophobic tail. These compounds are easily and inexpensively prepared on a commercial scale. Commercial surfactants, such as Brij, display a distribution in the number of oxyethylene groups, see section 1.1.2.1 for details of the synthesis and distribution of chain lengths. Individual POE surfactants (eg C₁₆EO₈), are much more difficult to prepare, and consequently more expensive.
Upon mixing amphiphiles with water a number of types of behaviour can be observed. At high dilution the amphiphiles exist as a solution of monomers. As the amphiphile concentration is increased, these monomers begin to form aggregates, with the polar head groups on the outside and the hydrocarbon tails towards the centre (figure 1.2a). This structure is called a micelle, and is formed when the amphiphile concentration is above a certain concentration (called the critical micelle concentration or CMC). Typically, the value of the CMC is less than 1 wt% of surfactant with respect to the total water content. The monomer concentration remains constant above the CMC, while the micelle concentration increases as the total amphiphile concentration is increased. As the concentration of the amphiphile in water increases further, provided the temperature is greater than the Kraft point (the temperature below which the amphiphiles solubility is too low to form micelles), amphiphiles exhibit lyotropic liquid crystal phase behaviour.

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>Structure</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>C_{16}EO_8</td>
<td>CH_3(CH_2)_{15}(OCH_2CH_2)_nOH</td>
<td>Octaethylene glycol monohexadecyl ether</td>
</tr>
<tr>
<td>C_{12}EO_8</td>
<td>CH_3(CH_2)_{11}(OCH_2CH_2)_nOH</td>
<td>Octaethylene glycol monododecyl ether</td>
</tr>
<tr>
<td>Brij 78</td>
<td>CH_3(CH_2)<em>{17}(OCH_2CH_2)</em>{20}OH</td>
<td>(average chain length)</td>
</tr>
<tr>
<td>Triton X-100</td>
<td>CH_3C(CH_2)_2CH_5C(CH_3)<em>2C_6H_4(OCH_2CH_2)</em>{16}OH</td>
<td>(average chain length)</td>
</tr>
<tr>
<td>Pluronics</td>
<td>HO(OCH_2CH_2)_x(OCH_2CH_2CH_2)_y(OCH_2CH_2)_zOH</td>
<td>variations on.</td>
</tr>
<tr>
<td>CTAB</td>
<td>CH_3(CH_2)_{16}N(CH_3)_3Br</td>
<td>Cetyltrimethylammonium Bromide</td>
</tr>
</tbody>
</table>

Table 1.1 Examples of some surfactants that have been used to prepare mesoporous materials. References refer to studies of their use in the synthesis of mesoporous silicas.

As the concentration of micelles in aqueous solution increases, the separation between micelle spacing steadily decreases until a stage where the micelles fuse into lyotropic liquid crystal phases. There are four basic types of lyotropic liquid crystal phase morphologies; these are the micellar cubic, hexagonal, bicontinuous cubic and lamellar
phases, as shown in figure 1.2b-e. The micellar cubic (I₁) phase, which forms at low surfactant concentrations (~10 – 20 wt%), is formed from close-packed micelles. As the concentration is increased the hexagonal phase (H₁) is formed (figure 1.2c), which consists of long cylindrical rods of amphiphilic molecules arrange in an hexagonal array. The lamellar phase (Lₐ) is formed at still higher concentrations, in which the amphiphilic molecules form flat bilayers separated from each other by water (figure 1.2e). A less common phase is the cubic phase (V₁), which often lies between the H₁ and Lₐ phase and has a complex interconnecting three-dimensional structure (figure 1.2d). At the extreme where there is very little water in the system the surfactant molecules revert to the spherical micelles but with the headgroups on the inside, surrounding small amounts of water (figure 1.2f). The range of aggregate structures shown in figure 1.2 only represents the phases commonly found for POE surfactant systems. There are also a number of other lyotropic phases, such as inverse hexagonal (Hᵣ) and biphasic regions where there are distinct regions of one phase dispersed in another phase, such as (H₁ + Lₐ) where distinct regions of H₁ and Lₐ can be observed under a polarising optical microscope at low magnification (ca.100x).

These structures are stable because the hydrophobic component of the molecules are shielded from the water by the hydrophilic headgroups. The aggregation of amphiphiles to form micelles and lyotropic liquid crystal phases is driven by entropy, and occurs due to the hydrophobic effect. The enthalpy of formation of micelles is considered to be an endothermic process with ΔH approximately 1-2 kJ mol⁻¹ of surfactant. Since micelles form readily above the CMC, then the entropy of formation (ΔS) of micelles must also be positive. This must be the case because the change in Gibbs free energy for any spontaneously occurring process must be negative. The Gibbs free energy change is related to the enthalpy and entropy of formation in accordance with equation 1.1.

\[ ΔG = ΔH - TΔS \]  

Therefore, if ΔH is positive then ΔS must also be positive if ΔG is to be negative. Experimentally the entropy of formation of micelles has been determined to be ~140 J K⁻¹ mol⁻¹. This can be rationalised by considering the interaction between monomeric amphiphiles and the bulk aqueous environment. When water molecules surround a hydrocarbon the water forms an ordered clathrate cage in which each water
molecules is, on average, hydrogen bonded to 3.5 - 4 neighbours. This is greater than the average hydrogen bonding in bulk water, 3 – 3.5 hydrogen bonds per water molecule, and hence greater order than in the bulk liquid water due to the directional nature of hydrogen bonds. When micelles are formed there is a net increase in disorder due to the loss of the clathrate cage surrounding the hydrocarbon/hydrophobic segments of the amphiphiles. This is the origin of the hydrophobic effect.

The larger structures, formed at higher concentrations of surfactant than that required for micelles, are said to be liquid crystalline. This is because the molecules are oriented on average along some preferred direction, producing fluid but structurally anisotropic phases. The molecules in a liquid crystal phase do not have the positional and orientational order of a solid, nor do they have the total disorder associated with a liquid, but tend to lie somewhere between the two extremes. The liquid crystal phases formed by mixtures of surfactant and water are termed lyotropic phases. As with thermotropic liquid crystals altering the temperature can alter the phase. However, in lyotropic systems, as was explained previously, altering the water content can also change the structure of the phase. The variables of temperature and composition are commonly used to plot phase diagrams for amphiphilic molecules. Phase diagrams are constructed from observations made by polarised light microscopy, X-ray diffraction and NMR.
Chapter 1

Introduction to Mesoporous Materials

Table 1.1

<table>
<thead>
<tr>
<th>Name</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>a) Micellar Solution</td>
<td><img src="image1.png" alt="Micellar Solution" /></td>
</tr>
<tr>
<td>b) Micellar Cubic phase</td>
<td><img src="image2.png" alt="Micellar Cubic phase" /></td>
</tr>
<tr>
<td>c) Hexagonal Phase</td>
<td><img src="image3.png" alt="Hexagonal Phase" /></td>
</tr>
<tr>
<td>d) Cubic Phase (V)</td>
<td><img src="image4.png" alt="Cubic Phase (V)" /></td>
</tr>
<tr>
<td>e) Lamellar Phase</td>
<td><img src="image5.png" alt="Lamellar Phase" /></td>
</tr>
<tr>
<td>f) Inverse micellar Solution</td>
<td><img src="image6.png" alt="Inverse micellar Solution" /></td>
</tr>
</tbody>
</table>

Figure 1.2 Examples of surfactant aggregate structures formed in lyotropic systems.
The phase diagram for \( \text{C}_{16}\text{EO}_8 \) with water shows that the liquid crystalline behaviour of this material is diverse, with large regions over which the \( H_1 \) and \( L_\alpha \) phases are stable (figure 1.3D). In addition to the lyotropic phases and micellar solution domains, the phase diagram also exhibits a phase separated region (\( L_1 + W \)), which is characterised by
a solution containing areas rich in micelles surrounded by water. The temperature at which a micellar solution phase separates is known as the cloud point. The name arises from the turbid nature of an Li+ W solution. A further region of the phase diagram, at low temperatures, consists of solid surfactant that is not in solution. The line that separates the lyotropic phases from the solid region is known as the Kraft boundary, and defines the crystal solubility boundary of the surfactant. Below the boundary the surfactant is present as crystals of surfactant surrounded by water. Phase behaviour in lyotropic systems is not purely a function of composition-temperature space but is also strongly influenced by the molecular structure of the surfactant. The ratio of the headgroup volume, defined by molecular size and degree of hydration, to the length of the hydrophobic tail, determines how the amphiphiles pack, hence the preferred curvature of the structures formed.

Comparison of the phase diagrams for the polyoxyethylene surfactants C_{12}EO_{4}, C_{12}EO_{6}, C_{12}EO_{8}, and C_{16}EO_{8} with water (figure 1.3.) shows the effect of headgroup size on the phase stability of lyotropic liquid crystal phases for a fixed alkyl chain length. With C_{12}EO_{4} the size of the headgroup and tail are relatively even, favouring the formation of a lamellar structure (L_{a}) over a wide range of composition and temperature. At a high weight percentage of C_{12}EO_{4} an inverse micellar solution is favoured due to the lack of water. As the headgroup becomes larger relative to the alkyl tail there is a shift to more curved structure. The phase diagram of C_{12}EO_{6} shows a much smaller lamellar phase, which is only present at higher weight percentages of C_{12}EO_{6} because the headgroup volume is smaller due to reduced hydration. At lower weight percent composition the more curved hexagonal phase, H_{I}, and cubic phase, V_{I}, are favoured. As the headgroup size is increased further, the hexagonal phase becomes stable over a wide range of composition and temperature and the micellar cubic phase, I_{t}, is now present. The lamellar phase is greatly reduced in size as such a flat structure is now unfavourable. Increasing the length of the hydrocarbon tail, as in the case of C_{16}EO_{8} versus C_{12}EO_{8}, has a similar effect on the phase behaviour as decreasing the size of the headgroup. Consequently, C_{16}EO_{8} exhibits a similar phase diagram to C_{12}EO_{6}. A minimum alkyl chain length of 8 carbons is necessary to form a lyotropic liquid crystal phase, for a C_{8} chain only a lamellar phase is formed.
1.1.2.1 Synthesis of the Pluronic Group of Surfactants

The Pluronic family of surfactants produced by BASF are ABA triblock oligomers, either \( \text{EO}_x\text{PO}_y\text{EO}_x \) or \( \text{PO}_x\text{EO}_y\text{PO}_x \). They are synthesised using anionic living polymerisation. Unlike radical polymerisation, the growing chains can only react with the monomer units. There is no termination reaction, therefore, under ideal conditions the number of units in a block will follow a Poisson distribution centred on the nominal number of units; equation 2 gives the distribution of block length. The number of units quoted for each block is the average number, which is determined by the ratio of monomer to initiator. For Pluronic P123 (\( \text{EO}_{20}\text{PO}_{70}\text{EO}_{20} \)) the EO blocks will have an average of 20 units, and a distribution peak with a FWHM of 10 units. The PO block will have an average of 70 units, and a distribution peak with a FWHM of 20 units. For Pluronic F127 (\( \text{EO}_{106}\text{PO}_{70}\text{EO}_{106} \)) the EO blocks will have an average of 106 units, and a distribution peak with a FWHM of 26 units. The PO block will have an average of 70 units, and a distribution peak with a FWHM of 20 units. The poly(ethylene oxide) headgroup of the Brij family of surfactants is also synthesised by anionic living polymerisation.

\[
\text{Mole fraction of } n\text{-mer} = \left( \frac{\alpha^n e^{-\alpha}}{n!} \right) \text{ where } \alpha = \text{ratio of monomer:initiator} \tag{2}
\]

and \( n \) is the number units in the chain.

1.1.3 The synthesis of mesoporous materials

The presence of surfactant is key to the preparation of ordered mesoporous materials. The concentration at which the surfactant is present determines the mechanism by which the mesoporous structure is formed. In the Mobil synthesis, of M41S materials, the surfactant concentrations are low (1-10 wt\%)\(^{2,9}\). At these concentrations the surfactant is present as a micellar solution, ruling out the existence of a homogeneous liquid crystal phase in the synthesis mixture. In 1995 it was shown that regular mesoporous silicas could be prepared at much higher surfactant concentrations, such that lyotropic liquid crystal phases were acting as structure directing agents\(^3\). At concentrations below that of the CMC of the surfactant, no mesoporous structure is observed. There have been several reviews of the synthesis of mesoporous materials\(^{13-16}\).
1.1.3.1 Mobil synthesis – low surfactant concentrations under hydrothermal conditions

The Mobil synthesis produces mesoporous materials using alkyltrimethylammonium ions, with alkyl chain lengths of 8-18 carbon atoms (figure 1.4). The radius of the uniformly sized pores that result upon removal of the surfactant by calcination or solvent extraction is directly correlated to the length of the alkyl chain. Larger pores can be synthesised if an additional hydrophobic organic species, such as 1,3,5 trimethyl benzene, is added to swell the self-assembled structures.

There is a clear resemblance between the hexagonal array of surfactant-filled pores found in these materials and the hexagonal topology of the H$_3$ liquid crystal phase. This suggests that surfactant aggregates act as structure-directing agents in the synthesis of MCM-41. The surfactant concentrations used are too low, in a purely aqueous system, for any liquid crystalline structures to be formed, therefore silicate ions must play a critical role in the formation a liquid crystal state and the stabilisation of the micellar arrays, forming a ‘Silicatropic’ liquid crystal phase. Three key processes in this self-assembly method were identified.

(1) Multidentate binding of silicate oligomers to the cationic surfactant.
(2) Preferential silicate polymerisation in the interface region due to the high concentration of silicate species in this region, and the partial screening of their negative charges by the surfactant.
(3) Charge density matching between the surfactant and the silicate.
This results in a biphasic mixture that contains a large quantity of water with small regions rich in silicate-encapsulated, rod-like, micelles. These inorganic-organic composite species are arranged in the hexagonal order of MCM-41 (figure 1.5).

\[ \text{H}_2\text{O} \quad \text{Si(OH)}_3\text{O}^{-} \]

Figure 1.5 Proposed mechanism for the formation of MCM-41 via silicate encapsulated, rod like micelles.

The mesoporous silica produced by the Mobil synthesis showed poor hydrothermal stability. A great deal of research has been done to find the optimum reaction conditions, looking at temperature, time, pH, silica:surfactant ratio, and additives to produce greater hydrothermal stability, improved long range order, and tuneable pore size with a narrower distribution\(^{17-21}\). Postsynthesis hydrothermal restructuring was also found to increase the order and stability of the M41S family\(^{22}\). There are a large number of variations on the Mobil method, but they all rely on self-assembly of micelles at low surfactant concentration. Critical to the method is the charge interaction between the surfactant head group and the forming material. This limits the materials that can be produced to inorganic oxides, such as silicas, aluminosilicates and metal oxides. For example, neutral templating routes have been developed using non-ionic surfactants (a primary amine or polyethylene oxide) and non-ionic silicon esters such as TEOS as precursors\(^{23,24}\). The template is thought to interact with the silica precursor through hydrogen bonding. These resemble the M41S materials, but with less long range order and thicker walls giving greater thermal stability upon calcination. A neutral alkoxide/polyoxyethylene and block copolymer surfactant templating route also produces hexagonally and cubically ordered mesoporous silicas at low temperatures.
1.1.3.2 Direct liquid crystal templating – high surfactant concentrations

Direct liquid crystal templating of mesoporous materials is possible by the use of high surfactant concentrations. The characteristic phase of the surfactant-water system can be used as a direct mould for the forming oxide ceramic or metal. In 1995 it was shown that mesoporous silicas, with pore morphologies identical to the M41S materials, could be produced in the homogeneous lyotropic liquid crystal phases of non-ionic POE surfactants (C_{16}EO_{8} and C_{12}EO_{8})\textsuperscript{3}.

\begin{align*}
a) \quad & =\text{Si(OMe)} + \text{H}_2\text{O} \rightarrow =\text{Si(OH)} + \text{MeOH} \\
b) \quad & 2 =\text{Si(OH)} \rightarrow =\text{SiOSi} = + \text{H}_2\text{O} \\
c) \quad & =\text{Si(OH)} + =\text{Si(OMe)} \rightarrow =\text{SiOSi} = + \text{MeOH}
\end{align*}

**Figure 1.5** The hydrolysis and condensation reactions of TMOS to form silica gel. a) hydrolysis of an alkoxy group, b) condensation of two silanol groups and c) condensation of a silanol and an alkoxy group.

In the direct liquid crystal templating method, a source of silica is provided by a silicon alkoxide (tetramethyl orthosilicate, TMOS) that is hydrolysed by acidified water. The reaction of water with TMOS results in a sequence of hydrolysis and condensation reactions, which eventually leads to the formation of amorphous silica (figure 1.5). Under acidic conditions, the condensation and hydrolysis are decoupled, see figure 1.6. The alkoxide is rapidly hydrolysed, followed by a slower condensation of the solid. It is necessary to remove the methanol produced by hydrolysis using a vacuum, as the methanol causes the loss of the lyotropic liquid crystal phase. A schematic of the synthesis is shown in figure 1.7. The final silica material is known as a gel because the silica can be thought of as a single macromolecule which extends throughout the solution. If the smallest dimension of the gel is greater than a few millimetres, the object is generally called a monolith. The area of materials chemistry which involves the preparation of gels from alkoxides is known as sol-gel science. Not only can the pore structure be moulded by the surfactant aggregates, but also the shape of the container in which the reaction is carried out can predetermine the macroscopic structure.
The direct templating route to mesoporous materials from non-ionic surfactant phases allows the templating of materials where there is very weak interaction between the surfactant headgroup and reactants. However, the presence of the surfactant and the necessity for a liquid crystal phase places a number of restrictions on any synthesis:

- The reaction to form the solid material must occur under aqueous conditions.
- The precursor to the solid must be highly soluble in water.
- Any reactants or products must not destroy the liquid crystal phase of the surfactant, or if a destructive product is produced, then rapid removal must be possible. For example, the hydrolysis of TMOS produces phase destroying methanol that can be rapidly removed under gentle vacuum.
- The synthesis temperature is limited by the temperature stability of the lyotropic liquid crystal phase used.
- The reaction must satisfy one of the following:
  i) Be sufficiently slow enough to allow thorough mixing of the reagents.
  ii) Occur at some interface between the liquid crystal phase and the reagent, which initiates formation of the inorganic network.
- The resulting mesoporous material must not be affected by the extraction of the surfactant template.

![Relative rates of hydrolysis and condensation of silicon alkoxide, versus pH, reproduced from D. W. Schraefer.](image)

**Figure 1.6** Relative rates of hydrolysis and condensation of silicon alkoxide, versus pH, reproduced from D. W. Schraefer\textsuperscript{25a,b}. 

\[1-14\]
1.1.3.3 Direct liquid crystal templating vs. self-assembly

Direct liquid crystal templating has a number of advantages over the dilute concentration self-assembly route; these are discussed below.

Predictability and variation in the phase

The pore morphology can be predicted from the phase in which the reaction is carried out. In the Mobil method there is no simple way of predicting the type of material produced. There are some limitations though, if the chosen phase is stable over a small temperature/concentration region it may not be stable in the presence of silicate ions, with another phase being formed instead. In addition, the direct template method is not limited to hexagonal, lamellar and cubic phases, but has the possibility of being extended to inverse phases.

Particle size

The direct templating route produces silicas whose overall particle size is much larger than those produced by the Mobil method. Typically, materials prepared using low surfactant concentrations consist of micron sized particles. In the direct liquid crystal templating method a continuous solid gel is produced rather than a precipitate. Recently,
large (~1 cm) optically transparent mesoporous silica monoliths have been prepared via direct templating from a hexagonal phase of Pluronics 123\textsuperscript{26}.

**Extending the range of Mesoporous materials**

The method is not limited to inorganic oxides as there is no necessity for an interaction between the precursor and the surfactant system. The use of a non-ionic surfactant, in the direct templating method, means that charge interactions are not important. Non-ionic surfactants have been used in adaptations of the Mobil method but it appears that the silicate species induce the phase separation to form a hexagonal structure. By suitable choice of a precursor it should be possible to produce a variety of mesoporous materials, from polymers to metals, directly in the liquid crystal phase.

### 1.1.4 Synthesis of mesoporous metal oxides and metals

A number of attempts to synthesis transition metal analogues of MCM-41 material have been made over the past few years, particularly titanium, niobium, and tantalum oxides. All have used the low surfactant concentration self-assembly route. Antonelli et al\textsuperscript{27-30} have used two approaches;

1. Using soluble and reactive metal alkoxides as precursors for the metal oxide framework.

2. Ligation of the surfactant headgroup directly to the metal alkoxide prior to hydrolysis and condensation reactions. This approach is called ligand assisted templating (LAT).

A titanium oxide analogue of MCM-41 was synthesised using the first approach\textsuperscript{27}. Acetyl acetone was used to slow down the rapid hydrolysis and condensation of the titanium alkoxide, allowing the appropriate interactions with the surfactant head group. There was partial structural collapse upon calcination, lowering the surface area to 200 m\textsuperscript{2} g\textsuperscript{-1}.

A niobium oxide analogue of MCM-41 was synthesised using the second approach, LAT. A primary amine surfactant was used ligated to niobium ethoxide\textsuperscript{28,29}. This was successful in producing high surface area, 600 m\textsuperscript{2} g\textsuperscript{-1}, cubic and hexagonal mesoporous...
materials. Mesoporous tantalum oxide$^{30}$ has also successfully been prepared by the LAT approach using primary amine complexes of Ta(OEt)$_5$, with surface areas of over 500 m$^2$g$^{-1}$. The surfactant in the LAT synthesis is removed by acid washes, therefore avoiding the calcination step.

There has also been interest in synthesising mesoporous zirconia recently. Ciesla et al$^{31}$ synthesised hexagonally ordered mesoporous zirconia using two different precursors. One zirconia source used was Zr(SO$_4$)$_2$.H$_2$O, using CTAB as the template. The structure needed to be stabilised by treatment with phosphoric acid, promoting the condensation of unreacted Zr-OH groups, and increasing the polymerisation of the framework. The material was stable to calcination, but suffered a $\sim$25% framework contraction. The material had a high surface area, $\sim$300 m$^2$g$^{-1}$. Another ZrO$_2$ precursor used was zirconium propoxide, with a strongly acidic CTAB solution as the template. Addition of (NH$_4$)$_2$SO$_4$ was necessary to reduce the reactivity of the precursor.

Stucky et al$^{32}$ have synthesised hexagonally-ordered ZrO$_2$, TiO$_2$, Ta$_2$O$_5$, Nb$_2$O$_5$, WO$_3$, SnO$_2$, using chloride precursors, and ethanolic solutions of Pluronic 123. The surface areas were in the range of 125-205 m$^2$g$^{-1}$.

Cubic and hexagonal mesoporous manganese oxides that are stable to calcination have been synthesised from oxidation of MnCl$_2$, and CTAB as the template$^{33}$. Thermally stable mesoporous hafnium oxide$^{34}$ was synthesised from hydrolysed HfCl$_4$ under pH controlled conditions via the Mobile route. The specific surface area of 204 m$^2$g$^{-1}$ is slightly low, even considering the molecular mass difference between SiO$_2$ and HfO$_2$ (60 vs 136).

Mesoporous metals such as platinum and palladium have been successfully produced via direct templating from the H$_1$ phase of Brij 56 via both chemical and electrochemical reduction of the metal salts$^{35,36,37}$.

1.1.5 Direct templating of ordered porous materials with templates other than surfactant

Lyotropic liquid crystal phases of surfactants are not the only structures that have been used as direct templates for ordered mesoporous materials. Mesoporous and macroporous materials have also been templated from bacteria, viruses and monodisperse colloidal spheres. Tobacco mosaic virus (TMV) is a rod-like particle 300 nm long and 18 nm in diameter which at high concentrations associate into a nematic liquid crystal phase,
similar to the H₁ phase of lyotropic liquid crystal systems. Mesoporous silica was
templated from the nematic phase of TMV using a mixture of tetraethoxy silane and
aminopropyl triethoxy silane as the silica precursors. TEM imaging showed the silica had
the same hexagonal structure as MCM-41. After calcination the silica had a pore
diameter of 11 nm and a wall thickness of 10 nm \(^{38}\). Bacteria have also been used as
templates for hexagonal mesoporous silica. High concentrations of cylindrical bacteria
also organise into structures similar to that of the H₁ lyotropic liquid crystal phase. Using
tetraethoxy silane as the silica precursor, ordered porous silica with 300-500 nm diameter
pores and 50-100 nm thick walls was templated from the bacterial phase \(^{39}\).

Hierarchically order porous silica structures have also been formed using double
templating techniques. Strands of spiders silk have been dip-coated in TEOS/Pluronic
P123/water solutions, which forms a mesoporous silica coating on the silk strand.
Calcination removes both the surfactant and silk thread leaving a hollow silica fibre 1-2
μm in diameter with 60 nm thick silica walls that contain hexagonally ordered
mesoporous channels that run parallel to the fibre direction \(^{40}\).

A range of macroporous metals and metal oxides have been templated using close-
packed monodisperse latex spheres or colloidal silica particles as templates. The metal or
metal oxide structure is formed in the space between the close packed particles, then the
particles are selectively removed, either chemically or via calcination, leaving a
macroporous structure of connected spherical pores \(^{41}\). Monodisperse colloidal polymer
spheres can be synthesised with diameters of 20 – 1000 nm, but so far only latex spheres
with diameters > 120 nm have been used templating of ordered macroporous materials.
Macroporous silica and titania were synthesised via sol-gel chemistry using close-packed
latex spheres with diameters between 190 and 275 nm as templates \(^{42}\). Macroporous thin
films of gold, platinum, palladium and cobalt \(^{43,44}\) have been electrochemically deposited
through close-packed monodisperse polystyrene spheres, producing cavities with
diameters between 400 and 1000 nm. These macroporous materials have a range of
potential applications such as photonic materials, data storage and biosensors.

1.1.6 Applications of mesoporous materials

The narrow pore size distributions and well-defined channel architectures of mesoporous
silicas makes them very attractive alternatives to zeolites. when larger pore sizes are
required. Already MCM-41 materials have been shown to have potential applications as supports for industrial catalysts\textsuperscript{45}. Mesoporous materials can be used as templated to grow nanowires of a uniform, controllable diameter. Nanowires of silicon and germanium have been grown in the channels of H\textsubscript{1} mesoporous silicas\textsuperscript{46,47}. Thin films of cubic mesoporous silica have been used in NO gas sensors, resulting in a more sensitive sensor. The thin films of mesoporous metals have potential for use as gas sensors\textsuperscript{48}. Inclusion of optically active components in the high surface area mesoporous materials allows for rapid diffusion for optical sensor applications\textsuperscript{49}. Mesoporous metal and metal oxides are also under investigation for use as electrodes in supercapacitors as the high surface area of mesoporous structures should allow devices to provide high power density and high energy density\textsuperscript{50}.

### 1.2 Summary and overview of thesis

The work described in this thesis is concerned with the development of ordered mesoporous silicas by direct templating from lyotropic liquid crystal phases using the method described by Attard et al\textsuperscript{13}. Of particular interest was the synthesis of cubic mesoporous silicas with a high degree of interconnectivity in the pore system and the ability to tune the pore diameter and wall thickness over a significant range and the extension of the range of pore diameters and wall thickness accessible for H\textsubscript{1} mesoporous silicas. This was done using the cheap poly(ethylene oxide) surfactant Brij 78 and the poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) block copolymers Pluronic P123 and F127. The factors affecting the degree of structural ordering of directly templated silicas was also studied.

Work described in chapter 2 details the investigation of the direct templating of H\textsubscript{1} mesoporous silica from fumed silica under hydrothermal condition using CTAB as a template, showing that the direct templating method can be extended to hydrothermal conditions.

Work described in chapter 3 gives details of the study of the range of pore size/wall thickness of H\textsubscript{1} silicas available using the H\textsubscript{1} phase of Pluronic P123 as a template. The factors affecting the structural ordering were also studied by looking at a wide range of reaction compositions.
The work presented in chapters 4 and 5 is concerned with templating cubic mesoporous silicas from the I$_t$ phase of Brij 78 and Pluronic F127 respectively, allowing access to a wide range of pore diameters and wall thickness. The factors affecting the structural ordering were also studied by looking at a wide range of reaction compositions.

The final piece of work, described in chapter 6, is an investigation into the effects of the addition of organic molecules with various hydrophobicity to TMOS/surfactant/0.5 M HCl$_{aq}$ ternary mixtures. The purpose of this study was to try to access pore diameter/wall thickness combinations that were not possible with the ternary mixture alone, specifically larger pore diameters through swelling of the hydrophobic core of the surfactant micelles.

1.3 References


48. Hayward, R. C.; Alberius-Henning, P.; Chmelka, B. F.; Stucky, G. D.


Chapter 2

Hydrothermal synthesis of mesoporous H\textsubscript{1} silica
2.1 Background and objectives

In 1992 the Mobil researchers synthesised the first MCM-41 silicas, using alkaline hydrothermal conditions, from colloidal silica using low concentrations, 10-15 wt% of alkyl trimethyl ammonium surfactants. At this concentration and temperature the solution is micellar, L₁, resulting in the mesoporous silica being formed via a self assembly route and precipitating as a fine powder. No attempt has been made to directly template the H₃ or V₁ phases of lyotropic liquid crystals under hydrothermal conditions. In this chapter direct templating of H₁ silica under hydrothermal conditions will be investigated. By direct templating under hydrothermal condition, it may be possible to more easily control the wall thickness and pore diameter than via the MCM-41 route. This will require a high surfactant concentration, 35-70 wt%, and a high silica to water ratio. The solubility of amorphous silica is strongly pH dependent above pH 9, as well as temperature dependent, see Fig. 2.1. CTAB was chosen as the surfactant because it has a hexagonal phase that is stable under high alkalinity up to 200°C, see figure 2.2.

**Figure 2.1** Solubility of amorphous silica as a function of pH and temperature. The left diagram shows silica solubility as a function of pH, between 2 and 10, at 22°C. The right diagram shows solubility as a function of temperature and pH under alkaline conditions.
Figure 2.2 Phase diagram of CTAB + water. $L_{cr}$ – liquid phase + crystal, mixture below Krafft temperature.
Chapter 2

Hydrothermal Synthesis of Mesoporous $H_2$ Silica

2.2 Experimental

2.2.1 Preparation of mesoporous silica

Fumed silica particles (<0.011μm, Aldrich), hexadecyl trimethyl ammonium bromide (CTAB, microselect >99%, Fluka Biochemika), and 1.0 M sodium hydroxide solution were mixed in a sealed RB flask to produce a homogeneous mixture. This required a heat/vortex mix/cool/mechanically mix cycle. The mixture was heated to 60 – 70°C using a hot air gun then vortex mixed for 30 seconds. The mixture was then transferred to a 23ml Teflon cup (filling it no more than 2/3 full). This was then placed inside a Parr Acid Digest Bomb (Fig. 2.3) and left in an oven at 115°C for between 7 and 15 days. Once cooled to room temperature the sample was washed to remove the NaOH (1500 ml of doubly distilled water was filtered over the sample), dried overnight at 65°C prior to calcination. CTAB was removed by calcination at 450°C under N$_2$ for 7 hours, followed by O$_2$ for 15 hours (heating rate 10°C min$^{-1}$).

Fumed silica was chosen as the silica source because of the very small particle size, hence a high surface area to volume ratio, allowing fast dissolution. A series of syntheses were carried out to find the concentration of alkali required to produce H$_2$-SiO$_2$. An estimate of a reasonable CTAB:fumed silica ratio was calculated based upon earlier direct templating synthesis using TMOS and Brij 56$^4$. A mixture of 1:0.55 CTAB:fumed silica and 50 wt% CTAB (w.r.t H$_2$O) was left at 115°C for 7 days. Initially 25 mM NaOH was used, but there was little change to the silica. In subsequent syntheses, the base concentration was increased until, at 0.7 M NaOH, analysis of the silica with powder X-ray diffraction and...
Chapter 2

Hydrothermal Synthesis of Mesoporous Si\(_2\)Silica

N\(_2\) adsorption isotherms showed the presence of a small amount of ordered mesoporous structure.

The series of samples presented in this chapter were produced with the ratio of 1.0 M NaOH\(_{aq}\) to CTAB kept constant (1.5:1 by mass) while varying the amount of fumed silica. The compositions of these samples can be found in appendix 3. Each sample was given a unique label.

In this chapter, the phrase "concentration of surfactant" is used to denote the weight percentage (wt%) of surfactant with respect to the alkaline solution content only. For example, a reaction mixture containing 2.07 g of fumed silica, 4.50 g of CTAB and 6.75 g of 1.0 M NaOH was said to have a surfactant concentration of 40 wt%.

2.2.2 Characterisation of mesoporous silicas

Characterisation was carried out to determine surface area, pore diameter and wall thickness using the complementary techniques of transmission electron microscopy, small angle powder X-ray diffraction and nitrogen adsorption isotherms following the procedures outlined in appendix 1.

2.3 Results

2.3.1 Characterisation of mesoporous silicas

2.3.1.1 Observations of the calcined silica samples

<table>
<thead>
<tr>
<th>Sample label</th>
<th>Ratio of CTAB:Silica (w/w)</th>
<th>Time at 115°C / days</th>
<th>Physical description of calcined silica</th>
</tr>
</thead>
<tbody>
<tr>
<td>la</td>
<td>1:0.37</td>
<td>7</td>
<td>Mostly particles ≤ 3 mm, some coarse powder</td>
</tr>
<tr>
<td>lb</td>
<td>1:0.46</td>
<td>7</td>
<td>Particles ≤ 4 - 5 mm down to coarse powder</td>
</tr>
<tr>
<td>lc</td>
<td>1:0.54</td>
<td>7</td>
<td>½ Particles ≤ 4-5 mm, ½ powder, some fine.</td>
</tr>
<tr>
<td>ld</td>
<td>1:0.54</td>
<td>13</td>
<td>½ Particles ≤ 4-5 mm, ½ powder, some fine.</td>
</tr>
<tr>
<td>le</td>
<td>1:0.64</td>
<td>7</td>
<td>Particles ≤ 3 - 4 mm down to fine powder</td>
</tr>
<tr>
<td>lf</td>
<td>1:0.73</td>
<td>7</td>
<td>Particles ≤ 3 mm down to fine powder</td>
</tr>
<tr>
<td>lg</td>
<td>1:0.73</td>
<td>15</td>
<td>½ Particles ≤ 5 mm, ½ powder, some fine.</td>
</tr>
<tr>
<td>lh</td>
<td>1:0.90</td>
<td>14</td>
<td>Mostly powder, some very fine, some particles ≤ 3 mm</td>
</tr>
</tbody>
</table>

Table 2.1 Particle size observations of calcined mesoporous silica samples.

The homogeneous mixture of CTAB, fumed silica and 1.0M NaOH\(_{aq}\) that was placed in the Teflon cup was an opaque putty like solid, the firmness of which varied depending on
the percentage of fumed silica. Table 2.1 contains observations of the particle size of the silica samples after calcinations. The white, opaque silica particles are generally no larger than 5 mm. Samples 1a and 1b do not contain any fine powder, but as the silica content increase so does the amount of fine powder.

2.3.1.2 **Powder X-ray diffraction of the silicas**

<table>
<thead>
<tr>
<th>Sample label</th>
<th>Ratio of CTAB:Silica (w/w)</th>
<th>Position of first reflection /2θ ±0.02°</th>
<th>Peak width at half height of first reflection /°</th>
<th>d spacing for first reflection /±0.05nm</th>
<th>Pore to pore distance, ( a_0 ) for an ( H_4 ) structure /nm ±0.05nm</th>
<th>Change in d spacing upon calcination / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>la</td>
<td>1:0.37</td>
<td>2.02</td>
<td>0.17</td>
<td>4.37</td>
<td>5.05</td>
<td>-11</td>
</tr>
<tr>
<td>lb</td>
<td>1:0.46</td>
<td>2.06</td>
<td>0.20</td>
<td>4.29</td>
<td>4.95</td>
<td>-6</td>
</tr>
<tr>
<td>Ic</td>
<td>1:0.54</td>
<td>2.04</td>
<td>0.27</td>
<td>4.33</td>
<td>5.00</td>
<td>-6</td>
</tr>
<tr>
<td>Id</td>
<td>1:0.54</td>
<td>2.04</td>
<td>0.30</td>
<td>4.33</td>
<td>5.00</td>
<td>-5</td>
</tr>
<tr>
<td>le</td>
<td>1:0.64</td>
<td>1.94</td>
<td>0.33</td>
<td>4.55</td>
<td>5.25</td>
<td>-13</td>
</tr>
<tr>
<td>If</td>
<td>1:0.73</td>
<td>2.06</td>
<td>0.40</td>
<td>4.29</td>
<td>4.95</td>
<td>-5</td>
</tr>
<tr>
<td>Ig</td>
<td>1:0.73</td>
<td>1.98</td>
<td>0.35</td>
<td>4.46</td>
<td>5.15</td>
<td>-8</td>
</tr>
<tr>
<td>Ih</td>
<td>1:0.90</td>
<td>1.96</td>
<td>0.57</td>
<td>4.50</td>
<td>5.20</td>
<td>-5</td>
</tr>
</tbody>
</table>

**Table 2.2** Peak positions and peak widths at half height for powder X-ray diffraction patterns of as-synthesised mesoporous silica. \( a_0 \) is the separation between adjacent pores.

Powder X-ray diffraction was carried out on as-synthesised silica samples and on calcined silica samples. Table 2.2 summarises the X-ray diffraction data obtained for the as-synthesised silicas that have been hydrothermally treated but have not been calcined. All samples showed four peaks that could be indexed to an \( H_4 \) structure. There were also several peaks attributable to CTAB crystals which are present at room temperature. All the samples have a pore separation close to 5.0 nm. The increase in the CTAB:fumed silica ratio as the series progresses from sample 1a to 1h has two effects. Firstly there is a slight increase in pore separation, ~4%. Secondly there is a gradual decrease in the long range order of the structure, as measured by the FWHM of the first peak which increases from 0.17° for sample 1a to 0.57° for sample 1h. Samples 1c and 1d, which have the same composition but sample 1d was heated for twice as long, are identical within experimental error. Samples 1f and 1g, which also have same composition but sample 1g was heated for twice as long, show a slight difference in pore separation and FWHM which may just be outside experimental error. Table 2.1 also contains the ratio of the pore separation of the calcined silica to the pore separation of the as-synthesised silica. The framework contracts
between 5 to 13% upon calcinations, which is comparable to literature values for MCM-41 silicas which is typically 5 – 20% framework contraction depending on the synthesis conditions. The FWHM also increases between 6 – 35% upon calcination, which indicates uneven contraction of the framework as the density of the silica walls increases.

<table>
<thead>
<tr>
<th>Sample label</th>
<th>Ratio of CTAB:Silica (w/w)</th>
<th>Position of first reflection /°</th>
<th>Peak width at half height of first reflection /°</th>
<th>d spacing for first reflection /°</th>
<th>Further peaks and indexing /°</th>
<th>Pore to pore distance for an H1 structure /nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>1:0.37</td>
<td>2.26</td>
<td>0.23</td>
<td>3.91</td>
<td>3.92, 4.56. 6.00</td>
<td>4.51</td>
</tr>
<tr>
<td>1b</td>
<td>1:0.46</td>
<td>2.20</td>
<td>0.25</td>
<td>4.01</td>
<td>3.82, 4.42, 5.84</td>
<td>4.63</td>
</tr>
<tr>
<td>1c</td>
<td>1:0.54</td>
<td>2.18</td>
<td>0.30</td>
<td>4.05</td>
<td>3.84, 4.40, 5.84</td>
<td>4.68</td>
</tr>
<tr>
<td>1d</td>
<td>1:0.54</td>
<td>2.16</td>
<td>0.26</td>
<td>4.09</td>
<td>3.78, 4.36, 5.78</td>
<td>4.72</td>
</tr>
<tr>
<td>1e</td>
<td>1:0.64</td>
<td>2.22</td>
<td>0.42</td>
<td>3.98</td>
<td>3.84, 4.42, 5.90</td>
<td>4.59</td>
</tr>
<tr>
<td>1f</td>
<td>1:0.73</td>
<td>2.16</td>
<td>0.52</td>
<td>4.09</td>
<td>3.82, 4.36, 5.82</td>
<td>4.72</td>
</tr>
<tr>
<td>1g</td>
<td>1:0.73</td>
<td>2.14</td>
<td>0.37</td>
<td>4.13</td>
<td>3.78, 4.36, 5.74</td>
<td>4.76</td>
</tr>
<tr>
<td>1h</td>
<td>1:0.90</td>
<td>2.06</td>
<td>0.78</td>
<td>4.29</td>
<td>3.84, 4.34, 5.78</td>
<td>4.95</td>
</tr>
</tbody>
</table>

Table 2.3 Peak positions and peak widths at half height for powder X-ray diffraction patterns of calcined mesoporous silica.

Figure 2.4 shows the X-ray diffraction patterns obtained for the calcined silicas with the data summarized in table 2.3. All samples showed four peaks that could be indexed to an H1 structure. No further peaks were observed at higher angles. There is a slight but gradual increase in the pore separation as the CTAB:fumed silica ratio is increased, mirroring the uncalcined samples. A 2.4x increase in fumed silica content only results in a 10% increase in pore separation, 4.5 nm to 5.0 nm. The long range order also decreases as the silica content is increased, as shown by the FWHM of the first peak increasing from 0.23° for sample 1a to 0.78° for sample 1h. The other peaks also broaden, becoming less well resolved. The 3^rd^ peak becomes a shoulder on the 2^nd^ peak and the 4^th^ peak decreases in intensity. Samples 1c and 1d have the same composition but sample 1d was heated for twice as long. This resulted in sample 1d having a slightly smaller FWHM and slightly greater pore separation. Samples 1f and 1g have the same composition but sample 1g was heated for twice as long. This resulted in sample 1g having a significantly smaller FWHM and slightly greater pore separation. At a CTAB:fumed silica ratio of 1:0.54 the extra heating time has little effect on the structure, but at 1:0.73 the extra heating does have a significant effect on the long range order of the structure. The long range order is greater than H1 silica templated using the Brij class of surfactants and TMOS, which only show...
three X-ray diffraction peaks at best. The silicas synthesised in this chapter show similar long range order to the first MCM-41 silicas produced, but subsequent optimisation of MCM-41 synthesis has increased the long-range order, with the number of X-ray peaks increased from 4 to 7.

**Figure 2.4** Powder X-ray diffraction patterns obtained for silica, prepared from 40wt% CTAB. Plots have been displaced to allow all patterns to be clearly viewed on one plot. The plots have also been scaled in the y-axis to allow easy comparison of FWHM. The inset graph shows a
magnified plot in the region of the 2\textsuperscript{nd}, 3\textsuperscript{rd} and 4\textsuperscript{th} peaks. Labels, eg la 1:0.37, correspond to the unique code for each material and the mass ratio of CTAB:Fumed silica.

### 2.3.1.3 Nitrogen adsorption isotherm analysis of silicas

<table>
<thead>
<tr>
<th>Sample label</th>
<th>Ratio of CTAB:Silica (w/w)</th>
<th>i) Pore-pore distance from XRD/\textpm nm</th>
<th>ii) Pore-pore distance from TEM/\textpm 0.5 nm</th>
<th>BET surface area/m\textsuperscript{2}g\textsuperscript{-1}</th>
<th>Pore volume/cm\textsuperscript{3}g\textsuperscript{-1}</th>
<th>ii) Pore size from N\textsubscript{2} adsorption analysis/nm</th>
<th>FWHM/nm</th>
<th>Wall thickness i-ii/nm*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fumed silica</td>
<td>-</td>
<td>-</td>
<td>192</td>
<td>0.30</td>
<td>3.2\textpm 0.1</td>
<td>0.2</td>
<td>1.31</td>
<td></td>
</tr>
<tr>
<td>la</td>
<td>1:0.37</td>
<td>4.51</td>
<td>3.79</td>
<td>832</td>
<td>0.69</td>
<td>3.3\textpm 0.2</td>
<td>0.3</td>
<td>1.33</td>
</tr>
<tr>
<td>lb</td>
<td>1:0.46</td>
<td>4.63</td>
<td>4.07</td>
<td>865</td>
<td>0.78</td>
<td>3.3\textpm 0.2</td>
<td>0.3</td>
<td>1.38</td>
</tr>
<tr>
<td>lc</td>
<td>1:0.54</td>
<td>4.68</td>
<td>3.91</td>
<td>702</td>
<td>0.62</td>
<td>3.3\textpm 0.2</td>
<td>0.3</td>
<td>1.22</td>
</tr>
<tr>
<td>ld</td>
<td>1:0.54</td>
<td>4.72</td>
<td>4.22</td>
<td>738</td>
<td>0.68</td>
<td>3.5\textpm 0.2</td>
<td>0.3</td>
<td>1.09</td>
</tr>
<tr>
<td>le</td>
<td>1:0.64</td>
<td>4.59</td>
<td>4.14</td>
<td>571</td>
<td>0.54</td>
<td>3.5\textpm 0.2</td>
<td>0.4</td>
<td>1.32</td>
</tr>
<tr>
<td>lf</td>
<td>1:0.73</td>
<td>4.72</td>
<td>4.00</td>
<td>512</td>
<td>0.50</td>
<td>3.4\textpm 0.2</td>
<td>0.4</td>
<td>1.26</td>
</tr>
<tr>
<td>lg</td>
<td>1:0.73</td>
<td>4.76</td>
<td>4.26</td>
<td>512</td>
<td>0.51</td>
<td>3.5\textpm 0.2</td>
<td>0.4</td>
<td>1.45</td>
</tr>
<tr>
<td>lh</td>
<td>1:0.90</td>
<td>4.95</td>
<td>-</td>
<td>413</td>
<td>0.46</td>
<td>3.5\textpm 0.2</td>
<td>0.4</td>
<td></td>
</tr>
</tbody>
</table>

| Table 2.4 | BET surface areas, pore volumes, and pore diameter for silica series. * Wall thickness was obtained by subtracting the pore size (ii) from the pore to pore distance (i). |

The nitrogen adsorption isotherms and the pore size distributions obtained from them for the calcined silica samples are shown in figures 2.5 and 2.6 respectively with the data summarised in table 2.4. The silica source, fumed silica, is included in the plots for comparison. It can be seen that there is no mesoporosity present in the fumed silica; The surface area comes from external surface area of the very fine particles and any microporosity present, while the pore volume is due space between particles and any micropores. The mesoporous silicas have pore diameters in the range of 3.2 – 3.5 nm, with a very narrow pore size distribution. The FWHM are all in the range of 0.2 – 0.4 nm, which is better than for H\textsubscript{1} silica templated from the Brij class of surfactant with TMOS, which are generally 0.7 – 2.1 nm. This can be attributed to the difference in head group, CTAB has a small, rigid cationic head group while Brij surfactants have larger more flexible polyethylene oxide head groups. There is a gradual increase in the FWHM as the CTAB:fumed silica ratio is increased. There is a small pore diameter increases from 3.2 nm to 3.5 nm as the CTAB:fumed silica ratio in increased for 1:0.37 to 1:0.54. The pore diameter remains at this value as the ratio is increased further. The high specific surface area and pore volumed for samples la and lb are characteristic of mesoporous silica, but
these values decrease as the fumed silica content is increased, with little change in pore diameter and wall thickness. The $N_2$ adsorption isotherm also starts to resemble the fumed silica plot as the silica content is increased. These results, combined with the observations of the particle size distribution for the calcined silica samples, which show that there is an increasing amount of fine silica powder present from a CTAB:Fumed silica ratio of 1:0.54 and greater, show that above a CTAB:Fumed silica ratio of 1:0.54, no further silica can be added between the CTAB micelles and any extra silica remains a fine non-porous powder. Samples 1c and 1d have the same composition, but sample 1d was heated for twice as long, which resulted in sample 1d having a slightly larger pore diameter, and thinner walls. Samples 1f and 1g have the same composition, but sample 1g was heated for twice as long. This had little effect on the surface area, pore diameter or pore volume.
Figure 2.5 Nitrogen adsorption/desorption isotherms for calcined silicas, prepared using 40 wt% CTAB. Labels, e.g., la 1:0.90, correspond to the unique code for each material and the mass ratio of CTAB:Fumed silica. Note the plots have been displaced on the volume axis so that they all fit on one plot.
Figure 2.6 Pore size distributions calculated from nitrogen adsorption curves of calcined silicas, prepared using 40wt% CTAB. Labels, eg 1a 1:0.90, correspond to the unique code for each material and the mass ratio of CTAB:fumed silica. Note the plots have been displaced on the dV/’dr axis so they can all be viewed clearly on one plot.
2.3.1.4 TEM studies of silica samples

Sample: la 1:0.37

Sample: lb 1:0.46

Sample: lc 1:0.54
Chapter 2
Hydrothermal Synthesis of Mesoporous H₄ Silica

when the channels were viewed side-on. Samples la, lb, ld and lg all showed small regions of hexagonally ordered pores when viewed down the channels. There appears to
Figure 2.7 TEM micrographs for H$_i$ silicas prepared from 40wt% CTAB and 1:0.37-0.90 mass ratio of CTAB:Fumed silica. Two representative micrographs are shown for each sample. Labels, eg. la 1:0.90, correspond to the unique code for each material and the mass ratio of CTAB:fumed silica. All scale bars are 50 nm.

Figure 2.7 shows representative TEM images for calcined silica samples. The structural order observed in the TEM images supports the structural order determined by X-ray and N$_2$ adsorption isotherm data. The values for pore to pore separation obtained from the TEM images are consistently smaller than the values obtained from X-ray diffraction, in the range of 10-15% smaller, despite calibration of the microscope. A possible explanation is shrinkage caused by electron beam damage, which was observed to damage to the structure over a period of minutes. Samples 1a to 1g showed well ordered H$_i$ structure when the channels were viewed side-on. Samples 1a, 1b, 1d and 1g all showed small regions of hexagonally ordered pores when viewed down the channels. There appears to
be a preferential orientation of the sample on the TEM grids as it is much easier to find samples with the channels oriented perpendicular to the observer than channels oriented parallel to the observer. For samples 1c and 1e, H₂ ordered channels are observed side on, but the only areas observed down the channels showed a disordered pore system, which is not representative of the sample as a whole. Sample 1h showed no ordered structure, despite the X-ray and N₂ adsorption evidence. The sample contains significant amounts of fine non-porous silica powder as well as H₂ structured silica, so it is possible the small amount of sample used for TEM imaging wasn't representative of the sample as a whole and that insufficient time was spent looking for correctly oriented particles.

2.3.1.5 Summary of results for H₂ silica

Table 2.3 summarises the pore diameter, wall thickness, surface area and pore volume for the H₂ silica samples in the series. All the samples are highly ordered mesoporous silicas that are templates of the H₂ phase of CTAB. Upon calcination there is a 5 – 13 % contraction of the framework that results in a slight broadening of the X-ray diffraction peaks, showing a decrease in long range structural order. From sample 1a to 1h, there is a gradual decrease in the long range order of the structure, the X-ray peaks become broader and less resolved, but all samples do exhibit 4 peaks. As the CTAB:fumed silica ratio is increased from 1:0.37 to 1:0.54 the pore diameter increases slightly from 3.2 nm to 3.5 nm. Above 1:0.54 the pore diameter is constant with a slight increase in the wall thickness. It is not possible to accommodate any more silica in the walls by increasing their thickness, and as a result the extra silica added remains a fine non-porous powder. This is confirmed by the surface area and pore volume measurements, which gradually decrease to roughly half the value of sample 1b, despite little change in pore diameter and wall thickness. The wall thickness is in the range of 1.1 – 1.4 nm, which is thicker than those of MCM-41 silica synthesised using CTAB¹ which are typically 0.8 – 1.0 nm, but the pore diameter is comparable MCM-41 silica which are in the range of 3.0 - 3.8 nm.
Chapter 2

Hydrothermal Synthesis of Mesoporous $H_1$ Silica

2.4 Discussion

2.4.1 Defects in $H_1$ silica structure

Figure 2.8 shows a range of defects that can be present in the $H_1$ phase of lyotropic liquid crystals\(^6\), which include dislocations where rods abruptly terminate or extra rods are present, disclinations where the rods rotate 180° about an axis, and screw dislocations where the rods rotate 120° about an axis. It is also possible to have combined defects such as a screw dislocation with a transverse edge dislocation.

![Figure 2.8](image)

**Figure 2.8** Examples of defects in hexagonal mesophases. **A** - $\theta \pi$ disclination  **B** - transverse edge dislocation  **C** - screw dislocation  **D** - longitudinal edge dislocation. The hatched sections of rods indicate the presence of a supplementary layer. Diagrams are reproduced from Bouligand et al.\(^6\)

Dislocation and disclination defects have been observed in MCM-41 materials\(^7\). Since the mesoporous silica is a direct template of the $H_1$ phase of CTAB, such defects should also be present in the silica. TEM studies of the $H_1$ silicas showed a number of types of defects to be present in the structure, examples of which are shown in figure 2.9. Figures 2.9.a and 2.9.b show a gradual curvature of the channels. Figure 2.9.b shows $\theta \pi$ disclination. Figure 2.9.c shows transverse edge dislocations and a screw dislocation. Figure 2.9.d shows a very disordered channel structure where the channels change direction frequently.
Longitudinal dislocations were not observed in the TEM images, but this is probably because only a few regions where found were the channels orientated parallel to the observer and these were very small.

![TEM micrographs for H₃ silicas prepared from 40wt% CTAB showing defects in the hexagonal structure. All scale bars are 50 nm.](image)

**Figure 2.9** TEM micrographs for H₃ silicas prepared from 40wt% CTAB showing defects in the hexagonal structure. All scale bars are 50 nm.

### 2.4.2 Surface area and pore volume – theoretical and measured

The theoretical surface area and pore volume were calculated using the pore diameter obtained from the N₂ adsorption isotherm and the pore to pore separation obtained from the X-ray diffraction data. The simple geometric model used, detailed in appendix 3, makes a number of assumptions. The silica walls are assumed to be smooth with the density of amorphous silica. The model does not take into account the pore size distribution, only an average pore diameter is used, and the external surface area of the
silica is neglected. The external surface area will be negligible compared to the internal surface area for large particles, 6 m²g⁻¹ for a 0.5 μm diameter sphere, but will be significant for very small particles, 60 m²g⁻¹ for a 0.05 μm diameter sphere. For these silica samples, the assumptions made in the model are generally reasonable. The pore size distribution is relatively narrow and the samples are composed of large particles. The roughness of the walls and external surface and the density of the silica walls are unknown factors that could lead to error in the theoretical value.

<table>
<thead>
<tr>
<th>Sample label</th>
<th>Ratio of CTAB:TMOS (w/w)</th>
<th>Predicted BET surface area /m²g⁻¹</th>
<th>BET surface area /m²g⁻¹ ±50 m²g⁻¹</th>
<th>Predicted Pore volume /cm³g⁻¹</th>
<th>Pore volume /±0.01 cm³g⁻¹</th>
<th>Pore size from N₂ adsorption analysis /nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>la</td>
<td>1:0.37</td>
<td>477</td>
<td>832</td>
<td>0.38</td>
<td>0.69</td>
<td>3.2±0.1</td>
</tr>
<tr>
<td>lb</td>
<td>1:0.46</td>
<td>471</td>
<td>865</td>
<td>0.39</td>
<td>0.78</td>
<td>3.3±0.2</td>
</tr>
<tr>
<td>lc</td>
<td>1:0.54</td>
<td>452</td>
<td>702</td>
<td>0.37</td>
<td>0.62</td>
<td>3.3±0.2</td>
</tr>
<tr>
<td>ld</td>
<td>1:0.54</td>
<td>517</td>
<td>738</td>
<td>0.45</td>
<td>0.68</td>
<td>3.5±0.2</td>
</tr>
<tr>
<td>le</td>
<td>1:0.64</td>
<td>580</td>
<td>571</td>
<td>0.51</td>
<td>0.54</td>
<td>3.5±0.2</td>
</tr>
<tr>
<td>lf</td>
<td>1:0.73</td>
<td>475</td>
<td>512</td>
<td>0.40</td>
<td>0.50</td>
<td>3.4±0.2</td>
</tr>
<tr>
<td>lg</td>
<td>1:0.73</td>
<td>500</td>
<td>512</td>
<td>0.44</td>
<td>0.51</td>
<td>3.5±0.2</td>
</tr>
<tr>
<td>lh</td>
<td>1:0.90</td>
<td>431</td>
<td>413</td>
<td>0.38</td>
<td>0.46</td>
<td>3.5±0.2</td>
</tr>
</tbody>
</table>

Table 2.5 Theoretical and measures surface area and pore volume values for the silica samples.

The theoretical and measured surface area and pore volumes are summarised in table 2.5. Samples 1a and 1b do not contain the finely powdered silica which is present in increasing amounts in later samples, therefore should give the most accurate comparison between the theoretical and measured values. Both the pore volume and surface area for these two samples are approximately 80-100% greater than the theoretical values. The microporosity of the silica walls is not taken into account in the simple model, leading to a possible underestimation of the surface area and pore volume. The micropore volumes were calculated from the N₂ isotherms using the α₃-plot method⁸, see appendix 1.B, but none of the samples showed any measurable micropore volume. The surface roughness and any error in the silica density should account for the difference between theoretical and measured values. As the percentage of finely powder silica increases, the measured values become much closer to the theoretical values, which suggests that the powder is similar to the non-porous fumed silica.
2.4.3 Proposed mechanism and effects of structural formation

The negatively charged dissolved silica species are attracted to the positive trimethyl ammonium head group of CTAB, displacing bromine or hydroxyl ion as the counter ions, coating the CTAB rods with silicate species which then can react with neighbouring silicate species. This silicate shell around the CTAB rods can then grow through further deposition of silica until adjacent silica shell join together and the space between them infills with silica.

The silica is initially particles with diameters in the order of hundreds of nm. This fumed silica has a surface area of 180 m\(^2\) g\(^{-1}\). The surface area eventually increases to 700-800 m\(^2\) g\(^{-1}\) when the mesoporous structure is formed. Under aqueous conditions the silica surface will be covered with silanol groups (Si-OH) at a density of approximately 6.6 silanol groups per nm\(^2\). Due to the surface area increase, water is consumed breaking the Si-O-Si bonds and forming silanol groups. The quantity of water used is not significant. In the syntheses carried out in this chapter only 1 - 2% of the total water present will be used, which will not significantly effect the CTAB concentration.

The pKa of silanol groups on a silica surface ranges from 6.8 to 9.2, the pKa increases as the surface deprotonates\(^2\), therefore under the highly alkaline conditions used the surface will deprotonate. Due to the large amount of silica present relative to the amount of water, 1.65 – 4.0 g of silica to 6.75 g of water, this will significantly affect the pH of the solution. There will be an initial drop in pH when the silica and basic solution are mixed, followed by a further gradual decrease in pH as the mesoporous structure is formed due to the increase in silica surface area. The initial pH drop will increase as the fumed silica used is increased, sample 1d will drop the pH to 13, but by sample 1g there isn’t sufficient base to deprotonate the complete surface resulting in a significant drop in pH, the increase in silanol pKa as the surface deprotonates will help limit this decrease. This drop in pH will decrease the solubility of the fumed silica, slowing the rate of structural formation.

Formation of the H\(_{1}\) structure will increase the number of silanol groups significantly, by a maximum of 4 times, further decreasing the pH and silica solubility. Despite the decrease in pH, the silica solubility remains great enough to form H\(_{1}\) silica in the time given, 7 – 15 days, as the elevated temperature also increases the silica solubility significantly.
2.5 Conclusions and further work

Mesoporous silica was successfully templated from the H₃ phase of CTAB under alkaline hydrothermal conditions using fumed silica as the silica source. TEM, powder X-ray diffraction and N₂ adsorption/desorption isotherms were used as complementary techniques to characterise the structure of the silicas. The concentration of base is important, below 0.7 M NaOH no mesoporous silica was formed. The mesoporous silica synthesised were all carried out using 1.0M NaOH. All samples had good long range order with a narrow pore size distribution. The best samples showed more ordered structures than the best H₃ silicas templated using Brij 56 and TMOS at 45°C⁴, four X-ray diffraction peaks verses three, and narrower pore size distributions, peak half-height widths of 0.3 nm verses 0.7 nm. The pore diameters were between 3.2 and 3.5 nm, which is slightly smaller than the 3.7 nm for MCM-41 silicas templated from CTAB¹. The wall thickness is significantly greater than the MCM-41 silicas, 1.1 - 1.4 nm compared with 0.8 – 1.0 nm. Despite increasing the silica content, it was not possible to increase the wall thickness any further. Above a CTAB:Fumed silica ratio of 1:0.54, only a small percentage of extra silica increases the wall thickness, the vast majority remains as fine amorphous silica powder. The particles size is in the range of 0.5 – 5 mm, compared with MCM-41 silicas which are a fine powder.

2.6 References


Chapter 3

Synthesis of Mesoporous Silica using Pluronic P123
3.1 Background and objectives

There has been significant research into synthesis mesoporous silica via the Mobil route, using low surfactant concentrations. A range of surfactant types have been used, with both ionic and non-ionic headgroups, and a range of chain lengths. This has allowed access to a wide range of pore diameters 3-30 nm. By contrast there has been very little research using higher surfactant concentration where lyotropic liquid crystal phases can be used as direct templates for mesoporous materials. A range of Brij surfactants have been successfully used as direct lyotropic liquid crystal templates for mesoporous silica and metals. The hexagonal phase (H₁) of the non-ionic surfactant Brij 56 (CH₃(CH₂)₁₅(OCH₂CH₂)₁₀OH) was used as a direct template for H₁ mesoporous silica, producing pore diameters up to 3.8 nm. The use of lyotropic liquid crystals phases of amphiphilic triblock polymers, such as EOₓPOᵧEOₓ, as direct templates should allow access to larger pore diameters than are possible with the Brij family of surfactants due to larger micelles.

![Figure 3.1 Phase diagram for Pluronic P123 + distilled water](image)

The published phase diagram of non-ionic triblock polymer EO₂₀PO₇₀EO₂₀ (Pluronic P123 from BASF) and water, Figure 3.1, exhibits an extensive H₁ phase stable across a wide range of temperature and composition. The extensive H₁ phase of Pluronic P123 was of interest because it allows the synthesis of mesoporous silica with wide range of pore diameter and wall thickness. In this chapter, a considerable area of the Pluronic
P123/TMOS/0.5 M HCl\textsubscript{(aq)} ternary diagram was explored to determine the mesoporous silica structures can be templated from high concentrations of Pluronic P123.

3.2 Experimental

3.2.1 Phase diagram of Pluronic P123/water

A phase diagram was constructed for Pluronic P123 using polarised light microscopy as outlined in appendix 1.D. Samples were prepared at 5 wt% intervals from 5 to 95 wt%. Pluronic P123 was used as supplied by BASF.

3.2.2 Preparation of mesoporous silica

The route followed for preparing mesoporous silica was based on a method described by Attard et.al\textsuperscript{5}. Pluronic P123 was dissolved in TMOS with gentle heating in a sealed flask. The resulting mixture was left to cool to room temperature and the required amount of 0.5 M HCl\textsubscript{(aq)} was then added. After leaving the hydrolysis reaction to proceed for ca. 1 minute the methanol produced by the hydrolysis was removed on a rotary evaporator, taking 10-20 min. Removal was determined by visual inspection. After methanol removal, the silica gel was cured in a sealed reaction flask in an oven at 45°C for one week. Surfactant removal was achieved by calcination in a tube furnace at 450°C under N\textsubscript{2} for 7 hours, followed by O\textsubscript{2} for 15 hours (heating rate 10°C min\textsuperscript{-1}). The following list describes the series of materials that were prepared.

- Series 1 – The ratio of 0.5 M HCl\textsubscript{(aq)} to Pluronic P123 was kept constant (1:1 by mass) while varying the amount of TMOS.

- Series 2 – The ratio of Pluronic P123 to TMOS was kept constant (1:1.5 by mass) while varying the amount of 0.5 M HCl\textsubscript{(aq)}.

- Series 3 - The ratio of 0.5 M HCl\textsubscript{(aq)} to TMOS was kept constant (1:1.5 by mass) while varying the amount of Pluronic P123.

For the purpose of simplicity, and to make comparisons between series easier, for the remainder of the chapter the phrase "concentration of surfactant" will denote the weight percentage (wt%) of surfactant with respect to the acid solution content only. For
Chapter 3  

Synthesis of Mesoporous Silica using Pluronic P123

example, a reaction mixture containing 0.9 g of TMOS, 0.3 g of Pluronic P123 and 0.7 g of 0.5 M HCl was said to have a surfactant concentration of 30 wt%.

The compositions of all the samples prepared are listed in appendix 2 and are also shown on the ternary diagram in figure 3.2. The error in a sample composition is ± 0.5 % (by mass) for each component. An explanation of how ternary diagrams are constructed and should be read is given in appendix 1.E. Each sample is given a unique label, made up of the series number and a letter denoting its position in the series (e.g. 2a), so that results can be cross-referenced throughout the chapter.

![Ternary Diagram](image)

**Figure 3.2** Ternary diagram showing all of the silica samples prepared from Pluronic P123 + TMOS + 0.5 M HCl mixtures.
3.2.3 Characterisation of mesoporous silicas

Characterisation was carried out by transmission electron microscopy, small angle powder X-ray diffraction, and nitrogen adsorption isotherms following the procedures as outlined in appendix 1.

3.3 Results

3.3.1 Phase diagram of Pluronic P123/water

![Phase diagram for Pluronic P123 + distilled water.](image)

**Figure 3.3** Phase diagram for Pluronic P123 + distilled water. C – birefringent phase, coloured, circular air bubbles

Figure 3.3 shows the phase diagram that was constructed for Pluronic P123 with distilled water. The diagram is significantly different from the diagram in the literature, see figure 3.1. The micellar cubic phase, I, is much smaller, the L\textsubscript{1} to I\textsubscript{1} transition occurs at ~26 wt % compared to ~15 wt% for figure 3.1. The I\textsubscript{1} to H\textsubscript{1} transition is also shifted, ~36 wt% compared to ~32 wt%. The micellar solution, L\textsubscript{1}, is also much larger. Both phase diagrams were constructed using polarising optical microscopy and used Pluronic P123 as received from BASF. There are a number of possible reasons for the discrepancies between the diagrams. The most likely is that the samples have different head group and/or tail chain length due to errors in synthesis. The samples could also have degraded over time or have been contaminated.
3.3.2 Characterisation of mesoporous silicas in series 1 – vary TMOS content

In series 1 the ratio of Pluronic P123:0.5 M HCl(aq) was kept constant at 1:1 (by mass) while the amount of TMOS was varied. A binary mixture of Pluronic P123 and 0.5 M HCl(aq) with a ratio of 1:1 (by mass) forms an H₄ phase.

3.3.2.1 Powder X-ray diffraction of the silicas in series 1

<table>
<thead>
<tr>
<th>Series label</th>
<th>Ratio of P123: TMOS (w/w)</th>
<th>Position of first reflection /θ ± 0.02°</th>
<th>Peak width at half height of first reflection /θ ± 0.02°</th>
<th>d spacing for first reflection /±0.1 nm</th>
<th>Further peaks and indexing /θ ± 0.02°</th>
<th>Pore separation for an H₄ structure /± 0.1 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>la</td>
<td>1:0.25</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>lb</td>
<td>1:0.50</td>
<td>0.96</td>
<td>0.52</td>
<td>9.2</td>
<td>-</td>
<td>10.6</td>
</tr>
<tr>
<td>lc</td>
<td>1:0.75</td>
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<td>0.19</td>
<td>8.4</td>
<td>-</td>
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<td>0.20</td>
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<td>1.66, 1.96</td>
<td>10.7</td>
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<td>0.16</td>
<td>8.9</td>
<td>1.70, 1.99</td>
<td>10.3</td>
</tr>
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<td>0.95</td>
<td>0.17</td>
<td>9.3</td>
<td>1.67, 1.90</td>
<td>10.8</td>
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<tr>
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<td>0.99</td>
<td>0.17</td>
<td>8.9</td>
<td>1.73, 1.96</td>
<td>10.3</td>
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<td>0.17</td>
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<td>1.79, 2.04</td>
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<td>0.20</td>
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<td>1.72, 1.96</td>
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<td>0.52</td>
<td>7.6</td>
<td>-</td>
<td>8.8</td>
</tr>
</tbody>
</table>

Table 3.1 Peak positions and peak widths at half height for X-ray diffraction patterns obtained from calcined silicas in series 1, prepared from 50 wt% Pluronic P123.

Figure 3.4 shows the X-ray diffraction patterns obtained for calcined silicas in series 1, with the data summarised in table 3.1. All samples, except la, showed at least one peak. Those samples that exhibited more than one peak could be indexed to an H₄ structure, having d spacing ratios of 1:1/√3: 1/√4. No further peaks were observed at higher angles. For sample la, which has the lowest P123:TMOS ratio, there was no X-ray diffraction peak. Sample 1b shows a single broad peak. Further increase in TMOS content results in more ordered mesoporous silicas. For samples ld to lj, three peaks characteristic of well ordered H₄ silica are observed. The half height peak width of these samples is
approximately constant at 0.18°. At a ratio of 1:2.75 and above, only one peak was observed, with an increasing FWHM, showing a gradual decrease in long range order. The pore separation exhibited very little dependence on P123:TMOS ratio, except at ratios above 1:2.50 there is a gradual decrease in the separation, accompanied by an increase in the FWHM.

Figure 3.4 Powder X-ray diffraction patterns obtained for calcined silica samples in series 1, prepared from 50wt% Pluronic P123. Plots have been displaced to allow all patterns to be clearly viewed on one plot. The plots have also been scaled in the y-axis to allow easy comparison of FWHM. The inset graph shows a magnified plot in the region of the 2\textsuperscript{nd} and 3\textsuperscript{rd} peaks. Labels, eg la 1:0.25, correspond to the unique code for each material and the mass ratio of Pluronic P123:TMOS.
3.3.2.2 Nitrogen adsorption isotherm analysis of silicas in series 1

<table>
<thead>
<tr>
<th>Series label</th>
<th>Ratio of P123:TMOS (w/w)</th>
<th>Pore-pore distance from PXRD (±0.1 nm)</th>
<th>Pore-pore distance from TEM (±0.2 nm)</th>
<th>BET surface area/m²/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>la</td>
<td>1:0.25</td>
<td>-</td>
<td>-</td>
<td>750</td>
</tr>
<tr>
<td>lb</td>
<td>1:0.50</td>
<td>10.6</td>
<td>-</td>
<td>732</td>
</tr>
<tr>
<td>lc</td>
<td>1:0.75</td>
<td>9.7</td>
<td>8.3</td>
<td>781</td>
</tr>
<tr>
<td>ld</td>
<td>1:1.00</td>
<td>9.5</td>
<td>7.8</td>
<td>710</td>
</tr>
<tr>
<td>le</td>
<td>1:1.25</td>
<td>10.7</td>
<td>8.2</td>
<td>783</td>
</tr>
<tr>
<td>lf</td>
<td>1:1.50</td>
<td>10.3</td>
<td>10.1</td>
<td>725</td>
</tr>
<tr>
<td>lg</td>
<td>1:1.75</td>
<td>10.8</td>
<td>9.7</td>
<td>817</td>
</tr>
<tr>
<td>lh</td>
<td>1:2.00</td>
<td>10.3</td>
<td>9.3</td>
<td>648</td>
</tr>
<tr>
<td>li</td>
<td>1:2.25</td>
<td>9.9</td>
<td>9.1</td>
<td>437</td>
</tr>
<tr>
<td>lj</td>
<td>1:2.50</td>
<td>10.6</td>
<td>9.2</td>
<td>517</td>
</tr>
<tr>
<td>lk</td>
<td>1:2.75</td>
<td>9.9</td>
<td>9.1</td>
<td>350</td>
</tr>
<tr>
<td>li</td>
<td>1:3.00</td>
<td>9.4</td>
<td>-</td>
<td>482</td>
</tr>
<tr>
<td>lm</td>
<td>1:3.50</td>
<td>9.3</td>
<td>-</td>
<td>413</td>
</tr>
<tr>
<td>ln</td>
<td>1:4.00</td>
<td>8.8</td>
<td>-</td>
<td>446</td>
</tr>
</tbody>
</table>

Table 3.2 BET surface areas, pore volumes, and pore for silicas in series 1, prepared from 50 wt% Pluronic P123. * Wall thickness was obtained by subtracting the pore size (ii) from the pore to pore distance (i).

The nitrogen adsorption/desorption isotherms and the pore size distributions obtained from them are shown in figures 3.5 and 3.6 respectively with the data summarised in table 3.2. Samples 1a and 1b, which have the lowest P123:TMOS ratios, are very disordered mesoporous silicas, the pore size distribution is very broad with no peak. Sample 1c has a very broad pore size distribution centred on 9.6 nm. As the TMOS content is increased further the pore size distribution narrows and shifts to 8.7 nm for sample 1e. For sample 1e to 1m, as the TMOS content is increased, there is a gradual decrease in pore diameter from 8.7 nm to 4 nm, accompanied by an increase in wall thickness, and decrease in specific surface area and pore volume. For samples 1m and 1n the pore size distribution is very broad. The surface areas of all the samples are large, in the range of 450 – 800 m²/g, characteristic of mesoporous silica. The decrease in pore volume and surface area as the wall thickness increases and the pore size decreases is as expected. The hysteresis that occurs at pressures greater than 0.4 P/Po is characteristic of materials with pore diameters greater than 3.8 nm and not due to bottlenecking or pore blocking. 

3-8
Figure 3.5 Nitrogen adsorption/desorption measurements for calcined silicas in series 1, prepared from 50 wt\% Pluronic P123. Labels, eg 1a 1:0.25, correspond to the unique code for each material and the mass ratio of Pluronic P123:TMOS. Note the plots have been displaced on the volume axis so that they all fit on one plot.
Figure 3.6 Pore size distributions calculated from nitrogen adsorption curves for calcined silicas in series 1, prepared from 50wt% Pluronic P123. Labels, eg 1a 1:0.25, correspond to the unique code for each material and the mass ratio of Pluronic P123:TMOS. Note the plots have been displaced on the dVp/dr axis so they can all be viewed clearly on one plot.
3.3.2.3 TEM studies of silicas in series 1

Sample: 1a 1:0.25

Sample: 1b 1:0.50

Sample: 1c 1:0.75
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Sample: 1g 1:1.75

Sample: 1h 1:2.00

Sample: 1i 1:2.25
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Sample: Ij 1:2.50

Sample: Ia 1:2.75

Sample: Ik 1:2.75

Sample: II 1:3.00

Sample: Ij 1:2.50

Sample: Ia 1:2.75

Sample: Ik 1:2.75

Sample: II 1:3.00

As with the TEM images in chapter 2, the values for pore separation are consistently smaller than the values obtained from X-ray diffraction, in the range of 10-15% smaller, despite calibration of the microscope. Unlike the hydrothermally synthesised
Figure 3.7. TEM micrographs for H₄ silicas prepared from 50wt% Pluronic P123 and 1:0.25-4.0 mass ratio of P123:TMOS. Two representative micrographs are shown for each sample. Labels, eg 1a 1:0.25, correspond to the unique code for each material and the mass ratio of P123:TMOS. All scale bars are 50 nm.

Figure 3.7 shows representative TEM images for silicas in series 1, with data summarised in table 3.2. The structural order observed in the TEM images of series 1 supports the structural order determined by X-ray diffraction and N₂ adsorption isotherm data. At low TMOS ratios no ordered mesoporous structure was observed. At Pluronic P123:TMOS ratios between 1:1.00 and 1:2.50, ordered H₄ materials were observed. The TEM images corroborate the X-ray diffraction spectra and N₂ sorption isotherms for the progressive decrease in structural order as the Pluronic P123:TMOS ratio is increased from 1:2.75 to 1:4.00. As with the TEM images in chapter 2, the values for pore separation are consistently smaller than the values obtained from X-ray diffraction, in the range of 10-15% smaller, despite calibration of the microscope. Unlike the hydrothermally synthesised
silica in chapter 1, very few defects were observed in the structure. This is attributed to the lower temperature and pressure used in the synthesis. No edge dislocations or $\pi\pi$ disclinations were observed, but bends and curvature were seen in the channels. In the best samples, channels have remained parallel over a micrometre or more. This explains why it was much easier, compared to the hydrothermal silicas, to find areas where you are looking straight down the pores. It is difficult to get accurate pore diameter measurements from TEM images because it is necessary to find a very thin sample correctly aligned. It was only possible to make measurements for samples 1e to 1-g and 1i. The pore diameter values were approximately 5 - 6 nm, which is smaller than the pore diameter calculated from N$_2$ adsorption isotherms which decreases from 8.7 nm for sample 1e down to 6.8 nm for sample 1e.

### 3.3.2.4 Summary of results for series 1

Sample 1a is a disordered porous silica. Sample 1b and 1c are very disordered H$_1$ silica. The most ordered H$_1$ silicas are found in the Pluronic P123:TMOS ratio region of 1:1.00 to 1:2.50, samples 1d to 1j. The X-ray diffraction patterns all have 3 peaks with 1$^{st}$ peak half-height widths of 0.18°. For Pluronic P123:TMOS ratios 1:2.75 to 1:4.00 the H$_1$ structure becomes progressively more disordered. The pore diameter also decreases from 6.8 nm to less than 3.5 nm, accompanied by an increase in wall thickness from 3.8 nm to 5.3 nm.
3.3.3 Characterisation of mesoporous silicas in series 2 – vary 0.5 M HCl\textsubscript{(aq)} content

In series 2 the ratio of Pluronic P123:TMOS was kept constant at 1:1.5 (by mass) while the amount of 0.5 M HCl(aq) was varied. The Pluronic P123:0.5 M HCl(aq) ratios were kept within the range that gave an H\textsubscript{1} phase for binary Pluronic P123/water mixtures.

3.3.3.1 Powder X-ray diffraction of the silicas in series 2

Figure 3.8 shows the X-ray diffraction patterns obtained for series 2 with the data summarised in table 3.3. All samples gave at least one peak. Those samples that exhibited more than one peak could be indexed to an H\textsubscript{1} structure. No further peaks were observed at higher angles. The half height peak widths are constant through out the series, except for a slight increase for samples 2e and 2f. There is an increase in the pore separation as the series progresses from 2a to 2f, from 10.3 nm to 11.4 nm. Samples 2b to 2d have clearly defined 2\textsuperscript{nd} and 3\textsuperscript{rd} peaks, exhibiting the best long range structural order of the samples, with the samples at either end of the series showing lower long range structural order.

<table>
<thead>
<tr>
<th>Series label</th>
<th>Wt% P123</th>
<th>Position of first reflection /2θ ±0.02°</th>
<th>Peak width at half height of first reflection /±0.02°</th>
<th>d spacing for first reflection /±0.1 nm</th>
<th>Further peaks and indexing /2θ ±0.02°</th>
<th>Pore to pore distance for an H\textsubscript{1} structure /±0.1 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a</td>
<td>40</td>
<td>0.97</td>
<td>0.16</td>
<td>9.1</td>
<td>Broad hump</td>
<td>10.3</td>
</tr>
<tr>
<td>2b</td>
<td>45</td>
<td>0.96</td>
<td>0.15</td>
<td>9.2</td>
<td>1.66, 1.93</td>
<td>10.6</td>
</tr>
<tr>
<td>2c</td>
<td>50</td>
<td>0.97</td>
<td>0.15</td>
<td>9.1</td>
<td>1.68, 1.97</td>
<td>10.3</td>
</tr>
<tr>
<td>2d</td>
<td>55</td>
<td>0.94</td>
<td>0.15</td>
<td>9.4</td>
<td>1.65, 1.92</td>
<td>10.6</td>
</tr>
<tr>
<td>2e</td>
<td>60</td>
<td>0.92</td>
<td>0.16</td>
<td>9.6</td>
<td>1.59, 1.84</td>
<td>10.9</td>
</tr>
<tr>
<td>2f</td>
<td>65</td>
<td>0.89</td>
<td>0.19</td>
<td>9.9</td>
<td>1.51, 1.78</td>
<td>11.2</td>
</tr>
<tr>
<td></td>
<td>70</td>
<td>0.87</td>
<td>0.22</td>
<td>10.2</td>
<td>Broad hump</td>
<td>11.4</td>
</tr>
</tbody>
</table>

Table 3.3 Peak positions and peak widths at half height for XRD patterns obtained from mesoporous silicas for series 2, prepared using varying amounts of 0.5 M HCl\textsubscript{(aq)}.
Figure 3.8 Powder X-ray diffraction patterns obtained for silica series 2, prepared using varying amounts of 0.5 M HCl(aq). Plots have been displaced to allow all patterns to be clearly viewed on one plot. The plots have also been scaled in the y-axis to allow easy comparison of FWHM. The inset graph shows a magnified plot in the region of the 2nd and 3rd peaks. Labels, eg 2a (40 wt%), correspond to the unique code for each material and the weight percent of Pluronic P123 used.
3.3.3.2 Nitrogen adsorption isotherm analysis of silicas in series 2

<table>
<thead>
<tr>
<th>Series label</th>
<th>Wt% P123</th>
<th>i) Pore-pore distance from XRD/TEM/Å</th>
<th>ii) Pore size from N₂ adsorption analysis/Å</th>
<th>BET surface area/m² g⁻¹</th>
<th>Pore volume/cm³ g⁻¹</th>
<th>FWHM/nm</th>
<th>Wall thickness i-ii/Å*</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a</td>
<td>40</td>
<td>10.3</td>
<td>9.4</td>
<td>646</td>
<td>0.85</td>
<td>7.4±0.6</td>
<td>2.1</td>
</tr>
<tr>
<td>2b</td>
<td>45</td>
<td>10.6</td>
<td>9.5</td>
<td>823</td>
<td>1.04</td>
<td>8.7±0.8</td>
<td>1.6</td>
</tr>
<tr>
<td>2c</td>
<td>50</td>
<td>10.3</td>
<td>9.4</td>
<td>725</td>
<td>0.97</td>
<td>8.7±0.8</td>
<td>1.8</td>
</tr>
<tr>
<td>2d</td>
<td>55</td>
<td>10.6</td>
<td>10.0</td>
<td>652</td>
<td>0.92</td>
<td>8.0±0.7</td>
<td>1.6</td>
</tr>
<tr>
<td>2e</td>
<td>60</td>
<td>10.9</td>
<td>9.3</td>
<td>617</td>
<td>0.79</td>
<td>9.6±1.0</td>
<td>1.8</td>
</tr>
<tr>
<td>2f</td>
<td>65</td>
<td>11.2</td>
<td>9.3</td>
<td>531</td>
<td>0.87</td>
<td>8.7±0.8</td>
<td>1.3</td>
</tr>
<tr>
<td>2g</td>
<td>70</td>
<td>11.4</td>
<td>9.2</td>
<td>476</td>
<td>0.98</td>
<td>10.1±1.0</td>
<td>5.6</td>
</tr>
</tbody>
</table>

Table 3.4 BET surface areas, pore volumes, and pore for silicas in series 2. * Wall thickness was obtained by subtracting the pore size (ii) from the pore to pore distance (i).

The nitrogen adsorption/desorption isotherms and the pore size distributions obtained from them are shown in figures 3.9 and 3.10 respectively with data summarised in table 3.4. Samples 2b to 2e are the most ordered samples of the series, having pore size distribution half height peak widths of ca. 1.6nm. The samples at either end of the series, 2a and 2f, have broader pore size distributions. There is a gradual decrease in wall thickness through the series from 2a to 2f, but there is a large uncertainty in the pore size measurements. The hysteresis that occurs at pressures greater than 0.4 P/P₀ is characteristic of materials with pore diameters greater than 3.8 nm and not due to bottlenecking or pore blocking.\[^{9,10}\]
Figure 3.9 Nitrogen adsorption/desorption measurements for calcined silicas in series 2, prepared using varying amounts of 0.5 M HCl(aq). Labels, eg 2a (40 wt%), correspond to the unique code for each material and the weight percent of Pluronic P123 used. Note the plots have been displaced on the volume axis so that they all fit a single plot.
Figure 3.10 Pore size distributions calculated from nitrogen adsorption curves for calcined silicas in series 2, prepared using varying amounts of 0.5 M HCl\textsubscript{(aq)}. Labels, eg 2a (40 wt%), correspond to the unique code for each material and the weight percent of Pluronic P123 used. Note the plots have been displaced on the dV\textsubscript{p}/dr axis so they can all be viewed clearly on one plot.
3.3.3.3 TEM studies of silicas in series 2

Sample: 2a 40wt%

Sample: 2a 40wt%

Sample: 2b 45wt%

Sample: 2b 45wt%

Sample: 1f 50wt%

Sample: 1f 50wt%
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Figure 3.11 TEM micrographs for H; silicas prepared from 40-70wt% Pluronic P123 and 1:1.5 mass ratio of P123:TMOS. Two representative micrographs are shown for each sample. Labels, eg 2a 40wt%, correspond to the unique code for each material. All scale bars are 50 nm.

Figure 3.11 shows representative TEM images of silicas in series 2, with data summarised in table 3.4. The structural order observed in the TEM images of series 2 supports the structural order as determined by X-ray diffraction and N₂ adsorption isotherms. The images show well ordered H₁ silicas for samples 2a to 2d. Samples 2e and 2f are less well ordered. It is difficult to get accurate pore diameter measurements from TEM images, it is necessary to find a very thin sample correctly aligned. It was only possible to get measurements for samples 1f and 2g, the values were approximately 5 - 6 nm, this is smaller than N₂ adsorption derived pore diameter, 8.7 and 8.0 nm respectively. As was found in series 1, the average pore separations measured from the TEM images are 10-15% smaller than the pore separation determined by X-ray diffraction.

3.3.3.4 Summary of results for series 2 silicas

All samples produced ordered H₁ silicas. There is a gradual decrease in wall thickness from 2.9 nm for sample 2a to 1.3 nm for sample 2f, accompanied by an increase in pore diameter from 7.4 nm to 10.1 nm. Sample 2b showed the greatest long range structural order, having the best resolved 2nd and 3rd X-ray diffraction peaks. From sample 2b to 2f these secondary peaks become less resolved and then disappear.
3.3.4 Characterisation of mesoporous silicas in series 3 - vary Pluronic P123 content

In series 3 the ratio of 0.5 M HCl(aq):TMOS was kept constant at 1:1.5 (by mass) while the amount of Pluronic P123 was varied. The Pluronic P123:0.5 M HCl(aq) ratios were kept within the range of ratios that gave an H1 phase for binary Pluronic P123/water mixtures.

3.3.4.1 Powder X-ray diffraction of the silicas in series 3

Figure 3.12 Powder X-ray diffraction patterns obtained for silica series 3, prepared using varying amounts of Pluronic P123. Plots have been displaced to allow all patterns to be clearly viewed on one plot. The plots have also been scaled in the y-axis to allow easy comparison of FWHM. The inset graph shows a magnified plot in the region of the 2nd and 3rd peaks. Labels, eg 2a (40wt%), correspond to the unique code for each material and the weight percent of Pluronic P123 used.
Figure 3.12 shows the X-ray diffraction patterns obtained for series 3 with the data summarised in table 3.5. All samples gave at least one peak. Those samples that exhibited more than one peak could be indexed to an H1 structure. No further peaks were observed at higher angles. Samples 3a to 3c show good long range structural order, with similar repeat distances and narrow peak widths. The three peaks become more resolved from sample 3a to 3c. Sample 3d is slightly less ordered, with a broad second peak. Samples 3e and 3f showed a single weak, broad peak at a much smaller d spacing.

3.3.4.2 Nitrogen adsorption isotherm analysis of the silicas in series 3

The nitrogen adsorption/desorption isotherms and pore size distributions obtained from them are shown in figures 3.13 and 3.14 respectively with the data summarised in table 3.6. From sample 3a to 3d there is a gradual increase in the pore size from 6.8 nm to 10.2 nm, accompanied by a decrease in wall thickness. Samples 3e and 3f don’t show any ordered mesoporosity. Their pore volumes are significantly lower than the other samples. The hysteresis that occurs at pressures greater than 0.4 P/Po is characteristic of materials with pore diameters greater than 3.8 nm and not due to bottlenecks or pore blocking.9,10
<table>
<thead>
<tr>
<th>Series label</th>
<th>Wt% P123</th>
<th>i) Pore-pore distance from XRD/± 0.1 nm</th>
<th>ii) Pore-pore distance from TEM/±0.2 nm</th>
<th>BET surface area/m²/g⁻¹ ±50 m²/g⁻¹</th>
<th>Pore volume/cm³/g⁻¹</th>
<th>ii) Pore size from N₂ adsorption analysis/nm</th>
<th>FWHM/nm</th>
<th>Wall thickness i-ii/nm*</th>
</tr>
</thead>
<tbody>
<tr>
<td>3a</td>
<td>40</td>
<td>10.7</td>
<td>10.6</td>
<td>772</td>
<td>0.76</td>
<td>6.8±0.6</td>
<td>1.5</td>
<td>3.9±0.7</td>
</tr>
<tr>
<td>3b</td>
<td>45</td>
<td>10.8</td>
<td>11.2</td>
<td>828</td>
<td>0.95</td>
<td>8.7±0.7</td>
<td>1.8</td>
<td>2.1±0.8</td>
</tr>
<tr>
<td>1f</td>
<td>50</td>
<td>10.3</td>
<td>10.4</td>
<td>725</td>
<td>0.97</td>
<td>8.7±0.7</td>
<td>1.8</td>
<td>1.6±0.8</td>
</tr>
<tr>
<td>3c</td>
<td>55</td>
<td>10.8</td>
<td>12.7</td>
<td>779</td>
<td>1.13</td>
<td>10.2±1.0</td>
<td>2.8</td>
<td>0.7±1.1</td>
</tr>
<tr>
<td>3d</td>
<td>60</td>
<td>10.5</td>
<td>10.8</td>
<td>838</td>
<td>0.88</td>
<td>9.6±1.0</td>
<td>1.4</td>
<td>0.9±1.0</td>
</tr>
<tr>
<td>3e</td>
<td>65</td>
<td>4.0</td>
<td>3.5</td>
<td>566</td>
<td>0.39</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3f</td>
<td>70</td>
<td>3.5</td>
<td>3.3</td>
<td>629</td>
<td>0.38</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

**Table 3.6** BET surface areas, pore volumes, and pore for silicas in series 3. * Wall thickness was obtained by subtracting the pore size (ii) from the pore to pore distance (i).
Figure 3.13 Nitrogen adsorption/desorption measurements for calcined silicas in series 3, prepared using varying amounts of Pluronic P123. Labels, e.g., 3a, correspond to the unique code for each material and the weight percent of Pluronic P123 used. Note the plots have been displaced on the volume axis so that they all fit a single plot.
Figure 3.14 Pore size distributions calculated from nitrogen adsorption curves for calcined silicas in series 3, prepared using varying amounts of Pluronic P123. Labels, e.g., 3a, correspond to the unique code for each material and the weight percent of Pluronic P123 used. Note the plots have been displaced on the $dV_p/dr$ axis so they can all be viewed clearly on one plot.
3.3.4.3 TEM studies of silicas in series 3

Sample: 3a 1:2.25 40wt%

Sample: 3a 1:2.25 40wt%

Sample: 3b 1:1.82 45wt%

Sample: 3b 1:1.82 45wt%

Sample: 1f 1:1.5 50wt%

Sample: 1f 1:1.5 50wt%
Samples 3c and 3d are disordered porous silicas with slightly lower surface areas and pore volumes than the H2 silica. TEM images and X-ray diffraction show a small percentage of the material is ordered, possibly disordered thin with ~4 nm pore to pore separation.
Figure 3.15 TEM micrographs for H<sub>1</sub> silicas prepared from 40-70wt% Pluronic P123 and 1:0.64-2.25 mass ratio of P123:TMOS. Two representative micrographs are shown for each sample. Labels, e.g. 3a 40wt% 2.25, correspond to the unique code for each material, the ratio of P123:TMOS, and the weight percent of Pluronic P123 used. All scale bars are 50 nm.

Figure 3.15 shows representative TEM images of silicas in series 3, with data summarised in table 3.6. The structural order observed in the TEM images is in agreement with the structural order determined by the X-ray diffraction and N<sub>2</sub> adsorption measurements. Samples 3a to 3c exhibit a well ordered H<sub>1</sub> structure. Sample 3d is slightly disordered H<sub>1</sub> silica, while samples 3e and 3f are mostly amorphous silica, with some regions showing the disordered H<sub>1</sub> structure responsible for the broad, weak X-ray diffraction peaks at ca. 4nm. The average pore separation measured from the TEM images are in agreement with the pore separation determined by X-ray diffraction. The pore diameter, measured from the TEM images, for samples 3a to 1f is 5 nm, which is smaller than the N<sub>2</sub> adsorption derived pore diameter of 6.8 to 8.7 nm.

3.3.4.4 Summary of results for silicas in series 3

From samples 3a to 3d well ordered H<sub>1</sub> silicas with high surface areas (720-840m<sup>2</sup>g<sup>-1</sup>) and pore volumes (0.76-1.13cm<sup>3</sup>g<sup>-1</sup>) were produced. The pore separation is approximately constant at 10.6 nm. The pore diameter increases from 6.8 nm to 10 nm from sample 3a to 3d, while there is a commensurate decrease in wall thickness from 3.9 nm to ~0.9nm.

Samples 3e and 3f are disordered porous silicas with slightly lower surface areas and pore volumes than the H<sub>1</sub> silicas. TEM images and X-ray diffraction show a small percentage of the material is ordered, possibly disordered H<sub>1</sub> with ~4 nm pore to pore separation.
3.3.5 Comparison of results in series 1, 2 and 3

In the experimental section a ternary diagram was used to display the compositions used in series 1, 2 and 3 (figure 3.2). By plotting the experimental data for all silica samples on a ternary diagram it was possible to compare results between series and visualise how the structure produced varies with the composition of the initial reaction mixture. What follows are ternary diagrams representing the data obtained from powder X-ray diffraction, N₂ adsorption isotherms and TEM studies. After the data were plotted on the ternary diagrams contours were drawn in by hand. The positions of the contours were determined by joining up points were the data values were within a defined range. Where no data points were available, the boundary of the contour was deduced by extrapolating measurements from surrounding points, consequently the contours can only used as an aid to visualising trends in the data.
3.3.5.1 Structural order observed by TEM studies

The ternary diagram in figure 3.16 shows the variation in structural order of the mesoporous silicas, as observed using TEM, with initial reaction composition. There is a large central region where ordered H₁ silica is formed. Moving out from this region, the degree of ordering decreases. At the extremes, very disordered mesoporous silica is produced.
### 3.3.5.2 Peak widths for the first X-ray diffraction peak

The ternary diagram in figure 3.17 shows the variation in mesoporous structural ordering as determined by half height peak width for the first X-ray diffraction peak. The features of the diagram are in agreement with those of the ternary diagram of ordering observed from TEM studies (figure 3.16). There is a large central region of the ternary diagram that has the lowest peak width values, where the most ordered mesoporous silicas are formed. Moving out from this central region the peak width increase and the silica becomes less ordered. Sample 1a is so disordered that no X-ray diffraction peak is observed.
3.3.5.3 Pore diameters obtained from analysis of N\textsubscript{2} adsorption isotherms.

Figure 3.18 Ternary diagram showing the change in pore diameter with composition. Pore diameters were obtained from N\textsubscript{2} adsorption isotherms. n/a indicates the material was too disordered to determine an pore diameter.

Figure 3.18 shows the variation in pore diameter, as obtained from N\textsubscript{2} adsorption isotherms, with composition of the reaction mixture. In the bottom left corner of the diagram, where TMOS content is lowest, very disordered mesoporous silica is produced with a very broad pore distribution. At higher TMOS concentrations, moving towards the top of the diagram, there is a decrease in pore diameter.
3.3.5.4 Pore to pore distance obtained by X-ray diffraction

Figure 3.19 Ternary diagram showing the change in pore to pore distance, obtained from powder X-ray diffraction, with composition.

Figure 3.19 shows change in pore to pore distance, $a_{\text{c}}$, as a function of composition. At low TMOS and high Pluronic P123 concentrations, disordered silica with a small pore separation is produced. In the centre left region, the largest pore separation is found, 10.8 - 11.5 nm. At higher TMOS concentrations the pore separation decreases to 8 - 10 nm.
3.3.5.5 Wall thickness determined by pore size analysis and X-ray diffraction

Figure 3.20 Ternary diagram showing the change in wall thickness with initial reaction composition. The wall thickness was determined from pore size analysis of N₂ adsorption isotherms and powder X-ray diffraction data. n/a indicates the material was too disordered to determine an accurate wall thickness.

Figure 3.20 shows the wall thickness, determined by powder X-ray diffraction and N₂ isotherms, as a function of composition. In the lower left corner of the ternary diagram, where the TMOS concentration is low, the silicas are too disordered to measure the wall thickness. At higher TMOS concentrations, ordered mesoporous structures are formed with ~1 nm thick walls. As the TMOS content is increased, the wall thickness increases to 5 nm, after which the silica becomes disordered.
3.3.5.6 Surface area obtained from BET analysis

Figure 3.21 Ternary diagram showing the change in BET surface area with composition.

Figure 3.21 shows the BET surface area of the silicas as a function of composition. The central region and low TMOS concentration region show the highest surface areas. The surface area decreases with increasing TMOS concentration.
3.3.4.7 Pore volumes obtained from N\textsubscript{2} adsorption isotherms

By comparing the ternary diagrams it was observed that the most ordered H\textsubscript{3} silicon were obtained in a region of the ternary diagram on sample 1 that had a reaction time of 42 \textdegree\text{C} and 29 wt\% Pluronic P123. Pluronic P123 is a flexible polymer that can change the structure depending on the direction. Figure 3.23 summarises the structural changes diagrammatically.

Figure 3.22 shows the pore volume of silicas as a function of composition. The central region shows the highest pore volume. Moving from this region the pore volume gradually decreases.

Figure 3.22 Ternary diagram showing the change pore volume with composition.

Changing the amount of Pluronic P123 content for a fixed ratio of TMOS to 0.5 M HCl(aq) had significant effects on the silicon structure. Decreasing the Pluronic P123 content results in a decrease in pore diameter and an increase in wall thickness. There is little change in surface area and pore volume. There is a decrease in the long range ordering. Increasing the Pluronic P123 content initially increases the pore diameter and decreases the wall thickness, and then the pore diameter decreases.
3.3.4.8 Summary of ternary diagram analysis

By comparing the ternary diagrams it was observed that the most ordered H₃ silicas were obtained in a region of the ternary diagram centred on sample 1f, a sample common to the three series, that has an reaction composition of 42 wt% TMOS, 29 wt% 0.5 M HCl(aq) and 29 wt% Pluronic P123. Deviation from this region results in a variety of changes in structure depending on the direction. Figure 3.23 summarises the structural changes diagrammatically.

**Series 1 - Change in TMOS content for a fixed ratio of Pluronic P123 to 0.5 M HCl(aq)**

Changes in TMOS content have a large effect on the mesoporous structure. Decreasing the TMOS content from that used for sample 1f resulted in a gradual decrease in order, a decrease in wall thickness and a broadening of the pore size distribution, resulting in a disordered mesoporous silica with a very broad, peakless, pore size distribution. The surface areas remain high, with a slight decrease in pore volume. Increasing the amount of TMOS resulted in the gradual decrease in structural order, a decrease in pore diameter and a corresponding increase in wall thickness. There is also a decrease in surface area and pore volume as expected.

**Series 2 - Change in 0.5 M HCl(aq) content for a fixed ratio of Pluronic P123 to TMOS**

Changing the amount of 0.5 M HCl(aq) from that used for sample 1f had a slight effect on the silica structure. There was little change in surface area and pore volume. Decreasing the 0.5 M HCl(aq) content resulted in a slight increase in pore diameter and a decrease in wall thickness, with a slight decrease in ordering. At the extreme, the pore size distribution becomes significantly broader, accompanied by a decrease in ordering. Increasing the 0.5 M HCl(aq) content results in slightly thicker walls and a decrease in pore diameter. At the extreme the pore size distribution became broader and long range order decreases.

**Series 3 - Change in Pluronic P123 content for a fixed ratio of TMOS to 0.5 M HCl(aq)**

Changing the amount of Pluronic P123 from that used for sample 1f had significant effects on the silica structure. Decreasing the Pluronic P123 content results in a decrease in pore diameter and an increase in wall thickness. There is little change in surface area and pore volume. There is a decrease in the long range ordering. Increasing the Pluronic P123 content initially increases the pore diameter and decreases the wall thickness, and then the
structure becomes a disordered microporous system, with a lower surface area and pore volume.

**Series 1**
- Increasing TMOS
- Increasing wall thickness
- Decreasing pore diameter

**Series 2**
- Decreasing 0.5 M HCl(aq)
- Slight increase in pore size
- Slight decrease in wall thickness

**Series 3**
- Decreasing Pluronic P123
- Increase in wall thickness
- Decrease in pore diameter

**Series 3**
- Increasing Pluronic P123
- Increase in pore diameter
- Decrease in wall thickness
- Becomes disordered microporous silica

**Series 2**
- Increasing 0.5 M HCl(aq)
- Slight decrease in pore diameter
- Slight increase in wall thickness

**Series 1**
- Decreasing TMOS
- Decrease in wall thickness
- Broadening of pore size distribution
- Disordered mesoporous silica at extreme

**Figure 3.23** A diagrammatic summary of the changes that were observed in pore size, wall thickness and degree of structural ordering when the composition of the reaction mixture is changed from that of sample 1f.
3.4 Discussion

It can be seen from the ternary diagrams in section 3.3.5 that while mesoporous silicas are formed over a wide range of composition, there is a wide variation in pore diameter, wall thickness and structural order. In determining what controls the mesoporous structure of the silicas a number of factors have to be considered. These include the liquid crystal phase behaviour of Pluronic P123 in water, the hydrolysis reactions of TMOS, geometry, space filling, and the interaction of the surfactant headgroup with Si(OH)$_4$.

3.4.1 Hydrolysis and condensation of silica

Reaction steps:  
\[ \text{Si(OMe)}_4 + 4 \text{H}_2\text{O} \rightarrow \text{Si(OH)}_4 + 4 \text{MeOH} \rightarrow \text{SiO}_2 + 2 \text{H}_2\text{O} \]

Overall reaction:  
\[ \text{Si(OMe)}_4 + 2 \text{H}_2\text{O} \rightarrow \text{SiO}_2 + 4 \text{MeOH} \]

The mechanism for the formation of amorphous silica from the hydrolysis of TMOS was discussed in chapter 1. The first reaction step is the hydrolysis of TMOS to form nominally Si(OH)$_4$ and methanol. For this reaction to go to completion before condensation occurs it is necessary to have a molar ratio of TMOS to water of 1:4 or greater (mass ratio of 0.5 M HCl(aq):TMOS of 1:2.1). With less water some of the TMOS in only partially hydrolysed, but subsequent condensation of silanol groups produces water, which will allow further hydrolysis. The lower limit of TMOS to water is 1:2, any less water and complete hydrolysis is not possible. Lines a and b on the ternary diagram in figure 3.24 show the 2:1 and 4:1 water:TMOS molar ratio respectively. Above line a there is insufficient water present to completely hydrolyse TMOS. Between lines a and b there is insufficient water to completely hydrolyse the TMOS before condensation begins, so only the methanol produced in the initial hydrolysis is removed. The remaining methanol that is generated as condensation occurs will remain in the “aqueous” region and may cause disorder in the phase. The decrease in long range order of the silica is commensurate with the increase in the water:TMOS ratio and hence the amount of methanol in the system. The addition of small amounts of methanol to a lyotropic phase can decrease the long range order, higher levels will destabilise the phase. The H$_i$ phase formed from Pluronic P123/water mixtures can tolerate relatively high levels of methanol before an isotropic phase, L$_i$, is formed instead. For a H$_i$ phase formed from 50 wt% Pluronic P123, approximately 40% of the water volume can be replaced with methanol before an isotropic phase, L$_i$, is formed instead. The generation of methanol also increases the liquid volume...
present in the system, which may also cause a decrease in long range order of the phase. There is another possible source of disorder, the degree of long range order of an H₁ phase stabilised by a varying proportion of water and silanol groups is unknown.

### 3.4.2 Limitations on ternary diagram

![Ternary Diagram](image)

**Figure 3.24** Ternary diagram showing the compositions of TMOS/Pluronic P123/0.5 M HCl used to produce mesoporous silica. The 2:1 and 4:1 water:TMOS molar ratio lines are shown. The phase boundaries of the binary Pluronic P123 + water mixture at 45°C are also shown.

The 4:1 and 2:1 Water:TMOS molar ratios lines are marked on the ternary diagram in figure 3.24 showing the regions where complete hydrolysis is possible before condensation (below 4:1 line) and where some condensation is required before hydrolysis can be completed (between 4:1 and 2:1 line). The binary phase diagram of Pluronic P123 + water (figure 3.2) revealed that at 45°C, the temperature at which all the silicas were prepared, a micellar solution (L₁) existed below 28 wt% P123, a micellar cubic (l₁) phase between 28-36 wt%, a hexagonal (H₁) phase between 36-77 wt%, and lamellar (L₉) phase.
above 77 wt%. These phase boundaries of the binary Pluronic 123 + water mixture are marked on the ternary diagram. The interaction of Si(OH)₄ with the PEO head group is also significant. For the most ordered silicas, 0.5 M HCl[aq]:TMOS ratio about 1:2:1, there is just enough water present to completely hydrolyse the TMOS before condensation, there is extremely little water left to hydrate the surfactant head group. However, polarised light microscopy showed that H₁ phases were formed even in the absence of water. Lyotropic phases are also observed with solvents that, like water, are highly polar (eg glycerol and formamide)¹¹, so it is not surprising that the nominal Si(OH)₄ molecules can also stabilise the H₁ phase. As the condensation occurs, water is generated some of which is needed for further hydrolysis.

3.4.3 Geometry and space filling

The most ordered H₁ silica, those exhibiting the best long range order, are found in the water:TMOS mass ratio range of 1:1.2 – 1.8, samples 1e to 1g, 2b to 2c and 3b to 3c. At this ratio TMOS is completely hydrolysed before condensation, giving a Si(OH)₄:H₂O mole ratio of 1:0.6 – 3.0. Decreasing the amount of TMOS below the ideal results in a progressive decrease in the order and broadening of the pore size distribution. At the lowest ratio used, 1:0.25, the resulting silica showed no long range order and a pore size ranged from the microporous out to 10 nm. At this ratio, after hydrolysis the Si(OH)₄:H₂O mole ratio is 1:30, so condensation happens in a dilute solution and therefore forms a highly porous framework. As the water:TMOS mass ratio is increased above the ideal, 1:1.8, the long range order of the structure gradually decreases and ultimately becomes disordered. Above a water:TMOS mass ratio of 1:2.1 there in not enough water to completely hydrolyse the TMOS before condensation. A mixture of completely and partially hydrolyses TMOS replaces the aqueous phase between the cylindrical rods of surfactant, solvating the hydrophilic headgroups. As condensation occurs water is produced, allowing further hydrolysis, which produces methanol, which may disorder the liquid crystal phase. As the water:TMOS mass ratio approached absolute hydrolysis limit, 1:4.2, the structure formed becomes very disordered, the pore size distribution ranges from the microporous region out to 5nm with a slight peak at 3 nm. A water:TMOS mass ratio in the range of 1:1.2 - 1.8 doesn’t guarantee a well ordered structure, the amount of surfactant is also a factor. This was shown in series 3, where the water:TMOS mass ratio was held at 1:1.50 while the amount of surfactant was varied. Up to 60 wt% P123, well ordered mesoporous silica was produced, but at 65 and 70 wt% Pluronic P123 the H₁
phase was no longer stable, due was insufficient material between the rods of surfactant to stabilize the phase resulting in a disordered microporous silica being produced. In series 2, at 65 and 70 wt% a greater amount of TMOS was used, resulting in \( \text{H}_1 \) templated silica.

### 3.4.4 Microporosity and surface area: theoretical vs. measured

There has been much discussion in the literature on the microporous nature of mesoporous silica templated using surfactants with PEO head groups\(^{12,13,14}\). These silicas were prepared via a self-assembly route using TEOS and \(~3\) wt% surfactant, but these discussions are also valid for the silicas synthesised in this chapter. Part of the PEO head group penetrates into the \( \text{Si(OH)}_4 / \text{water} \) phase as condensation occurs, causing the silica wall to be microporous to a depth of \(~1\) nm. This microporosity contributes significantly to surface area and pore volume (10-20%). Attempts have been made to quantify the micropore volume using \( \alpha_s \) plots\(^{15}\), see appendix 1.B. The micropore volume cannot be accurately determined if the pore size distribution from the mesoporous channels and the pore size distribution for the micropore walls overlap. This leads to an underestimation of the micropore volume, even negative micropore volumes if the overlap is significant. The microporosity also causes the BET surface area calculation to return surface areas that are significantly greater than the true surface area. The pore size distributions for mesoporous silica templated from Pluronic P123 are significantly wider than those of silica templated from CTAB in chapter 2 or Brij 78 in chapter 4, which may be a result of the pore diameters being several times greater. From the TEM images of ordered mesoporous silica samples, the pore size distribution comes from variations in pore diameter along single pores, rather than a range of different sized pores. The wider pore size distribution, and larger error in pore diameter, hence wall thickness, introduce significant error into the theoretical surface area and pore volume which are calculated using a simple geometric model, see appendix 3 for details. Figure 3.25 shows the theoretical and measured surface area and pore volume of silicas in series 1. It can be seen that the error bars are significant for the large pore/thin walled samples, but decrease significantly for thicker walled samples.
Table 3.7 Theoretical and measured surface area and pore volume data for silicas in series 1.

<table>
<thead>
<tr>
<th>Sample label</th>
<th>Ratio of P123:TMOS (w/w)</th>
<th>Predicted BET surface area/m² g⁻¹ ±50 m² g⁻¹</th>
<th>Predicted Pore volume/cm³ g⁻¹</th>
<th>Predicted Total Pore volume/cm³ g⁻¹</th>
<th>Micropore volume/cm³ g⁻¹</th>
<th>Pore size from N₂ adsorption analysis /nm</th>
<th>FWHM /nm</th>
<th>Wall thickness /nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>1:0.25</td>
<td>-</td>
<td>750</td>
<td>-</td>
<td>0.72</td>
<td>0.05</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1b</td>
<td>1:0.50</td>
<td>-</td>
<td>732</td>
<td>-</td>
<td>0.74</td>
<td>0.02</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1c</td>
<td>1:0.75</td>
<td>1506</td>
<td>781</td>
<td>3.61</td>
<td>1.27</td>
<td>-0.06</td>
<td>9.6±0.1</td>
<td>7.5</td>
</tr>
<tr>
<td>1d</td>
<td>1:1.00</td>
<td>387</td>
<td>710</td>
<td>0.76</td>
<td>1.24</td>
<td>-0.06</td>
<td>7.9±0.7</td>
<td>3.8</td>
</tr>
<tr>
<td>1e</td>
<td>1:1.25</td>
<td>313</td>
<td>783</td>
<td>0.68</td>
<td>1.22</td>
<td>0.05</td>
<td>8.7±0.9</td>
<td>1.5</td>
</tr>
<tr>
<td>1f</td>
<td>1:1.50</td>
<td>383</td>
<td>725</td>
<td>0.83</td>
<td>0.97</td>
<td>0.01</td>
<td>8.7±0.9</td>
<td>1.6</td>
</tr>
<tr>
<td>1g</td>
<td>1:1.75</td>
<td>217</td>
<td>817</td>
<td>0.43</td>
<td>1.00</td>
<td>0.10</td>
<td>7.9±0.7</td>
<td>1.8</td>
</tr>
<tr>
<td>1h</td>
<td>1:2.00</td>
<td>253</td>
<td>648</td>
<td>0.49</td>
<td>0.82</td>
<td>0.05</td>
<td>7.8±0.7</td>
<td>1.5</td>
</tr>
<tr>
<td>1i</td>
<td>1:2.25</td>
<td>200</td>
<td>437</td>
<td>0.34</td>
<td>0.52</td>
<td>0.03</td>
<td>6.8±0.6</td>
<td>1.4</td>
</tr>
<tr>
<td>1j</td>
<td>1:2.50</td>
<td>159</td>
<td>517</td>
<td>0.27</td>
<td>0.61</td>
<td>0.04</td>
<td>6.8±0.6</td>
<td>1.4</td>
</tr>
<tr>
<td>1k</td>
<td>1:2.75</td>
<td>133</td>
<td>350</td>
<td>0.19</td>
<td>0.42</td>
<td>0.03</td>
<td>5.6±0.4</td>
<td>1.4</td>
</tr>
<tr>
<td>1l</td>
<td>1:3.00</td>
<td>121</td>
<td>482</td>
<td>0.15</td>
<td>0.42</td>
<td>0.02</td>
<td>4.9±0.3</td>
<td>1.9</td>
</tr>
<tr>
<td>1m</td>
<td>1:3.50</td>
<td>92</td>
<td>413</td>
<td>0.09</td>
<td>0.33</td>
<td>0.02</td>
<td>4.0±0.2</td>
<td>-</td>
</tr>
<tr>
<td>1n</td>
<td>1:4.00</td>
<td>-</td>
<td>446</td>
<td>-0.26</td>
<td>-</td>
<td>0.00</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Figure 3.25 shows the graphs of predicted and measured surface areas and pore volumes for series 1. At low P123:TMOS ratios it isn’t possible to predict the surface area and pore volume, nor measure the micropore volume due to the highly disordered nature of the porous structure. At higher ratios the micropore distribution tailed out to 3 nm and the pore size distribution from the mesopores also extends into the 3 nm region to varying degrees, causing the micropore volume to under estimated significantly. The presence of micropores causes the BET surface area to be overestimated. As micropore volume is not included in the theoretical model, the presence of micropores will result in a larger pore volume than predicted. For P123:TMOS ratios of ≥ 1:2, there is a significant increase in wall thickness and decrease in pore diameter, which means micropore volume will contribute a greater proportion of the total pore volume, as mesopore volume is proportional to the pore radius squared but micropore volume is proportional to the pore radius. Due to significant overlap of the micro and mesopore distributions, there is a large error in the calculated micropore volume as the pore diameter decreases, but there is other evidence of significant microporosity at smaller pore diameters. The difference in measured and predicted surface area increases, while the predicted surface area is decreasing, the measured surface area is, within error, constant. The predicted and measured total pore volume both decrease in this range, but the predicted pore volume is decreasing at a greater rate. This is consistent with a significant microporosity in the structure.
3.4.4.2 Predicted and measured surface area and pore volume for series 2

Figure 3.26 shows the graphs of predicted and measured surface area and pore volumes for series 2. Similar to series 1, it is difficult to determine the micropore volume with the $\alpha_s$– plot method due to merging of micropore and mesopore distributions. The measured surface area decreases as the wall thickness decreases and pore diameter increases slightly, while the predicted surface area increases slightly over this range. This is consistent with an over estimation of the surface area due to micropores, which decreases as the wall thickness decreases. The predicted pore volume starts out lower than the measured pore volume, but becomes closer as the wall thickness decreases.

<table>
<thead>
<tr>
<th>Sample label</th>
<th>Wt% P123</th>
<th>Predicted BET surface area /m$^2$g$^{-1}$</th>
<th>Predicted BET surface area /m$^2$g$^{-1}$</th>
<th>Predicted Pore volume /cm$^3$g$^{-1}$</th>
<th>Total Pore volume /cm$^3$g$^{-1}$</th>
<th>Micropore volume /cm$^3$g$^{-1}$</th>
<th>Pore size from $N_2$ adsorption analysis /nm</th>
<th>FWHM /nm</th>
<th>Wall thickness /nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a</td>
<td>40</td>
<td>216</td>
<td>646</td>
<td>0.40</td>
<td><strong>0.85</strong></td>
<td>-0.03</td>
<td>7.4±0.6</td>
<td>2.1</td>
<td>2.9</td>
</tr>
<tr>
<td>2b</td>
<td>45</td>
<td>328</td>
<td>823</td>
<td>0.71</td>
<td><strong>1.04</strong></td>
<td>0.06</td>
<td>8.7±0.8</td>
<td>1.6</td>
<td>1.9</td>
</tr>
<tr>
<td>1f</td>
<td>50</td>
<td>383</td>
<td>725</td>
<td>0.83</td>
<td><strong>0.97</strong></td>
<td>0.00</td>
<td>8.7±0.8</td>
<td>1.8</td>
<td>1.6</td>
</tr>
<tr>
<td>2c</td>
<td>55</td>
<td>243</td>
<td>652</td>
<td>0.49</td>
<td><strong>0.92</strong></td>
<td>0.05</td>
<td>8.0±0.7</td>
<td>1.6</td>
<td>2.6</td>
</tr>
<tr>
<td>2d</td>
<td>60</td>
<td>449</td>
<td>617</td>
<td>1.07</td>
<td><strong>0.79</strong></td>
<td>0.07</td>
<td>9.6±1.0</td>
<td>1.8</td>
<td>1.3</td>
</tr>
<tr>
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<td>253</td>
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<td><strong>0.87</strong></td>
<td>0.01</td>
<td>8.7±0.8</td>
<td>1.3</td>
<td>2.5</td>
</tr>
<tr>
<td>2f</td>
<td>70</td>
<td>445</td>
<td>476</td>
<td>1.12</td>
<td><strong>0.98</strong></td>
<td>0.00</td>
<td>10.1±1.0</td>
<td>5.6</td>
<td>1.3</td>
</tr>
</tbody>
</table>

Table 3.8 Theoretical and measured surface area and pore volume data for silicas in series 2.
3.4.4.3 Predicted and measured surface area and pore volume for series 3

Figure 3.27 show the graphs of predicted and measured surface area and pore volumes for series 3. Similar to series 1, it is difficult to determine the micropore volume with the $\alpha_i$-plot method due to merging of micropore and mesopore distributions, except for samples 3e and 3f, which showed no mesoporous structure, where the micropore volumes are close to the total pore volume. For the thicker walled/smaller pore diameter samples the predicted surface area and pore volume are substantially lower than the measured surface area and pore volumes, but the two values become closer as the wall thickness decreases and the pore diameter increases. This is consistent with a microporous wall structure.

<table>
<thead>
<tr>
<th>Sample label</th>
<th>Wt% P123</th>
<th>Predicted BET surface area /m²g⁻¹ ±50 m²g⁻¹</th>
<th>BET surface area /m²g⁻¹ ±50 m²g⁻¹</th>
<th>Predicted Pore volume /cm³g⁻¹</th>
<th>Total Pore volume /cm³g⁻¹</th>
<th>Micropore volume /cm³g⁻¹</th>
<th>Pore size from N₂ adsorption analysis /nm</th>
<th>FWHM /nm</th>
<th>Wall thickness /nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>3a</td>
<td>40</td>
<td>155</td>
<td>772</td>
<td>0.26</td>
<td>0.76</td>
<td>0.06</td>
<td>6.8±0.6</td>
<td>1.5</td>
<td>3.9</td>
</tr>
<tr>
<td>3b</td>
<td>45</td>
<td>299</td>
<td>828</td>
<td>0.65</td>
<td>0.95</td>
<td>0.09</td>
<td>8.7±0.7</td>
<td>1.8</td>
<td>2.1</td>
</tr>
<tr>
<td>3c</td>
<td>50</td>
<td>383</td>
<td>725</td>
<td>0.83</td>
<td>0.97</td>
<td>0.00</td>
<td>8.7±0.7</td>
<td>1.8</td>
<td>1.6</td>
</tr>
<tr>
<td>3d</td>
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<td>687</td>
<td>779</td>
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<td>1.13</td>
<td>0.07</td>
<td>10.2±1.0</td>
<td>2.8</td>
<td>0.7</td>
</tr>
<tr>
<td>3e</td>
<td>60</td>
<td>594</td>
<td>838</td>
<td>1.42</td>
<td>0.88</td>
<td>0.20</td>
<td>9.6±1.0</td>
<td>1.4</td>
<td>0.9</td>
</tr>
<tr>
<td>3f</td>
<td>65</td>
<td>-</td>
<td>566</td>
<td>-</td>
<td>0.39</td>
<td>0.24</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3f</td>
<td>70</td>
<td>-</td>
<td>629</td>
<td>-</td>
<td>0.38</td>
<td>0.23</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 3.9 Theoretical and measured surface area and pore volume data for silicas in series 3.
Figure 3.27 Graphs of predicted and measured surface area and pore volume for silicas in series 3. The error bars on the predicted surface area and pore volume are calculated from the error in pore diameter. The micropore volume is also plotted, calculated using the $\alpha_3$ – plot method.

### 3.5 Conclusions

From a study of the ternary reaction mixture of Pluronic P123, 0.5 HCl(aq), and TMOS, a more complete picture was obtained of the factors that determine the physical structure of the silica produced. TEM, X-ray diffraction and N$_2$ adsorption isotherms have all proven complementary techniques in determining the structural properties of the mesoporous silicas. By varying the proportions of Pluronic P123, TMOS and 0.5 M HCl(aq) it is possible to produce H$_1$-silica with pore diameters that range from 4 nm to 10 nm, and walls that range from ~1 nm to 5 nm in thickness. These two variables, in general, are dependent on each other, thick walls are accompanied by a small pore diameter, and vice versa, but there is some degree of independence for values in the middle of the ranges. The range of pore diameters and wall thickness of the silicas synthesised in this chapter are comparable with those the 2d-hexagonal silicas synthesised by Stucky et al., designated SBA-15, using 3 wt% Pluronic P123 and tetraethoxy silane under acidic conditions. The SBA-15 silicas had a wall thickness in the range of 3 – 6 nm and pore diameter in the range of 5 – 9 nm. Whereas the synthesis temperature controls the pore diameter and wall thickness of SBA-15 silicas, the structural parameters of the H$_1$-silica synthesised in this chapter are controlled by the ratio of reactants at a fixed synthesis temperature.
3.6 References


Chapter 4

Synthesis of mesoporous silica using Brij 78
**Chapter 4**

**Synthesis of mesoporous silica using Brij 78**

### 4.1 Background and objectives

When the phase diagram of Brij 78 (C_{18}H_{37}(OCH_{2}CH_{2})_{n}OH, n \sim 20) and water was constructed it revealed an micellar cubic phase (I\(_{c}\)) that extended over an unusually large range of temperature and composition, see Figure 4.2, which is due to the relatively large head group. The extent of the micellar cubic and hexagonal phase has been shown to increase with head group size for polyoxyethylene surfactants with a fixed alkyl chain length\(^1\), see figure 1.3. Micellar cubic phases consist of micelles packed on an ordered lattice. There had been no attempts to directly template mesoporous silica using the micellar cubic phases. If there were no connectivity between the micelles, a direct template would result in surfactant micelles embedded in a matrix of silica, making it impossible to remove the surfactant without destroying the silica matrix. If there is connectivity between the micelles or the presence of silicate species results in a micellar cubic phase with interconnectivity between the micelles, it is possible to directly template mesoporous silica. It is also possible that the addition of silicate species could cause the hexagonal phase (H\(_{1}\)) to be formed instead. Materials templated from cubic phases have a highly connected pore structure accessible from any orientation, unlike hexagonal (H\(_{1}\)) structures, which may be advantageous in future applications such as gas sensors\(^2\). In this chapter, the results of directly templating mesoporous silica from the micellar cubic phase of Brij 78 are presented.

### 4.2 Experimental

#### 4.2.1 Phase determination of Brij 78/water mixture

A phase diagram was constructed for Brij 78 using polarised light microscopy as outlined in appendix 1.D. Samples were prepared at 5 wt\% intervals from 5 to 95 wt\%. Brij 78 was used as supplied by Aldrich.

#### 4.2.2 Preparation of mesoporous silica

The route followed for preparing mesoporous silica was based on a method described by Attard et.al\(^3\). Brij 78 was dissolved in TMOS with gentle heating in a sealed flask. The resulting mixture was left to cool to room temperature and the required amount of 0.5 M HCl\(_{aq}\) was then added. After leaving the hydrolysis reaction to proceed for ca. 1 minute the methanol produced by the hydrolysis was removed on a rotary evaporator, taking 10-20min. Removal was determined by visual inspection. After methanol removal, the
silica gel was cured in a sealed reaction flask in an oven at 45°C for one week. Surfactant removal was achieved by calcination in a tube furnace at 450°C under N₂ for 7 hours, followed by O₂ for 15 hours (heating rate 10°C min⁻¹). A series of silica samples were prepared where the ratio of Brij 78 to 0.5 M HCl(aq) was kept constant at 1:1.5 by mass while the TMOS content was varied. The compositions of all the samples prepared are listed in appendix 2 and are also shown on the ternary diagram in figure 4.1. The error in a sample composition is ± 0.5 % (by mass) for each component. An explanation of how ternary diagrams are constructed and should be read is given in appendix 1.E. Each sample is given a unique label, with the letter denoting its position in the series (e.g. 1a). In this chapter, the phrase "concentration of surfactant" is used to denote the weight percentage (wt%) of surfactant with respect to the acid solution content only. For example, a reaction mixture containing 0.9 g of TMOS, 0.3 g of Brij 78 and 0.7 g of 0.5 M HCl was said to have a surfactant concentration of 30 wt%.

Figure 4.1 Ternary diagrams of all the silica samples prepared from Brij 78 + TMOS + 0.5 M HCl mixtures.
4.2.3 Characterisation of mesoporous silicas

Characterisation was carried out using transmission electron microscopy, small angle powder X-ray diffraction, and nitrogen adsorption isotherms following the procedures as outlined in appendix 1.

4.3 Results

4.3.1 Phase diagram of Brij 78/water mixtures

![Phase diagram for Brij 78 + distilled water. The bars for the 80wt% and 85wt% samples represent the temperature range over which the phase transition occurred. S – solid mixture of Brij 78/water.](image)

Figure 4.2 shows the phase diagram that was constructed for Brij 78. The key features of the phase diagram are the large micellar cubic phase (I_l) and hexagonal phase (H_l), which are stable up to relatively high temperatures for the Brij family of surfactants. X-ray diffraction was performed on the micellar cubic phase (I_l) phase (40 wt% Brij 78) at ca. 20°C. The micelles were determined to be packed in a primitive cubic lattice (7.9 nm unit cell). The d spacings have the ratios 1:1/\sqrt{2}:1/\sqrt{3}:1/\sqrt{4}:1/\sqrt{5}. The micellar cubic structure may vary with temperature and composition as shown by the study of the micellar cubic phase of C_{12}EO_{12}/water by Seddon et al. which has 3 different packing arrangements, Fm3m, Im3m and Pm3n in different regions of the micellar cubic phase\textsuperscript{12}. Micellar cubic phases have also been shown to only have one structural arrangement\textsuperscript{13}. 
4.3.2 Characterisation of silicas

In the series of silica samples prepared, the ratio of Brij 78 to 0.5 M HCl\textsubscript{(aq)} was kept constant at 1:1.5 (by mass), a ratio at which an I\textsubscript{1} phase is formed from a binary mixture of Brij 78 and water, while the amount of TMOS was varied. All samples produced a soft gel after the methanol was removed, which formed a solid after curing. The as-synthesised samples were isotropic under a POM, indicating a 3d cubic structure.

4.3.2.1 Powder X-ray diffraction of the silicas

<table>
<thead>
<tr>
<th>Series Label</th>
<th>Ratio of Brij78:TMOS (w/w)</th>
<th>Position of first reflection /\theta \pm 0.02^\circ</th>
<th>Peak width at half height of first reflection /\theta</th>
<th>d spacing for first reflection /\pm 0.05\text{nm}</th>
<th>Further peaks and indexing /\pm 0.02^\circ</th>
<th>Change in d spacing upon calcination /%</th>
</tr>
</thead>
<tbody>
<tr>
<td>la</td>
<td>1:0.6</td>
<td>1.72</td>
<td>~0.24</td>
<td>5.12</td>
<td>-</td>
<td>+13</td>
</tr>
<tr>
<td>lb</td>
<td>1:0.9</td>
<td>1.54</td>
<td>~0.24</td>
<td>5.74</td>
<td>-</td>
<td>-25</td>
</tr>
<tr>
<td>lc</td>
<td>1:1.2</td>
<td>1.48</td>
<td>0.25</td>
<td>5.98</td>
<td>-</td>
<td>-28</td>
</tr>
<tr>
<td>ld</td>
<td>1:1.5</td>
<td>1.52</td>
<td>0.15</td>
<td>5.82</td>
<td>-</td>
<td>-10</td>
</tr>
<tr>
<td>le</td>
<td>1:1.8</td>
<td>1.45</td>
<td>0.17</td>
<td>6.09</td>
<td>-</td>
<td>-11</td>
</tr>
<tr>
<td>lf</td>
<td>1:2.1</td>
<td>1.43</td>
<td>0.21</td>
<td>6.18</td>
<td>-</td>
<td>-13</td>
</tr>
<tr>
<td>lg</td>
<td>1:2.4</td>
<td>1.50</td>
<td>0.24</td>
<td>5.88</td>
<td>-</td>
<td>-12</td>
</tr>
<tr>
<td>lh</td>
<td>1:2.7</td>
<td>1.50</td>
<td>0.21</td>
<td>5.88</td>
<td>-</td>
<td>-12</td>
</tr>
<tr>
<td>li</td>
<td>1:3.1</td>
<td>1.54</td>
<td>0.21</td>
<td>5.75</td>
<td>-</td>
<td>-10</td>
</tr>
<tr>
<td>lj</td>
<td>1:4.0</td>
<td>1.73</td>
<td>0.17</td>
<td>5.12</td>
<td>-</td>
<td>-16</td>
</tr>
<tr>
<td>lk</td>
<td>1:5.0</td>
<td>1.75</td>
<td>0.26</td>
<td>5.06</td>
<td>-</td>
<td>-13</td>
</tr>
</tbody>
</table>

Table 4.1 Peak positions and peak widths at half height for powder X-ray diffraction patterns obtained from as-synthesised mesoporous silicas prepared from 40 wt% Brij 78.

Figure 4.3 shows the X-ray diffraction patterns obtained for as-synthesised silica samples with the data is summarised in table 4.1. All samples showed a single peak. No further peaks were observed at higher angles. At the lowest ratios of Brij 78:TMOS, 1:0.6 and 1:0.9, samples la and lb, the single weak peak is evidence of a very disordered mesoporous material. Increasing the ratio to 1:1.2 resulted in a more ordered structure with a stronger single peak. The d spacing peaks at 6.2 nm for sample 1f, with a gradual decrease either side. The half-height widths of the peaks are small, in the range of 0.15 to 0.26^\circ. For the more ordered samples, 1d to 1k, the d spacing contracts 10 – 16 % upon calcinations. The disordered structures 1b and 1c contract slightly more, 25 – 28 %.
indicating a less dense structure before calcination. The lowest TMOS content sample, la, shows a slight expansion of the framework upon calcinations, 13%.

**Figure 4.3** Powder X-ray diffraction patterns obtained for as-synthesised silica samples, prepared from 40wt% Brij 78. Plots have been displaced to allow all patterns to be clearly viewed on one plot. The plots have also been scaled in the y-axis to allow easy comparison of FWHM. Labels, eg 1a 1:0.6, correspond to the unique code for each material and the mass ratio of Brij 78:TMOS.
Table 4.2 Peak positions and peak widths at half height for powder X-ray diffraction patterns obtained from calcined mesoporous silicas prepared from 40 wt% Brij 78.

<table>
<thead>
<tr>
<th>Series label</th>
<th>Ratio of Brij78:TMOS (w/w)</th>
<th>Position of first reflection / 20 ±0.02°</th>
<th>Peak width at half height of first reflection /°</th>
<th>d spacing for first reflection /±0.05nm</th>
<th>Further peaks and indexing / 20 ±0.02°</th>
<th>Pore to pore distance for an H1 structure /nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>la</td>
<td>1:0.6</td>
<td>1.49</td>
<td>0.43</td>
<td>5.9</td>
<td>-</td>
<td>7.9</td>
</tr>
<tr>
<td>lb</td>
<td>1:0.9</td>
<td>2.05</td>
<td>0.44</td>
<td>4.3</td>
<td>-</td>
<td>5.5</td>
</tr>
<tr>
<td>lc</td>
<td>1:1.2</td>
<td>2.05</td>
<td>0.48</td>
<td>4.3</td>
<td>-</td>
<td>5.1</td>
</tr>
<tr>
<td>ld</td>
<td>1:1.5</td>
<td>1.71</td>
<td>0.17</td>
<td>5.2</td>
<td>2.90, 3.33</td>
<td>6.1</td>
</tr>
<tr>
<td>le</td>
<td>1:1.8</td>
<td>1.65</td>
<td>0.19</td>
<td>5.4</td>
<td>2.84, 3.25</td>
<td>6.4</td>
</tr>
<tr>
<td>lf</td>
<td>1:2.1</td>
<td>1.63</td>
<td>0.25</td>
<td>5.4</td>
<td>2.87, 3.22</td>
<td>6.4</td>
</tr>
<tr>
<td>lg</td>
<td>1:2.4</td>
<td>1.69</td>
<td>0.26</td>
<td>5.2</td>
<td>2.95, 3.45</td>
<td>6.2</td>
</tr>
<tr>
<td>lh</td>
<td>1:2.7</td>
<td>1.70</td>
<td>0.23</td>
<td>5.2</td>
<td>2.95, 3.45</td>
<td>6.2</td>
</tr>
<tr>
<td>li</td>
<td>1:3.1</td>
<td>1.71</td>
<td>0.28</td>
<td>5.2</td>
<td>2.97</td>
<td>6.2</td>
</tr>
<tr>
<td>lj</td>
<td>1:4.0</td>
<td>2.04</td>
<td>0.23</td>
<td>4.3</td>
<td>3.62 (broad)</td>
<td>5.6</td>
</tr>
<tr>
<td>lk</td>
<td>1:5.0</td>
<td>2.02</td>
<td>0.38</td>
<td>4.4</td>
<td>3.82 (broad)</td>
<td>5.6</td>
</tr>
</tbody>
</table>

Figure 4.4 shows the X-ray diffraction patterns obtained for calcined silica samples, with the data summarised in table 4.2. All samples showed at least one peak. Those samples that exhibited more than one peak could be indexed to an H1 structure, the d spacing ratios are 1: 1/√3:1/√4. No further peaks were observed at higher angles. There is a strong correlation between the degree of structural ordering in the as-synthesised and the calcined samples. Calcination resulted in a general increase in the FWHM, due to framework contraction, particularly in the more disordered samples. At the lowest ratios of Brij 78:TMOS, 1:0.6 and 1:0.9, samples 1a and 1b, the single broad X-ray peak is evidence of a very disordered mesoporous material. Increasing the ratio to 1:1.2 resulted a more ordered structure with a sharper single peak. In the Brij 78:TMOS ratio region of 1:1.5 to 1:2.7, highly ordered mesoporous silica, with three characteristic peaks, were formed, with the d spacing approximately constant at 5.3 nm. The FWHM for these samples was in the range of 0.17 to 0.26°. At a ratio of 1:3.1 and above, the structural ordering decreases, with the 2nd and 3rd peaks become less resolved, merging into a single broad peak. There is also a small decrease in the d spacing to 4.4 nm.
Figure 4.4 Powder X-ray diffraction patterns obtained for calcined silica samples, prepared from 40wt% Brij 78. Plots have been displaced to allow all patterns to be clearly viewed on one plot. The plots have also been scaled in the y-axis to allow easy comparison of FWHM. The inset graph shows a magnified plot in the region of the 2\textsuperscript{nd} and 3\textsuperscript{rd} peaks. Labels, eg 1a 1:0.6, correspond to the unique code for each material and the mass ratio of Brij 78:TMOS. The dotted vertical lines on the x-axis denote the peak positions from the X-ray diffraction pattern of an I\textsubscript{1} phase of Brij 78 (40 wt% Brij 78 aqueous solution).
4.3.2.2 Nitrogen adsorption isotherm analysis of silicas

The nitrogen adsorption/desorption isotherms and the pore size distributions obtained from them are shown in figures 4.5 and 4.6 respectively with the data summarised in table 4.3. The wall thickness was calculated assuming an H\textsubscript{1} structure. All samples are porous with a high surface area, in the range of 546 – 1129 m\textsuperscript{2} g\textsuperscript{-1}. Samples 1a and 1b have very broad pore distributions that tail out to 6 nm. As the TMOS content is increased, the pore size distribution narrows while the pore diameter increases to a maximum value of 4.5 nm for sample 1d, which also has the thinnest walls, leading to the sample having the highest surface area, 1130 m\textsuperscript{2} g\textsuperscript{-1} and pore volume, 1.10 cm\textsuperscript{3} g\textsuperscript{-1}. As the Brij 78:TMOS is increases above 1:1.5 the pore diameter gradually decreases to 2.9 nm, while the half-height width stays approximately constant at 0.7 nm. At a Brij 78:TMOS ratio of 1:2.1 and above, the wall thickness remains constant at 2.6 nm, while the pore size gradually decreases to 2.9 nm. There is a gradual decrease in surface area and pore volume, which is expected with a decreasing pore diameter and constant wall thickness. The hysteresis that occurs at pressures greater than 0.4 P/P\textsubscript{o}, is characteristic of materials with pore diameters greater than 3.7 nm and not due to bottlenecking or pore blocking\textsuperscript{4,5}. Samples 1j and 1k, where capillary condensation occurs below 0.4 P/P\textsubscript{o} show no hysteresis.

<table>
<thead>
<tr>
<th>Sample label</th>
<th>Ratio of Brij 78:TMOS (w/w)</th>
<th>i) Pore-pore distance from XRD/ ±0.05 nm</th>
<th>BET surface area/m\textsuperscript{2} g\textsuperscript{-1} ±50 m\textsuperscript{2} g\textsuperscript{-1}</th>
<th>BET pore volume/cm\textsuperscript{3} g\textsuperscript{-1}</th>
<th>n) Pore size from N\textsubscript{2} adsorption analysis /nm</th>
<th>TWHM /nm</th>
<th>Wall thickness i-n /nm*</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>1.06</td>
<td>7.9</td>
<td>855</td>
<td>0.63</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1b</td>
<td>1.09</td>
<td>5.5</td>
<td>899</td>
<td>0.82</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1c</td>
<td>1.12</td>
<td>5.1</td>
<td>955</td>
<td>0.80</td>
<td>3.5±0.2</td>
<td>2.1</td>
<td>1.6±0.7</td>
</tr>
<tr>
<td>1d</td>
<td>1.15</td>
<td>6.1</td>
<td>1129</td>
<td>1.10</td>
<td>4.5±0.2</td>
<td>1.0</td>
<td>1.6±0.7</td>
</tr>
<tr>
<td>1e</td>
<td>1.18</td>
<td>6.4</td>
<td>876</td>
<td>0.74</td>
<td>4.0±0.2</td>
<td>0.7</td>
<td>2.4±0.7</td>
</tr>
<tr>
<td>1f</td>
<td>1.21</td>
<td>6.4</td>
<td>970</td>
<td>0.73</td>
<td>3.8±0.2</td>
<td>0.8</td>
<td>2.6±0.7</td>
</tr>
<tr>
<td>1g</td>
<td>1.24</td>
<td>6.2</td>
<td>833</td>
<td>0.59</td>
<td>3.5±0.2</td>
<td>0.6</td>
<td>2.7±0.7</td>
</tr>
<tr>
<td>1h</td>
<td>1.27</td>
<td>6.2</td>
<td>850</td>
<td>0.57</td>
<td>3.5±0.2</td>
<td>0.7</td>
<td>2.7±0.7</td>
</tr>
<tr>
<td>1i</td>
<td>1.31</td>
<td>6.2</td>
<td>847</td>
<td>0.57</td>
<td>3.5±0.2</td>
<td>0.8</td>
<td>2.7±0.7</td>
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<tr>
<td>1j</td>
<td>1.40</td>
<td>5.6</td>
<td>641</td>
<td>0.38</td>
<td>3.0±0.1</td>
<td>0.6</td>
<td>2.6±0.6</td>
</tr>
<tr>
<td>1k</td>
<td>1.50</td>
<td>5.6</td>
<td>546</td>
<td>0.30</td>
<td>2.9±0.1</td>
<td>0.7</td>
<td>2.7±0.6</td>
</tr>
</tbody>
</table>

Table 4.3 BET surface areas, pore volumes, and pore diameter for silicas, prepared from 40 wt% Brij 78

* Wall thickness was obtained by subtracting the pore size (ii) from the pore to pore distance (i), as calculated for a H\textsubscript{1} structure
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Figure 4.5 Nitrogen adsorption/desorption isotherms of calcined silicas prepared from 40 wt% Brij 78. Labels, eg la 1:0.6, correspond to the unique code for each material and the mass ratio of Brij 78:TMOS. Note the plots have been displaced on the volume axis so that they all fit on one plot.
4.3.2.3 TEM studies of silica samples

Figure 4.7 shows representative TEM images for the silicas prepared from 40wt% Brij 78, with the data summarised in table 4.4. The structural order observed in the TEM images of the series support the structural order as determined by X-ray diffraction and N₂ adsorption isotherms. TEM images of sample 1a and 1b show a very disordered porous structure, while sample 1c shows evidence of some ordered structure. TEM images of samples 1d to 1j show a well ordering mesoporous structure, but 1i and 1j show some decrease in order. Sample 1k shows a further decrease in order.
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Sample: 1a 1:0.6

Sample: 1a 1:0.9

Sample: 1c 1:1.2

Sample: 1c 1:1.2
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Sample 1 g:1:2.4

Sample 1 g:1:2.4

Sample 1 g:1:2.4

Sample 1 g:1:1.2

Sample 1 g:1:2

Sample 1 g:1:2.7

Sample 1 h:1:2.4

Sample 1 h:1:2.7

Sample 1 h:1:2.7

Sample 1 h:1:1.2
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Figure 4.7: TEM micrographs for silicas prepared from 40wt% Brij 78 and 1:1.6 - 3:1 mass ratio of Brij 78:TMOS. Representative micrographs are shown for each sample. Labels, e.g. 1h:1:2.7, correspond to the unique code for each material and the mass ratio of Brij 78:TMOS. All scale bars are 50 nm.
Figure 4.7. TEM micrographs for silicas prepared from 40wt% Brij 78 and 1:0.6 – 5.0 mass ratio of Brij 78:TMOS. Representative micrographs are shown for each sample. Labels, e.g. la 1:0.6, correspond to the unique code for each material and the mass ratio of Brij 78:TMOS. All scale bars are 50 nm.
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**Synthesis of mesoporous silica using Brij 78**

<table>
<thead>
<tr>
<th>Series label</th>
<th>Ratio of Brij78: TMOS (w/w)</th>
<th>d spacing for first reflection /±0.05nm</th>
<th>TEM Parallel lines /±0.3 nm</th>
<th>TEM Hexagonal /±0.3 nm</th>
<th>TEM cubic/±0.3 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ia</td>
<td>1:0.6</td>
<td>5.9</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ib</td>
<td>1:0.9</td>
<td>4.3</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ic</td>
<td>1:1.2</td>
<td>4.3</td>
<td>4.3</td>
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<td>-</td>
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<td>4.5</td>
<td>4.4</td>
</tr>
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<td>4.9</td>
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<td>5.2</td>
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<td>4.8</td>
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<td>4.8</td>
</tr>
<tr>
<td>Ik</td>
<td>1:5.0</td>
<td>4.4</td>
<td>4.9</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 4.4 Repeat distances from TEM images. The d spacing of the first powder X-ray diffraction peak is also included in the table for comparison to these measurements.

The powder X-ray diffraction data is consistent with the silica sample having the same 2d hexagonal mesoporous structure as the silicas in Chapter 2 and 3, but the polarising optical microscopy observations of the as-synthesised samples showed the samples are isotropic, indicative of a cubic phase. For the most ordered silica samples, the TEM images are also not consistent with a 2d hexagonal structure, a cubic arrangement of pores is observed in addition to the parallel fringes and hexagonal ordered pores that are observed for a 2d hexagonal system. The more disordered samples also displayed a “worm-like” structure, and a TEM image of sample Id shows an interesting cubic projection, but this is the only region seen with that structure. This means that either there are two different structures present, which is not supported by the pore size distribution, X-ray data and polarising optical microscopy observations, or that the three different types of TEM images observed are projections of a single, undetermined, cubic structure. If the different types of TEM images observed are the different projection of a single structure, there should be a constant relationship between the repeat distanced in the different projections. The repeat distances measured from the TEM images are between 4 and 6 nm. There is a loose relationship between the different projections. In general, the hexagonal repeat distances are slightly greater than those of the cubic or parallel fringes, which are similar. The d spacing of the first powder X-ray diffraction
peak is generally slightly less the repeat distance of the hexagonal projection. There is too much scatter in the measurements, probably caused by different amounts of beam damage in the sample and local variation in repeat distances, to determine ratios between the repeat distances.

### 4.3.2.4 Summary of results for series

All silica samples prepared from 40 wt% Brij 78 are mesoporous with relatively high surface areas and pore volumes. There is a large variation in the degree of structural ordering, pore diameter, and pore size distribution. The silica framework undergoes a contraction of between 10 to 28 percent upon removal of the surfactant by calcination, which causes a decrease in long range structural ordering, as measured by the half-height width of the powder X-ray peak. The exact mesoporous structure has not been determined, but the polarising optical microscopy and TEM imaging are consistent with a cubic structure. The powder X-ray diffraction of the most ordered samples gave 3 peaks with d spacing ratios of $1:1/\sqrt{3}:1/\sqrt{4}$ which is consistent with a 2d hexagonal structure. In the literature, there are no cubic structures where the first three peaks have these ratios. The X-ray diffraction pattern of the $I_1$ phase of Brij 78 gave five peaks with d spacing ratios of $1:1/2:1/\sqrt{3}:1/\sqrt{4}:1/\sqrt{5}$, therefore the silica structure is not a direct template of the $I_1$ phase. To allow comparisons between silicas, a 2d hexagonal structure is assumed when calculating the wall thickness. At the low TMOS concentrations used, highly disordered mesoporous silicas with very broad pore size distributions are produced, but as the TMOS concentration is increased, the structure becomes more ordered. At a Brij 78 to TMOS ratio of 1:1.5, a very ordered mesoporous structure is formed, with a 4.5 nm pore diameter and 1.6 nm thick walls. As the TMOS concentration is increased further the wall thickness increases to 2.6 nm and remains constant while the pore diameter gradually decrease to 2.9 nm, which is accompanied by a gradual decrease in long range structure ordering as shown by the $2^{nd}$ and $3^{rd}$ X-ray peaks broadening into a single peak.
4.4 Discussion

It was not possible to precisely determine the mesoporous structure, as the polarising optical microscopy and TEM images showed an undetermined cubic structure, while the powder X-ray diffraction was consistent with a 2d hexagonal structure. All the silica samples prepared have the same mesoporous structure, but the TEM images and X-ray diffraction patterns do not match any of the published cubic structures. The mesoporous structure produced is not a direct template of the micellar cubic phase of Brij 78, which has a primitive cubic arrangement spherical micelles, as the X-ray diffraction pattern is different. In the presence of silicate species, the micellar cubic phase appears to rearrange into a continuous cubic phase.

The hydrolysis and condensation of TMOS, geometry and space filling, discussed in chapter 3, section 3.4.1 are also valid for the silicas produced in this chapter. Similarly to the H₃-SiO₂ produced in chapter 3, the most ordered sample were formed when there is relatively little water left after the TMOS is hydrolysed. The samples with the most ordered mesoporous structures, samples 1d to 1h, have TMOS:water molar ratios in the range of 1:5.3 - 8.4, giving a Si(OH)₄:water molar ratio of 1:1.3 - 4.4 after hydrolysis. With more water present the mesoporous structure is more disordered, but with less water there is a slight decrease in long range order. In the region of the ternary diagram explored, see figure 4.6, the “Si(OH)₄” oligomers formed by hydrolysis of TMOS stabilise a lyotropic liquid crystal phase, but it was not the micellar cubic phase present with just a binary Brij 78/water mixture, instead a continuous cubic phase was formed.
4.4.1 Limitations of the ternary diagram

**Figure 4.8** Ternary diagram showing the compositions of TMOS/Brij 78/0.5 M HCl used to produce mesoporous silica. The 2:1 and 4:1 water TMOS molar ratio lines are shown. The phase boundaries of the binary Brij 78 + water mixture at 45°C are also shown.

The 4:1 and 2:1 Water:TMOS molar ratios lines are marked on the ternary diagram in figure 4.8 showing the regions where complete hydrolysis is possible before condensation (below 4:1 line) and where some condensation is required before hydrolysis can be completed (between 4:1 and 2:1 line). The binary phase diagram of Brij 78 + water (figure 4.1) revealed that at 45°C, the temperature at which all the silicas were prepared, a micellar solution existed below 28 wt% Brij 78, a micellar cubic phase between 28-56 wt%, an hexagonal phase between 56-78 wt%, and above 78 wt% a lamellar phase exists. These phase boundaries of the binary Brij 78 + water mixture are marked on the ternary diagram.
4.4.2 Microporosity of the silicas

Like Pluronic P123, Brij 78 has a poly oxyethylene head group, part of the which can penetrate into the Si(OH)₄/water phase as condensation occurs, causing the silica wall to be microporous up to a depth of ~1 nm. This microporosity contributes significantly to surface area and pore volume (10-20%). Attempts have been made to quantify the micropore volume using αₛ-plots, see appendix 1.B. The microporosity causes the BET surface area calculation to return surface areas that are significantly greater than the true surface area.

![Total Pore Volume and Micropore Volume](image)

**Figure 4.9** Plot of total pore volume and micropore volume vs. Brij 78:TMOS mass ratio for silica samples. The micropore volume is calculated using the αₛ-plot method.

The graph in figure 4.9 shows the total pore volume, as measured by nitrogen adsorption, and micropore volume, as calculated by the αₛ-plot method, of the silicas as a function of the Brij 78:TMOS ratio. At low Brij 78:TMOS ratios, where the mesoporous structure is very disordered, the pore size distribution is very broad there is significant overlap with the micropore distribution. This results in an underestimation of the micropore volume, which causes negative micropore volume values to be calculated.

At higher Brij 78:TMOS ratios there is less overlap between the micropore and mesopore distributions as the structure is more ordered, giving more accurate micropore volumes. At a Brij 78:TMOS ratio of 1:2.1 and greater, the pore diameter decreases with a fixed
wall thickness, the micropore volume becomes a greater percentage of the total pore volume. The micropore volume peaks at 20% of the total pore volume for silica sample 1k, which has the thickest walls and smallest pore diameter. This is expected, since the micropore volume is generated by the PEO head group of the surfactant penetrating the silica walls, hence the micropore volume is proportional to the pore radius while the while the pore volume due to the mesopore is proportional to the radius squared, therefore as the pore diameter decreases the micropore volume becomes a greater percentage of the total pore volume. The exact mesoporous structure has not been determined, therefore the theoretical surface area and pore volume can't be calculated from a geometric model, but the significant micropore volumes will cause the BET surface area to be overestimated.

4.5 Conclusions

Using the complementary techniques of TEM, powder X-ray diffraction and N2 adsorption/desorption isotherms, a series of mesoporous cubic silicas have been characterised. It was not possible to precisely determine the mesoporous structure, but it appears to be some type of cubic structure from the polarising optical microscopy and TEM images. The type of cubic structure could not be determined from the X-ray diffraction pattern. All the ordered silica samples prepared have the same cubic mesoporous structure. The mesoporous silica structure produced is not a direct template of the micellar cubic phase of Brij 78 that is formed from a binary mixture of water and Brij 78, as the X-ray diffraction patterns are different. The mesoporous structure could be determined using high resolution TEM and electron crystallography on a well ordered silica sample. Further exploration of the Brij 78/TMOS/0.5 M HCl(aq) ternary diagram may produce mesoporous silica with different cubic structures.

Similarly to the H1-SiO2 produced in chapter 3 using Pluronic P123, the most ordered sample were formed when there is relatively little water left after the TMOS is hydrolysed. The most ordered mesoporous structures had a TMOS:water molar ratio of 1:5.3 - 8.4, giving Si(OH)4:water molar ratio of 1:1.3 - 4.4 after complete hydrolysis. With more water present, the more disordered the mesoporous structure, but with less water there is a slight decrease in long range order.
The range of pore diameters produced by the Brij 78 templated silicas, 2.9 nm to 4.5 nm, is comparable to those of silica templated from the hexagonal phase of Brij 56\textsuperscript{10,11}. Brij 56 is has a smaller head group than Brij 78 with a slightly shorter alkyl chain, favouring the formation of the hexagonal phase (H\textsubscript{1}).

The Brij family of surfactants, with a fixed alkyl chain length and a distribution in head group size, are an intermediate between ionic surfactants such as CTAB, where the head group size and tail length are the same for each surfactant molecule, and oligomeric surfactants such as the Pluronic family, where there is a distribution of head group size and hydrophobic chain length. This is reflected in the pore size distribution of the most ordered silicas produced from each surfactant. The narrowest pore size distribution from CTAB templated silica in chapter 2 had a FWHM of 0.3 nm, while for Brij 78 in this chapter it is 0.6 nm, and for Pluronic P123 in chapter 3 it was 1.4 nm.

### 4.6 References


Chapter 5

Synthesis of Mesoporous Silica using Pluronic F127
5.1 Background and objectives

![Phase Diagram of Pluronic F127 + Distilled Water](image)

**Figure 5.1** Published phase diagram of Pluronic F127 + distilled water\(^1\). This phase diagram was checked against the sample of Pluronic F127 used for the syntheses in this chapter and was found to be in agreement. The L\(_1\) to I\(_1\) transition at 15 wt% was determined to be within 2°C of the measured sample.

The published phase diagram of non-ionic triblock polymer EO\(_{106}\)PO\(_{70}\)EO\(_{106}\), Pluronic F127 (from BASF) and water\(^1\), Figure 5.1, exhibits an extensive micellar cubic phase, stable across a wide range of temperature and composition, far greater than that of Brij 78. This is due to a large headgroup, which favours the formation of highly curved structures. In 1998, Stucky et al.\(^2\) used Pluronic F127 at a low concentration, 3-5 wt%, to produce a cubic mesoporous silica via self-assembly, which they designated SBA-16. The powder X-ray diffraction determined that the space group to be Im3m, but it wasn’t until 2000 that Sakamoto et al.\(^3\) determined the pore structure. Using high-resolution TEM to produce a density map, the structure of Stucky’s SBA-16 sample was determined to consist of 9.5 nm diameter spherical cavities arranged in a body-centre-cubic array connected by 2.3 nm wide channels. The mesoporous silica templated from the micellar cubic phase of Brij 78, which was investigated in Chapter 4, produced silica with an undetermined cubic structure. Silica had not been templated from the micellar cubic phase of Pluronic F127, so
the structure that would be formed was unknown. It was possible that the structure formed would have the same cubic structure as silica templated from Brij 78, the SBA-16 cubic structure, another cubic structure, or a hexagonal structure. The structure formed could have also been dependent on the composition used. The extensive micellar cubic phase of Pluronic F127 was also of interest because it allows the synthesis of mesoporous silica with wide range of pore diameter and wall thickness. In this chapter, a considerable area of the Pluronic F127/TMOS/0.5 M HCl(aq) ternary diagram was explored to determine what mesoporous silica structures can be templated from high concentrations of Pluronic F127.

5.2 Experimental

5.2.1 Preparation of mesoporous silica

The route followed for preparing mesoporous silica was based on a method described by Attard et.al\(^4\). Pluronic F127 was dissolved in TMOS with gentle heating in a sealed flask. The resulting mixture was left to cool to room temperature and the required amount of 0.5 M HCl(aq) was then added. After leaving the hydrolysis reaction to proceed for ca. 1 minute the methanol produced by the hydrolysis was removed on a rotary evaporator, taking 10-20 min. Removal was determined by visual inspection. After methanol removal, the silica gel was cured in sealed reaction flask in an oven at 45°C for one week. Surfactant removal was achieved by calcination in a tube furnace at 450°C under N\(_2\) for 7 hours, followed by O\(_2\) for 15 hours (heating rate 10°C min\(^{-1}\)). Three series of mesoporous silicas were templated from Pluronic F127, as listed below.

- Series 1 – The ratio of 0.5 M HCl(aq) to Pluronic F127 was kept constant (1:1 by mass) while varying the amount of TMOS.

- Series 2 – The ratio of Pluronic F127 to TMOS was kept constant (1:1.5 by mass) while varying the amount of 0.5 M HCl(aq).

- Series 3 – The ratio of 0.5 M HCl(aq) to TMOS was kept constant (1:1.5 by mass) while varying the amount of Pluronic F127.
The compositions of all the samples prepared are listed in appendix 2 and are also shown on the ternary diagram in figure 5.2. The error in a sample composition is ± 0.5 % (by mass) for each component. An explanation of how ternary diagrams are constructed and should be read is given in appendix 1.E. Each sample is given a unique label, with the letter denoting its position in the series (e.g. 1a) so that results can be cross-referenced throughout the chapter. The phrase "concentration of surfactant" is used to denote the weight percentage (wt%) of surfactant with respect to the acid solution content only. For example, a reaction mixture containing 0.9 g of TMOS, 0.3 g of Pluronic F127 and 0.7 g of 0.5 M HCl was said to have a surfactant concentration of 30 wt%.

![Ternary diagram of silica samples](image)

**Figure 5.2** Ternary diagram of all the silica samples prepared from Pluronic F127 + TMOS + 0.5 M HCl mixtures.
5.2.2 Characterisation of mesoporous silicas

Characterisation was carried out using transmission electron microscopy, small angle powder X-ray diffraction, nitrogen adsorption isotherms following the procedures outlined in appendix 1.

5.3 Results

5.3.1 Characterisation of silicas in series 1 – Vary TMOS content

In series 1, the ratio of Pluronic F127 to 0.5 M HCl(aq) was kept constant at 1:1 (by mass) while the amount of TMOS was varied. A binary mixture of Pluronic F127 and 0.5 M HCl(aq) with a ratio of 1:1 (by mass) forms an I$_1$ phase.

5.3.1.1 Powder X-ray diffraction of silicas in series 1

<table>
<thead>
<tr>
<th>Series label</th>
<th>Ratio of F127:TMOS (w/w)</th>
<th>Position of first reflection /$\theta$ ± 0.02$^\circ$</th>
<th>Peak width at half height of first reflection /$^\circ$</th>
<th>$d$ spacing for first reflection /±0.1 nm</th>
<th>Further peaks /$\theta$ ± 0.02$^\circ$</th>
<th>Pore to pore distance for an I$_1$ structure /± 0.1 nm</th>
</tr>
</thead>
<tbody>
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<td>la</td>
<td>1:0.25</td>
<td>0.97 0.30</td>
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<td>-</td>
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<td>-</td>
<td>9.8</td>
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</tr>
<tr>
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<td>11.5</td>
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<td>1.49</td>
<td>11.9</td>
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</tr>
<tr>
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<td>0.85 0.12</td>
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<td>1.46, 1.69</td>
<td>12.0</td>
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<td>1.38</td>
<td>13.1</td>
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</tr>
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<td>1:2.25</td>
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<td>10.5</td>
<td>1.46</td>
<td>12.1</td>
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</tr>
<tr>
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<td>1:2.50</td>
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<td>10.9</td>
<td>1.48</td>
<td>12.6</td>
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</tr>
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<td>-</td>
<td>11.0</td>
<td></td>
</tr>
</tbody>
</table>

Table 5.1 Peak positions and peak widths at half height for X-ray diffraction patterns obtained from calcined mesoporous silicas samples prepared from 50 wt% Pluronic F127.
Chapter 5

Synthesis of mesoporous silica using Pluronic F127

Figure 5.3 Powder X-ray diffraction patterns obtained for calcined silica samples in series 1, prepared from 50wt% Pluronic F127. Plots have been displaced to allow all patterns to be clearly viewed on one plot. The plots have also been scaled in the y-axis to allow easy comparison of FWHM. The inset graph shows a magnified plot in the region of the 2nd and 3rd peaks. Labels, eg 1a 1:0.25, correspond to the unique code for each material and the mass ratio of Pluronic F127:TMOS.

Figure 5.3 shows the X-ray diffraction patterns obtained for calcined silica samples in series 1, with the data summarised in table 5.1. All samples showed at least one peak. The samples that exhibited more than one peak could be indexed to a H1 structure, with d spacing ratios of 1:1/√3: 1/√4. No further peaks were observed at higher angles. Samples 1a and 1b both showed a single very broad, weak peak at slightly smaller d spacings than...
the other samples in the series. The peak widths of the first peaks, with the exception of sample 1a, are relatively narrow. From sample 1b to 1g (1:0.5 to 1:1.75 F127:TMOS) the FWHM is approximately constant at 0.12°, after which it gradually increases to 0.21° for sample 1n. From sample 1a the structural order gradually increases, with a second peak appearing for samples 1c, 1d and 1e. Samples 1f and 1g showed the greatest degree of structural order, with 3 peaks, after which the long range structural order decreases, only a second peak is observed which gradually broadens then disappears by sample 1n. The d spacing gradually increases from sample 1a to sample 1h, 8.4 nm to 11.4 nm, after which the d spacing gradually decreases to 9.5 nm for sample 1n.

5.3.1.2 Nitrogen adsorption isotherm analysis of silicas in series 1

<table>
<thead>
<tr>
<th>Series label</th>
<th>Ratio of F127:TMOS</th>
<th>i) Pore-pore distance from XRD/±0.1 nm</th>
<th>BET surface area/m²g⁻¹</th>
<th>Pore volume/cm³g⁻¹</th>
<th>ii) Pore size from N₂ adsorption analysis/nm</th>
<th>FWHM/nm</th>
<th>Wall thickness i-ii / nm*</th>
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</thead>
<tbody>
<tr>
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<td>1:0.25</td>
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<td>413</td>
<td>0.78</td>
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<td>-</td>
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<td>10.5</td>
<td>753</td>
<td>1.01</td>
<td>7.3±0.5</td>
<td>5.8</td>
<td>2.5±0.6</td>
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<tr>
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<td>1:0.75</td>
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<td>738</td>
<td>1.34</td>
<td>9.6±1.0</td>
<td>4.8</td>
<td>1.9±1.1</td>
</tr>
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<td>8.0±0.7</td>
<td>2.2</td>
<td>3.9±0.8</td>
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<td>1:1.25</td>
<td>11.3</td>
<td>828</td>
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<td>7.4±0.5</td>
<td>2.2</td>
<td>3.7±0.6</td>
</tr>
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<td>1:1.50</td>
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<td>0.80</td>
<td>7.0±0.5</td>
<td>1.4</td>
<td>5.3±0.6</td>
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<td>839</td>
<td>0.76</td>
<td>7.6±0.6</td>
<td>2.1</td>
<td>4.4±0.7</td>
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<td>725</td>
<td>0.70</td>
<td>8.8±0.9</td>
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<td>4.3±1.0</td>
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<td>5.3±0.6</td>
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</tbody>
</table>

Table 5.2 BET surface areas, pore volumes, and pore for silicas in series 1, prepared from 50 wt% Pluronic F127. * Wall thickness was obtained by subtracting the pore size (ii) from the pore to pore distance (i), as calculated for a H₃ structure.
Figure 5.4 Nitrogen adsorption/desorption isotherms of calcined silicas in series 1, 50 wt% Pluronic F127. Labels, eg 1a 1:0.25, correspond to the unique code for each material and the mass ratio of Pluronic F127:TMOS. Note the plots have been displaced on the volume axis so that they all fit on one plot.
Figure 5.5 Pore size distributions calculated from nitrogen adsorption isotherms of calcined silicas in series 1, prepared using 50wt% Pluronic F127. Labels, eg 1a 1:0.25, correspond to the unique code for each material and the mass ratio of Pluronic F127:TMOS. Note the plots have been displaced on the dV_p/dr axis so they can all be viewed clearly on one plot.

The nitrogen adsorption/desorption isotherms and the pore size distributions obtained from them for series 1 are shown in figures 5.4 and 5.5 respectively, with the data summarised in table 5.2. The wall thickness was calculated assuming an H_1 structure. Sample 1a has a very broad pore distribution, which tails out to 16 nm. As the TMOS content is increased, the pore size distribution narrows and the pore diameter decreases from 9.6 nm to 7.0 nm for sample 1f. The pore size then increases to 8.8 nm for sample
From sample 1h to 1n the pore size gradually decreases from 8.8 nm to 5.0 nm. The corresponding increase in wall thickness, from 4.3 nm to 6.0 nm, is smaller due to gradual decrease in d spacing for these samples. The increase in wall thickness and decrease in pore diameter is accompanied by the expected decrease in surface area and pore volume. The surface areas of all the samples are large, in the range of 413 – 962 m² g⁻¹. The half height peak widths of the pore size distributions are in the range of 1.4 – 2.2 nm for samples 1d to 1n. The pore volume peaks at 1.36 cm³ g⁻¹ for sample 1d, with it decreasing gradually for samples either side. The hysteresis observed in the isotherms that occurs at pressures greater than 0.4 P/P is characteristic of materials with pore diameters greater than 3.7 nm⁶,⁷ and not due to bottlenecking or pore blocking.

5.3.1.3 TEM studies of silicas in series 1

Figure 5.6 shows representative TEM images for calcined silicas in series 1, with the data summarised in table 5.3. The structural order observed in the TEM images of series 1 silicas supports the degree of structural order as determined by X-ray diffraction and N₂ adsorption isotherm data. TEM images of samples 1a and 1b show a disordered structure, sample 1c show some regions of ordered structure. At Pluronic F127 ratios between 1:1.0 and 1:2.75, highly ordered materials were observed. There is a decrease in structural ordering when the Pluronic F127:TMOS ratio is increased from 1:3.0 to 1:4.0, the TEM images get progressively less ordered as the amount of TMOS is increased.
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Sample: la 1:0.25

Sample: lb 1:0.50

Sample: lc 1:0.75
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Sample: 1c 1:0.75

Sample: 1d 1:1.00

Sample: 1c 1:0.75

Sample: 1d 1:1.00

Sample: 1d 1:1.00

Sample: 1d 1:1.00
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Sample: 1e 1:1.25

Sample: 1e 1:1.25

Sample: 1e 1:1.25

Sample: 1e 1:1.25

Sample: 1f 1:1.50

Sample: 1f 1:1.50
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Sample: If 1:1.50

Sample: Ig 1:1.75

Sample: Ig 1:1.75

Sample: Ig 1:1.75

Sample: Ig 1:1.75

Sample: Ig 1:1.75
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Synthesis of mesoporous silica using Pluronic F127

Sample: Ih 1:2.00

Sample: li 1:2.25
Chapter 5

Synthesis of mesoporous silica using Pluronic F127

Sample: li 1:2.25

Sample: li 1:2.50

Sample: lj 1:2.25

Sample: lj 1:2.50
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Figure 5.6 TEM micrographs for calcined silica samples in series 1, prepared using 30 wt% Pluronic F127 and a P123/TMOS ratio of 1:0.25-4.00 (by mass). Representative micrographs are shown for each sample. Labels, eg 1k 1:2.75, correspond to the unique code for each sample. All scale bars are 50 nm.
Figure 5.6 TEM micrographs for calcined silicas samples in series 1, prepared using 50wt% Pluronic F127 and a F127:TMOS ratio of 1:0.25-4.00 (by mass). Representative micrographs are shown for each sample. Labels, eg 1a 1:0.25, correspond to the unique code for each material. All scale bars are 50 nm.
Table 5.3 Repeat distances from TEM images of series 1. The d spacing of the first powder X-ray diffraction peak is also included in the table for comparison to these measurements.

As with the silicas produced in chapter 4, the powder X-ray diffraction data are consistent with these silica samples having a 2d hexagonal mesoporous structure, i.e. the same as the hexagonal phase (H1) templated silicas in chapter 2 and 3. TEM studies of the most ordered silica samples show a cubic arrangement of pores in addition to the parallel fringes and hexagonal ordered pores that are observed for a 2d hexagonal system. A disordered “worm-hole” like structure is also observed for many of the samples. If the different types of TEM images observed are different projections of a single structure, there should be a constant relationship between the repeat distanced in these different projections. There are trends in the repeat distances, which are between 7 and 12 nm. In general, the hexagonal repeat distances are slightly greater than those of the cubic or parallel fringes, which are similar. The d spacing of the first powder X-ray diffraction peak is generally slightly less than the repeat distance of the hexagonal projection. There is too much scatter in the measurements, probably caused by differing amounts of beam damage done to the sample and local variation in repeat distances, to determine ratios between the repeat distances.
5.3.1.4 Summary of results for silicas in series 1

Samples 1a and 1b are disordered porous silicas. Sample 1c has a disordered cubic structure. The most ordered cubic structures are found in the Pluronic F127:TMOS ratios of 1:1.00 to 1:2.75, samples 1d to 1h. Samples 1f and 1g show the greatest long range structural order, being the only samples with three X-ray diffraction peaks, with a gradual decrease in structural ordering as the TMOS concentration is increased further. For Pluronic F127:TMOS ratios 1:3.00 to 1:4.00 the cubic structure becomes progressively more disordered until no structural ordering is observed. For Pluronic F127:TMOS ratios of 1:1.00 to 1:1.75 the pore diameter is between 7 to 8 nm, with a wall thickness of roughly 4 nm. From Pluronic F127:TMOS ratios of 1:2.00 to 1:4.00, the pore size gradually decreases from 8.8 nm to 5.0 nm, with a corresponding increase in wall thickness, from 4.3 nm to 6.0 nm.
5.3.2 Characterisation of mesoporous silicas in series 2 – vary 0.5 M HCl(aq) content

In series 2, the ratio of Pluronic F127 to TMOS was kept constant at 1:1.5 (by mass) while the amount of 0.5 M HCl(aq) was varied. The Pluronic F127 to 0.5 M HCl(aq) ratios were kept within a range that gave an I, phase for a binary mixture of Pluronic F127 and water.

5.3.2.1 Powder X-ray diffraction of the silicas in series 2

<table>
<thead>
<tr>
<th>Series label</th>
<th>Wt% Pluronic F127</th>
<th>Position of first reflection /°</th>
<th>Peak width at half height of first reflection /°</th>
<th>d spacing for first reflection /nm</th>
<th>Further peaks /°</th>
<th>Pore to pore distance for an H1 structure /±0.1 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a</td>
<td>25</td>
<td>1.06</td>
<td>~0.30</td>
<td>8.3</td>
<td>-</td>
<td>9.6</td>
</tr>
<tr>
<td>2b</td>
<td>30</td>
<td>0.90</td>
<td>0.11</td>
<td>9.9</td>
<td>-</td>
<td>11.4</td>
</tr>
<tr>
<td>2c</td>
<td>35</td>
<td>0.87</td>
<td>0.15</td>
<td>10.1</td>
<td>-</td>
<td>11.7</td>
</tr>
<tr>
<td>2d</td>
<td>40</td>
<td>0.94</td>
<td>0.22</td>
<td>9.4</td>
<td>-</td>
<td>10.9</td>
</tr>
<tr>
<td>2e</td>
<td>45</td>
<td>0.90</td>
<td>0.15</td>
<td>9.8</td>
<td>1.55, 1.81</td>
<td>12.3</td>
</tr>
<tr>
<td>2f</td>
<td>50</td>
<td>0.83</td>
<td>0.12</td>
<td>10.7</td>
<td>1.42, 1.67</td>
<td>12.3</td>
</tr>
<tr>
<td>2f</td>
<td>55</td>
<td>0.82</td>
<td>0.11</td>
<td>10.8</td>
<td>1.39, 1.59</td>
<td>12.5</td>
</tr>
<tr>
<td>2g</td>
<td>60</td>
<td>0.87</td>
<td>0.16</td>
<td>10.1</td>
<td>1.49, 1.74</td>
<td>11.7</td>
</tr>
<tr>
<td>2h</td>
<td>65</td>
<td>0.83</td>
<td>0.12</td>
<td>10.7</td>
<td>1.46, 1.67</td>
<td>12.3</td>
</tr>
</tbody>
</table>

Table 5.4 Peak positions and peak widths at half height for X-ray diffraction patterns obtained from calcined mesoporous silicas samples in series 2, prepared using varying amounts of 0.5 M HCl(aq).

Figure 5.7 shows the X-ray diffraction patterns obtained for calcined silica sample in series 2, with the data summarised in table 5.4. All samples showed at least one peak. The samples that exhibited more than one peak could be indexed to an H1 structure. No further peaks were observed at higher angles. Samples 2a and 2b both showed a single very weak peak, at slightly smaller d spacing than the other samples in the series. The FWHM of the first peaks, with the exception of sample 2a, are relatively narrow. From sample 2b to 2h, the FWHM varies within the range 0.11 – 0.22°. From sample 2a to 2h, the long range structural order gradually increases, with a second and third peak appearing for samples 2e to 2h. The third peak is a weak shoulder on the second peak. The d spacing gradually increases from sample 2a to sample 2h, 8.3 nm to 10.7 nm.

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Figure 5.7 Powder X-ray diffraction patterns obtained for calcined silica samples of series 2, prepared using varying amounts of 0.5 M HCl(aq). Plots have been displaced to allow all patterns to be clearly viewed on one plot. The plots have also been scaled in the y-axis to allow easy comparison of FWHM. The inset graph shows a magnified plot in the region of the 2nd and 3rd peaks. Labels, eg 2a (40 wt%), correspond to the unique code for each material and the weight percent of Pluronic F127 used.
5.3.2.2 Nitrogen adsorption isotherm analysis of silicas in series 2

The nitrogen adsorption/desorption isotherms and the pore size distributions obtained from them for series 2 are shown in figures 5.8 and 5.9 respectively, with the data summarised in table 5.5. The wall thickness was calculated assuming an H₁ structure.

Samples 2a has a very broad pore distribution, which tails out to 16 nm. As the TMOS content is increased, the pore size distribution narrows, with the pore diameter remaining in the range 6.8 – 7.4 nm for samples 2a to 1f. From sample 2f to 2h the pore size distribution broadens slightly, with a pore size of 8.7 nm. The general trend is for the wall thickness to decrease from sample 2a to 2h. The surface areas of all the samples are large, in the range of 757 – 914 m² g⁻¹. The pore volumes are in the range of 0.80 - 1.06 cm³ g⁻¹. The hysteresis observed in the isotherms that occurs at pressures greater than 0.4 P/P₀ is characteristic of materials containing pore with diameters greater than 3.7 nm⁵,⁶.

<table>
<thead>
<tr>
<th>Series label</th>
<th>Ratio of F127:TMOS (w/w)</th>
<th>i) Pore-pore distance from XRD / nm</th>
<th>BET surface area /m²g⁻¹ ±50 m²g⁻¹</th>
<th>Pore volume /cm³g⁻¹</th>
<th>ii) Pore size from N₂ adsorption analysis /nm</th>
<th>FWHM /nm</th>
<th>Wall thickness i-ii /nm*</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a</td>
<td>25</td>
<td>9.6</td>
<td>914</td>
<td>1.06</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2b</td>
<td>30</td>
<td>11.4</td>
<td>881</td>
<td>0.98</td>
<td>6.8±0.5</td>
<td>-</td>
<td>4.6±0.6</td>
</tr>
<tr>
<td>2c</td>
<td>35</td>
<td>11.7</td>
<td>907</td>
<td>0.98</td>
<td>7.3±0.6</td>
<td>-</td>
<td>4.4±0.7</td>
</tr>
<tr>
<td>2d</td>
<td>40</td>
<td>10.9</td>
<td>758</td>
<td>0.88</td>
<td>7.4±0.6</td>
<td>1.8</td>
<td>3.5±0.7</td>
</tr>
<tr>
<td>2e</td>
<td>45</td>
<td>12.3</td>
<td>837</td>
<td>0.90</td>
<td>7.4±0.6</td>
<td>2.2</td>
<td>4.9±0.7</td>
</tr>
<tr>
<td>1f</td>
<td>50</td>
<td>12.3</td>
<td>756</td>
<td>0.80</td>
<td>7.0±0.5</td>
<td>1.4</td>
<td>5.3±0.6</td>
</tr>
<tr>
<td>2f</td>
<td>55</td>
<td>12.5</td>
<td>985</td>
<td>1.00</td>
<td>8.7±0.9</td>
<td>1.9</td>
<td>3.8±1.0</td>
</tr>
<tr>
<td>2g</td>
<td>60</td>
<td>11.7</td>
<td>732</td>
<td>1.01</td>
<td>8.7±0.9</td>
<td>3.1</td>
<td>3.0±1.0</td>
</tr>
<tr>
<td>2h</td>
<td>65</td>
<td>12.3</td>
<td>757</td>
<td>0.91</td>
<td>8.7±0.9</td>
<td>2.5</td>
<td>3.6±1.0</td>
</tr>
</tbody>
</table>

Table 5.5 BET surface areas, pore volumes, and pore for silicas in series 2. * Wall thickness was obtained by subtracting the pore size (ii) from the pore to pore distance (i), as calculated for a H₁ structure.
Figure 5.8 Nitrogen adsorption/desorption isotherms of calcined silicas in series 2, prepared using varying amounts of 0.5 M HCl(aq). Labels, eg 2a (40 wt%), correspond to the unique code for each material and the weight percent of Pluronic F127 used. Note the plots have been displaced on the volume axis so that they all fit a single plot.
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Figure 5.9 Pore size distributions calculated from nitrogen adsorption curves of calcined silicas in series 2, prepared using varying amounts of 0.5 M HCl\textsubscript{(aq)}. Labels, eg 2a (40 wt%), correspond to the unique code for each material and the weight percent of Pluronic F127 used. Note the plots have been displaced on the dV\textsubscript{p}/dr axis so they can all be viewed clearly on one plot.

5.3.2.3 TEM studies of silicas in series 2

Figure 5.10 shows representative TEM images for silicas in series 2, with the data summarised in table 5.6. The structural order observed in the TEM images of series 2 are in agreement with the degree of structural order determined by the powder X-ray diffraction and N\textsubscript{2} adsorption isotherm data. TEM images of sample 2a show a disordered porous structure. Samples 2b to 2d show an increasing degree of structural ordering of \textit{l}\textsubscript{1} silica. Samples 2e to 2h show a well ordered mesoporous structure.
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Sample: 2a 25wt%
Sample: 2a 25wt%

Sample: 2b 30wt%
Sample: 2b 30wt%

Sample: 2b 30wt%
Sample: 2b 30wt%
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Sample: 2c 35wt%

Sample: 2d 40wt%
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Sample: 2f 55wt%

Sample: 2f 55wt%

Sample: 2g 60wt%

Sample: 2g 60wt%

Sample: 2g 60wt%

Sample: 2g 60wt%
**Figure 5.10** TEM micrographs of calcined silicas samples in series 2, prepared from 25-65wt% Pluronic F127 with a F127:TMOS ratio of 1:1.5 (by mass). Representative micrographs are shown for each sample. Labels, eg 2a 40wt%, correspond to the unique code for each material and the weight percent of Pluronic F127 used. All scale bars are 50 nm.
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<table>
<thead>
<tr>
<th>Series label</th>
<th>Wt% Pluronic F127</th>
<th>d spacing for first reflection /±0.05nm</th>
<th>TEM Parallel lines /±0.3 nm</th>
<th>TEM Hexagonal /±0.3 nm</th>
<th>TEM cubic/ ±0.3nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a</td>
<td>25</td>
<td>8.3</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2b</td>
<td>30</td>
<td>9.9</td>
<td>8.8</td>
<td>-</td>
<td>9.9</td>
</tr>
<tr>
<td>2c</td>
<td>35</td>
<td>10.1</td>
<td>7.7</td>
<td>10.1</td>
<td>8.4</td>
</tr>
<tr>
<td>2d</td>
<td>40</td>
<td>9.4</td>
<td>8.5</td>
<td>9.8</td>
<td>8.1</td>
</tr>
<tr>
<td>2e</td>
<td>45</td>
<td>9.8</td>
<td>8.4</td>
<td>9.4</td>
<td>8.2</td>
</tr>
<tr>
<td>2f</td>
<td>50</td>
<td>10.7</td>
<td>9.6</td>
<td>11.2</td>
<td>8.7</td>
</tr>
<tr>
<td>2g</td>
<td>60</td>
<td>10.1</td>
<td>9.1</td>
<td>9.4</td>
<td>9.1</td>
</tr>
<tr>
<td>2h</td>
<td>65</td>
<td>10.7</td>
<td>9.3</td>
<td>10.5</td>
<td>8.9</td>
</tr>
</tbody>
</table>

Table 5.6 Repeat distances from TEM images of series 2. The d spacing of the first powder X-ray diffraction peak is also included in the table for comparison to these measurements.

As with the silicas in series 1, the TEM images are not consistent with the 2d hexagonal structure indicated by the X-ray diffraction data. The repeat distances measured from the TEM images are between 8 and 11 nm. There is a loose relationship between the different projections. In general, the hexagonal repeat distances are slightly greater than those of the cubic or parallel fringes, which are similar. The d spacing of the first powder X-ray diffraction peak is generally slightly less the repeat distance of the hexagonal projection. There is too much scatter in the measurements, probably caused by differing amounts of beam damage done to the sample and local variation in repeat distances, to determine ratios between the repeat distances.

5.3.2.4 Summary of results for silicas in series 2

Sample 2a is a disordered porous silica. The other samples show a cubic structure. Sample 2b shows a very disordered cubic structure, which becomes progressively more ordered from sample 2a to 2d. Samples 2e to 2h show good long range, having three X-ray diffraction peaks. There is a decrease in wall thickness from 2b to 2h, 4.6 nm to 3.6 nm, accompanied by an increase in the pore diameter from 7.3 nm to 8.7 nm. The pore size distribution of sample 2a is very broad, centred on 7.0 nm. The pore size distribution narrows as the series progresses, but stays centred on 7.0 nm.
5.3.3 Characterisation of mesoporous silicas in series 3 - vary Pluronic F127 content

In series 3, the ratio of 0.5 M HCl(aq) to TMOS was kept constant at 1:1.5 (by mass) while the amount of Pluronic F127 was varied. The Pluronic F127 to 0.5 M HCl(aq) ratios were kept within the range of ratios that gave an I₃ phase for a binary mixture of Pluronic F127 and water.

5.3.3.1 Powder X-ray diffraction of the silicas in series 3

<table>
<thead>
<tr>
<th>Series label</th>
<th>Wt% Pluronic F127</th>
<th>Position of first reflection /θ ±0.02°</th>
<th>Peak width at half height of first reflection /±0.02°</th>
<th>d spacing for first reflection /±0.1 nm</th>
<th>Further peaks /θ /±0.02°</th>
<th>Pore to pore distance for an H₁ structure /±0.1 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>3a</td>
<td>25</td>
<td>0.95</td>
<td>0.19</td>
<td>9.3</td>
<td>-</td>
<td>10.8</td>
</tr>
<tr>
<td>3b</td>
<td>30</td>
<td>0.84</td>
<td>0.15</td>
<td>10.5</td>
<td>-</td>
<td>12.1</td>
</tr>
<tr>
<td>3c</td>
<td>35</td>
<td>0.86</td>
<td>0.14</td>
<td>10.2</td>
<td>-</td>
<td>11.8</td>
</tr>
<tr>
<td>3d</td>
<td>40</td>
<td>0.86</td>
<td>0.16</td>
<td>10.2</td>
<td>-</td>
<td>11.8</td>
</tr>
<tr>
<td>3e</td>
<td>45</td>
<td>0.84</td>
<td>0.12</td>
<td>10.6</td>
<td>1.43</td>
<td>12.2</td>
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<tr>
<td>3f</td>
<td>50</td>
<td>0.83</td>
<td>0.12</td>
<td>10.7</td>
<td>1.42, 1.66</td>
<td>12.3</td>
</tr>
<tr>
<td>3g</td>
<td>55</td>
<td>0.87</td>
<td>0.13</td>
<td>10.1</td>
<td>1.49</td>
<td>11.7</td>
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<tr>
<td>3h</td>
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<td>0.11</td>
<td>9.9</td>
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<tr>
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<td>0.84</td>
<td>0.11</td>
<td>10.5</td>
<td>1.41, 1.64</td>
<td>12.1</td>
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</table>

*Table 5.7* Peak positions and peak widths at half height for powder X-ray diffraction patterns obtained from calcined mesoporous silicas samples in series 3, prepared using varying amounts of Pluronic F127.

Figure 5.11 shows the X-ray diffraction patterns obtained for calcined silica samples in series 3, with the data summaries in table 5.7. All samples showed at least one peak. The samples that exhibited more than one peak could be indexed to an H₁ structure. No further peaks were observed at higher angles. Sample 3a showed a single very weak peak, at slightly smaller d spacing than the other samples in the series. The degree of long range order increases through the series. The FWHM of the first peaks decreases through the series, from sample 3a to 3h, the FWHM decreases from 0.19° to 0.11°. Samples 3e to 3h exhibit 2 or 3 peaks, showing good long range order. The d spacing for samples 3b to 3h are in the range of 9.9 nm to 10.7 nm.
Figure 5.11 Powder X-ray Diffraction patterns obtained for calcined silica samples in series 3, prepared using varying amounts of Pluronic F127. Plots have been displaced to allow all patterns to be clearly viewed on one plot. The plots have also been scaled in the y-axis to allow easy comparison of FWHM. The inset graph shows a magnified plot in the region of the 2$^\text{nd}$ and 3$^\text{rd}$ peaks. Labels, eg 2a (40wt%), correspond to the unique code for each material and wt% of Pluronic F127 used.
5.3.3.2 Nitrogen adsorption isotherm analysis of the silicas in series 3

The nitrogen adsorption/desorption isotherms and the pore size distributions obtained from them for series 3 are shown in figures 5.12 and 5.13 respectively with the data summarised in table 5.8. The wall thickness was calculated assuming an H$_1$ structure. Samples 3a has a very broad pore distribution, which tails out to 6 nm. The wall thickness decreases through the series, from 6.1 nm for sample 3b to 1.9 nm for sample 3h. This is accompanied by an increase in the pore diameter from 6.0 nm for sample 3b to 10.2 nm for sample 3h. The pore size distribution broadens slightly from 3b to 3h. The surface areas of all the samples are large, in the range of 670 – 974 m$^2$g$^{-1}$. The pore volume increases through the series, from 0.36 to 1.45 cm$^3$g$^{-1}$, as the pore diameter increases and the wall thickness decreases. The hysteresis that occurs at pressures greater than 0.4 P/P$_0$ is characteristic of materials with pore diameters greater than 3.7 nm$^5$ and not due to bottlenecking or pore blocking.

<table>
<thead>
<tr>
<th>Series label</th>
<th>Wt% Pluronic F127</th>
<th>i) Pore-pore distance from XRD/ nm</th>
<th>BET surface area /m$^2$g$^{-1}$ ±50 m$^2$g$^{-1}$</th>
<th>Pore volume /cm$^3$g$^{-1}$</th>
<th>ii) Pore size from N$_2$ adsorption analysis /nm</th>
<th>FWHM /nm</th>
<th>Wall thickness i-ii /nm*</th>
</tr>
</thead>
<tbody>
<tr>
<td>3a</td>
<td>25</td>
<td>10.8</td>
<td>670</td>
<td>0.36</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3b</td>
<td>30</td>
<td>12.1</td>
<td>729</td>
<td>0.45</td>
<td>6.0±0.4</td>
<td>1.7</td>
<td>6.1±0.5</td>
</tr>
<tr>
<td>3c</td>
<td>35</td>
<td>11.8</td>
<td>833</td>
<td>0.60</td>
<td>6.8±0.5</td>
<td>1.8</td>
<td>5.0±0.6</td>
</tr>
<tr>
<td>3d</td>
<td>40</td>
<td>11.8</td>
<td>974</td>
<td>0.76</td>
<td>7.0±0.5</td>
<td>1.8</td>
<td>4.8±0.6</td>
</tr>
<tr>
<td>3e</td>
<td>45</td>
<td>12.2</td>
<td>866</td>
<td>0.83</td>
<td>8.0±0.7</td>
<td>1.7</td>
<td>4.2±0.8</td>
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<tr>
<td>3f</td>
<td>50</td>
<td>12.3</td>
<td>756</td>
<td>0.80</td>
<td>7.0±0.5</td>
<td>1.4</td>
<td>5.3±0.6</td>
</tr>
<tr>
<td>3g</td>
<td>55</td>
<td>11.7</td>
<td>850</td>
<td>1.11</td>
<td>8.4±0.7</td>
<td>2.4</td>
<td>3.3±0.8</td>
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<tr>
<td>3h</td>
<td>60</td>
<td>11.5</td>
<td>834</td>
<td>1.29</td>
<td>9.6±1.0</td>
<td>2.3</td>
<td>1.9±1.1</td>
</tr>
</tbody>
</table>

Table 5.8 BET surface areas, pore volumes, and pore for silicas in series 3, prepared using varying amounts of Pluronic F127. * Wall thickness was obtained by subtracting the pore size (ii) from the pore to pore distance (i), as calculated for a H$_1$ structure.
Figure 5.12 Nitrogen adsorption/desorption isotherms of calcined silicas in series 3, prepared using varying amounts of Pluronic F127. Labels, eg 3a, correspond to the unique code for each material and the wt% of Pluronic F127. Note the plots have been displaced on the volume axis so that they all fit a single plot.
Figure 5.13 Pore size distributions calculated from nitrogen adsorption curves for calcined silicas in series 3, prepared using varying amounts of Pluronic F127. Labels, eg 3a, correspond to the unique code for each material, and the wt% of Pluronic F127 used. Note the plots have been displaced on the dV/dr axis so they can all be viewed clearly on one plot.
5.3.3.3 TEM studies of silicas in series 3

<table>
<thead>
<tr>
<th>Sample</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>3a</td>
<td>1:4.5, 25wt%</td>
</tr>
<tr>
<td>3b</td>
<td>1:3.5, 30wt%</td>
</tr>
</tbody>
</table>

Sample: 3a 1:4.5, 25wt%
Sample: 3b 1:3.5, 30wt%
Chapter 5

Synthesis of mesoporous silica using Pluronic F127

Sample: 3d 1:2.25 40wt%

Sample: 3d 1:2.25 40wt%

Sample: 3e 1:1.8 45wt%

Sample: 3e 1:1.8 45wt%

Sample: 3e 1:1.8 45wt%

Sample: 3e 1:1.8 45wt%
Chapter 5

Synthesis of mesoporous silica using Pluronic F127

Sample: If 1:1.50 50wt%
Sample: If 1:1.50 50wt%
Sample: If 1:1.50 50wt%
Sample: If 1:1.50 50wt%

Sample: 3f 1:1.23 55wt%
Sample: 3f 1:1.23 55wt%
Sample: 3f 1:1.23 55wt%
Sample: 3f 1:1.23 55wt%
Sample; 3f 1:1.23 55wt%

Sample; 3g 1:1.0 60wt%

Sample: 3g 1:1.0 60wt%
Figure 5.14 TEM micrographs for calcined silicas in series 3, prepared using 25-65wt% Pluronic F127 and a F127:TMOS ratio of 1:0.81-4.50 (by mass). Representative micrographs are shown for each sample. Labels, eg 3a 2.25 40wt%, correspond to the unique code for each material, the ratio of F127:TMOS, and the weight percent of Pluronic F127 used. All scale bars are 50 nm.

Figure 5.14 shows representative TEM images for silicas in series 3, with the data summarised in table 5.9. The TEM images of series 3 support degree of structural ordering of the mesoporous silica as determined by the powder X-ray diffraction and N₂ adsorption isotherm data. TEM images of sample 3a show a disordered porous structure. TEM images of sample 3b show a disordered porous structure. Samples 3c to 3f show a well ordering porous structure. Samples 3g and 3h do not appear as well ordered, contrary to the X-ray diffraction and N₂ isotherms. These samples have large pores with very thin walls, making them most susceptible to electron beam damage.
<table>
<thead>
<tr>
<th>Series label</th>
<th>Wt% Pluronic F127</th>
<th>d spacing for first reflection /±0.05nm</th>
<th>TEM Parallel lines /±0.05nm</th>
<th>TEM Hexagonal /±0.3 nm</th>
<th>TEM cubic/ ±0.3nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>3a</td>
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<td>9.3</td>
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<td>-</td>
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<td>10.5</td>
<td>8.9</td>
<td>8.3</td>
<td>10.0</td>
</tr>
</tbody>
</table>

Table 5.9 Repeat distances from TEM images of series 3. The d spacing of the first powder X-ray diffraction peak is also included in the table for comparison to these measurements.

As with the silicas in series 1, the TEM images are not consistent with the 2d hexagonal structure indicated by the X-ray diffraction data. The repeat distances measured from the TEM images are between 8 and 11 nm. There is a loose relationship between the different projections. In general, the hexagonal repeat distances are slightly greater than those of the cubic or parallel fringes, which are similar. The d spacing of the first powder X-ray diffraction peak is generally slightly less than the repeat distance of the hexagonal projection. There is too much scatter in the measurements, probably caused by differing amounts of beam damage done to the sample and local variation in repeat distances, to determine ratios between the repeat distances.
5.3.3.4 Summary of results for silicas in series 3

Samples 3a has a disordered mesoporous structure with a very broad pore distribution. The structural order increases from samples 3b to 3h, as the pore diameter increases from 6.0 nm for sample 3b to 10.2 nm for sample 3h, and the wall thickness decreases from 6.0 nm for sample 3b to 1.9 nm for sample 3h. The pore size distribution broadens slightly from 3b to 3h. The X-ray diffraction peak widths for the first peaks decreases through the series, from 0.19° for sample 3a to 0.11° for sample 3h. Samples 3e to 3h exhibit two or three X-ray diffraction peaks, showing good long range structural order.

5.3.4 Comparison of results in series 1, 2 and 3

In the experimental section a ternary diagram was used to display the compositions used in series 1, 2 and 3 (figure 5.2). By plotting the experimental data for all silica samples on a ternary diagram it was possible to compare results between series and visualise how the structure produced varies with the composition of the initial reaction mixture. What follows are ternary diagrams representing the data obtained from powder X-ray diffraction, N₂ adsorption isotherms and TEM studies. After the data were plotted on the ternary diagrams contours were drawn in by hand. The positions of the contours were determined by joining up points were the data values were within a defined range. Where no data points were available, the boundary of the contour was deduced by extrapolating measurements from surrounding points, consequently the contours can only used as an aid to visualising trends in the data.
5.3.4.1 Structural ordering observed by TEM studies

Figure 5.15 Ternary diagram representing the degree of order of the mesoporous structure from the TEM studies.

The ternary diagram in figure 5.15 shows the variation in structural ordering of the mesoporous silicas, as observed using TEM images, with initial reaction composition. The most ordered silicas are observed in a circular region centred on 25 wt% Pluronic F127, 25 wt% 0.5 M HCl$_{aq}$ and 50 wt% TMOS. Moving out of this region, the structural ordering decreases progressively, becoming very disordered at the extreme, with no discernable structural ordering.
5.3.4.2 Peak widths of the first X-ray diffraction peak

The ternary diagram in figure 5.16 shows the variation in mesoporous structural ordering as determined by half height peak width for the first X-ray diffraction peak. At very low TMOS and Pluronic F127 concentrations very disordered materials are formed. Generally, the peak widths are relatively small. The best region is the bottom left where the TMOS concentrations are low and Pluronic F127 concentrations are relatively high. There is an increase in the peak width as the TMOS concentration is increased.
5.3.4.3 Pore diameters obtained from analysis of N₂ adsorption isotherms

Figure 5.17 Ternary diagram showing the change in pore diameter with composition. Pore diameters were obtained from N₂ adsorption isotherms. n/a indicates the material was too disordered to determine an pore diameter.

Figure 5.17 shows the variation in pore diameter, as obtained from N₂ adsorption isotherms, with initial reaction mixture. The largest pores diameters are found at high Pluronic F127 concentrations and low TMOS concentrations. The pore diameter decreases with increasing TMOS concentrations and decreasing Pluronic F127 concentrations.
5.3.4.4 Pore to pore distance obtained by X-ray diffraction

Figure 5.18 shows the change in pore to pore distance, $a_o$, as a function of composition. The pore to pore distance is calculated assuming a $H_3$ structure. The shortest separations are found at the extremes of TMOS concentrations, with the largest values in the central and upper region of the diagram.
5.3.4.5 Wall thickness determined by pore size analysis and X-ray diffraction

Figure 5.19 Ternary diagram showing the change in wall thickness with composition. The wall thickness was determined from pore size analysis of N₂ adsorption isotherms and X-ray diffraction data. n/a indicates the material was too disordered to determine an accurate wall thickness.

Figure 5.19 shows the wall thickness, determined by X-ray diffraction and N₂ isotherms, as a function of composition. The wall thickness was calculated assuming an H₁ structure to allow comparisons to be made between the samples. The thinnest walls are found at bottom left side, where TMOS concentrations are low and Pluronic F127 concentrations are high. As the TMOS concentration is increased, and Pluronic F127 concentration is decreased, the walls become progressively thicker. At very low TMOS concentrations, very disordered silicas are formed; this is also true for the lowest Pluronic F127 concentration used.
5.3.4.6 Surface area obtained from BET analysis

Figure 5.20 Ternary diagram showing the change in BET surface area with composition. The lowest surface areas are at the extremes of TMOS content, where the walls are at the thickest, or where the structure is very disordered with thin walls. The highest surface areas are in the central region of the diagram.
5.3.4.7 Pore volumes obtained from N\textsubscript{2} adsorption isotherms

The three series share a common sample, if, with a composition of 42 wt% TMOS, 29 wt% 0.5 M HCl, and 29 wt% Pluronic F127. The mesoporous silica produced in this region of the ternary diagram is well-ordered. Deviation from this structure arises from the variety of changes in structure of the mesoporous silica. Figure 5.21 assesses the structural changes diagrammatically. Series 1- Change in TMOS content for a fixed ratio of Pluronic F127 to 0.5 M HCl. Changes in TMOS content have a large effect on the mesoporous structure. Decreasing the TMOS content from 42 wt% TMOS results in a gradual decrease in structural order, a decrease in pore diameter and a decrease in porosity. This resulted in the mesoporous structure having broader pores, pore size distribution, and a decrease in pore volume. Figure 5.21 shows the pore volume of silicas as a function of composition. The pore volume approximately follows the pore diameter ternary diagram. The highest pore volumes are found at the left of the diagram, where the TMOS concentrations are low and Pluronic F127 concentrations are high, where the silicas have large pores and thin walls. The pore volume decreases as the TMOS content is increased and the Pluronic F127 content decreased.

Figure 5.21 Ternary diagram showing the variation in pore volume with composition.
5.3.4.8 Summary of ternary diagram analysis

The three series share a common sample, 1f, with a composition of 42 wt% TMOS, 29 wt% 0.5 M HCl(aq) and 29 wt% Pluronic F127. The mesoporous silica produced in this region of the ternary diagram is well ordered. Deviation from this region results in a variety of changes in structure depending on the direction. Figure 5.22 summarises the structural changes diagrammatically.

Series 1 - Change in TMOS content for a fixed ratio of Pluronic F127 to 0.5 M HCl(aq)
Changes in TMOS content have a large effect on the mesoporous structure. Decreasing the TMOS content from that of sample 1f resulted in a gradual decrease in structural order, a decrease in wall thickness and a broadening of the pore size distribution. At the extreme this resulted in disordered mesoporous silica with a very broad, peakless, pore size distribution. The surface areas remain high, with a slight decrease in pore volume. Increasing the amount of TMOS resulted in the gradual decrease in structural ordering, a decrease in pore diameter and a corresponding increase in wall thickness. There is also a decrease in surface area and pore volume as expected.

Series 2 - Change in 0.5 M HCl(aq) content for a fixed ratio of Pluronic F127 to TMOS
Changing the amount of 0.5 M HCl(aq) from that used for sample 1f had a slight effect on the silica structure. There was little change in surface area and pore volume. Decreasing the 0.5 M HCl(aq) content resulted in an increase in pore diameter and a decrease in wall thickness, with a slight broadening of the pore size distribution. The structural ordering was unchanged. Increasing the 0.5 M HCl(aq) content results in slightly thicker walls, a decrease in pore diameter, and a decrease in long range ordering. At the extreme the silica becomes very disordered with a very broad pore size distribution and a very broad X-ray diffraction peak.

Series 3 - Change in Pluronic F127 content for a fixed ratio of TMOS to 0.5 M HCl(aq)
Changing the amount of Pluronic F127 from that used for sample 1f had significant effects on the silica structure. Decreasing the Pluronic F127 content results in a decrease in pore diameter and an increase in wall thickness, accompanied by a decrease in surface area and pore volume. There is also a decrease in the long range ordering. Increasing the Pluronic F127 content increases the pore diameter and decreased the wall thickness. There is a
Slight decrease in surface area but an increase in pore volume. The structural ordering is maintained.

**Series 1**
- Increasing TMOS
  - Decrease in pore size
  - Increase in wall thickness

**Series 2**
- Decreasing 0.5 M HCl\(_{\text{aq}}\)
  - Decrease in wall thickness
  - Increase in pore size

**Series 3**
- Increasing Pluronic F127
  - Increase in pore size
  - Decrease in wall thickness
  - Increase in pore volume

**Series 2**
- Increasing 0.5 M HCl\(_{\text{aq}}\)
  - Small decrease in pore size
  - Small decrease in wall thickness

**Series 1**
- Decreasing TMOS
  - Slight decrease in pore size
  - Decrease in wall thickness
  - Broadening pore size distribution

**Series 3**
- Decreasing Pluronic F127
  - Small decrease in pore size
  - Increase in wall thickness
  - Decrease in pore volume

**Figure 5.22** A diagrammatic summary of the changes that were observed in pore size, wall thickness and degree of structural ordering when the composition of the reaction mixture is changed from 29 wt% Pluronic F127, 29 wt% 0.5 M HCl\(_{\text{aq}}\), and 42 wt% TMOS, the composition at which the three series intersect.
5.4 Discussion

It can be seen from the ternary diagrams in section 5.3.4 that while cubic mesoporous silicas are formed over a wide range of composition there is a wide variation in pore diameter, wall thickness and long range structural order. In determining what controls the mesoporous structure of the silicas a number of factors have to be considered. These include liquid crystal phase behaviour of Pluronic F127 in water, the hydrolysis reactions of TMOS, geometry, space filling, and the interaction of the surfactant headgroup with Si(OH)₄. The hydrolysis and condensation of TMOS which was discussed in chapter 3, section 3.4.1, is also valid for the silicas produced in this chapter.

5.4.1 Limitations of the ternary diagram

![Figure 5.23 Ternary diagram showing the compositions of TMOS/Pluronic F127/0.5 M HCl used to produce mesoporous silica. The 2:1 and 4:1 water:TMOS molar ratio lines are shown. The phase boundaries of the binary Pluronic F127 + water mixture at 45°C are also shown.](image-url)
The 4:1 and 2:1 Water:TMOS molar ratios lines are marked on the ternary diagram in figure 5.23 showing the regions where complete hydrolysis is possible before condensation (below 4:1 line) and where some condensation is required before hydrolysis can be completed (between 4:1 and 2:1 line). The binary phase diagram of Pluronic F127 + water (figure 5.1) revealed that at 45°C, the temperature at which all the silicas were prepared, a micellar solution existed below 13 wt% Pluronic F127, a micellar cubic phase between 13-71 wt% and a micellar cubic + crystal phase above 71 wt%. These phase boundaries of the binary Pluronic F127 + water mixture are marked on the ternary diagram.

5.4.2 Geometry and Space filling

There are two important factors determining the degree of structural ordering of the mesoporous silicas; The weight percentage of Pluronic F127 and the 0.5 M HCl(aq) to TMOS ratio. In series 1 the Pluronic F127 content was fixed at 50 wt% w.r.t 0.5 M HCl(aq). The most ordered mesoporous structures were produced using a 0.5M HCl(aq):TMOS ratio range of 1:1.5 – 1.75, samples 1f and 1g. At this ratio TMOS is completely hydrolysed, giving a Si(OH)₄:H₂O mole ratio of 1:0.83 – 1.63. Decreasing the amount of TMOS below the ideal, results in a progressive decrease in structural order and broadening of the pore size distribution. At the lowest ratio used, 1:0.25, this resulted in silica with a single broad, weak X-ray diffraction peak and a pore size distribution ranged from the microporous out to 17 nm. At this ratio, after hydrolysis the Si(OH)₄:H₂O mole ratio is 1:30, so condensation happens in a dilute solution and therefore forms a highly porous framework. As the 0.5M HCl(aq):TMOS ratio is increased above the ideal, 1:1.75, the structure becomes progressively more disordered, the X-ray diffraction peaks broaden, with the 2ⁿᵈ and 3ʳᵈ peaks disappearing, but a reasonable degree of order is retained at up to the 2:1 water:TMOS hydrolysis limit. Above a 0.5 M HCl(aq):TMOS ratio of 1:2.1 there in not enough water to completely hydrolyse the TMOS. A mixture of completely and partially hydrolyses TMOS replaces the aqueous phase between the surfactant phase, solvating the hydrophilic head group. As condensation occurs water is produced, allowing further hydrolysis, which produces methanol, which may disorder the liquid crystal phase. As the 0.5 M HCl(aq):TMOS mass ratio approaches the absolute hydrolysis limit, 1:4.2, the structure formed becomes more disordered. The weight percent of Pluronic F127 also has a strong influence on the degree of structural ordering. In series 3 the 0.5M HCl(aq):TMOS ratio was kept at 1:1.5. As the weight percentage of Pluronic F127 was decreased from 50
to 25, the structural ordering gradually decreased, resulting in a very broad pore size
distribution and X-ray diffraction peak at 25wt% Pluronic F127. The silica samples
showed more ordering than those of series 2 samples with a comparable weight percent of
Pluronic F127 due to a higher percentage of TMOS. At greater than 50 wt% Pluronic
F127, in series 3, the structural ordering was increased slightly at a 0.5M HCl\(_{(aq)}\):TMOS
ratio of 1:1.5. For series 2 silicas of a comparable weight percentage of Pluronic F127 to
the series 3 silicas, they had a higher TMOS content and showed less structural ordering.
Mesoporous silicas templated from Pluronic F127 showed greater structural order as the
weight percentage of Pluronic F127 was increased, compared to mesoporous silicas
templated from Pluronic P123 which showed good structural order over a wide range of
weight percent of Pluronic P123, but the mesoporous structure became very disordered
above 60wt% Pluronic P123

5.4.3 Micropore and mesopore volume

Like Pluronic P123, Pluronic F127 has a poly oxyethylene head group, part of the which
can penetrate into the Si(0H)\(_4\)/water phase as condensation occurs, causing the silica wall
to be microporous up to a depth of \(\sim 1\) nm\(^8,9,10\). Pluronic F127 has a much larger
headgroup, EO\(_{107}\), compared to that of P123, EO\(_{20}\), which may lead to a greater degree of
microporosity. Attempts have been made to quantify the micropore volume using \(\alpha_s\) –
plots\(^7\), see appendix 1.B. There are significant errors in the calculated values of micropore
volume due an overlap in the micropore and mesopore distributions causing the micropore
volume to be underestimated, and even returning negative values when there is significant
overlap. The microporosity in the silica walls causes the BET surface area calculation to
return surface areas that are significantly greater than the true surface area. The exact
mesoporous structure has not been determined, therefore the theoretical surface area and
pore volume can’t be calculated from a geometric model.
5.4.3.1 Micropore volume for series 1

![Graph of measured total pore volume and calculated micropore volume of silicas in series 1. The micropore volume is calculated using the $\alpha_s$-plot method, see appendix 1.B.](image)

The graph in figure 5.24 shows the total pore volume, as measured by nitrogen adsorption, and micropore volume, as calculated by the $\alpha_s$-plot method, of the silicas in series 1 as a function of the Pluronic F127:TMOS ratio. At low Pluronic F127:TMOS ratios, where the mesoporous structure is very disordered, the pore size distribution is very broad with a significant overlap with the micropore distribution. This results in an underestimation of the micropore volume, which causes negative micropore volume values to be calculated.

At higher Pluronic F127:TMOS ratios there is less overlap between the micropore and mesopore distributions as the structure is more ordered, giving more accurate micropore volumes. At a Pluronic F127:TMOS ratio of 1:2.0 and greater, the pore diameter decreases and the wall thickness increases, therefore the micropore volume becomes a greater percentage of the total pore volume. The micropore volume increases to 30% of the total pore volume at a F127:TMOS ratio of 1:2.75 and above. This is expected, since the micropore volume is generated by the PEO head group of the surfactant penetrating the silica walls, hence the micropore volume is proportional to the pore radius while the while the pore volume due to the mesopore is proportional to the radius squared, therefore as the pore diameter decreases the micropore volume becomes a greater percentage of the total pore volume.
5.4.3.2 Micropore volume for series 2

The graph in figure 5.25 shows the total pore volume, as measured by nitrogen adsorption, and micropore volume, as calculated by the $\alpha_s$-plot method, of the silicas in series 2 as a function of weight percent Pluronic F127. As the weight percent of Pluronic F127 increases, there is a slight increase in pore diameter accompanied by a slight decrease in wall thickness. There is also a large increase in structural order as the weight percent of Pluronic F127 is increased. As a result there is only a slight change in total pore volume in the series. The apparent gradual increase in micropore volume present is due to gradual decrease in overlap between the mesopore and micropore distributions, allowing a more accurate micropore volume to be calculated.

5.4.3.3 Micropore volume for series 3

The graph in figure 5.26 shows the total pore volume, as measured by nitrogen adsorption, and micropore volume, as calculated by the $\alpha_s$-plot method, of the silicas in series 3 as a function of weight percent Pluronic F127. At low weight percent Pluronic F127, the walls are relatively thick and pore diameters are relatively small, resulting in a small pore volume and a high percentage of microporosity, 20-40%. As the weight percent of Pluronic F127 increases, there is a large increase in pore diameter accompanied with a
decrease in wall thickness. The structures are relatively ordered. This leads to the large increase in total pore volume seen in the graph and to the decrease in micropore volume. The error in the micropore calculation results in negative values for higher weight percent Pluronic F127 samples.

![Graph](image)

**Figure 5.26** Graph of measured total pore volume and calculated micropore volume of silicas in series 3. The micropore volume is calculated using the \( \alpha_s \) – plot method.

### 5.5 Conclusions

From a study of the ternary reaction mixture of Pluronic P127, 0.5 HCl\(_{aq}\), and TMOS, a more complete picture of the factors determine the physical structure of the silica produced was obtained. TEM, X-ray diffraction and \( N_2 \) adsorption isotherms have all proven complementary techniques in determining the structural properties of the mesoporous silicas. From the TEM and X-ray diffraction, the ordered mesoporous silicas produced in this chapter have the same cubic structure as the mesoporous silica produced from Brij 78 in Chapter 4. The mesoporous structure could be determined using high resolution TEM and electron crystallography on a well ordered sample. The pore diameters produced using Pluronic F127 are complementary to those of the Brij 78 templated silicas, which are in the range of 2.9 nm to 4.5 nm. By varying the proportions of Pluronic P127, TMOS and 0.5 M HCl\(_{aq}\), is it possible to produce mesoporous silica with pore diameters that range from 5 nm to 10 nm. and walls that range from 2 nm to 6
nm in thickness, assuming an H1 structure. These two variables, in general, are dependent on each other, thick walls are accompanied by a small pore diameter, and vice versa, but there is some degree of independence for values in the middle of the ranges. The range of pore diameters and wall thickness of the silicas synthesised in this chapter are comparable with those of SBA-16 silicas synthesised by Stucky et al.\textsuperscript{2}, using 3-6 wt% Pluronic F127 and tetraethoxy silane under acidic conditions. Whereas the pore diameter and wall thickness of SBA-16 silicas are controlled with the synthesis temperature, the structural parameters of the mesoporous silicas synthesised in this chapter are controlled using the ratio of reactants at a fixed synthesis temperature.

Similarly to the H1-SiO2 produced in Chapter 3 using Pluronic P123, the most ordered samples were formed when there is relatively little water left after the TMOS is hydrolysed. The most ordered mesoporous structures had a TMOS:water molar ratios of 1:4.8 – 5.6, giving a \textquotedblleft Si(OH)4 \textquotedblright:water molar ratio of 1:0.8 – 1.6 after complete hydrolysis. Below this ratio, the more water present, the more disordered the mesoporous structure, but with less water there is a slight decrease in structural order. Mesoporous silica templated with Pluronic P123 are well ordered over a range of weight percent of Pluronic P123, but become very disordered above 60 wt% Pluronic P123, but silicas templated from Pluronic F127 show an increasing degree of structural order as the weight percent of Pluronic F127 is increased.

5.6 References


Chapter 6

Synthesis of Mesoporous Silica using Pluronic P123 and F127 with Cosolvents/Cosurfactants
6.1 Background and objectives

The use of small hydrophobic molecules to swell the hydrophobic core of micelles allows the synthesis of ordered mesoporous silicas with larger pore diameter than those templated using surfactant alone. Work by Stucky et al. used 1,3,5 trimethyl benzene (TMB) as a swelling agent with a micellar solution of Pluronic P123 to produce mesoporous silica, designated SBA-15, with larger pore diameters than when using Pluronic P123 alone. They used a 3 wt% Pluronic P123 solution with a fixed mass of Pluronic P123, TEOS and acidified water, while the Pluronic P123:TMB mass ratio was varied between 1:0 and 1:1.5. This resulted in a pore diameter between 10 nm and 30 nm, which was proportional to the amount of trimethyl benzene added. Butanol, pentanol and hexanol were used as swelling agents in research by Feng et al. The silicas were prepared using 25 wt% Pluronic P123 or F127 (w.r.t to acidified water content) using the Attard synthesis. The mass of surfactant, TMOS and acidified water were kept constant while the mass ratio of surfactant:alcohol was varied between 1:0.49 and 1:0.72. The pore diameter was proportional to the amount of alcohol added and to the chain length of the alcohol, but the diameter only ranged between 7.7 and 10.6 nm, not showing the extensive swelling of the hydrophobic core observed by Stucky et al. with dilute solutions and trimethyl benzene.

There has also been interest in using a mixture of surfactants with the same tail-group size but different headgroup sizes as templates for mesoporous silica, allowing control of the micelle curvature, hence structure formed, unit cell parameter, and pore size. The micellar solutions of 5 wt% surfactant mixtures of C_{12}EO_x, C_{16}EO_x, C_{18}EO_x and EO_xPO_{70}EO_x were used as templates, where x is the average number of EO units achieved by blending the available surfactants, to produce a range of hexagonal and cubic mesoporous silica structures. J. D. Holmes et al. used mixtures of Pluronic P123 (EO_{20}PO_{70}EO_{20}) and Pluronic P65 (EO_{20}PO_{30}EO_{20}) as templates for H_1 mesoporous silica using the Attard method. By varying the mixture they were able to tune the pore diameter between the values for the two surfactants individually, 7.0 nm and 4.6 nm, as the volume of the hydrophobic core was varied.

In this chapter the aim was to use a range of cosolvents and cosurfactants to access pore size/wall thickness combinations for mesoporous silica that were not accessible when using Pluronic P123 or F127 alone as the templates in chapters 3 and 5 respectively.
The work presented in this chapter used a range of organic molecules of varying hydrophobicities as cosolvents with either 50 wt% (w.r.t 0.5 M HCl\text{aq}) Pluronic P123 or F127 as the template. A series of silica samples were prepared using surfactant:cosolvent ratios in the range of 1:0.13 to 1:1 for each additive. The cosolvents used were 1,3,5 trimethyl benzene, 1-decanol, ethanediol, 1,3 propanediol, 1,4 butanediol and 2,2 dimethoxy propane. Mixtures of Pluronic P123 or F127 with Brij 72 (C_{16}EO_{2}), Brij 76 (C_{18}EO_{10}), and Brij 78 (C_{18}EO_{20}), were also used as direct templates. There is a large difference in size between the Brij and Pluronic surfactants that may have caused them to act more like cosolvents than cosurfactants, particularly with Pluronic F127.

### 6.3 Experimental

#### 6.1.1 Preparation of mesoporous silica

The route followed for preparing mesoporous silica was based on a method described by Attard et.al\textsuperscript{5}. Either Pluronic F127 or P123, which ever was required, and Brij cosurfactant, if it was required, was dissolved in TMOS with gentle heating in a sealed flask. The resulting mixture was left to cool to room temperature and the required amount of organic additive and 0.5 M HCl\text{aq} was then added. After leaving the hydrolysis reaction to proceed for about 1 minute the methanol produced by the hydrolysis was removed on a rotary evaporator, taking 10-20 min. Removal was determined by visual inspection. After methanol removal, the silica gel was cured in sealed reaction flask in an oven at 45°C for one week. Surfactant removal was achieved by calcination in a tube furnace at 450°C under N\textsubscript{2} for 7 hours, followed by O\textsubscript{2} for 15 hours (heating rate 10°C min\textsuperscript{-1}).

For Pluronic P123 with cosolvents/cosurfactants, the reaction composition was kept constant at 2.5g TMOS, 1.67g Pluronic P123 and 1.67g 0.5 M HCl\text{aq}. This gives a 50 wt% Pluronic P123 w.r.t. 0.5 M HCl\text{aq} with a P123:TMOS ratio of 1:1.5 (w/w), the same as sample 1f in chapter 3. The ratio of Pluronic P123:cosolvent/cosurfactant was then varied between 1:0.13 and 1:1. The additives used were 1,3,5 trimethyl benzene, 1-decanol, 1.2 ethanediol, 1.3 propanediol, 1.4 butanediol, 2.2 dimethoxy propane. Brij 72.
Chapters Synthesis of Mesoporous Silica using Pluronic P123 and F127 with Cosolvents/Cosurfactants

Brij 76, and Brij 78. For Pluronic P123 with Brij 78, a second series was produced where the total surfactant mass was kept at 1.67g with the Pluronic P123:Brij 78 ratio varied between 1:0.13 and 1:1.

For Pluronic F127 with cosolvents/cosurfactants, the reaction composition was kept constant at 2.5g TMOS, 1.43g Pluronic F127 and 1.43g 0.5 M HCl\(_{aq}\). This gives a 50 wt% Pluronic F127 w.r.t. 0.5 M HCl\(_{aq}\) with a F127:TMOS ratio of 1:1.75 (w/w), the same as sample 1g in chapter 5. The ratio of Pluronic F127:cosolvent/cosurfactant was then varied between 1:0.13 and 1:1. The additives used were 1,3,5 trimethyl benzene, 1-decanol, Brij 72, Brij 76 and Brij 78.

The compositions of all the samples prepared are listed in appendix 2. The error in a sample composition is ± 0.5 % (by mass) for each component. Each sample is given a unique label, the first letter, either P or F, denotes that Pluronic P123 or F127 was used, respectively, the two numbers denote the ratio of surfactant to cosolvent/cosurfactant used, 13,25,38,50 and 1 correspond to ratios of 1:0.13, 1:0.25, 1:0.38, 1:0.50, 1:1. The last three letters are abbreviations for the cosolvent/cosurfactant used either 1,3,5 trimethyl benzene (TMB), 1-decanol (DEC), ethanediol (ETD), 1,3 propanediol (PD), 1,4 butanediol (BUD), 2,2 dimehoxy propane (DMP), Brij 72 (B72), Brij 76 (B76) or Brij 78 (B78). In this chapter, the phrase "concentration of surfactant" is used to denote the weight percentage (wt%) of surfactant with respect to the acid solution content only. For example, a reaction mixture containing 0.9 g of TMOS, 0.5 g of Pluronic F127 and 0.5 g of 0.5 M HCl was said to have a surfactant concentration of 50 wt%.
6.3.3 Characterisation of mesoporous silicas

Characterisation was carried out by small angle powder X-ray diffraction and nitrogen adsorption isotherms following the procedures outlined in appendix 1.

6.4 Results

6.4.3 Pluronic P123 with cosolvents/copolymers

6.4.3.1 Pluronic P123 with 1,3,5 trimethyl benzene

6.4.3.1.1 Powder X-ray diffraction of silica

Figure 6.1 shows the powder X-ray diffraction patterns for the calcined silica samples with the data summarised in table 6.1. All samples, except PITMB, showed three peaks that could be indexed to a $H_1$ structure. As the quantity of TMB is increased, the pore separation increases gradually from 10.1 nm to 12.6 nm. There is a gradual decrease in the intensity of the first peak relative to the background, along with a broadening of the 2$^\text{nd}$ and 3$^\text{rd}$ peaks. At the highest TMB concentrations the structure is totally disordered, no X-ray peak in present.

<table>
<thead>
<tr>
<th>Series label</th>
<th>Ratio of P123: TMB (w/w)</th>
<th>Position of first reflection /°$2\theta$ $\pm0.02^\circ$</th>
<th>Peak width at half height of first reflection /°$2\theta$ $\pm0.02^\circ$</th>
<th>d spacing for first reflection / nm</th>
<th>Further peaks and indexing /°$2\theta$ $\pm0.02^\circ$</th>
<th>Pore to pore distance for an $H_1$ structure / nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>P123REF</td>
<td>1:0</td>
<td>1.01</td>
<td>0.15</td>
<td>8.74±0.1</td>
<td>1.73, 2.01</td>
<td>10.1±0.10</td>
</tr>
<tr>
<td>P25TMB</td>
<td>1:0.25</td>
<td>0.97</td>
<td>0.17</td>
<td>9.13±0.1</td>
<td>1.63, 1.94</td>
<td>10.5±0.10</td>
</tr>
<tr>
<td>P50TMB</td>
<td>1:0.50</td>
<td>0.81</td>
<td>0.12</td>
<td>10.88±0.15</td>
<td>1.41, 1.62</td>
<td>12.6±0.15</td>
</tr>
<tr>
<td>PITMB</td>
<td>1:1.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 6.1 Peak positions and peak widths at half height for X-ray diffraction patterns obtained from calcined mesoporous silicas prepared from Pluronic P123 with 1,3,5 trimethyl benzene.
6.4.3.1.2 Nitrogen adsorption/desorption isotherm analysis of silicas

The nitrogen adsorption/desorption isotherms and the pore size distributions obtained from them are shown in figure 6.2 and 6.3 respectively, with the data summarised in table 6.2. As the quantity of TMB is increased, the pore diameter is gradually increased from 8.7 nm to 11.4 nm. This is also accompanied by an increase in the FWHM of the pore size distribution. The maximum pore diameter of 11.4 nm is significantly greater than the maximum pore diameter of 10.0 nm in chapter 3. At the highest P123:TMB ratio of 1:1, the pore size distribution becomes very broad with no peak, from the microporous region it tails out to 3.5 nm.

<table>
<thead>
<tr>
<th>Series label</th>
<th>Ratio of P123: TMB (w/w)</th>
<th>i) Pore-pore distance from XRD/ nm</th>
<th>BET surface area /m²g⁻¹ ±50 m²g⁻¹</th>
<th>ii) Pore size from N₂ adsorption analysis /nm</th>
<th>FWHM /nm</th>
<th>Wall thickness i-ii /nm*</th>
</tr>
</thead>
<tbody>
<tr>
<td>P123REF</td>
<td>1:0</td>
<td>10.1±0.10</td>
<td>725</td>
<td>8.7±0.9</td>
<td>1.9</td>
<td>1.4±1.0</td>
</tr>
<tr>
<td>P25TMB</td>
<td>1:0.25</td>
<td>10.5±0.10</td>
<td>776</td>
<td>9.6±1.0</td>
<td>3.6</td>
<td>0.9±1.1</td>
</tr>
<tr>
<td>P50TMB</td>
<td>1:0.5</td>
<td>12.6±0.15</td>
<td>728</td>
<td>11.4±1.3</td>
<td>3.4</td>
<td>1.2±1.4</td>
</tr>
<tr>
<td>P1TMB</td>
<td>1:1.0</td>
<td>-</td>
<td>619</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 6.2 BET surface areas, pore volumes, and pore diameter for silicas from Pluronic P123 with 1,3,5 trimethyl benzene. * Wall thickness was obtained by subtracting the pore size (ii) from the pore to pore distance (i).
Figure 6.2 Nitrogen adsorption/desorption isotherms of calcined silicas, prepared using Pluronic P123 with 1,3,5 trimethyl benzene. Note the plots have been displaced on the volume axis so that they all fit on one plot. Labels on the right correspond to a unique code for each sample.

Figure 6.3 Pore size distributions calculated from nitrogen adsorption isotherms of calcined silicas prepared using Pluronic P123 with 1,3,5 trimethyl benzene. Note the plots have been displaced on the dV_p/dr axis so they can all be viewed clearly on one plot. Labels on the right correspond to a unique code for each sample.
6.4.3.2 Pluronic P123 with 1-decanol

6.4.3.2.1 Powder X-ray diffraction of silica

Figure 6.4 shows the powder X-ray diffraction patterns for the calcined silica samples, with the data summarised in Table 6. The addition of 1-decanol results in a single X-ray peak, that is much broader than that of the sample without decanol, at a much lower d spacing. For a P123:decanol ratio of 1:0.25 and 1:0.50 the d spacing is ~5 nm, but at 1:1 it increases to 7.6 nm.

<table>
<thead>
<tr>
<th>Series label</th>
<th>Ratio of P123: Decanol (w/w)</th>
<th>Position of first reflection /2θ ±0.02°</th>
<th>Peak width at half height of first reflection /±0.02°</th>
<th>d spacing for first reflection / nm</th>
<th>Further peaks and indexing /2θ ±0.02°</th>
<th>Pore to pore distance for an H1 structure / nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>P123REF</td>
<td>1:0</td>
<td>0.99</td>
<td>0.16</td>
<td>8.9 ± 0.10</td>
<td>1.70, 1.99</td>
<td>10.3 ± 0.10</td>
</tr>
<tr>
<td>P25DEC</td>
<td>1:0.25</td>
<td>1.97</td>
<td>0.35</td>
<td>4.48 ± 0.05</td>
<td>-</td>
<td>5.2 ± 0.05</td>
</tr>
<tr>
<td>P50DEC</td>
<td>1:0.50</td>
<td>2.07</td>
<td>0.39</td>
<td>4.27 ± 0.05</td>
<td>-</td>
<td>4.9 ± 0.05</td>
</tr>
<tr>
<td>P1DEC</td>
<td>1:1.0</td>
<td>1.34</td>
<td>0.44</td>
<td>6.59 ± 0.05</td>
<td>-</td>
<td>7.6 ± 1.0</td>
</tr>
</tbody>
</table>

Table 6.3 Peak positions and peak widths at half height for X-ray diffraction patterns obtained from calcined mesoporous silicas prepared from Pluronic P123 with decanol.

Figure 6.4 Powder X-ray diffraction patterns obtained for calcined silica, prepared from Pluronic P123 with 1-decanol. Plots have been displaced to allow all patterns to be clearly viewed on one plot. The plots have also been scaled in the y-axis to allow easy comparison of FWHM. Labels on the right correspond to a unique code for each sample.
6.4.3.2.2 Nitrogen adsorption/desorption isotherm analysis of silicas

The nitrogen adsorption/desorption isotherms and the pore size distributions obtained from them are shown in figure 6.5 and 6.6 respectively, with the data summarised in table 6.4. The addition of 1-decanol causes the loss of ordered structure. The pore size distributions are very broad with no peak, from the micropore region tailing out to 5, 9, and 20 nm for P123:decanol ratios of 1:0.25, 1:0.50 and 1:1.0 respectively.

<table>
<thead>
<tr>
<th>Series label</th>
<th>Ratio of P123: Decanol (w/w)</th>
<th>i) Pore-pore distance from XRD/ nm</th>
<th>BET surface area /m²g⁻¹ ±50 m²g⁻¹</th>
<th>Pore volume /±0.05 cm³g⁻¹</th>
<th>i) Pore size from N₂ adsorption analysis /nm</th>
<th>FWHM /nm</th>
<th>Wall thickness i-ii /nm*</th>
</tr>
</thead>
<tbody>
<tr>
<td>P123REF</td>
<td>1:0</td>
<td>10.3±0.10</td>
<td>725</td>
<td>0.97</td>
<td>8.7±0.9</td>
<td>1.9</td>
<td>1.6±1.0</td>
</tr>
<tr>
<td>P25DEC</td>
<td>1:0.25</td>
<td>5.2±0.05</td>
<td>480</td>
<td>0.31</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>P50DEC</td>
<td>1:0.5</td>
<td>4.9±0.05</td>
<td>535</td>
<td>0.35</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>P1DEC</td>
<td>1:1.0</td>
<td>7.6±1.0</td>
<td>555</td>
<td>0.57</td>
<td>-</td>
<td>-</td>
<td>-</td>
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</tbody>
</table>

Table 6.4 BET surface areas, pore volumes, and pore diameter for silicas from Pluronic P123 with decanol. * Wall thickness was obtained by subtracting the pore size (ii) from the pore to pore distance (i).

Figure 6.5 Nitrogen adsorption/desorption isotherms of calcined silicas, prepared using Pluronic P123 with 1-decanol. Note the plots have been displaced on the volume axis so that they all fit on one plot. Labels on the right correspond to a unique code for each sample.
Figure 6.6 Pore size distributions calculated from nitrogen adsorption isotherms of calcined silicas prepared using Pluronic P123 with 1-decanol. Note the plots have been displaced on the dVp/dr axis so they can all be viewed clearly on one plot. Labels on the right correspond to a unique code for each sample.

6.4.3.3 Pluronic P123 with ethanediol

6.4.3.3.1 Powder X-ray diffraction of silica

Figure 6.7 shows the powder X-ray diffraction patterns obtained for the calcined silica samples, with the data summarised in Table 6.5. All samples showed at least one peak. Those that showed further peaks could be indexed to a H₁ structure. At P123:ethanediol ratios of 1:0.25 and 1:0.50, the pore separation is 10.5 nm, but at 1:1 the pore separation increases to 11.3 nm with a slight broadening of the 1ˢᵗ peak and merging of the 2ⁿᵈ and 3ʳᵈ peak.

<table>
<thead>
<tr>
<th>Series label</th>
<th>Ratio of P123: Ethanediol (w/w)</th>
<th>Position of first reflection /2θ ±0.02°</th>
<th>Peak width at half height of first reflection /±0.02°</th>
<th>d spacing for first reflection / nm</th>
<th>Further peaks and indexing /2θ ±0.02°</th>
<th>Pore to pore distance for an H₁ structure / nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>P123REF</td>
<td>1:0</td>
<td>0.99</td>
<td>0.16</td>
<td>8.9±0.1</td>
<td>1.70, 1.99</td>
<td>10.3±0.1</td>
</tr>
<tr>
<td>P25ETD</td>
<td>1:0.25</td>
<td>0.97</td>
<td>0.14</td>
<td>9.1±0.1</td>
<td>1.66, 1.92</td>
<td>10.5±0.1</td>
</tr>
<tr>
<td>P50ETD</td>
<td>1:0.50</td>
<td>0.96</td>
<td>0.14</td>
<td>9.2±0.1</td>
<td>1.65, 1.91</td>
<td>10.6±0.1</td>
</tr>
<tr>
<td>PIETD</td>
<td>1:1.0</td>
<td>0.90</td>
<td>0.15</td>
<td>9.8±0.1</td>
<td>1.79</td>
<td>11.3±0.1</td>
</tr>
</tbody>
</table>

Table 6.5 Peak positions and peak widths at half height for X-ray diffraction patterns obtained from calcined mesoporous silicas prepared from Pluronic P123 with ethanediol.
6.4.3.3.2 Nitrogen adsorption/desorption isotherm analysis of silicas

The nitrogen adsorption/desorption isotherms and the pore size distributions obtained from them are shown in figure 6.8 and 6.9 respectively, with the data summarised in table 6.6. As the quantity of ethanediol is increased the pore diameter decreases from 8.7 to 6.8 nm, with a small decrease in the peak width. The wall thickness increases from 1.6 nm to 4.5 nm. There is a corresponding decrease in pore volume and surface area.

<table>
<thead>
<tr>
<th>Series label</th>
<th>Ratio of P123: Ethanediol (w/w)</th>
<th>i) Pore-pore distance from XRD/ nm</th>
<th>BET surface area /m²g⁻¹</th>
<th>Pore volume /±0.05 cm³g⁻¹</th>
<th>ii) Pore size from N₂ adsorption analysis /nm</th>
<th>FWHM /nm</th>
<th>Wall thickness i-ii /nm*</th>
</tr>
</thead>
<tbody>
<tr>
<td>P123REF</td>
<td>1:0</td>
<td>10.3±0.1</td>
<td>725</td>
<td>0.97</td>
<td>8.7±0.9</td>
<td>1.9</td>
<td>1.6±1.0</td>
</tr>
<tr>
<td>P25ETD</td>
<td>1:0.25</td>
<td>10.5±0.1</td>
<td>659</td>
<td>0.90</td>
<td>7.5±0.6</td>
<td>1.5</td>
<td>3.0±0.7</td>
</tr>
<tr>
<td>P50ETD</td>
<td>1:0.5</td>
<td>10.6±0.1</td>
<td>651</td>
<td>0.92</td>
<td>7.6±0.6</td>
<td>1.8</td>
<td>3.0±0.7</td>
</tr>
<tr>
<td>P1ETD</td>
<td>1:1.0</td>
<td>11.3±0.1</td>
<td>662</td>
<td>0.89</td>
<td>6.8±0.5</td>
<td>1.6</td>
<td>4.5±0.5</td>
</tr>
</tbody>
</table>

Table 6.6 BET surface areas, pore volumes, and pore diameter for silicas from Pluronic P123 with ethanediol.* Wall thickness was obtained by subtracting the pore size (ii) from the pore to pore distance (i).

Figure 6.8 Nitrogen adsorption/desorption isotherms of calcined silicas, prepared using Pluronic P123 with ethanediol. Note the plots have been displaced on the volume axis so that they all fit on one plot. Labels on the right correspond to a unique code for each sample.
Figure 6.9 Pore size distributions calculated from nitrogen adsorption isotherms of calcined silicas prepared using Pluronic P123 with ethanediol. Note the plots have been displaced on the dV/dP axis so they can all be viewed clearly on one plot. Labels on the right correspond to a unique code for each sample.

6.4.3.4 Pluronic P123 with 1,3 propanediol

6.4.3.4.1 Powder X-ray diffraction of silica

Figure 6.10 shows the powder X-ray diffraction patterns for the calcined silica samples, with the data summarised in table 6.7. All samples showed at least one peak. Those that showed further peaks could be indexed to a H structure. With the addition of propanediol the pore separation decreases to 9.4 nm. Increasing the propanediol cause an increase in the peak width of the 1st peak and the loss of the 2nd and 3rd peaks.

<table>
<thead>
<tr>
<th>Series label</th>
<th>Ratio of P123:Propanediol (w/w)</th>
<th>Position of first reflection /θ ±0.02°</th>
<th>Peak width at half height of first reflection /±0.02°</th>
<th>d spacing for first reflection / nm</th>
<th>Further peaks and indexing /θ ±0.02°</th>
<th>Pore to pore distance for an H structure / nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>P123REF</td>
<td>1:0</td>
<td>0.99</td>
<td>0.16</td>
<td>8.9±0.1</td>
<td>1.70, 1.99</td>
<td>10.3±0.1</td>
</tr>
<tr>
<td>P25PD</td>
<td>1:0.25</td>
<td>1.09</td>
<td>0.15</td>
<td>8.1±0.1</td>
<td>1.90, 2.17</td>
<td>9.4±0.1</td>
</tr>
<tr>
<td>P50PD</td>
<td>1:0.50</td>
<td>1.07</td>
<td>0.16</td>
<td>8.3±0.1</td>
<td>1.87, 2.16</td>
<td>9.6±0.1</td>
</tr>
<tr>
<td>P1PD</td>
<td>1:1.0</td>
<td>1.1</td>
<td>0.27</td>
<td>8.0±0.1</td>
<td>-</td>
<td>9.3±0.1</td>
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</tbody>
</table>

Table 6.7 Peak positions and peak widths at half height for X-ray diffraction patterns obtained from calcined mesoporous silicas prepared from Pluronic P123 with propanediol.
Figure 6.10 Powder X-ray diffraction patterns obtained for calcined silica, prepared from Pluronic P123 with propanediol. Plots have been displaced to allow all patterns to be clearly viewed on one plot. The plots have also been scaled in the y-axis to allow easy comparison of FWHM. The inset graph shows a magnified plot in the region of the 2nd and 3rd peaks. Labels on the right correspond to a unique code for each sample.

6.4.3.4.2 Nitrogen adsorption/desorption isotherm analysis of silicas

The nitrogen adsorption/desorption isotherms and the pore size distributions obtained from them are shown in figure 6.11 and 6.12 respectively, with the data summarised in table 6.8. As the quantity of propanediol is increased the pore diameter decreases from 8.7 to 5.0 nm, with a decrease in the peak width, except for the greater propanediol content where the peak width increases. The wall thickness increases from 1.6 nm to 4.3 nm. There is a corresponding decrease in pore volume and surface area.

<table>
<thead>
<tr>
<th>Series label</th>
<th>Ratio of P123: Propanediol (w/w)</th>
<th>i) Pore-pore distance from XRD/ nm</th>
<th>BET surface area / m²g⁻¹</th>
<th>Pore volume / ±0.05 cm³g⁻¹</th>
<th>ii) Pore size from N₂ adsorption analysis /nm</th>
<th>FWHM / nm</th>
<th>Wall thickness i-ii / nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>P123REF</td>
<td>1:0</td>
<td>10.3±0.1</td>
<td>725</td>
<td>0.97</td>
<td>8.7±0.9</td>
<td>1.9</td>
<td>1.6±1.0</td>
</tr>
<tr>
<td>P25PD</td>
<td>1:0.25</td>
<td>9.4±0.1</td>
<td>612</td>
<td>0.73</td>
<td>6.3±0.5</td>
<td>1.1</td>
<td>2.9±0.6</td>
</tr>
<tr>
<td>P50PD</td>
<td>1:0.5</td>
<td>9.6±0.1</td>
<td>609</td>
<td>0.68</td>
<td>5.6±0.4</td>
<td>1.1</td>
<td>4.0±0.5</td>
</tr>
<tr>
<td>P1PD</td>
<td>1:1.0</td>
<td>9.3±0.1</td>
<td>544</td>
<td>0.56</td>
<td>5.0±0.3</td>
<td>2.5</td>
<td>4.3±0.4</td>
</tr>
</tbody>
</table>

Table 6.8 BET surface areas, pore volumes, and pore diameter for silicas from Pluronic P123 with propanediol * Wall thickness was obtained by subtracting the pore size (ii) from the pore to pore distance (i).
Figure 6.11 Nitrogen adsorption/desorption isotherms of calcined silicas, prepared using Pluronic P123 with propanediol. Note the plots have been displaced on the volume axis so that they all fit on one plot. Labels on the right correspond to a unique code for each sample.

Figure 6.12 Pore size distributions calculated from nitrogen adsorption isotherms of calcined silicas prepared using Pluronic P123 with propanediol. Note the plots have been displaced on the $dV_p/dr$ axis so they can all be viewed clearly on one plot. Labels on the right correspond to a unique code for each sample.
6.4.3.5 Pluronic P123 with 1,4 butanediol

6.4.3.5.1 Powder X-ray diffraction of silica

Figure 6.13 shows the powder X-ray diffraction patterns for the calcined silica samples, with the data summarised in table 6.9. All samples, except P1BUD, showed at least one peak. Those that showed further peaks could be indexed to a H$_1$ structure. As the quantity of butanediol is increased, the pore separation increases from 10.3 nm to 8.5 nm. At the highest P123:butanediol ratio of 1:1, the 2$^{\text{nd}}$ and 3$^{\text{rd}}$ peaks disappear.

<table>
<thead>
<tr>
<th>Series label</th>
<th>Ratio of P123: Butanediol (w/w)</th>
<th>Position of first reflection /2(\theta) ±0.02°</th>
<th>Peak width at half height of first reflection /±0.02°</th>
<th>d spacing for first reflection / nm</th>
<th>Further peaks and indexing /2(\theta) ±0.02°</th>
<th>Pore to pore distance for an H$_1$ structure / nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>P123REF</td>
<td>1:0</td>
<td>0.99</td>
<td>0.16</td>
<td>8.9±0.1</td>
<td>1.70, 1.99</td>
<td>10.3±0.1</td>
</tr>
<tr>
<td>P25BUD</td>
<td>1:0.25</td>
<td>1.12</td>
<td>0.16</td>
<td>7.9±0.1</td>
<td>1.98, 2.24</td>
<td>9.1±0.1</td>
</tr>
<tr>
<td>P50BUD</td>
<td>1:0.50</td>
<td>1.07</td>
<td>0.15</td>
<td>8.3±0.1</td>
<td>1.87, 2.16</td>
<td>9.6±0.1</td>
</tr>
<tr>
<td>P1BUD</td>
<td>1:1.0</td>
<td>1.2</td>
<td>0.15</td>
<td>7.3±0.1</td>
<td>-</td>
<td>8.5±0.1</td>
</tr>
</tbody>
</table>

Table 6.9 Peak positions and peak widths at half height for X-ray diffraction patterns obtained from calcined mesoporous silicas prepared from Pluronic P123 with butanediol.

Figure 6.13 Powder X-ray Diffraction patterns obtained for calcined silica, prepared from Pluronic P123 with butanediol. Plots have been displaced to allow all patterns to be clearly viewed on one plot. The plots have also been scaled in the y-axis to allow easy comparison of FWHM. The inset graph shows a magnified plot in the region of the 2$^{\text{nd}}$ and 3$^{\text{rd}}$ peaks. Labels on the right correspond to a unique code for each sample.
6.4.3.5.2 Nitrogen adsorption/desorption isotherm analysis of silicas

The nitrogen adsorption/desorption isotherms and the pore size distributions obtained from them are shown in figure 6.14 and 6.15 respectively, with the data summarised in table 6.10. As the quantity of butanediol is increased the pore diameter decreases from 8.7 nm to 4.2 nm with decrease in the peak width, except for the greater butanediol content where the peak width increases. The wall thickness increases from 1.6 nm to 4.3 nm. There is a corresponding decrease in pore volume and surface area.

<table>
<thead>
<tr>
<th>Series label</th>
<th>Ratio of P123: Butanediol (w/w)</th>
<th>i) Pore-pore distance from XRD/ nm</th>
<th>BET surface area / m² g⁻¹ ±0.05 m² g⁻¹</th>
<th>Pore volume / cm³ g⁻¹</th>
<th>ii) Pore size from N₂ adsorption analysis / nm</th>
<th>FWHM / nm</th>
<th>Wall thickness t-1 / nm*</th>
</tr>
</thead>
<tbody>
<tr>
<td>P123REF</td>
<td>1:0</td>
<td>10.3±0.1</td>
<td>725</td>
<td>0.97</td>
<td>8.7±0.9</td>
<td>1.9</td>
<td>1.6±1.0</td>
</tr>
<tr>
<td>P25BUD</td>
<td>1:0.25</td>
<td>9.1±0.1</td>
<td>665</td>
<td>0.76</td>
<td>5.7±0.5</td>
<td>1.3</td>
<td>3.4±0.6</td>
</tr>
<tr>
<td>P50BUD</td>
<td>1:0.5</td>
<td>9.6±0.1</td>
<td>645</td>
<td>0.71</td>
<td>6.3±0.5</td>
<td>1.0</td>
<td>3.3±0.6</td>
</tr>
<tr>
<td>P1BUD</td>
<td>1:1.0</td>
<td>8.5±0.1</td>
<td>684</td>
<td>0.55</td>
<td>4.2±0.2</td>
<td>2.4</td>
<td>4.3±0.3</td>
</tr>
</tbody>
</table>

Table 6.10 BET surface areas, pore volumes, and pore diameter for silicas from Pluronic P123 with butanediol.* Wall thickness was obtained by subtracting the pore size (ii) from the pore to pore distance (i).

Figure 6.14 Nitrogen adsorption/desorption isotherms of calcined silicas, prepared using Pluronic P123 with butanediol. Note the plots have been displaced on the volume axis so that they all fit on one plot. Labels on the right correspond to a unique code for each sample.
Chapter 6 Synthesis of Mesoporous Silica using Pluronic P123 and P127 with Cosolvents/Cosurfactants

6.4.3.6 Pluronic P123 with 2,2 dimethoxy propane

6.4.3.6.1 Powder X-ray diffraction of silica

Figure 6.16 shows the powder X-ray diffraction patterns for the calcined silica, with the data summarised in table 6.11. Also samples showed three or four peaks that could be indexed to an H1 structure. The addition of 2,2 dimethoxy propane resulted in a shift in the pore separation to 10.9 nm with a decrease in the 1\textsuperscript{st} peak width to 0.13°. The 2\textsuperscript{nd} and 3\textsuperscript{rd} peaks became better resolved and a 4\textsuperscript{th} peak was also present, indicating better long range order in the structure.

<table>
<thead>
<tr>
<th>Series label</th>
<th>Ratio of P123: diMeO propane (w/w)</th>
<th>Position of first reflection /2θ ±0.02°</th>
<th>Peak width at half height of first reflection /±0.02°</th>
<th>d spacing for first reflection /± 0.05 nm</th>
<th>Further peaks and indexing /2θ ±0.02°</th>
<th>Pore to pore distance for an H1 structure /±nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>P123REF</td>
<td>1:0</td>
<td>0.99</td>
<td>0.16</td>
<td>8.9±0.1</td>
<td>1.70, 1.99</td>
<td>10.3±0.1</td>
</tr>
<tr>
<td>P25DMP</td>
<td>1:0.25</td>
<td>0.94</td>
<td>0.13</td>
<td>9.4±0.1</td>
<td>1.63,1.91,2.50</td>
<td>10.9±0.1</td>
</tr>
<tr>
<td>P50DMP</td>
<td>1:0.50</td>
<td>0.94</td>
<td>0.13</td>
<td>9.4±0.1</td>
<td>1.65,1.93,2.52</td>
<td>10.8±0.1</td>
</tr>
<tr>
<td>P1DMP</td>
<td>1:1.0</td>
<td>0.93</td>
<td>0.13</td>
<td>9.5±0.1</td>
<td>1.62,1.91,2.47</td>
<td>11.0±0.1</td>
</tr>
</tbody>
</table>

Table 6.11 Peak positions and peak widths at half height for X-ray diffraction patterns obtained from calcined mesoporous silicas prepared from Pluronic P123 with 2,2 dimethoxy propane.
6.4.3.6.2 Nitrogen adsorption/desorption isotherm analysis of silicas

The nitrogen adsorption/desorption isotherms and the pore size distributions obtained from them are shown in figure 6.17 and 6.18 respectively, with the data summarised in table 6.12. The surface areas are in the range of 725 - 795 m² g⁻¹ and pore volumes 0.90-1.01 cm³ g⁻¹. At a P123:dimethoxy propane ratio of 1:0.25 the pore diameter decreases to 8.0 nm while the wall thickness increases to 2.9 nm. As the dimethoxy propane content increases the pore size increases to 8.7 nm and the wall thickness decreases to 2.3 nm.

<table>
<thead>
<tr>
<th>Series label</th>
<th>Ratio of P123: dimethoxy propane (w/w)</th>
<th>i) Pore-pore distance from XRD/ nm</th>
<th>BET surface area /m² g⁻¹ ±50 m² g⁻¹</th>
<th>Pore volume /±0.05 cm³ g⁻¹</th>
<th>ii) Pore size from N₂ adsorption analysis /nm</th>
<th>FWHM /nm</th>
<th>Wall thickness i-ii /nm*</th>
</tr>
</thead>
<tbody>
<tr>
<td>P123REF</td>
<td>1:0</td>
<td>10.3±0.1</td>
<td>725</td>
<td>0.97</td>
<td>8.7±0.9</td>
<td>1.9</td>
<td>1.6±1.0</td>
</tr>
<tr>
<td>P25DMP</td>
<td>1:0.25</td>
<td>10.9±0.1</td>
<td>795</td>
<td>1.01</td>
<td>8.0±0.7</td>
<td>1.6</td>
<td>2.9±0.8</td>
</tr>
<tr>
<td>P50DMP</td>
<td>1:0.5</td>
<td>10.8±0.1</td>
<td>730</td>
<td>0.97</td>
<td>8.1±0.7</td>
<td>1.6</td>
<td>2.7±0.8</td>
</tr>
<tr>
<td>P1DMP</td>
<td>1:1.0</td>
<td>11.0±0.1</td>
<td>729</td>
<td>0.90</td>
<td>8.7±0.9</td>
<td>1.8</td>
<td>2.3±1.0</td>
</tr>
</tbody>
</table>

Table 6.12 BET surface areas, pore volumes, and pore diameter for silicas from Pluronic P123 with 2,2 dimethoxy propane* Wall thickness was obtained by subtracting the pore size (ii) from the pore to pore distance (i).
Figure 6.17 Nitrogen adsorption/desorption isotherms of calcined silicas, prepared using Pluronic P123 with 2,2 dimethoxy porpane. Note the plots have been displaced on the volume axis so that they all fit on one plot. Labels on the right correspond to a unique code for each sample.

Figure 6.18 Pore size distributions calculated from nitrogen adsorption isotherms of calcined silicas prepared using Pluronic P123 with 2,2 dimethoxy porpane. Note the plots have been displaced on the dV_p/dr axis so they can all be viewed clearly on one plot. Labels on the right correspond to a unique code for each sample.
6.4.3.7 Pluronic P123 with Brij 72

6.4.3.7.1 Powder X-ray diffraction of silica

Figure 6.19 shows the powder X-ray diffraction patterns for the calcined silica samples and with the data summarised in table 6.13. All samples showed at least two peaks. The addition of Brij 72 caused a decrease in long range order; The peak widths increase to 0.27°, and the 2\textsuperscript{nd} and 3\textsuperscript{rd} peaks merge into a single peak. There is a small shift in the pore separation to 9.8 nm.

<table>
<thead>
<tr>
<th>Series label</th>
<th>Ratio of P123: Brij 72 (w/w)</th>
<th>Position of first reflection /2\theta ±0.02°</th>
<th>Peak width at half height of first reflection /°±0.02°</th>
<th>d spacing for first reflection / nm</th>
<th>Further peaks and indexing /2\theta ±0.02°</th>
<th>Pore to pore distance for an H\textsubscript{1} structure / nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>P123REF</td>
<td>1:0</td>
<td>0.99</td>
<td>0.16</td>
<td>8.9±0.1</td>
<td>1.70: 1.99</td>
<td>10.3±0.1</td>
</tr>
<tr>
<td>P25B72</td>
<td>1:0.25</td>
<td>1.00</td>
<td>0.21</td>
<td>8.9±0.1</td>
<td>1.93</td>
<td>10.2±0.1</td>
</tr>
<tr>
<td>P50B72</td>
<td>1:0.50</td>
<td>1.04</td>
<td>0.27</td>
<td>8.5±0.1</td>
<td>2.19</td>
<td>9.8±0.1</td>
</tr>
</tbody>
</table>

Table 6.13 Peak positions and peak widths at half height for X-ray diffraction patterns obtained from calcined mesoporous silicas prepared from Pluronic P123 with Brij 72.

Figure 6.19 Powder X-ray diffraction patterns obtained for calcined silica, prepared from Pluronic P123 with Brij 72. Plots have been displaced to allow all patterns to be clearly viewed on one plot. The plots have also been scaled in the y-axis to allow easy comparison of FWHM. Labels on the right correspond to a unique code for each sample.
6.4.3.7.2 Nitrogen adsorption/desorption isotherm analysis of silicas

The nitrogen adsorption/desorption isotherms and the pore size distributions obtained from them are shown in figure 6.20 and 6.21 respectively, with the data summarised in table 6.14. At a P123:Brij 72 ratio of 1:0.25 there is very little change in the structure, but at a ratio of 1:0.5 the pore diameter decreases to 6.7 nm and pore size distribution broadens significantly, accompanied by a decrease in pore volume.

<table>
<thead>
<tr>
<th>Series label</th>
<th>Ratio of P123: Brij 72 (w/w)</th>
<th>i) Pore-pore distance from XRD/ nm</th>
<th>BET surface area /m² g⁻¹ ±50 m² g⁻¹</th>
<th>Pore volume /±0.05 cm³ g⁻¹</th>
<th>ii) Pore size from N₂ adsorption analysis /nm</th>
<th>FWHM /nm</th>
<th>Wall thickness i-ii /nm*</th>
</tr>
</thead>
<tbody>
<tr>
<td>P123REF</td>
<td>1:0</td>
<td>10.3±0.1</td>
<td>725</td>
<td>0.97</td>
<td>8.7±0.9</td>
<td>1.9</td>
<td>1.6±1.0</td>
</tr>
<tr>
<td>P25B72</td>
<td>1:0.25</td>
<td>10.2±0.1</td>
<td>851</td>
<td>0.90</td>
<td>8.7±0.9</td>
<td>1.9</td>
<td>1.5±1.0</td>
</tr>
<tr>
<td>P50B72</td>
<td>1:0.50</td>
<td>9.8±0.1</td>
<td>697</td>
<td>0.57</td>
<td>6.7±0.5</td>
<td>4.0</td>
<td>3.1±0.6</td>
</tr>
</tbody>
</table>

Table 6.14 BET surface areas, pore volumes, and pore diameter for silicas from Pluronic P123 with Brij 72. * Wall thickness was obtained by subtracting the pore size (ii) from the pore to pore distance (i).

**Figure 6.20** Nitrogen adsorption/desorption isotherms of calcined silicas, prepared using Pluronic P123 with Brij 72. Note the plots have been displaced on the volume axis so that they all fit on one plot. Labels on the right correspond to a unique code for each sample.
Figure 6.21 Pore size distributions calculated from nitrogen adsorption isotherms of calcined silicas prepared using Pluronic P123 with Brij 72. Note the plots have been displaced on the dV/Δr axis so they can all be viewed clearly on one plot. Labels on the right correspond to a unique code for each sample.

6.4.3.8 Pluronic P123 with Brij 76

6.4.3.8.1 Powder X-ray diffraction of silica

Figure 6.22 shows the powder X-ray diffraction patterns for the calcined silica with the data summarised in table 6.15. All samples, except P1B76, showed at least one peak. Those that showed further peaks could be indexed to a H₃ structure. The addition Brij 76 resulting in an increase in long range order for samples with a P123:Brij 76 ratio of 1:0.13 to 1:0.5. The samples show a 4th peak, accompanied better resolution of the 2nd and 3rd peaks. As the Brij 76 content increases the pore separation decreases from 10.3 nm to 9.1 nm. With a P123:Brij 76 ratio of 1:1 the is no X-ray peak present, denoting a lack of ordered mesoporous structure.
### Table 6.15

<table>
<thead>
<tr>
<th>Series label</th>
<th>Ratio of P123: Brij 76 (w/w)</th>
<th>Position of first reflection /2θ ±0.02°</th>
<th>Peak width at half height of first reflection /±0.02°</th>
<th>d spacing for first reflection / nm</th>
<th>Further peaks and indexing /2θ ±0.02°</th>
<th>Pore to pore distance for an H1 structure / nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>P123REF</td>
<td>1:0</td>
<td>0.99</td>
<td>0.16</td>
<td>8.9±0.1</td>
<td>1.70, 1.99</td>
<td>10.3±0.1</td>
</tr>
<tr>
<td>P13B76</td>
<td>1:0.13</td>
<td>0.99</td>
<td>0.13</td>
<td>8.9±0.1</td>
<td>1.71, 2.02, 2.60</td>
<td>10.3±0.1</td>
</tr>
<tr>
<td>P25B76</td>
<td>1:0.25</td>
<td>1.04</td>
<td>0.14</td>
<td>8.5±0.1</td>
<td>1.81, 2.11, 2.76</td>
<td>9.8±0.1</td>
</tr>
<tr>
<td>P38B76</td>
<td>1:0.38</td>
<td>1.05</td>
<td>0.16</td>
<td>8.4±0.1</td>
<td>1.81, 2.15, 2.76</td>
<td>9.7±0.1</td>
</tr>
<tr>
<td>P50B76</td>
<td>1:0.50</td>
<td>1.12</td>
<td>0.18</td>
<td>7.9±0.1</td>
<td>1.95, 2.25, 2.88</td>
<td>9.1±0.1</td>
</tr>
<tr>
<td>P1B76</td>
<td>1:1.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

**Figure 6.22** Powder X-ray diffraction patterns obtained for calcined silica, prepared from Pluronic P123 with Brij 76. Plots have been displaced to allow all patterns to be clearly viewed on one plot. The plots have also been scaled in the y-axis to allow easy comparison of FWHM. The inset graph shows a magnified plot in the region of the 2nd and 3rd peaks. Labels on the right correspond to a unique code for each sample.
6.4.3.8.2 Nitrogen adsorption/desorption isotherm analysis of silicas

The nitrogen adsorption/desorption isotherms and the pore size distributions obtained from them are shown in figure 6.23 and 6.24 respectively, with the data summarised in table 6.16. As the Brij 76 content is increased the pore diameter gradual decreases from 8.7 nm to 7.3 nm, with a slight broadening of the pore size distribution, while the wall thickness is constant at 1.8 nm. At P123:Brij 76 ratio of 1:1 the pore size distribution becomes very broad with no peak, tailing to 9 nm. There is a corresponding decrease in surface area and pore volume as the pore size decreases.

<table>
<thead>
<tr>
<th>Series label</th>
<th>Ratio of P123: Brij 76 (w/w)</th>
<th>i) Pore-pore distance from XRD/ nm</th>
<th>BET surface area /m² g⁻¹ ±50 m² g⁻¹</th>
<th>Pore volume /±0.05 cm³ g⁻¹</th>
<th>ii) Pore size from N₂ adsorption analysis /nm</th>
<th>FWHM /nm</th>
<th>Wall thickness i-ii /nm*</th>
</tr>
</thead>
<tbody>
<tr>
<td>P123REF</td>
<td>1:0</td>
<td>10.3±0.1</td>
<td>725</td>
<td>0.97</td>
<td>8.7±0.9</td>
<td>1.9</td>
<td>1.6±1.0</td>
</tr>
<tr>
<td>P13B76</td>
<td>10.13</td>
<td>10.3±0.1</td>
<td>867</td>
<td>1.23</td>
<td>8.3±0.7</td>
<td>1.6</td>
<td>2.0±0.8</td>
</tr>
<tr>
<td>P25B76</td>
<td>1:0.25</td>
<td>9.8±0.1</td>
<td>901</td>
<td>1.22</td>
<td>8.0±0.7</td>
<td>1.5</td>
<td>1.8±0.8</td>
</tr>
<tr>
<td>P38B76</td>
<td>1:0.38</td>
<td>9.7±0.1</td>
<td>780</td>
<td>0.88</td>
<td>8.0±0.7</td>
<td>2.1</td>
<td>1.7±0.8</td>
</tr>
<tr>
<td>P50B76</td>
<td>1:0.50</td>
<td>9.1±0.1</td>
<td>558</td>
<td>0.67</td>
<td>7.3±0.5</td>
<td>2.0</td>
<td>1.8±0.6</td>
</tr>
<tr>
<td>P1B76</td>
<td>1:1</td>
<td>-</td>
<td>592</td>
<td>0.38</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 6.16 BET surface areas, pore volumes, and pore diameter for silicas from Pluronic P123 with Brij 76. * Wall thickness was obtained by subtracting the pore size (ii) from the pore to pore distance (i).
Figure 6.23 Nitrogen adsorption/desorption isotherms of calcined silicas, prepared using Pluronic P123 with Brij 76. Note the plots have been displaced on the volume axis so that they all fit on one plot. Labels on the right correspond to a unique code for each sample.

Figure 6.24 Pore size distributions calculated from nitrogen adsorption isotherms of calcined silicas prepared using Pluronic P123 with Brij 76. Note the plots have been displaced on the dV_p/dr axis so they can all be viewed clearly on one plot. Labels on the right correspond to a unique code for each sample.
6.4.3.9 Pluronic P123 with Brij 78

6.4.3.9.1 Powder X-ray diffraction of silica

Figure 6.25 shows the powder X-ray diffraction patterns for the calcined silica with the data summarised in table 6.17. All samples showed at least two peaks that could be indexed to a H1 structure. As the Brij 78 content is increased there is a gradual decrease in pore separation from 10.3 nm to 8.1 nm. With a P123:Brij 78 ratio of 1:0.13 to 1:0.38 there is an increase in long range order as there is a 4th peak and better resolution of the 2nd and 3rd peaks. Increasing the P123:Brij 78 ratio further results in a decrease in long range order with the loss of 4th peak and the merging of the 2nd and 3rd peaks.

<table>
<thead>
<tr>
<th>Series label</th>
<th>Ratio of P123: Brij 78 (w/w)</th>
<th>Position of first reflection /θ ±0.02°</th>
<th>Peak width at half height of first reflection /θ±0.02°</th>
<th>d spacing for first reflection / nm</th>
<th>Further peaks and indexing /θ ±0.02°</th>
<th>Pore to pore distance for an H1 structure / nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>P123REF</td>
<td>1:0</td>
<td>0.99</td>
<td>0.16</td>
<td>8.9±0.10</td>
<td>1.70, 1.99</td>
<td>10.3±0.1</td>
</tr>
<tr>
<td>P13B78</td>
<td>1:0.13</td>
<td>1.03</td>
<td>0.12</td>
<td>8.6±0.10</td>
<td>1.78, 2.10, 2.71</td>
<td>9.9±0.1</td>
</tr>
<tr>
<td>P25B78</td>
<td>1:0.25</td>
<td>1.05</td>
<td>0.13</td>
<td>8.4±0.10</td>
<td>1.81, 2.15, 2.75</td>
<td>9.7±0.1</td>
</tr>
<tr>
<td>P38B78</td>
<td>1:0.38</td>
<td>1.15</td>
<td>0.14</td>
<td>7.6±0.10</td>
<td>1.97, 2.32, 2.99</td>
<td>8.8±0.1</td>
</tr>
<tr>
<td>P50B78</td>
<td>1:0.50</td>
<td>1.20</td>
<td>0.15</td>
<td>7.4±0.10</td>
<td>2.07, 2.39</td>
<td>8.5±0.1</td>
</tr>
<tr>
<td>P1B78</td>
<td>1:1.0</td>
<td>1.27</td>
<td>0.19</td>
<td>7.0±0.05</td>
<td>2.97</td>
<td>8.1±0.1</td>
</tr>
</tbody>
</table>

Table 6.17 Peak positions and peak widths at half height for X-ray diffraction patterns obtained from calcined mesoporous silicas prepared from Pluronic P123 with Brij 78.
6.4.3.9.2 Nitrogen adsorption/desorption isotherm analysis of silicas

The nitrogen adsorption/desorption isotherms and the pore size distributions obtained from them are shown in figure 6.26 and 6.27 respectively, with the data summarised in table 6.18. As the quantity of Brij 78 is increased, the pore diameter is gradually decreased from 8.7 nm to 6.3 nm.

<table>
<thead>
<tr>
<th>Series label</th>
<th>Ratio of P123: Brij 78 (w/w)</th>
<th>i) Pore-pore distance from XRD/ nm</th>
<th>BET surface area /m² g⁻¹ ±50 m² g⁻¹</th>
<th>ii) Pore size from N₂ adsorption analysis /nm</th>
<th>FWHM /nm</th>
<th>Wall thickness (i-ii)/nm*</th>
</tr>
</thead>
<tbody>
<tr>
<td>P123REF</td>
<td>1:0</td>
<td>10.3±0.1</td>
<td>725</td>
<td>0.97</td>
<td>8.7±0.9</td>
<td>1.6±1.0</td>
</tr>
<tr>
<td>P13B78</td>
<td>10.13</td>
<td>9.9±0.1</td>
<td>757</td>
<td>1.13</td>
<td>8.7±0.9</td>
<td>1.7±1.0</td>
</tr>
<tr>
<td>P25B78</td>
<td>1:0.25</td>
<td>9.7±0.1</td>
<td>840</td>
<td>1.23</td>
<td>8.3±0.7</td>
<td>1.7±1.4</td>
</tr>
<tr>
<td>P38B78</td>
<td>1:0.38</td>
<td>8.8±0.1</td>
<td>767</td>
<td>1.19</td>
<td>7.9±0.7</td>
<td>1.6±0.8</td>
</tr>
<tr>
<td>P50B78</td>
<td>1:0.50</td>
<td>8.5±0.1</td>
<td>841</td>
<td>1.22</td>
<td>7.0±0.5</td>
<td>1.5±1.5</td>
</tr>
<tr>
<td>P1B78</td>
<td>1:1</td>
<td>8.1±0.1</td>
<td>828</td>
<td>1.18</td>
<td>6.3±0.5</td>
<td>2.5±1.8</td>
</tr>
</tbody>
</table>

Table 6.18 BET surface areas, pore volumes, and pore diameter for silicas from Pluronic P123 with Brij 78. * Wall thickness was obtained by subtracting the pore size (ii) from the pore to pore distance (i).
Figure 6.26 Nitrogen adsorption/desorption isotherms of calcined silicas, prepared using Pluronic P123 with Brij 78. Note the plots have been displaced on the volume axis so that they all fit on one plot. Labels on the right correspond to a unique code for each sample.

Figure 6.27 Pore size distributions calculated from nitrogen adsorption isotherms of calcined silicas prepared using Pluronic P123 with Brij 78. Note the plots have been displaced on the dV_p/dr axis so they can all be viewed clearly on one plot. Labels on the right correspond to a unique code for each sample.
6.4.3.10 Pluronic P123 with Brij 78 (50 wt% surfactant)

6.4.3.10.1 Powder X-ray diffraction of silica

Figure 6.28 shows the powder X-ray diffraction patterns for the calcined silica with the data summarised in table 6.19. All samples showed at least two peaks that could be indexed to a H\(_1\) structure. As the Brij 78 content is increased there is a gradual decrease in pore separation from 10.3 nm to 8.9 nm. With a P123:Brij 78 ratio of 1:0.13 to 1:0.50 there is an increase in long range order as there is a 4\(^{th}\) peak and better resolution of the 2\(^{nd}\) and 3\(^{rd}\) peaks. Increasing the P123:Brij 78 ratio further results in a decrease in long range order with the loss of 3\(^{rd}\) and 4\(^{th}\) peaks.

<table>
<thead>
<tr>
<th>Series label</th>
<th>Ratio of P123: Brij 78 (w/w)</th>
<th>Position of first reflection /(\theta) ±0.02°</th>
<th>Peak width at half height of first reflection /±0.02°</th>
<th>d spacing for first reflection /nm</th>
<th>Further peaks and indexing /(\theta) ±0.02°</th>
<th>Pore to pore distance for an H(_1) structure /±nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>P123REF</td>
<td>1:0</td>
<td>0.99</td>
<td>0.16</td>
<td>8.9±0.1</td>
<td>1.70, 1.99</td>
<td>10.3±0.1</td>
</tr>
<tr>
<td>P13B78C</td>
<td>1:0.13</td>
<td>1.07</td>
<td>0.16</td>
<td>8.2±0.1</td>
<td>1.86, 2.18, 2.91</td>
<td>9.5±0.1</td>
</tr>
<tr>
<td>P25B78C</td>
<td>1:0.25</td>
<td>1.12</td>
<td>0.14</td>
<td>7.9±0.1</td>
<td>1.94, 2.25, 2.99</td>
<td>9.1±0.1</td>
</tr>
<tr>
<td>P38B78C</td>
<td>1:0.38</td>
<td>1.12</td>
<td>0.14</td>
<td>7.9±0.1</td>
<td>1.90, 2.25, 2.97</td>
<td>9.1±0.1</td>
</tr>
<tr>
<td>P50B78C</td>
<td>1:0.50</td>
<td>1.09</td>
<td>0.17</td>
<td>8.1±0.1</td>
<td>1.84, 2.18, 2.82</td>
<td>9.3±0.1</td>
</tr>
<tr>
<td>P1B78C</td>
<td>1:1.0</td>
<td>1.14</td>
<td>0.28</td>
<td>7.7±0.1</td>
<td>1.92</td>
<td>8.9±0.1</td>
</tr>
</tbody>
</table>

Table 6.19 Peak positions and peak widths at half height for X-ray diffraction patterns obtained from calcined mesoporous silicas prepared from Pluronic P123 with Brij 78, 50wt% surfactant.
Figure 6.28 Powder X-ray diffraction patterns obtained for calcined silica, prepared from Pluronic P123 with Brij 78. Plots have been displaced to allow all patterns to be clearly viewed on one plot. The plots have also been scaled in the y-axis to allow easy comparison of FWHM. The inset graph shows a magnified plot in the region of the 2nd, 3rd and 4th peaks. Labels on the right correspond to a unique code for each sample.

6.4.3.10.2 Nitrogen adsorption/desorption isotherm analysis of silicas

The nitrogen adsorption/desorption isotherms and the pore size distributions obtained from them are shown in figure 6.29 and 6.30 respectively, with the data summarised in table 6.20. As the quantity of TMB is increased, the pore diameter is gradually decreased from 8.7 nm to 6.3 nm.

<table>
<thead>
<tr>
<th>Series label</th>
<th>Ratio of P123: Brij 78 (w/w)</th>
<th>i) Pore-pore distance from XRD/ nm</th>
<th>BET surface area /m²g⁻¹ ±50 m²g⁻¹</th>
<th>Pore volume /±0.05 cm³g⁻¹</th>
<th>ii) Pore size from N₂ adsorption analysis /nm</th>
<th>FWHM /nm</th>
<th>Wall thickness i-ii /nm*</th>
</tr>
</thead>
<tbody>
<tr>
<td>P123REF</td>
<td>1:0</td>
<td>10.3±0.1</td>
<td>725</td>
<td>0.97</td>
<td>8.7±0.9</td>
<td>1.9</td>
<td>1.6±1.0</td>
</tr>
<tr>
<td>P13B78C</td>
<td>10.13</td>
<td>9.5±0.1</td>
<td>858</td>
<td>1.12</td>
<td>7.3±0.5</td>
<td>1.7</td>
<td>2.2±0.6</td>
</tr>
<tr>
<td>P25B78C</td>
<td>1:0.25</td>
<td>9.1±0.1</td>
<td>869</td>
<td>1.15</td>
<td>8.0±0.7</td>
<td>1.4</td>
<td>1.1±0.8</td>
</tr>
<tr>
<td>P38B78C</td>
<td>1:0.38</td>
<td>9.1±0.1</td>
<td>884</td>
<td>1.11</td>
<td>7.5±0.6</td>
<td>1.4</td>
<td>1.4±0.7</td>
</tr>
<tr>
<td>P50B78C</td>
<td>1:0.50</td>
<td>9.3±0.1</td>
<td>862</td>
<td>1.04</td>
<td>7.3±0.5</td>
<td>1.5</td>
<td>2.0±0.6</td>
</tr>
<tr>
<td>P1B78C</td>
<td>1:1</td>
<td>8.9±0.1</td>
<td>916</td>
<td>0.96</td>
<td>6.3±0.5</td>
<td>2.9</td>
<td>2.6±0.6</td>
</tr>
</tbody>
</table>

Table 6.20 BET surface areas, pore volumes, and pore diameter for silicas from Pluronic P123 with Brij 78, 50wt% surfactant. * Wall thickness was obtained by subtracting the pore size (ii) from the pore to pore distance (i).
**Figure 6.29** Nitrogen adsorption/desorption isotherms of calcined silicas, prepared using Pluronic P123 with Brij 78, 50wt% surfactant. Note the plots have been displaced on the volume axis so that they all fit on one plot. Labels on the right correspond to a unique code for each sample.

**Figure 6.30** Pore size distributions calculated from nitrogen adsorption isotherms of calcined silicas prepared using Pluronic P123 with Brij 78, 50wt% surfactant. Note the plots have been displaced on the dV/dr axis so they can all be viewed clearly on one plot. Labels on the right correspond to a unique code for each sample.
6.4.3.11 TEM studies of selected silica samples

Due to time constraints TEM studies were only performed on a few of the samples in this chapter. The lack of TEM for most of the samples is not a problem, as it has been shown in previous chapters that there is a consistent correspondence between the degree of structural order observed in the TEM, small angle X-ray diffraction and the pore size distribution.

Representative TEM images of sample P50TMB are shown in figure 6.31.A and B. The images show an ordered mesoporous structure with an average pore separation of 11.7 nm and pore diameter of 7 – 9 nm. These values are slightly smaller than the X-ray diffraction and N$_2$ isotherm measurements.

Representative TEM images of sample P50PD are shown in figure 6.31.C and D. The images show an ordered mesoporous structure with an average pore separation of 9.3 nm, which is in agreement with X-ray diffraction measurements.

Representative TEM images sample P1BUD are shown in figure 6.31. E and F. The images show a disordered mesoporous structure that is consistent with broad pore size distribution and single X-ray diffraction peak.

Representative TEM images sample P25DMP are shown in figure 6.31. The images show an ordered mesoporous structure with an average pore separation of 9.6 nm and pore diameter of 6 nm. These values are slightly smaller than the X-ray diffraction and N$_2$ isotherm measurements.

Representative TEM images sample P50B78C are shown in figure 6.31. H to K. The images show an ordered mesoporous structure with an average pore separation of 8.4 nm. This value is slightly smaller than the X-ray diffraction measurement.

The TEM measurements of studied samples are support the X-ray diffraction and N$_2$ adsorption measurements, but give slightly smaller values for pore separations and pore diameters as seen before in previous chapters.
Figure 6.31 Representative TEM images of samples P50TMB, P50PD, PIBUD, P25TMP and P50B78C. All scale bars are 50 nm.
Figure 6.31 Representative TEM images of samples P50TMB, P50PD, P1BUD, P25DMP and P50B78C. All scale bars are 50 nm.
6.4.3.12 Summary of Pluronic P123 with cosolvents/cosurfactants

The results for the addition of cosolvents/cosurfactants to Pluronic P123 are summarised by the diagram in figure 6.32.

- **Ethanediol**: decrease in pore diameter and an increase in wall thickness
- **1, 3, 5 trimethyl benzene**: increase in pore diameter, decrease in wall thickness
- **1-decanol**: loss of mesoporous structure
- **Propanediol**: decrease in pore diameter and an increase in wall thickness
- **2, 2 dimethyl propane**: increase in pore diameter and order
- **Brij 72**: decrease in pore diameter and an increase in wall thickness
- **Brij 76**: decrease in pore diameter and an increase in wall thickness
- **Brij 78**: decrease in pore diameter and an increase in wall thickness

Figure 6.32 Diagram showing the effect of the addition of cosolvents/cosurfactants to Pluronic P123 on the mesoporous silicas templated from these mixtures.
The addition of increasing amounts of 1,3,5 trimethyl benzene results in an increase in the pore diameter from 8.7 nm to 11.4 nm with a broadening of the pore size distribution but with little change in the wall thickness. At a P123:TMB ratio of 1:1 there is a loss of ordered to the mesoporous structure, with a pore size distribution that is broad with no peak, tailing out to 3.5 nm.

The addition of 1-decanol is very detrimental to the ordered mesoporous structure. At the lowest P123:1-decanol ratio used, 1:0.25, the silica produced had a disordered mesoporous structure with a very broad pore size distribution with no peak that tails out to 5 nm. As the decanol content was increases, the pore size distribution remained broad with no peak, but tailed out further to 9 nm then 20 nm.

The addition of diols caused a reduction in pore diameter and an increase in wall thickness. The reduction in pore size in proportional to alky chain length. The addition of increasing amounts of ethanediol results in a decrease in the pore diameter from 8.7 nm to 6.8 nm with an increase in the wall thickness from 1.6 nm to 4.5 nm. The addition of increasing amounts of 1,3 propanediol results in a decrease in the pore diameter from 8.7 nm to 5.0 nm with an increase in the wall thickness from 1.6 nm to 4.3 nm. The addition of increasing amounts of 1,4 butanediol results in a decrease in the pore diameter from 8.7 nm to 4.2 nm with an increase in the wall thickness from 1.6 nm to 4.3 nm.

The addition of 2,2 dimethoxy propane results in an increase in long range structural order, a $4^{th}$ X-ray diffraction peak is present with better resolution of the $2^{nd}$ and $3^{rd}$ peaks. There pore diameter varies between 8.0 and 8.7 nm and the wall thickness increases to 2.3 – 2.9 nm.

The addition of increasing amounts of Brij 72 results in a decrease in the pore diameter from 8.7 nm to 6.7 nm with an increase in the wall thickness to 3.1 nm. Increasing Brij 72 content resulted in a progressive decrease in long range structural order.

The addition of increasing amounts of Brij 76 results in a decrease in the pore diameter from 8.7 nm to 7.3 nm with little change in the wall thickness. At P123:brij 78 ratios of 1:0.13, 1:0.25 and 1:0.38 the mesoporous structure showed increased long range order, with a $4^{th}$ X-ray peak present, but further increase in the Brij 76 content decreases the long range order. The addition of increasing amounts of Brij 78 results in a decrease in
the pore diameter from 8.7 nm to 6.3 nm with little change in the wall thickness. At P123:Brij 78 ratios of 1:0.13, 1:0.25 and 1:0.38 the mesoporous structure showed increased long range order, with a 4\textsuperscript{th} X-ray peak present, but further increase in the Brij 78 content decreases the long range order. The addition of increasing amounts of Brij 78 (50 wt\% surfactant) results in a decrease in the pore diameter from 8.7 nm to 6.3 nm with little change in the wall thickness. At P123:Brij 78 ratios of 1:0.13 to 1:0.5 the mesoporous structure showed increased long range order, with a 4\textsuperscript{th} X-ray peak present, but further increase in the Brij 78 content decreases the long range order.

6.4.4 Pluronic F127 with cosolvents/cosurfactants

6.4.4.1 Pluronic F127 with 1,3,5 trimethyl benzene

6.4.4.1.1 Powder X-ray diffraction of silica

Figure 6.33 shows the powder X-ray diffraction patterns for the calcined silica samples and with the data summarised in table 6.21. All samples showed at least one peak. Those that showed further peaks could be indexed to an H\textsubscript{1} structure. As the quantity of TMB is increased, the d spacing increases gradually from 10.4 nm to 14.9 nm. There is a gradual decrease in the intensity of the 1\textsuperscript{st} peak compared to the background intensity. The 2\textsuperscript{nd} and 3\textsuperscript{rd} peaks become of equal intensity.

<table>
<thead>
<tr>
<th>Series label</th>
<th>Ratio of F127: TMB (w/w)</th>
<th>Position of first reflection /θ (\pm 0.02^\circ)</th>
<th>Peak width at half height of first reflection /° (\pm 0.02^\circ)</th>
<th>d spacing for first reflection / nm</th>
<th>Further peaks and indexing / 2θ (\pm 0.02^\circ)</th>
<th>Pore to pore distance for an H\textsubscript{1} structure / nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>F127REF</td>
<td>1:0</td>
<td>0.85</td>
<td>0.12</td>
<td>10.40±0.10</td>
<td>1.46, 1.69</td>
<td>12.0±0.15</td>
</tr>
<tr>
<td>F25TMB</td>
<td>1:0.25</td>
<td>0.75</td>
<td>0.11</td>
<td>11.71±0.15</td>
<td>1.33, 1.48</td>
<td>13.5±0.2</td>
</tr>
<tr>
<td>F38TMB</td>
<td>1:0.38</td>
<td>0.66</td>
<td>0.10</td>
<td>13.44±0.20</td>
<td>1.16, 1.33</td>
<td>15.5±0.25</td>
</tr>
<tr>
<td>F50TMB</td>
<td>1:0.50</td>
<td>0.64</td>
<td>0.06</td>
<td>13.71±0.20</td>
<td>1.12, 1.27</td>
<td>15.8±0.25</td>
</tr>
<tr>
<td>F1TMB</td>
<td>1:1.0</td>
<td>0.59</td>
<td>0.07</td>
<td>14.91±0.25</td>
<td>-</td>
<td>17.2±0.3</td>
</tr>
</tbody>
</table>

Table 6.21 Peak positions and peak widths at half height for X-ray diffraction patterns obtained from calcined mesoporous silicas prepared from Pluronic F127 with 1,3,5 trimethyl benzene.
Figure 6.33 Powder X-ray diffraction patterns obtained for calcined silica, prepared from Pluronic F127 with 1,3,5 trimethyl benzene. Plots have been displaced to allow all patterns to be clearly viewed on one plot. The plots have also been scaled in the y-axis to allow easy comparison of FWHM. The inset graph shows a magnified plot in the region of the 2\textsuperscript{nd} and 3\textsuperscript{rd} peaks. Labels on the right correspond to a unique code for each sample.

6.4.4.1.2 Nitrogen adsorption/desorption isotherm analysis of silicas

The nitrogen adsorption/desorption isotherms and the pore size distributions obtained from them are shown in figures 6.34 and 6.35 respectively, with the data summarised in table 6.22. As the quantity of TMB is increased the pore diameter increases from 7.0 nm to 13.9 nm, but this is accompanied by a broadening of the pore size distribution with the half height peak width increasing from 1.4 nm to 6.3 nm. The wall thickness decreases from 5.0 nm down to ~3 nm. The surface areas are all in the range 690 – 760 m\textsuperscript{2}g\textsuperscript{-1} and the pore volumes are in the range of 0.77 – 0.82 cm\textsuperscript{3}g\textsuperscript{-1}.
Table 6.22 BET surface areas, pore volumes, and pore diameter for silicas from Pluronic F127 with 1,3,5 trimethyl benzene.* Wall thickness was obtained by subtracting the pore size (ii) from the pore to pore distance (i), as calculated for a H₃ structure.

<table>
<thead>
<tr>
<th>Series label</th>
<th>Ratio of F127: TMB (w/w)</th>
<th>i) Pore-pore distance from XRD/ nm</th>
<th>BET surface area /m²g⁻¹ ±50 m²g⁻¹</th>
<th>Pore volume /cm³g⁻¹ ±0.05</th>
<th>ii) Pore size from N₂ adsorption analysis /nm</th>
<th>FWHM /nm</th>
<th>Wall thickness i-ii /nm*</th>
</tr>
</thead>
<tbody>
<tr>
<td>F127REF</td>
<td>1.0</td>
<td>12.0±0.15</td>
<td>756</td>
<td>0.80</td>
<td>7.0±0.5</td>
<td>1.4</td>
<td>5.0±0.7</td>
</tr>
<tr>
<td>F25TMB</td>
<td>1:0.25</td>
<td>13.5±0.2</td>
<td>721</td>
<td>0.77</td>
<td>9.6±1.0</td>
<td>3.6</td>
<td>3.92±1.2</td>
</tr>
<tr>
<td>F38TMB</td>
<td>1:0.38</td>
<td>15.5±0.25</td>
<td>716</td>
<td>0.82</td>
<td>10.7±1.1</td>
<td>3.3</td>
<td>4.8±1.4</td>
</tr>
<tr>
<td>F50TMB</td>
<td>1:0.50</td>
<td>15.8±0.25</td>
<td>692</td>
<td>0.81</td>
<td>13.9±1.8</td>
<td>6.0</td>
<td>1.93±2.2</td>
</tr>
<tr>
<td>F1TMB</td>
<td>1:1.0</td>
<td>17.2±0.3</td>
<td>716</td>
<td>0.77</td>
<td>13.9±1.8</td>
<td>6.3</td>
<td>3.32±2.1</td>
</tr>
</tbody>
</table>

Figure 6.34 Nitrogen adsorption/desorption isotherms of calcined silicas, prepared using Pluronic F127 with 1,3,5 trimethyl benzene. Note the plots have been displaced on the volume axis so that they all fit on one plot. Labels on the right correspond to a unique code for each sample.
Figure 6.35 Pore size distributions calculated from nitrogen adsorption isotherms of calcined silicas prepared using Pluronic F127 with 1,3,5 trimethyl benzene. Note the plots have been displaced on the dVp/dr axis so they can all be viewed clearly on one plot. Labels on the right correspond to a unique code for each sample.

6.4.4.2 Pluronic F127 with 1-decanol

6.4.4.2.1 Powder X-ray diffraction of silica

Figure 6.36 shows the X-ray diffraction patterns obtained for the calcined silica samples with the data summarised in table 6.23. All samples showed at least one peak. With a F127:decanol ratio of 1:0.25, there is a slight decrease in the d spacing and a decrease in long range order, the 2\textsuperscript{nd} and 3\textsuperscript{rd} peaks disappear and the 1\textsuperscript{st} peak width increases to 0.17\(^{\circ}\). Increasing the ratio to 1:0.5 results in the peak broadening further and the d spacing decreasing to 7.1 nm.

<table>
<thead>
<tr>
<th>Series label</th>
<th>Ratio of F127:Decanol (w/w)</th>
<th>Position of first reflection /2(\theta) ±0.02(^{\circ})</th>
<th>Peak width at half height of first reflection /±0.02(^{\circ})</th>
<th>d spacing for first reflection / nm</th>
<th>Further peaks and indexing /2(\theta) ±0.02(^{\circ})</th>
<th>Pore to pore distance for an H(_1) structure /nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>F127REF</td>
<td>1:0</td>
<td>0.85</td>
<td>0.12</td>
<td>10.4±0.1</td>
<td>1.46, 1.69</td>
<td>12.0±0.15</td>
</tr>
<tr>
<td>F25DEC</td>
<td>1:0.25</td>
<td>0.89</td>
<td>0.17</td>
<td>10.0±0.1</td>
<td>-</td>
<td>11.5±0.10</td>
</tr>
<tr>
<td>F50DEC</td>
<td>1:0.50</td>
<td>1.25</td>
<td>0.18</td>
<td>7.1±0.05</td>
<td>-</td>
<td>8.1±0.10</td>
</tr>
</tbody>
</table>

Table 6.23 Peak positions and peak widths at half height for X-ray diffraction patterns obtained from calcined mesoporous silicas prepared from Pluronic F127 with 1-decanol.
Figure 6.36 Powder X-ray diffraction patterns obtained for calcined silica, prepared from Pluronic F127 with 1-decanol. Plots have been displaced to allow all patterns to be clearly viewed on one plot. The plots have also been scaled in the y-axis to allow easy comparison of FWHM. Labels on the right correspond to a unique code for each sample.

6.4.4.2.2 Nitrogen adsorption/desorption isotherm analysis of silicas

The nitrogen adsorption/desorption isotherms and the pore size distributions obtained from them are shown in figures 6.37 and 6.38 respectively, with the data summarised in table 6.24. With a F127:decanol ratio of 1:0.25 the pore diameter increases to 8.7 nm and the pore size distribution broaden, the half height peak width increases to 3.3 nm. The wall thickness also decreases to 3.2 nm. At a ratio of 1:0.5 the pore size distribution becomes very broad ranging from the microporous to 4.0 nm with no peak, resulting in the surface area decreasing to 518 m²g⁻¹ and the pore volume to 0.28 cm³g⁻¹.

<table>
<thead>
<tr>
<th>Series label</th>
<th>Ratio of F127:Decanol (w/w)</th>
<th>i) Pore-pore distance from XRD/ nm</th>
<th>BET surface area /m²g⁻¹ ±50 m²g⁻¹</th>
<th>Pore volume /±0.05 cm³g⁻¹</th>
<th>ii) Pore size from N₂ adsorption analysis /nm</th>
<th>FWHM /nm</th>
<th>Wall thickness i-ii /nm*</th>
</tr>
</thead>
<tbody>
<tr>
<td>F127REF</td>
<td>1:0</td>
<td>12.0±0.15</td>
<td>756</td>
<td>0.80</td>
<td>7.0±0.5</td>
<td>1.4</td>
<td>5.0±0.7</td>
</tr>
<tr>
<td>F25DEC</td>
<td>1:0.25</td>
<td>11.5±0.10</td>
<td>796</td>
<td>0.96</td>
<td>8.7±0.9</td>
<td>3.3</td>
<td>3.2±1.0</td>
</tr>
<tr>
<td>F50DEC</td>
<td>1:0.5</td>
<td>8.1±0.10</td>
<td>518</td>
<td>0.28</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 6.24 BET surface areas, pore volumes, and pore diameter for silicas from Pluronic F127 with 1-decanol. * Wall thickness was obtained by subtracting the pore size (ii) from the pore to pore distance (i), as calculated for a H₁ structure.
Figure 6.37 Nitrogen adsorption/desorption measurements for calcined silicas, Pluronic F127 with 1-decanol. Note the plots have been displaced on the volume axis so that they all fit on one plot. Labels on the right correspond to a unique code for each sample.

Figure 6.38 Pore size distributions calculated from nitrogen adsorption isotherms of calcined silicas, prepared using Pluronic F127 with 1-decanol. Note the plots have been displaced on the dV/dr axis so they can all be viewed clearly on one plot. Labels on the right correspond to a unique code for each sample.
6.4.4.3 Pluronic F127 with Brij 72

6.4.4.3.1 Powder X-ray diffraction of silica

Figure 6.39 shows the X-ray diffraction patterns obtained for the calcined silica samples with the data summarised in table 6.25. All samples showed three peaks that could be indexed to an H\textsubscript{i} structure, except sample F1B72 that showed a single broad peak. At a F127:Brij 72 ratio of 1:0.25 there is an increase in the d spacing to 11.8 nm, but decreases to 10.3 – 10.9 nm as the Brij 72 content is increased. At a ratio of 1:1 the there is a single broad peak at a d spacing of 6.3 nm, much lower than the other samples.

<table>
<thead>
<tr>
<th>Series label</th>
<th>Ratio of F127: Brij 72 (w/w)</th>
<th>Position of first reflection /° ±0.02°</th>
<th>Peak width at half height of first reflection /° ±0.02°</th>
<th>d spacing for first reflection / nm</th>
<th>Further peaks and indexing /° ±0.02°</th>
<th>Pore to pore distance for an H\textsubscript{i} structure /nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>F127REF</td>
<td>1:0</td>
<td>0.85</td>
<td>0.12</td>
<td>10.4±0.1</td>
<td>1.46, 1.69</td>
<td>12.0±0.15</td>
</tr>
<tr>
<td>F25B72</td>
<td>1:0.25</td>
<td>0.75</td>
<td>0.11</td>
<td>11.8±0.2</td>
<td>1.35, 1.52</td>
<td>13.6±0.20</td>
</tr>
<tr>
<td>F38B72</td>
<td>1:0.38</td>
<td>0.86</td>
<td>0.13</td>
<td>10.3±0.1</td>
<td>1.51, 1.73</td>
<td>11.9±0.15</td>
</tr>
<tr>
<td>F50B72</td>
<td>1:0.50</td>
<td>0.81</td>
<td>0.11</td>
<td>10.9±0.1</td>
<td>1.41, 1.63</td>
<td>12.5±0.15</td>
</tr>
<tr>
<td>F1B72</td>
<td>1:1.0</td>
<td>1.41</td>
<td>0.25</td>
<td>6.3±0.1</td>
<td>-</td>
<td>7.2±0.10</td>
</tr>
</tbody>
</table>

Table 6.25 Peak positions and peak widths at half height for X-ray diffraction patterns obtained from calcined mesoporous silicas prepared from Pluronic F127 with Brij 72.
Chapters Synthesis of Mesoporous Silica using Pluronic P123 and F127 with Cosolvents/Cosurfactants

Figure 6.39 Powder X-ray diffraction patterns obtained for calcined silica, prepared from Pluronic F127 with Brij 72. Plots have been displaced to allow all patterns to be clearly viewed on one plot. The plots have also been scaled in the y-axis to allow easy comparison of FWHM. The inset graph shows a magnified plot in the region of the 2\textsuperscript{nd} and 3\textsuperscript{rd} peaks. Labels on the right correspond to a unique code for each sample.

6.4.4.3.2 Nitrogen adsorption/desorption isotherm analysis of silicas

The nitrogen adsorption/desorption isotherms and the pore size distributions obtained from them are shown in figures 6.40 and 6.41 respectively, with the data summarised in table 6.26. The lowest F127:Brij 72 ratio, 1:0.25, increases the pore diameter to 9.6 nm with a small increase in the peak width and the wall thickness decreases to 4.0 nm. Increasing the ratio to 1:0.38 and 1:0.50 results in a slight decrease in pore diameter to 9.0 nm and the wall thickness to ~3.5 nm. At a ratio of 1:1, the pore size distribution becomes very broad, ranging from the microporous out to 6 nm, with no peak, which results in a halving of the pore volume to 0.46 cm\textsuperscript{3} g\textsuperscript{-1}. 
Table 6.26 BET surface areas, pore volumes, and pore diameter for silicas from Pluronic P123 with Brij 72. * Wall thickness was obtained by subtracting the pore size (ii) from the pore to pore distance (i), as calculated for a H\(_2\) structure.

<table>
<thead>
<tr>
<th>Series label</th>
<th>Ratio of F127/Brij 72 (w/w)</th>
<th>i) Pore-pore distance from XRD/(\frac{\text{nm}}{})</th>
<th>BET surface area/(\text{m}^2\text{g}^{-1}) (\pm 50\text{ m}^2\text{g}^{-1})</th>
<th>Pore volume/(\pm 0.05\text{ cm}^3\text{g}^{-1})</th>
<th>ii) Pore size from (N_2) adsorption analysis/(\text{nm})</th>
<th>FWHM/(\text{nm})</th>
<th>Wall thickness/(\text{nm})*</th>
</tr>
</thead>
<tbody>
<tr>
<td>F127REF</td>
<td>1:0</td>
<td>12.0(\pm 0.15)</td>
<td>756</td>
<td>0.80</td>
<td>7.0(\pm 0.5)</td>
<td>1.4</td>
<td>5.0(\pm 0.7)</td>
</tr>
<tr>
<td>F25B72</td>
<td>1:0.25</td>
<td>13.6(\pm 0.20)</td>
<td>865</td>
<td>0.89</td>
<td>9.6(\pm 1.0)</td>
<td>2.1</td>
<td>4.0(\pm 1.2)</td>
</tr>
<tr>
<td>F38B72</td>
<td>1:0.38</td>
<td>11.9(\pm 0.15)</td>
<td>911</td>
<td>1.06</td>
<td>8.7(\pm 0.9)</td>
<td>2.2</td>
<td>3.2(\pm 1.1)</td>
</tr>
<tr>
<td>F50B72</td>
<td>1:0.5</td>
<td>12.5(\pm 0.15)</td>
<td>763</td>
<td>0.98</td>
<td>9.0(\pm 0.9)</td>
<td>2.2</td>
<td>3.5(\pm 1.1)</td>
</tr>
<tr>
<td>F1B72</td>
<td>1:1.0</td>
<td>7.2(\pm 0.10)</td>
<td>647</td>
<td>0.46</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

**Figure 6.40** Nitrogen adsorption/desorption measurements for calcined silicas, prepared using Pluronic F127 with Brij 72. Note the plots have been displaced on the volume axis so that they all fit on one plot. Labels on the right correspond to a unique code for each sample.
Figure 6.41 Pore size distributions calculated from nitrogen adsorption isotherms of calcined silicas, prepared using Pluronic F127 with Brij 72. Note the plots have been displaced on the \( dV_p/dr \) axis so they can all be viewed clearly on one plot. Labels on the right correspond to a unique code for each sample.

6.4.4.4 Pluronic F127 with Brij 76

6.4.4.4.1 Powder X-ray diffraction of silica

Figure 6.42 shows the X-ray diffraction patterns obtained for the calcined silica samples with the data summarised in table 6.27. All samples showed at least one peak. Those that showed further peaks could be indexed to an \( H_1 \) structure. The addition of Brij 76 causes the d spacing to decrease to 9.5 nm and a reduction of the long range order. The 3\(^{rd} \) X-ray peak is lost and the 1\(^{st} \) peak width broadens at higher Brij 76 content.

<table>
<thead>
<tr>
<th>Series label</th>
<th>Ratio of F127: Brij 76 (w/w)</th>
<th>Position of first reflection /2θ ±0.02°</th>
<th>Peak width at half height of first reflection /±0.02°</th>
<th>d spacing for first reflection / nm</th>
<th>Further peaks and indexing /2θ ±0.02°</th>
<th>Pore to pore distance for an ( H_1 ) structure / nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>F127REF</td>
<td>1:0</td>
<td>0.85</td>
<td>0.12</td>
<td>( 10.40±0.1 )</td>
<td>( 1.46, 1.69 )</td>
<td>12.0±0.15</td>
</tr>
<tr>
<td>F25B76</td>
<td>1:0.25</td>
<td>0.93</td>
<td>0.12</td>
<td>( 9.5±0.1 )</td>
<td>( 1.59, 1.86 )</td>
<td>11.0±0.10</td>
</tr>
<tr>
<td>F50B76</td>
<td>1:0.50</td>
<td>0.94</td>
<td>0.14</td>
<td>( 9.4±0.1 )</td>
<td>1.59</td>
<td>10.9±0.10</td>
</tr>
</tbody>
</table>

Table 6.27 Peak positions and peak widths at half height for X-ray diffraction patterns obtained from calcined mesoporous silicas prepared from Pluronic F127 with Brij 76.

6-46
6.4.4.4.2 Nitrogen adsorption/desorption isotherm analysis of silicas

The nitrogen adsorption/desorption isotherms and the pore size distributions obtained from them are shown in figures 6.43 and 6.44 respectively, with the data summarised in table 6.28. At a F127:Brij 76 of 1:0.25 the pore diameter increases to 8.7 nm and the wall thickness decreases to 2.3 nm, resulting in a corresponding increase in pore volume and surface area. Increasing the ratio to 1:0.5 causes the pore diameter to decrease to 8.0 nm, but the pore volume also decreases significantly.

<table>
<thead>
<tr>
<th>Series label</th>
<th>Ratio of F127: Brij 76 (w/w)</th>
<th>i) Pore-pore distance from XRD/nm</th>
<th>BET surface area/m²g⁻¹ ±50 m²g⁻¹</th>
<th>Pore volume/cm³g⁻¹±0.05</th>
<th>ii) Pore size from N₂ adsorption analysis/nm</th>
<th>FWHM/nm</th>
<th>Wall thickness i-ii/nm*</th>
</tr>
</thead>
<tbody>
<tr>
<td>F127REF</td>
<td>1:0</td>
<td>12.0±0.15</td>
<td>756</td>
<td>0.80</td>
<td>7.0±0.5</td>
<td>1.4</td>
<td>5.0±0.7</td>
</tr>
<tr>
<td>F25B76</td>
<td>1:0.25</td>
<td>11.0±0.10</td>
<td>807</td>
<td>1.03</td>
<td>8.7±0.9</td>
<td>2.3</td>
<td>2.3±1.1</td>
</tr>
<tr>
<td>F50B76</td>
<td>1:0.5</td>
<td>10.9±0.10</td>
<td>714</td>
<td>0.57</td>
<td>8.0±0.7</td>
<td>1.8</td>
<td>2.9±0.8</td>
</tr>
</tbody>
</table>

Table 6.28 BET surface areas, pore volumes, and pore diameter for silicas from Pluronic P123 with Brij 76. * Wall thickness was obtained by subtracting the pore size (ii) from the pore to pore distance (i), as calculated for a H₁ structure.
Figure 6.43 Nitrogen adsorption/desorption measurements for calcined silicas, prepared using Pluronic F127 with Brij 76. Note the plots have been displaced on the volume axis so that they all fit on one plot. Labels on the right correspond to a unique code for each sample.

Figure 6.44 Pore size distributions calculated from nitrogen adsorption isotherms of calcined silicas, prepared using Pluronic F127 with Brij 76. Note the plots have been displaced on the dV/đr axis so they can all be viewed clearly on one plot. Labels on the right correspond to a unique code for each sample.
6.4.4.5 Pluronic F127 with Brij 78

6.4.4.5.1 Powder X-ray diffraction of silica

Figure 6.45 shows the X-ray diffraction patterns obtained for the calcined silica samples with the data summarised in table 6.29. All samples showed three peaks that could be indexed to an H1 structure. As the Brij 78 content is increases the d spacing decreases to 9.0 nm with a slight broadening of the peak width.

<table>
<thead>
<tr>
<th>Series label</th>
<th>Ratio of F127: Brij 78 (w/w)</th>
<th>Position of first reflection /θ₀ ±0.02°</th>
<th>Peak width at half height of first reflection /θ₀ ±0.02°</th>
<th>d spacing for first reflection / nm</th>
<th>Further peaks and indexing /θ₀ ±0.02°</th>
<th>Pore to pore distance for an H1 structure / nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>F127REF</td>
<td>1:0</td>
<td>0.85</td>
<td>0.12</td>
<td>10.40±0.10</td>
<td>1.46, 1.69</td>
<td>12.0±0.15</td>
</tr>
<tr>
<td>F25B78</td>
<td>1:0.25</td>
<td>0.95</td>
<td>0.12</td>
<td>9.3±0.10</td>
<td>1.64, 1.88</td>
<td>10.8±0.10</td>
</tr>
<tr>
<td>F50B78</td>
<td>1:0.50</td>
<td>0.98</td>
<td>0.14</td>
<td>9.0±0.10</td>
<td>1.70, 1.98</td>
<td>10.4±0.10</td>
</tr>
</tbody>
</table>

Table 6.29 Peak positions and peak widths at half height for X-ray diffraction patterns obtained from calcined mesoporous silicas prepared from Pluronic F127 with Brij 78.

Figure 6.45 Powder X-ray diffraction patterns obtained for calcined silica, prepared from Pluronic F127 with Brij 72. Plots have been displaced to allow all patterns to be clearly viewed on one plot. The plots have also been scaled in the y-axis to allow easy comparison of FWHM. The inset graph shows a magnified plot in the region of the 2nd and 3rd peaks. Labels on the right correspond to a unique code for each sample.
6.4.4.5.2 Nitrogen adsorption/desorption isotherm analysis of silicas

The nitrogen adsorption/desorption isotherms and the pore size distributions obtained from them are shown in figures 6.46 and 6.47 respectively, with the data summarised in table 6.30. With the addition of Brij 78 the pore diameter increases to 8.0 nm with a broadening of the peak width and the wall thickness decreases to 2.4 nm, resulting in an increase in the surface area and pore volume.

<table>
<thead>
<tr>
<th>Series label</th>
<th>Ratio of F127: Brij 78 (w/w)</th>
<th>i) Pore-pore distance from XRD/ nm</th>
<th>ii) Pore size from N\textsubscript{2} adsorption analysis /nm</th>
<th>BET surface area /m\textsuperscript{2}/g\textsuperscript{-1}</th>
<th>Pore volume /cm\textsuperscript{3}/g\textsuperscript{-1}</th>
<th>FWHM /nm</th>
<th>Wall thickness i-ii /nm*</th>
</tr>
</thead>
<tbody>
<tr>
<td>F127REF</td>
<td>1:0</td>
<td>12.0±0.15</td>
<td>756</td>
<td>0.80</td>
<td>7.0±0.5</td>
<td>1.4</td>
<td>5.0±0.7</td>
</tr>
<tr>
<td>F25B78</td>
<td>1:0.25</td>
<td>10.8±0.10</td>
<td>899</td>
<td>0.98</td>
<td>8.0±0.9</td>
<td>2.1</td>
<td>2.8±1.0</td>
</tr>
<tr>
<td>F50B78</td>
<td>1:0.5</td>
<td>10.4±0.10</td>
<td>756</td>
<td>1.06</td>
<td>8.0±0.9</td>
<td>2.0</td>
<td>2.4±1.0</td>
</tr>
</tbody>
</table>

Table 6.30 BET surface areas, pore volumes, and pore diameter for silicas from Pluronic P123 with Brij 78. * Wall thickness was obtained by subtracting the pore size (ii) from the pore to pore distance (i), as calculated for a H\textsubscript{1} structure.

Figure 6.46 Nitrogen adsorption/desorption measurements for calcined silicas, prepared using Pluronic F127 with Brij 76. Note the plots have been displaced on the volume axis so that they all fit on one plot. Labels on the right correspond to a unique code for each sample.
Figure 6.47 Pore size distributions calculated from nitrogen adsorption isotherms of calcined silicas, prepared using Pluronic F127 with Brij 76. Note the plots have been displaced on the dV_p/dr axis so they can all be viewed clearly on one plot. Labels on the right correspond to a unique code for each sample.

6.4.4.6 TEM studies of selected silica samples

Due to time constraints TEM studies were only preformed on a few of the samples in this chapter. It has been shown in previous chapters that there is a consistent correspondence between the degree of structural order observed in the TEM, small angle X-ray diffraction and the pore size distribution.

Representative TEM images of sample F50TMB are shown in figure 6.48. A to D. The images show an ordered mesoporous structure. The parallel fringes are 12.0 nm apart and the hexagonal pores are 14.6 nm apart with a pore diameter of 8 - 10 nm. The pore diameters measured are significantly different from the 14 nm diameter obtained from N_2 isotherm measurements, but the pore size distribution is very wide. A disordered structure is also observed.

Representative TEM images of sample F50B78 are shown in figure 6.48. E and F. The images show an ordered mesoporous structure. The parallel fringes are 7.4 nm apart and the hexagonal pores are 8.8 nm apart.
Figure 6.48 Representative TEM images of samples F50TMB and F50B78. All scale bars are 50 nm.
6.4.4.7 Summary of Pluronic F127 with cosolvents/cosurfactants

The results for the addition of cosolvents/cosurfactants to Pluronic P127 are summarised by the diagram in figure 6.49.

The addition of increasing amounts of 1,3,5 trimethyl benzene result in an increase in pore diameter from 7.0 nm to 13.9 nm but with a significant broadening of the pore size distribution. There is also a decrease in the wall thickness from 5.0 nm to 3.3 nm.

The addition of 1-decanol initially produced an increase in pore diameter to 8.7 nm, but further decanol result in a mesoporous silica with no ordered structure and a very broad, pore size distribution, with no peak, that tails out to 4 nm.

The addition of Brij 72 results in an increase in the pore diameter to 9 nm - 9.6 nm, accompanied by a decrease in wall thickness to 3 – 4 nm. Too much Brij 72 is detrimental to the structural order, at a F127:Brij 72 ratio of 1:1 the silica produced is very disordered, the pore size distribution is very broad with no peak, tailing out to 6.0 nm.

The addition of Brij 76 results in an increase in the pore diameter to 8 nm – 8.7 nm, accompanied by a decrease in wall thickness to 2 – 3 nm. There is a decrease in long range structural order as the Brij 76 content is increases, at a F127:Brij 76 ratio of 1:0.5 the 3rd X-ray peak is lost. The addition of Brij 78 results in an increase in the pore diameter to 8 nm, accompanied by a decrease in wall thickness to 2.5 – 3 nm.
**1, 3, 5 trimethyl benzene**
Increase in pore diameter
Decrease in long-range order

1-decanol
small increase in pore diameter, then mesoporous structure is lost.

Brij 78
small increase in pore diameter, thinner walls, less order.

Brij 72
small increase in pore diameter, then mesoporous structure is lost.

Brij 76
small increase in pore diameter, thinner walls, less order.

**Figure 6.49** Diagram showing the effect of the addition of cosolvents/cosurfactants to Pluronic F127 on the mesoporous silicas templated from these mixtures.

### 6.5 Discussion

#### 6.5.1 Addition of alky diols to Pluronic P123

The addition of 1,2 Ethanediol to the reaction mixture results in a progressive decrease in pore diameter and an increase in wall thickness as amount of ethanediol used is increased. This was to be expected as ethanediol is relatively hydrophilic, so has the same effect as using greater amounts of water, the pore size and wall thickness are similar to those of sample 3a in chapter 3, 6.8 nm pore diameter with 4.5 nm wall...
thickness. The addition of 1,3 propanediol and 1,4 butanediol produces unexpected result. Both are more hydrophobic than ethanediol therefore should show greater partitioning into the hydrophobic core, resulting in a smaller reduction in pore size, or possibly pore swelling with butanediol, but the opposite happens. With the addition of 1,3 propanediol the pore diameter is decreased further to 5.0 nm with a wall thickness of 4.3 nm. The addition of more hydrophobic butanediol causes an even greater decrease in pore diameter, 4.2 nm with 4.3 nm wall thickness.

6.5.2 Mixture of Pluronic P123, F127 and Brij 72, 76, 78

The mixtures of Pluronic P123 (EO$_{20}$PO$_{70}$EO$_{20}$) with Brij 72, 76, and 78 behaved much as expected. Brij 78 and Pluronic P123 both have the same headgroup, but Brij 78 has a much smaller tailgroup, resulting in a decrease in the micelle radius as the proportion of Brij 78 is increased, resulting in a decrease in the pore diameter from 8.7 nm to 6.3 nm. Brij 76 has a smaller headgroup, resulting in a smaller decrease in pore diameter to 7.3 nm before ordered structure is lost. The addition of Brij 76 and 78 resulting in an increase in long range structural order, as an additional, weak, 4$^\text{th}$ X-ray peak is present. Brij 72 has a much smaller headgroup, resulting in a mismatch between the surfactants, causing a decrease in structural order and a broadening of the pore size distribution.

The mixtures of Pluronic F127 (EO$_{106}$PO$_{70}$EO$_{106}$) with Brij 72, 76, and 78 behaved in the opposite way to with Pluronic P123. Due to the F127 headgroup much larger than Brij headgroups, 5 – 50x larger, the Brij headgroup has little effect on the curvature, but the alkyl tail acts to swell the hydrophobic core, resulting in an increased pore diameter. If too much Brij is present the ordered structure is lost. The addition of Brij 72 increases the pore diameter up to 9.0 nm while decreasing the wall thickness to 3.5 nm. As the size of the Brij headgroup is increased the micelle swelling decreases. With Brij 76 the pore diameter increases up to 8.7 nm, and with Brij 78 up to 8.0 nm.

6.5.3 Comparison of the wall thickness and pore diameters produced

The pore diameter and wall thickness of all ordered H$_4$ silicas presented in chapters 3 and 6 are plotted on the graph in Figure 6.50. In his Thesis$^5$, N. Coleman templated ordered
H₁ silicas from the H₁ phase of Brij 56 (C₁₆H₃₃(OCH₂CH₂)₉OH), the results of which are included in the graph in Figure 6.50 for comparison because a similar region of the surfactant/TMOS/0.5 M HCl(aq) ternary diagram was explored compared to Pluronic P123 in chapter 3. The silica samples templated from Brij 56 are scattered about a line where the sum of the pore diameter and wall thickness is equal to 5.5 nm, over a pore diameter range of 2.5 - 4.0 nm. Due to the larger hydrophobic core and headgroup, the silica samples templated from Pluronic P123 exhibit larger pores over a greater range, they are scattered about a line where the sum of the pore diameter and wall thickness is equal to 12 nm, over a pore diameter range of 4 - 10 nm. The addition of ethanediol, propanediol, butanediol, 2,2 dimethoxy propane to the reaction mixture produced silicas with wall thickness/pore diameter combinations that are also scattered about the line where the sum of the pore diameter and wall thickness equals 12 nm. The addition of TMB increased maximum pore diameter available by 1 nm to 11 nm. The addition of Brij 72, 76, 78 to reaction mixture results in silicas with walls 1-1.5 nm thinner at the same pore diameter as the sample templated from Pluronic P123.

The pore diameter and wall thickness of all ordered cubic silicas presented in chapters 4, 5, and 6 are plotted on the graph in Figure 6.51. The silica samples templated from Brij 78 are scattered along about a line where the sum of the pore diameter and wall thickness is equal to 6 nm, over a pore diameter range of 3.0 – 4.5 nm. As with Pluronic P123, due to the larger hydrophobic core and headgroup, the silica samples templated from Pluronic F127 exhibit larger pores over a greater range, they are scattered about a line where the sum of the pore diameter and wall thickness is equal to 12 nm, over a pore diameter range of 5 - 10 nm. The addition of TMB increased the pore diameter available for the same range of wall thickness and increased the maximum pore diameter to 14 nm. The addition of Brij 72, 76, and 78 results in pore diameter/wall thickness combinations that are in the range of those produced by the use of Pluronic F127 alone.
Figure 6.50 Graph showing pore diameter versus wall thickness of all ordered H₄ silicas presented in this thesis. The H₄ silicas templated from Brij 56/TMOS/0.5 M HCl(aq) by N. R. B. Coleman are included for comparison, were a similar region of the ternary diagram was explored as with Pluronic P123.
Figure 6.51 Graph showing pore diameter versus wall thickness for all ordered cubic silicas presented in chapters 4, 5, and 6.
6.6 Conclusions

A range of cosolvent and cosurfactants were used with Pluronic P123 and F127 to template mesoporous silicas in an attempt to produce pore diameter and wall thickness combinations not achievable when Pluronic P123 or F127 were used alone as templates. Swelling of the micelles with hydrophobic molecules was of particular interest as this leads to an increasing the maximum pore diameter achievable. The results are summarised by the diagrams in Figures 6.32 and 6.49.

1,3,5 trimethyl benzene was effective at swelling the hydrophobic core of Pluronic P123 and F127 micelles. For Pluronic P123 the pore diameter was increased from 8 nm to 11.7 nm before the addition of TMB caused a loss of ordered pore structure, which is slightly larger than the 10 nm of the largest pore diameter produced in chapter 3. The larger headgroup of Pluronic F127 allowed greater swelling of the hydrophobic core by TMB, taking the pore diameter from 7 nm to 13.9 nm, which is greater than the 11 nm of the largest pore diameter produced in chapter 5. These increases in pore diameter are not as extensive the range of pore diameters produced by Stucky et al\textsuperscript{1} using TMB to swell micelles in 5wt\% Pluronic P123, where silicas with pore diameters of 10 – 30 nm were achieved. In contrast to the addition of TMB, the use of decanol as a swelling agent with 50 wt\% Pluronic P123 or F127 resulted in loss of all ordered mesoporous structure. The silica produced was highly porous, but had a very broad pore distribution. This is in contrast to the micelle swelling observed by Feng et. al\textsuperscript{2} when the shorter alkyl chain alcohols pentanol and hexanol were used. Trimethyl benzezene was the only additive used in this chapter that significantly increased the pore diameter. Further attempts to increase the pore diameter by swelling with hydrophobic additives could use straight chain and cyclic alcohols, and cyclic hydrocarbons, e.g. toluene, naphthalene.

The pore diameter and wall thickness for all ordered H\textsubscript{1} silica in this thesis are plotted in figure 6.50. The silica sample templated from Pluronic P123 in chapter 3 have pore diameter and wall thickness combinations that are scattered around the line where the sum of pore diameter and wall thickness equals 12 nm, with a pore diameter between 4 to 10 nm. The samples produced with the addition of ethanediol, propanediol, butanediol and 2,2 dimethoxy propane resulted in samples that were also scattered along this line.
The pore diameter and wall thickness for all ordered I₃ templated silicas in this thesis are plotted in figure 6.51. The silica sample templated from Pluronic P127 in chapter 5 have pore diameter and wall thickness combinations that are scattered around the line where the sum of pore diameter and wall thickness equals 12 nm, with a pore diameter between 5 to 10 nm. Due to a larger hydrophobic core, silicas templated from Pluronic P123 and F127 have significantly greater pore diameters than silicas templated from Brij 56 and 78. Pluronic P123 and F127 templated silicas have pore diameters in the range of 4 –10 nm, while those from Brij 56 and 78 have pore diameters in the range of 3 – 4.5 nm.

The addition of Brij 72, 76, and 78 to Pluronic P123 results in a decrease in pore diameter. The walls were also thinner than silicas with comparable pore diameters that were templated from Pluronic P123 alone. The reduction in pore diameter is because of the similarity in headgroup size between P123 and Brij 76 and 78, but difference in the hydrophobic chain lengths causing an increase in curvature of the micelles, hence smaller radius. The addition of Brij 72, 76, and 78 to Pluronic F127 resulted in micelle swelling due to F127 having a much larger headgroup than the Brij surfactants used. The alkyl chain of the Brij swelled the hydrophobic core while the headgroup had little effect.

The addition of 2, 2 dimethyl propane to Pluronic P123 resulted in very little change in the pore diameter, a small increase the wall thickness and an increase in long range order; The powder X-ray diffraction pattern showed an extra peak for all concentrations of 2,2 dimethyl propane used.

6.7 References

Chapter 7

Summary and Conclusions
Chapter 7

Summary and Conclusions

7.1 Summary and conclusions

A range of mesoporous silicas were templated from lyotropic liquid phases of CTAB, Brij 78, Pluronic P123 and Pluronic F127. The regularity and morphology of the mesoporous structures were examined using small angle X-ray diffraction, transmission electron microscopy and N₂ adsorption isotherms as a function of the reaction composition.

Mesoporous silica was successfully templated from the H₁ phase of CTAB under strongly alkaline (>0.7 M NaOH) hydrothermal conditions using fumed silica as the silica source. The sample showed good long range order, having 4 small angle X-ray diffraction peaks, and a narrow pore size distribution (0.4 nm full-width at half-maximum). The pore diameters were between 3.2 and 3.5 nm, which is slightly smaller than the 3.7 nm for MCM-41 silicas templated from CTAB¹. The wall thickness is significantly greater than the MCM-41 silicas, 1.1 - 1.4 nm compared with 0.8 - 1.0 nm. TEM studies of the silicas revealed a number of defects in the H₁ structure such as +π disclinations, transverse edge dislocations and a screw dislocation, see figure 2.9.

The remaining silicas were synthesised from TMOS/surfactant/0.5 M HCl(aq) mixtures at 45°C using the method described by Attard et al.², where a vacuum was used to remove the methanol produced by hydrolysis of TMOS. The central region of the TMOS/surfactant/0.5 M HCl(aq) ternary diagram was explored, where the surfactant concentration is relatively high. The most ordered mesoporous silicas were produced when there was very little water left after the hydrolysis of the TMOS, 1:5-7 TMOS:water molar ratio. If not enough TMOS is present the condensation takes place in a more dilute solution, causing the formation of a disorder H₁ structure with a very broad pore distribution. With more TMOS, where all the water present is used to hydrolyze TMOS, there is a gradual decrease in order up to the 1:2 TMOS:water molar ratio hydrolysis limit, but a reasonable degree of order is retained. The ideal TMOS:water ratio is only one requirement for a well-ordered mesoporous silica, the liquid crystal template must also have good long range order. With higher than ideal TMOS concentrations there is very little water left after the hydrolysis of TMOS. However, polarised light microscopy showed that for Pluronic P123 the H₁ phases were formed even in the absence of water. Lyotropic phases are also observed with solvents that, like
water, are highly polar (eg glycerol and formamide\(^3\)), so it is not surprising that the nominal Si(OH)\(_4\) molecules can also stabilise the H\(_1\) phase.

The Pluronic P123 and F127 templated silica samples showed greater long range structural order as the surfactant concentration was increased, but for P123 at higher concentrations a greater amount of TMOS was necessary to stabilise the H\(_1\) phase.

Mesoporous silicas with a H\(_1\) mesostucture were templated from the H\(_1\) phase of Pluronic P123. The pore size and wall thickness of all the ordered H\(_1\) silicas produced are plotted in figure 6.50. The pore diameter and wall thickness combinations are scattered around the line where the sum of pore diameter and wall thickness equals 12 nm, with a pore diameter between 5 to 10 nm. TEM studies of these silicas did not show the disclination and dislocation defects seen for the silicas templated from the H\(_1\) phase of CTAB under hydrothermal conditions. The channels were observed to be straight for several microns. A few samples were observed with slight bends in the channels.

Mesoporous silicas with an undetermined three dimensional cubic mesostucture were templated from the I\(_1\) phase of Pluronic F127. The pore size and wall thickness of all the ordered I\(_1\) templated silicas produced are plotted in figure 6.51. The pore diameter and wall thickness combinations are scattered around the line where the sum of pore diameter and wall thickness equals 12 nm, with a pore diameter between 5 to 10 nm. Mesoporous silicas with the same undetermined 3d cubic mesostucture were templated from the I\(_1\) phase of Brij 78. The pore diameter and wall thickness combinations are scattered around the line where the sum of pore diameter and wall thickness equals 6 nm, with a pore diameter between 3 to 4.5 nm. Due to a larger hydrophobic core, silicas templated from Pluronic P123 and F127 have significantly greater pore diameters than silicas templated from Brij 56 and 78.

The diagrams in figure 3.23 and 5.22 show the effect on the silica mesostructure from varying the amount of each component in the ternary mixtures TMOS/Pluronic P123/0.5 M HCl\(_{aq}\) and TMOS/Pluronic F127/0.5 M HCl\(_{aq}\), respectively. In general, increasing the amount of TMOS at a fixed water:surfactant ratio results in a decrease in the pore diameter, with an increase in wall thickness. Increasing the surfactant concentration increases the pore diameter and decreases the wall thickness. Increasing the water concentration increases the wall thickness and decreases the pore diameter.
The surface areas and pore volumes of the H<sub>t</sub> silicas templated from Pluronic P123 were predicted from the pore diameters and wall thickness measurements using a simple geometric model. The theoretical surface areas and pore volumes were significantly smaller than measured values. The differences were greatest for the thick-walled samples with small pore diameters. This is consistent with silica walls containing micropores created by the penetration of part of the poly(ethylene oxide)head group into the silica gel while condensation is occurring.

The Brij family of surfactants, with a fixed alkyl chain length and a distribution in head group size, are intermediate between ionic surfactants such as CTAB, where the head group size and tail length are the same for each surfactant molecule, and oligomeric surfactants such as the Pluronic family, where there is a distribution in the number of units in the poly(ethylene oxide) and poly(propylene oxide) blocks. This variation in size is reflected in the width of the pore size distribution of the most ordered silicas templated from each surfactant. The silicas templated from CTAB, where the headgroup size and alkyl tail length are fixed, have the narrowest pore size distribution with a FWHM of 0.3 nm, while for silica templated from Brij 78 the narrowest pore size distribution has a FWHM of 0.6 nm, and for silicas templated from Pluronic P123 and F127 the narrowest pore size distribution has a FWHM of 1.4 nm. The CTAB and Brij 78 templated silicas have similar pore diameters, while the pore diameters of the most ordered silicas templated from Pluronic P123 and F127 are roughly double those of CTAB and Brij 78 template silicas.

The range of pore diameters and wall thickness of the silicas templated from the H<sub>t</sub> phase of Pluronic PI23 are comparable with those the H<sub>t</sub> silicas synthesised by Stucky et al., designated SBA-15, using 3 wt% Pluronic P123 and tetraethoxy silane under acidic conditions. The SBA-15 silicas had a wall thickness in the range of 3 – 6 nm and pore diameter in the range of 5 – 9 nm. Whereas the pore size and wall thickness of SBA-15 silicas are controlled with the synthesis temperature; the structural parameters of the H<sub>t</sub>-silica synthesised in this chapter are controlled using the ratio of reactants at a fixed synthesis temperature.

The addition of hydrophobic additives to the ternary TMOS/surfactant/0.5 M HCl<sub>(aq)</sub> mixture was investigated for Pluronic P123 and F127, the results of which are summarised in the diagrams of figures 6.32 and 6.49 respectively. The addition of 1,3,5 trimethyl benzene was effective at swelling the hydrophobic core pore of the Pluronic P123 and F127 micelles. For Pluronic P123 the pore size was increased from 8 nm to
11.7 nm before the addition of TMB caused a loss of ordered pore structure, which is slightly larger than the 10 nm of the largest pore produced in chapter 3. The larger headgroup of Pluronic F127 allowed greater swelling of the hydrophobic core, taking the pore size from 7 nm to 13.9 nm, which is larger than the 11 nm of the largest pore produced in chapter 5. These increases in pore diameter are not as extensive as the range of pore diameters produced by Stucky et al. using TMB to swell micelles in 5wt% Pluronic P123, where silicas with pore diameters of 10 – 30 nm were achieved. In contrast to the addition of TMB, the use of decanol as a swelling agent with 50 wt% Pluronic P123 or F127 resulted in loss of all ordered mesoporous structure. The silica produced was highly porous, but had a very broad pore distribution. This is in contrast to the micelle swelling observed by Feng et al. where the shorter chain alky alcohols pentanol and hexanol were used. A range of Pluronic P123/Brij 78 mixtures were used to template ordered H1 mesoporous silica with a pore diameter tuneable between 8.7 nm and 6.3 nm. The total surfactant concentration was kept at 50 wt%, but the Brij 78 content was varied between 0 and 50% of the surfactant mass. Pluronic P123 and Brij 78 have the same EO20 headgroup but different hydrophobic tails, hence the packing parameter/micelle radius is dependent on the mixture used, allowing the pore diameter to be varied between the pore diameters obtained using the two surfactants separately as templates. This principle was demonstrated by J. D. Holmes et al. using mixtures of Pluronic P123 (EO20PO70EO20) and Pluronic P65 (EO20PO30EO20) as templates for H1 mesoporous silica using the Attard method. By varying the mixture they were able to tune the pore diameter between 7.0 nm and 4.6 nm

7.2 References

Appendix 1 Techniques

1.A Transmission electron microscopy

Transmission electron microscopy is widely used to examine the nanostructure of inorganic materials. Light microscopy is limited by the wavelength of visible light making it impossible ever to resolve detail finer than 300 nm. By imaging a sample using electrons it is theoretically possible to view structures as small as 0.02 nm. Electrons accelerated through a potential of 200 kV have a wavelength of 0.0025 nm. In practice, with a good TEM, a resolution of 0.2 nm is achievable. An electron beam is formed by a gun, which accelerates the electrons produced from a filament. The accelerating voltage that is applied can be varied depending on the sample of interest. For most inorganic materials a relatively high accelerating voltage of 200kV is required so that the beam can penetrate the sample. However, in some cases this high voltage can cause local heating of the sample, which over time destroys any microstructure that may be present. Focusing and magnification is achieved using a series of electromagnetic lenses. The electron beam is focused onto the specimen by the condenser lenses and magnification of the transmitted image is achieved using objective and projector lenses. Finally, the image is formed on a fluorescent screen. Figure 1a shows a schematic diagram of a transmission electron microscope.

![Figure 1a Schematic of a transmission electron microscope](image)
Appendix 1

Techniques

Experimental parameters
The procedures followed for obtaining TEM images of the mesoporous silicas using the JEOL 2000FX, equipped with a lanthanum hexaboride (LaB₆) filament, are described below:

a) Sample preparation
Samples for TEM observation were prepared by dropping a dispersion of the silica in distilled water onto a circular, 3.05 mm diameter, 400 mesh copper grid that supports a carbon film (supplied by Agar Scientific). The samples were ground to a fine powder in water using an agate pestle and mortar, and then dispersal was achieved by placing in an ultrasound bath for 15 minutes. One drop of the dispersion was placed on a grid, then dried in an oven at 70°C for 4 hours.

b) Inserting samples into the vacuum system
Once dried, two grids were placed in the metal sample holder, which was inserted into the vacuum system. Typically, it took 2-15 minutes before a sufficient vacuum was re-established for the electron beam to be switched on.

c) Image formation
The samples were examined at a magnification of ×120,000 using an acceleration voltage of 200 kV, which was sufficient to observe the nanostructure. The stability of the mesoporous silica samples under the electron beam varied depending on the wall thickness and degree of structural order. Typically, an ordered structure was destroyed within ~1-2 minute of exposure to the focused beam. Usually, the mesostructure was only observed at the thin edges of particles or on very thin particles.

e) Photography and digital image analysis
Underneath the viewing chamber was a camera that held a number of photographic plates. Once a suitable region of the sample had been found a plate was exposed and the image recorded. Typically about 5-10 representative pictures would be taken over a period of 30-40 minutes. Once the negatives had been removed from the vacuum system they were developed.
Digitisation of the negatives was carried out using an AGFA Duoscan T1200 scanner attached to a PC. The Duoscan had a special transparency tray that was designed for scanning negatives and could produce high-resolution scans of the original negative in 12-bit greyscale. Adjustment of brightness and contrast of the scanned images was carried out using Corel Photopaint 10. Measurements, from the images, such as pore to pore distance were carried out using Scion image.

**Analysis of results**

To properly assess the nature of any mesoporosity within a sample it was necessary to have a number of representative micrographs. In terms of structural order, the mesoporous silicas could be placed into four categories:

1) The silica did not have any mesoporosity.
2) The silica was mesoporous but disordered.
3) The silica was mesoporous and sufficiently ordered that the phase could be identified.
4) The silica was mesoporous and the phase easily identifiable.

The repeat distances in ordered structures observed were measured by averaging across a number of repeat units. To ensure the scale bar on the micrograph was accurate the TEM was calibrated using asbestos fibres with known lattice spacings. In H₃ materials, there is a tendency for the particles to lie with the channels parallel to the carbon film. Consequently, at first sight, the material appeared lamellar but on further investigation the end on view of the hexagonally arranged pores was revealed. Confirmation of a homogeneous hexagonal phase, throughout the material, could be obtained by measuring the ratio of the repeat distance of the pores, side on, to the repeat distance end on (figure 1b). Cubic structures show ordered patterns when electron beam is aligned with a lattice plane. This results in a number of different patterns for the same cubic structure, with the repeat distances related by a factor.
1.B Nitrogen adsorption/desorption isotherm acquisition and analysis

Introduction
Studying the adsorption/desorption of an inert gas, such as nitrogen, on the surface of a material can provide information about the surface area and pore size distribution of the material, and reveal any pore blocking within the structure. Routine surface area analysis is carried out by using commercially available instruments that record the adsorption and desorption of nitrogen before calculating a surface area from the collected data. Nitrogen adsorption/desorption studies are widely used in the study of mesoporous inorganic oxides and metals and have become a standard technique for characterising surfactant templated materials\(^4,5\), giving surface areas, pore volumes and pore size distributions for mesoporous materials. IUPAC classified pores into micropores, mesopores, and macropores using pore diameter, \(d\) (micropores: \(d < 2\) nm; mesopores: \(2\) nm \(< d < 50\) nm; macropores: \(d > 50\) nm)\(^4\). The physical adsorption mechanism changes with the pore diameter. Below the saturated vapour pressure, vapour condenses in the mesopores of which the walls are covered with adsorbed layers of gas. This mechanism is called capillary condensation.
Equipment description

Figure 1c The Gemini III 2375 analyser a) plumbing diagram b) drawing of the instrument. Reproduced from the Micrometrics operating manual.

Nitrogen adsorption/desorption experiments were carried out using a Micrometrics Gemini III 2375 Surface Area Analyser. The Gemini instrument automates the process of obtaining nitrogen adsorption/desorption curves and BET surface areas. It works by analysing the difference in the volume of nitrogen adsorbed by a tube containing the sample of interest and an empty reference tube. Both tubes are immersed in a single liquid nitrogen bath, which maintains isothermal conditions. Figure 1c shows a schematic of the components of the Gemini’s plumbing system.
Experimental parameters

For all the nitrogen adsorption/desorption experiments described in this thesis the following procedure was adopted:

1. Sample tubes were cleaned by washing with deionised water and rinsed with acetone before drying in an oven, at 60°C, overnight.
2. Samples were weighed out accurately (~20mg of silicas) into the analysis tube.
3. The instrument was set up with the following parameters before starting the analysis:
   - 40 adsorption points between \( P/P_\circ \) 0.01-0.95 and 32 desorption points.
   - Sample weight (see above)
   - Saturation pressure \( P_\circ \) – 760 mmHg
   - Evacuation rate 500 mmHg/min
   - Evacuation time 30 min
4. The automated BET analysis was carried out on adsorption points at relative pressures \( (P/P_\circ) \) between 0.05 and 0.30.
5. Pore volumes were obtained at a relative pressure \( (P/P_\circ) \) of ~0.95
6. The relative pressure and volume of nitrogen were entered in a spreadsheet to calculate a pore size distribution and a more accurate BET measurement that excludes pressures where capillary condensation occurs in the pores.

The first page of output after the analysis of a mesoporous silica was complete is shown in figure 1d.
Sample ID: 001  Started: 05/11/99  09:00:00
Sample weight: 0.0197g  Completed: 05/11/99 17:44:13
Evacuation rate: 500.0 mmHg/min  Evacuation time: 30 min
No free space correction applied  Saturation pressure: 760mmHg
Analysis mode: Equilibration  Equilibration time: 5 sec

**BET Multipoint Surface Area report**

| Surface area: | 1012 sq. m/g |
| Slope:        | 0.004253     |
| Y-intercept:  | 0.000050     |
| C:            | 85.727       |
| Vm:           | 232.406952   |
| Correlation coefficient: | 9.9994e-001 |

**BET Single Point Surface Area:** 978.6993 sq.m/g

**Adsorption Total Pore Volume at 0.9517 P/Po:** 0.8765 cc/g

**Analysis Log**

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*Figure 1d* First page of data output from the gemini analyser for a mesoporous silica.
Analysis of results

Nitrogen/adsorption desorption curves

In this technique, gas adsorption is carried out by exposing a solid (the adsorbant) to an adsorptive gas (the adsorbate) at different relative pressures at the boiling point of the liquid adsorbate at 1 atm. Nitrogen is the preferred adsorbate gas for BET measurements as it is relatively insensitive to the chemical nature of the surface. The quantity of nitrogen adsorbed by the solid at a given temperature is proportional to the mass of the solid, the pressure and the nature of the solid, the relationship between the amount of nitrogen adsorbed and the relative pressure can be expressed as:

\[ V = f(P/P_0)_{T,gas,solid} \]  

\( V \) is the amount or volume of nitrogen adsorbed by the solid, \( P \) is the vapour pressure and \( P_0 \) is the saturated vapour pressure. Adsorption isotherms, such as those in figure 1e were constructed by plotting the amount adsorbed \( V \) against the relative pressure \( P/P_0 \).

\[ \]

Figure 1e Typical adsorption isotherms\(^4\): Type I - microporous solids such as zeolites, Type II - non-porous solids or macroporous solids and Type IV - mesoporous solids.

At very low relative pressures, a monolayer of nitrogen molecules forms on the surface of the solid. As the pressure is increased, multilayers of nitrogen are formed. There is a second condensation process going on as the multilayers are formed. Capillary condensation fills any pores present in the material. The smallest pores are filled first at very low pressures. Further increases in the relative pressure result in the filling of steadily larger pores. If a sample has a narrow range of pore sizes then when a certain
relative pressure is reached the adsorption isotherm will contain a step as nitrogen is rapidly adsorbed into the pores. The wider the pore size range, the more stretched the step. Microporous solids such as zeolites have very large internal surface areas compared to their external surface areas and filling of the pores occurs at low relative pressures (Figure 1e.a). At the other extreme a macroporous solid does not exhibit pore filling until high relative pressures (Figure 1e.b). A mesoporous material exhibits pore filling at intermediate relative pressures; A hysteresis loop is associated with capillary condensation when the pore diameter is greater than 3.7 nm (figure 1e.c).

For the mesoporous materials described in this thesis nitrogen adsorption/desorption curves of V against \( P/P_0 \) were plotted using the output from the Gemini analyser. This data was then used to calculate the pore size distribution using the Doolimore and Heal method described below.

**Pore size analysis of nitrogen desorption isotherms**

It was mentioned in the previous section that the size of pores that are present and the range of pore sizes determine the form of a nitrogen adsorption/desorption isotherm. Pore size analysis takes this principle one step further by applying a mathematical analysis of the form of the isotherm to deduce a pore size distribution. A number of methods have been described in the literature for calculating pore size distributions. In essence, they are all based on the Kelvin equation (2), which relates the relative pressure at which capillary condensation occurs to the pore radius of mesopores.

\[
\ln \frac{P}{P_0} = \frac{-2\gamma V}{r_k RT} \quad (2)
\]

Where \( \gamma \) is the surface tension of adsorbate
V is the molar volume of adsorbate
R is the gas constant
T is the absolute temperature
\( r_k \) is the capillary condensate radius
\( P/P_0 \) is the relative pressure
Unfortunately, the Kelvin equation only accounts for capillary condensation and does not consider the adsorption of nitrogen multi-layers on the surface of the pores. For an accurate pore size determination the multi-layers must also be taken into account. When the capillary liquid is lost, multi-layers are left on the walls, and thus the radius of the meniscus of the capillary condensate is less than the actual radius of the pores \( r_p \) by the amount \( t \) (3).

\[ r_k = r_p - t \]  \hspace{1cm} (3)

The method of determining \( t \), the geometry of the pores and the pore size add to the complexity of pore size analysis and have been discussed in a number of publications. For the pore size analyses described in this thesis a calculation described by Dollimore and Heal was employed. This is based on the method of Barrett et al., (commonly known as the BJH method) but uses an improved route to determining multi-layer desorption. Equation 4 was used as the basis for determining the pore size distribution and from this a spreadsheet was drawn up as described by Dollimore and Heal.

\[ \Delta V_p = R_n(\Delta V_n - \Delta t_n \Sigma S_p + 2\pi t_n \Delta t_n \Sigma l_p) \]  \hspace{1cm} (4)

Where \( \Delta V_p \) is the change in pore volume between two relative pressures
\( \Delta V_n \) is the change in volume of the adsorbate between two relative pressures
\( R_n = (r_p)^2/(r_k + \Delta t_n)^2 \) \( (r_k \) – average capillary radius between two relative pressures)
\( \Delta t_n \) = change in multi-layer thickness between two relative pressures
\( S_p = 2\Delta V_p/r_p \) (surface area of the pores)
\( L_p = S_p/(2\pi r_p) \) (length of the cylindrical pores)
Figure 1f The cylindrical model used in pore size analysis and the multilayers of adsorbed nitrogen, of thickness \( t \).

The spreadsheet for the pore size analysis of mesoporous silica is shown in table 1a. The pore size distributions given in this thesis were obtained by plotting the values of \( \Delta V_p / \Delta r \) (\( dV_p/dr \)) against \( r_p \) for the adsorption branch of the isotherm. The pore size distribution is reliable for pore diameters > 2.0 nm, hence is not useful for measuring micropore diameters.

<table>
<thead>
<tr>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
<th>G</th>
<th>H</th>
</tr>
</thead>
<tbody>
<tr>
<td>P/P_o</td>
<td>V_{des}</td>
<td>V_{liq}</td>
<td>( \Delta V )</td>
<td>t</td>
<td>( \Delta t )</td>
<td>( r_k )</td>
<td>( r_p )</td>
</tr>
<tr>
<td>ml g^{-1}</td>
<td>ml</td>
<td>ml</td>
<td>Å</td>
<td>Å</td>
<td>Å</td>
<td>Å</td>
<td>Å</td>
</tr>
<tr>
<td>A1</td>
<td>B1</td>
<td>B1*0.00155</td>
<td>C2-C1</td>
<td>-4.3[(5/lnA1)^{1/3}]</td>
<td>E2-E1</td>
<td>-9.53/lnA1</td>
<td>E1+G1</td>
</tr>
<tr>
<td>A3</td>
<td>B3</td>
<td>B3*0.00155</td>
<td>C4-C3</td>
<td>-4.3[(5/lnA3)^{1/3}]</td>
<td>E4-E3</td>
<td>-9.53/lnA3</td>
<td>E3+G3</td>
</tr>
<tr>
<td>.</td>
<td>.</td>
<td>.</td>
<td>.</td>
<td>.</td>
<td>.</td>
<td>.</td>
<td>.</td>
</tr>
<tr>
<td>A_m</td>
<td>B_m</td>
<td>B_m*0.00155</td>
<td>C_{m-C_{m+1}}</td>
<td>-4.3[(5/lnA_m)^{1/3}]</td>
<td>E_{m-E_{m+1}}</td>
<td>-9.53/lnA_m</td>
<td>E_{m+G_m}</td>
</tr>
</tbody>
</table>
### Table 1a

The spreadsheet used for calculating pore size distributions from nitrogen desorption data. The data is ordered such that the first desorption point (i.e., where \( P/P_0 \) is close to 1) is at the bottom of the table. As some of the equations are recursive the data has to be inputted line by line. Columns A and B are obtained from the nitrogen desorption experiment and column W is plotted against X to obtain the pore size distribution.
BET surface area analysis

The specific surface area of powders is determined almost exclusively by the BET\(^9\) (Brunauer-Emmett-Teller) method. The surface area of a solid can be obtained by applying the BET model to the nitrogen adsorption data. The BET isotherm model is based on a multilayer coverage on the solid. The rate of adsorption onto the adsorptive sites of the solid is assumed to be equal to the desorption rate of the gas from the occupied sites. Thus, a linear equation can be derived, usually called the 'BET equation':

\[
\frac{P}{V(P_o - P)} = \frac{1}{V_mC} + \frac{(C-1)P}{V_mC P_o} \tag{5}
\]

where \(V_a\) is the moles of gas adsorbed per gram of adsorbent when the gas pressure is \(P\), \(V_m\) is the monolayer capacity of the surface, that is, the number of moles of gas per gram of adsorbent required to form a monolayer, \(P_o\) is the saturation gas pressure (vapour pressure of liquid adsorbate) at the temperature used, and \(C\) is a constant. When \(P/(P_o- P)\) verses \(P/P_o\) is plotted, there is a linear region at low pressure, regression of this region allows the values of \(V_m\) and \(C\) to be calculated from the slope and the \(y\) intercept.

\[
\text{slope} = \frac{(C - 1)}{V_mC} \tag{6}
\]

\[
\text{intercept} = \frac{1}{V_mC} \tag{7}
\]

From \(V_m\), the volume of gas adsorbed for monolayer coverage per gram of solid and \(a_m\), the average area occupied by one nitrogen molecule in the monolayer, the specific surface area of the solid can be calculated

\[
S_{BET} = \frac{V_m a_m N}{22.4 \times 10^{-3}} \tag{8}
\]
Where $S_{\text{BET}}$ is the specific surface area in $m^2 g^{-1}$, $V_m$ is in $m^2 g^{-1}$, $a_m$ in $m^2$.

The Gemini instrument automated the process of obtaining the nitrogen adsorption isotherms, but the surface areas given in this thesis were calculated using the BET method in a spreadsheet. BET analysis was generally carried out on the measurements between relative pressures of 0.05 and 0.30. If there were pores present in the sample with diameters less than 3.0 nm capillary condensation will take place at relative pressures below 0.3, therefore the upper relative pressure used in the BET analysis was reduced to a pressure below the start of capillary condensation. Some of the very disordered silica samples had an extremely broad pore size distribution, therefore there was no low pressure region free from capillary condensation, causing the BET analysis to return surface area values that are greater than the true surface areas.

**Estimating the micropore volume - $\alpha_s$ - plots**

No current theory is capable of providing a general mathematical description of micropore filling but it is sometimes possible to estimate the micropore volume of a silica sample by applying the $\alpha_s$- plot method\textsuperscript{10}, which is a comparative technique, to the $N_2$ adsorption isotherm. A $N_2$ adsorption isotherm of a non-porous silica sample is used as a reference against the porous sample. The volume of nitrogen adsorbed at each pressure measured is normalised to the volume adsorbed at 0.4 $P/P_\infty$ (relative pressure, $P_\infty$ – saturation pressure). The $\alpha_s$ is the reduced volume for the nonporous reference sample. The reduced volumes of the nonporous reference and the sample at the same pressure are then plotted against each other. The micropore adsorption occurs at very low pressures, within the first few data points, therefore the micropore volume can be measured by regression of the linear region at low values of $\alpha_s$ to give the intercept with the y-axis. The micropore volume can be calculated by converting the reduced volume of the y intercept to a real volume then converting to the volume of liquid nitrogen. The total pore volume can also be measured by regressing the linear region at the highest $\alpha_s$ values to give the intercept on the y-axis. Figure 1g shows example $\alpha_s$ – plots for porous materials. In order to determine the micropore volume accurately, the micropore and mesopore distributions need to be separate. If the micropore and mesopore distributions overlap.
this will result in the micropore volume being underestimated, or if the overlap is significant, negative values will be obtained.

Figure 1g Example $\alpha_s$ – plots of high surface area materials. The dashed lines represent regression of a linear region of the graph. For the fumed silica reference sample used $\alpha_s = 0.44$ for the lowest pressure.
1.C  Powder X-ray Diffraction

Introduction

Powder x-ray diffraction is routinely used to study polycrystalline solid state materials such as zeolites. It differs from single crystal X-ray diffraction in that the beam strikes a finely powdered sample, which ideally contains crystals, randomly oriented. The lattice planes of the crystals diffract the X-ray beam. Those planes oriented at the correct angle (Bragg angle 2θ) result in constructive interference of the X-ray beam providing a signal. The recorded powder X-ray patterns can be interpreted by using the Bragg equation nλ = 2dsinθ. Where λ is the wavelength of the incident beam and d is the lattice spacing. Commonly a Cu Kα1 radiation source is used (λ = 1.5406 Å) and detection of the scattered X-rays carried out by a scintillation counter. With such a setup the scattered X-rays result in Bragg reflections at wide angles (10-90°) for crystalline materials.

Characterisation of mesoporous materials by powder X-ray diffraction has become the analytical method of choice for analysing the quality, phase and repeat distance of the structure\(^1\). In the case of mesoporous silicas, the pore walls of the structures are amorphous and so at wide angles no sharp reflections are observed. However, at low angles (2θ <10°) the larger spacings of the mesopore structure are observed. These reflections, at low angles, can be used to help identify the type of mesopore structure (H₁, V₁ and L α). In addition, the narrower the peaks, and the greater the number of peaks in the diffraction pattern, the greater the long range structural order of the material.

Equipment description

Data were collected using a conventional diffractometer, Siemens D5000, employing copper radiation passed through a single crystal monochromator giving only Kα1 radiation figure 1h. The monochromatic X-ray beam was then collimated through an aperture diaphragm and directed onto the sample, mounted flush in a recessed aluminium or plastic holder. Diffracted X-rays were detected by a standard scintillation counter. The sample goniometer was rotated at a constant angular velocity and the detector moved at twice this velocity to ensure the diffraction angle, 2θ. Diffraction data were recorded on a Windows based PC.
Appendix 1  Techniques

Figure 1h A Schematic representation of the Siemens D5000 diffractometer

Experimental parameters

The silica samples were ground using a pestle and mortar for ca. 2 minutes. The resulting fine silica powder was then placed in an aluminium holder containing a circular indentation (ca. 30 mm in diameter and 1 mm deep), and the surface of the powder was made flush with the sides of the holder. Small angle scattering was recorded, using a step size of 0.02 2θ, with 1mm slits, 5 degree/min scan rate, and an acquisition time of 20-30 min.

Analysis of results

Small angle X-ray scattering

Small angle X-ray diffraction patterns were used to help identify the mesopore structure of the silica samples. Each order of diffraction has an associated reciprocal spacing, $S_{hkl} = 1/d_{hkl}$. The ratio of the reciprocal spacings of the diffraction lines allow powder patterns to be indexed to a particular mesophase symmetry (lamellar, hexagonal or cubic for lyotropic systems). The diffraction peaks for a lamellar phase are regularly spaced as $S_h/S_1 = h (1, 2, 3, 4,...)$. For the 2D hexagonal liquid crystal phase $S_{hl}/S_{10} = (h^2+k^2+hk)^{1/2}$ {1, $\sqrt{3}$, 2, $\sqrt{7}$, 3, $\sqrt{12}$, $\sqrt{13}$,...} and for the cubic structures $S_{hkl}/S_{100} = (h^2+k^2+l^2)^{1/2}$ {1, $\sqrt{2}$, $\sqrt{3}$, 2, $\sqrt{5}$, $\sqrt{6}$, $\sqrt{8}$, 3,...}. The various lyotropic cubic phases are further distinguished by characteristic systematic absences, which differ for each space group. The observed
reflections and their corresponding positions are summarised in table 1b. In order to
differentiate between the various liquid crystal phases a large number of orders of
diffraction are necessary. This is particularly true of cubic materials where there are a
variety of possible structures. Furthermore, powder X-ray diffraction cannot differentiate
between lattice planes that diffract at the same angle 2θ. Finally, the long range order in
a mesoporous material is not nearly as great as the regular arrangement of atoms in a
crystal. This means that the diffraction peaks, due to the mesoporous structure, are much
less sharp than those observed for a crystal. The combination of all these factors means
that a great deal of care must be taken when recording and interpreting X-ray diffraction
data of mesostructures. It is possible to improve the quality of the diffraction data by
using equipment specifically designed for low angle measurements. Other improvements
include the use of a highly monochromatic source of x-rays (e.g. synchrotron radiation)
and the collection of data over a long period of time.

$$\sin^2 \Theta = \frac{4}{3} \lambda^2 \left( \frac{h^2 + k^2 + hk}{a^2} \right)$$ (8)

$$\frac{1}{d_{hkl}} = 2 \left( \frac{h^2 + k^2 + hk}{a^2} \right)^{0.5}$$ (9)

$$a_o = \frac{2}{\sqrt{5}} d_{100}$$ (10)

For materials that index to a 2D-hexagonal ordering of pores, space group P6mm, the
relationship between the angle, θ, of the diffraction peak, the unit cell parameter, a_o, and
the miller indices is shown in equation 8. From this equation the separation between
adjacent pores, a_o, can be derived (equation 10). The wall thickness was calculated by
subtracting the pore size from the pore separation, a_o. With the exception of a few
extremely disordered mesoporous silicas, all the mesoporous silicas described in this
thesis produced at least one diffraction peak. The ordered H1 mesoporous silicas
templated from Pluronic P123 gave one major peak (100) and two minor peaks (110 and
200), and with a few very well ordered samples in Chapter 6 a fourth peak was present
(210). The ordered H1 mesoporous silicas templated from CTAB under hydrothermal
conditions gave one major peak (100) and three minor peaks (110, 200 and 210). As the H1 structure became more disordered the 110, 200 and 210 peaks rapidly disappeared leaving the 100 peak, which was retained even for very disordered structures. The peak width of the 100 peak dramatically increased for more disordered structures and the peak width at half height was used as a measure of disorder in the structure. The lower the long-range order in the mesoporous structure the broader the diffraction peak.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Space group</th>
<th>Selection rules</th>
<th>hkl list</th>
<th>spacing ratios, S_{hi}/S_{100}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lamellar (L_w)</td>
<td>h00: h = n</td>
<td>100, 200, 300</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hexagonal (H_x)</td>
<td>hk0: h + k = n</td>
<td>100, 110, 200, 210</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cubic (V_i)</td>
<td>Pm3n (223)</td>
<td>h, k, l permutable</td>
<td>200, 210, 220</td>
<td>2, 3, 8</td>
</tr>
<tr>
<td></td>
<td>hhl: l = 2n</td>
<td>200, 211, 220, 300</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>310, 222</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pn3m (224)</td>
<td>h, k, l permutable</td>
<td>110, 111, 200, 211</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>hhl: l = 2n</td>
<td>211, 220, 300, 310</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>222</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fm3m (225)</td>
<td>h, k, l permutable</td>
<td>111, 200, 220, 311</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>hkl: h+k, h+l, l+k = 2n</td>
<td>200, 220, 311</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0kl: k+l = 2n</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>hhl: h+l = 2n</td>
<td>311</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>h00: h = 2n</td>
<td>222</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fd3m (227)</td>
<td>h, k, l permutable</td>
<td>111, 220</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>hkl: h+k = 2n and h+l, l+k = 2n</td>
<td>111, 220</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 1b Selection rules for the space groups associated with lyotropic liquid crystal phases and the relative spacings of the first Bragg reflections. Note that only a selection of the cubic space groups are given for the more commonly found phases in lyotropic systems. Information obtained from the international tables of crystallography.

<table>
<thead>
<tr>
<th>Space Group</th>
<th>Selection Rules</th>
<th>First Bragg Reflections</th>
</tr>
</thead>
<tbody>
<tr>
<td>Im3m (229)</td>
<td>h, k, l permutable</td>
<td>110, 200, 211, 220, 310, 222</td>
</tr>
<tr>
<td></td>
<td>okl: k+l = 4n and k, l = 2n</td>
<td>( \sqrt{11} )</td>
</tr>
<tr>
<td></td>
<td>hkl: h+l = 2n</td>
<td>( \sqrt{12} )</td>
</tr>
<tr>
<td></td>
<td>h00: h = 4n</td>
<td>( \sqrt{13} )</td>
</tr>
<tr>
<td>Ia3d (230)</td>
<td>h, k, l permutable</td>
<td>211, 220, 321, 400</td>
</tr>
<tr>
<td></td>
<td>okl: k+l = 4n</td>
<td>( \sqrt{14} )</td>
</tr>
<tr>
<td></td>
<td>hkl: h+l = 2n</td>
<td>( \sqrt{15} )</td>
</tr>
<tr>
<td></td>
<td>h00: h = 4n</td>
<td>( \sqrt{16} )</td>
</tr>
</tbody>
</table>

1.D  Polarising optical microscopy and phase diagram construction
The polarised light microscope differs from a standard optical microscope in that the sample is observed through a pair of crossed, polaroid filters. One of the filters (the analyser) is situated above the sample, which is sandwiched between two glass plates, and one below (the polariser). When there is no sample present, the image on the microscope appears black as no light is transmitted.

Figure 1i  Schematic diagram of the positioning of polaroid filters in a polarised light microscope

An isotropic liquid has no effect on plane polarised light as the refractive indices of the material are the same in all directions. However, in a liquid crystal system there is ordering of the molecules, which in some cases this can result in anisotropy in the refractive index of the material. For lyotropic systems, hexagonal and lamellar phases have two different refractive indices at 90° to each other. These liquid crystal phases are said to be birefringent and each has a particular optical texture under a polarising microscope, allowing identification of the phases. Figure 1i shows some optical textures for the commonly found liquid crystal phases of lyotropic systems. In cubic systems there is no birefringence as light interacts with the material in a similar manner whatever the orientation. Micellar solutions are isotropic and therefore, along with cubic phases, appear black under the polarising microscope. Identification of the liquid crystal phase by polarised light microscopy is a combination of observations of optical textures.
and the viscosity of the phase. The viscosity often helps to differentiate between systems that appear identical under the microscope. For example, cubic phases can be differentiated from micellar solutions, as a cubic phase is very viscous with irregular shaped air bubbles trapped in the mixture whereas a micellar solution is very fluid with spherical bubbles.

<table>
<thead>
<tr>
<th>Mixture</th>
<th>Optical texture</th>
<th>Viscosity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Micellar solution (L₀)</td>
<td>Isotropic (figure 1i.a)</td>
<td>Very fluid with circular air bubbles</td>
</tr>
<tr>
<td>Phase seperated (L₀ + w)</td>
<td>Isotropic (figure 1i.b)</td>
<td>Very fluid with spherical regions rich in micelles Turbid solution</td>
</tr>
<tr>
<td>Micellar cubic phase (L₁)</td>
<td>Isotropic (figure 1i.c)</td>
<td>Viscous phase sometimes containing angular air bubbles</td>
</tr>
<tr>
<td>Hexagonal phase (H₀)</td>
<td>Feather texture (figure 1i.d,e)</td>
<td>Viscous phase containing angular air bubbles</td>
</tr>
<tr>
<td>Cubic phase (V₁)</td>
<td>Isotropic (black) (figure 1i.f)</td>
<td>Very viscous phase containing angular air bubbles</td>
</tr>
<tr>
<td>Lamellar phase (L₂)</td>
<td>Thread like texture (figure 1i.g) or Oily streak texture (figure 1i.f), becomes a mosaic like texture of heating (figure 1i.h)</td>
<td>Fairly viscous but less viscous than an H₀ phase – spherical air bubbles The viscosity of the phase can drop dramatically with heating</td>
</tr>
<tr>
<td>Inverse micelles (L⁻)</td>
<td>Isotropic (like figure 1i.a)</td>
<td>Fluid with spherical air bubbles</td>
</tr>
</tbody>
</table>

Table 1c Some pointers to identifying commonly found structures in lyotropic systems of ethylene oxide surfactants.
Figure 1j Photographs of various phases of Brij 97 and Brij 78 observed under POM. (A) – $L_1$ (B) – $L_1 + W$ (C) – $I_1$ (D) – $H_1$ (E) – $H_1$ cooled from $L_1$ phase (F) – $V_1$ (G) – $L_\alpha$ Threads (H) – $L_\alpha$ (I) – $L_\alpha$ oily streak- (slight motion blur). The polarisers are crossed for photos D, E, G, H, and I.
The construction of phase diagrams

The phase behaviour of the mixtures was investigated by polarised light microscopy using an Olympus BH-2 polarised light microscope equipped with a Linkam TMS90 heating stage and temperature control unit. The phase behaviour of each mixture was characterised by placing a small sample between a glass slide and cover slip and viewing under a polarised light microscope. Phase transition boundaries were located to an accuracy of ± 2°C by using heating/cooling rates of 0.2°C min⁻¹ across the boundary. Initially a regular series of mixtures was examined (e.g. 10 wt% increments in surfactant concentration) and a rough phase diagram constructed. From this further mixtures were prepared to better identify the positions of the phase boundaries.

For the phase diagrams constructed it was important to ensure that the surfactant mixtures were homogeneous. Samples for study were prepared by accurately weighing out the required amount of surfactant and aqueous solution into a glass vial. After sealing the vial, mixing was achieved by at least four heating/cooling cycles where the sample was heated to 80°C and cooled to room temperature. In addition, during cooling the compositions were vigorously shaken using a vortex mixture. All mixtures were allowed to equilibrate at room temperature overnight before analysis.
1. The construction of ternary diagrams

Ternary diagrams are useful tools for displaying 3 component data (ternary data) on a 2 dimensional diagram. The ternary diagrams in this thesis were constructed using the Tridraw software package\textsuperscript{12}. An example of how to read off the composition of a point on the ternary diagram is given in figure 1k.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{ternary_diagram.png}
\caption{An example of a ternary diagram. The composition of the three component system can be read as shown by the dashed lines. In this case, the composition at the indicated point is 60 wt\% TMOS, 12 wt\% HCl and 28 wt\% Pluronic P123.}
\end{figure}
References


2. Beta 3b of Scion Image (Image analysis software supplied by Scion Corp.)
http://www.scioncorp.com


12. Tridraw v2.6 by J I Hualde

## Appendix 2 Silica sample compositions

### 2.A Chapter 2 CTAB H₂SiO₂ compositions

<table>
<thead>
<tr>
<th>Sample label and Lab Book Reference</th>
<th>SiO₂:CTAB (w/w)</th>
<th>SiO₂/g</th>
<th>CTAB/g</th>
<th>Water/g</th>
<th>CTAB:TMOS equivalence</th>
<th>Days at 115°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>la TJGS/2357/58</td>
<td>0.37:1</td>
<td>1.65</td>
<td>4.50</td>
<td>6.75</td>
<td>1.0.94</td>
<td>7</td>
</tr>
<tr>
<td>lb TJGS/2541/3</td>
<td>0.46:1</td>
<td>2.07</td>
<td>4.50</td>
<td>6.75</td>
<td>1.1.17</td>
<td>7</td>
</tr>
<tr>
<td>lc TJGS/2357/61</td>
<td>0.54:1</td>
<td>2.45</td>
<td>4.50</td>
<td>6.75</td>
<td>1.1.37</td>
<td>7</td>
</tr>
<tr>
<td>ld TJGS/2357/62</td>
<td>0.54:1</td>
<td>2.45</td>
<td>4.50</td>
<td>6.75</td>
<td>1.1.37</td>
<td>13</td>
</tr>
<tr>
<td>le TJGS/2541/5</td>
<td>0.64:1</td>
<td>2.88</td>
<td>4.50</td>
<td>6.75</td>
<td>1.1.62</td>
<td>7</td>
</tr>
<tr>
<td>lf TJGS/2357/42</td>
<td>0.73:1</td>
<td>3.48</td>
<td>4.76</td>
<td>7.16</td>
<td>1.1.85</td>
<td>7</td>
</tr>
<tr>
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### 2.B Chapter 3 Pluronic P123 H₂SiO₂ compositions

#### Series 1 – Vary TMOS

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<th>Sample Label and Lab Book Reference</th>
<th>P123: TMOS by mass</th>
<th>TMOS /g</th>
<th>Pluronic P123 /g</th>
<th>0.5 M HCl(aq) /g</th>
<th>Total mass /g</th>
<th>Mole ratio of Water: TMOS</th>
<th>Mass fraction TMOS</th>
<th>Mass fraction Pluronic P123</th>
<th>Mass fraction 0.5 M HCl(aq)</th>
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### Series 2 – Vary Water

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<th>Pluronic P123 /g</th>
<th>0.5 M HCl(aq) /g</th>
<th>Total mass /g</th>
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<th>Mass fraction TMOS</th>
<th>Mass fraction Pluronic P123</th>
<th>Mass fraction 0.5 M HCl(aq)</th>
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<th>Total mass /g</th>
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<th>Mass fraction TMOS</th>
<th>Mass fraction Pluronic P123</th>
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## 2.C Chapter 4 Brij 78 compositions

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<th>Mass fraction Brij 78</th>
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## 2.D Chapter 5 Pluronic F127 compositions

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<th>TMOS/g</th>
<th>Pluronic F127/g</th>
<th>0.5 M HCl(aq)/g</th>
<th>Total mass/g</th>
<th>Mole ratio of Water: TMOS</th>
<th>Mass fraction TMOS</th>
<th>Mass fraction Pluronic F127</th>
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### Series 2 – Vary Water

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<th>Pluronic F127 /g</th>
<th>0.5 M HCl(aq) /g</th>
<th>Total mass /g</th>
<th>Mole ratio of Water:TMOS</th>
<th>Mass fraction TMOS</th>
<th>Mass fraction Pluronic F127</th>
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<td>13.14</td>
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<tr>
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<td>35</td>
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<td>7.27</td>
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<td>0.426</td>
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<tr>
<td>2d TJGS/2541/66</td>
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<td>2e TJGS/3100/31</td>
<td>45</td>
<td>2.50</td>
<td>1.67</td>
<td>2.04</td>
<td>6.21</td>
<td>6.89</td>
<td>0.403</td>
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</tr>
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<td>1f TJGS/2541/74</td>
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<td>2.00</td>
<td>2.00</td>
<td>7.00</td>
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<td>2g TJGS/2541/67</td>
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<td>0.473</td>
<td>0.316</td>
<td>0.210</td>
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<tr>
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<td>2.00</td>
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<td>6.08</td>
<td>3.04</td>
<td>0.493</td>
<td>0.329</td>
<td>0.178</td>
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### Series 3 – Vary Pluronic F127

<table>
<thead>
<tr>
<th>Sample Label and Lab Book Reference</th>
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<th>TMOS /g</th>
<th>Pluronic F127 /g</th>
<th>0.5 M HCl(aq) /g</th>
<th>Total mass /g</th>
<th>Mole ratio of Water:TMOS</th>
<th>Mass fraction TMOS</th>
<th>Mass fraction Pluronic F127</th>
<th>Mass fraction 0.5 M HCl(aq)</th>
</tr>
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<tbody>
<tr>
<td>3a TJGS/3100/67</td>
<td>25</td>
<td>4.00</td>
<td>0.89</td>
<td>2.67</td>
<td>7.56</td>
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<td>0.529</td>
<td>0.118</td>
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<tr>
<td>3b TJGS/3100/42</td>
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<td>1.00</td>
<td>2.33</td>
<td>6.83</td>
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<td>0.512</td>
<td>0.146</td>
<td>0.341</td>
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<td>0.90</td>
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<td>5.64</td>
<td>0.493</td>
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<td>1.67</td>
<td>5.28</td>
<td>5.64</td>
<td>0.473</td>
<td>0.210</td>
<td>0.316</td>
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<td>2.00</td>
<td>7.00</td>
<td>5.63</td>
<td>0.429</td>
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<td>0.286</td>
</tr>
<tr>
<td>3f TJGS/3100/66</td>
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<td>2.50</td>
<td>2.09</td>
<td>1.67</td>
<td>6.28</td>
<td>5.64</td>
<td>0.399</td>
<td>0.334</td>
<td>0.267</td>
</tr>
<tr>
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<td>60</td>
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<td>2.50</td>
<td>1.67</td>
<td>6.67</td>
<td>5.64</td>
<td>0.375</td>
<td>0.375</td>
<td>0.250</td>
</tr>
<tr>
<td>3h TJGS/3100/43</td>
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<td>2.50</td>
<td>3.10</td>
<td>1.67</td>
<td>7.27</td>
<td>5.64</td>
<td>0.344</td>
<td>0.426</td>
<td>0.230</td>
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</table>
## 2.E Chapter 6 Sample compositions

### Pluronic P123 with cosolvents

<table>
<thead>
<tr>
<th>Sample Label and Lab Book Reference</th>
<th>P123 by mass</th>
<th>TMOS /g</th>
<th>Pluronic P123 /g</th>
<th>0.5 M HCl(aq) /g</th>
<th>Total mass /g</th>
<th>Mole ratio of Water to TMOS</th>
<th>Mass fraction of TMOS</th>
<th>Mass fraction of Pluronic P123</th>
<th>Mass fraction of 0.5 M HCl(aq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P123REF TJGS/2541/58</td>
<td>11.50</td>
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<td>5.64</td>
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<td>0.286</td>
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</table>

### 1,3,5 trimethyl benzene

<table>
<thead>
<tr>
<th>Sample Label and Lab Book Reference</th>
<th>TMOS /g</th>
<th>Pluronic P123 /g</th>
<th>0.5 M HCl(aq) /g</th>
<th>1,3,5 trimethyl benzene /g</th>
<th>Total mass /g</th>
<th>Mass fraction of TMOS</th>
<th>Mass fraction of Pluronic P123</th>
<th>Mass fraction of 0.5 M HCl(aq)</th>
<th>Mass fraction of 1,3,5 trimethyl benzene</th>
</tr>
</thead>
<tbody>
<tr>
<td>P25TMB TJGS/2541/76</td>
<td>2.50</td>
<td>1.67</td>
<td>1.67</td>
<td>0.42</td>
<td>6.26</td>
<td>0.399</td>
<td>0.267</td>
<td>0.267</td>
<td>0.067</td>
</tr>
<tr>
<td>P50TMB TJGS/2541/77</td>
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<td>1.67</td>
<td>1.67</td>
<td>0.84</td>
<td>6.68</td>
<td>0.374</td>
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<td>0.250</td>
<td>0.126</td>
</tr>
<tr>
<td>P1TMB TJGS/2541/78</td>
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<td>1.67</td>
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### 1-decanol

<table>
<thead>
<tr>
<th>Sample Label and Lab Book Reference</th>
<th>TMOS /g</th>
<th>Pluronic P123 /g</th>
<th>0.5 M HCl(aq) /g</th>
<th>Decanol /g</th>
<th>Total mass /g</th>
<th>Mass fraction of TMOS</th>
<th>Mass fraction of Pluronic P123</th>
<th>Mass fraction of 0.5 M HCl(aq)</th>
<th>Mass fraction of decanol</th>
</tr>
</thead>
<tbody>
<tr>
<td>P25DEC TJGS/3100/19</td>
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<td>0.267</td>
<td>0.267</td>
<td>0.267</td>
</tr>
<tr>
<td>P50DEC TJGS/3100/20</td>
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<td>0.84</td>
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</tr>
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<td>P1DEC TJGS/3100/21</td>
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### 1,2 ethanediol

<table>
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<tr>
<th>Sample Label and Lab Book Reference</th>
<th>TMOS /g</th>
<th>Pluronic P123 /g</th>
<th>0.5 M HCl(aq) /g</th>
<th>Ethanediol /g</th>
<th>Total mass /g</th>
<th>Mass fraction of TMOS</th>
<th>Mass fraction of Pluronic P123</th>
<th>Mass fraction of 0.5 M HCl(aq)</th>
<th>Mass fraction of ethanediol</th>
</tr>
</thead>
<tbody>
<tr>
<td>P25ETD TJGS/3100/13</td>
<td>2.50</td>
<td>1.67</td>
<td>1.67</td>
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<td>0.267</td>
<td>0.267</td>
</tr>
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### 1,3 propanediol

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<th>TMOS /g</th>
<th>Pluronic P123 /g</th>
<th>0.5 M HCl(aq) /g</th>
<th>Propane diol /g</th>
<th>Total mass /g</th>
<th>Mass fraction TMOS</th>
<th>Mass fraction Pluronic P123</th>
<th>Mass fraction 0.5 M HCl(aq)</th>
<th>Mass fraction propane diol</th>
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<tr>
<td>P25PD TJGS/3100/2</td>
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<td>1.67</td>
<td>0.42</td>
<td>6.26</td>
<td>0.399</td>
<td>0.267</td>
<td>0.267</td>
<td>0.067</td>
</tr>
<tr>
<td>P50PD TJGS/3100/3</td>
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<td>1.67</td>
<td>0.84</td>
<td>6.68</td>
<td>0.374</td>
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<td>0.250</td>
<td>0.126</td>
</tr>
<tr>
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<td>1.67</td>
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### 1,4 butanediol

<table>
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<th>0.5 M HCl(aq) /g</th>
<th>Butanediol /g</th>
<th>Total mass /g</th>
<th>Mass fraction TMOS</th>
<th>Mass fraction Pluronic P123</th>
<th>Mass fraction 0.5 M HCl(aq)</th>
<th>Mass fraction butanediol</th>
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<tbody>
<tr>
<td>P25BUD TJGS/3100/5</td>
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<td>0.267</td>
<td>0.067</td>
</tr>
<tr>
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<td>0.126</td>
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### Brij 72

<table>
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<th>TMOS /g</th>
<th>Pluronic P123 /g</th>
<th>0.5 M HCl(aq) /g</th>
<th>Brij 72 /g</th>
<th>Total mass /g</th>
<th>Mass fraction TMOS</th>
<th>Mass fraction Pluronic P123</th>
<th>Mass fraction 0.5 M HCl(aq)</th>
<th>Mass fraction Brij 72</th>
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<tbody>
<tr>
<td>P25B72 TJGS/3100/46</td>
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<td>1.67</td>
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<td>0.267</td>
<td>0.067</td>
</tr>
<tr>
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<td>1.67</td>
<td>1.67</td>
<td>0.84</td>
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<td>0.374</td>
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</table>

### Brij 76

<table>
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<th>Pluronic P123 /g</th>
<th>0.5 M HCl(aq) /g</th>
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<th>Total mass /g</th>
<th>Mass fraction TMOS</th>
<th>Mass fraction Pluronic P123</th>
<th>Mass fraction 0.5 M HCl(aq)</th>
<th>Mass fraction Brij 76</th>
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<tr>
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<td>2.50</td>
<td>1.67</td>
<td>1.67</td>
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<td>0.413</td>
<td>0.276</td>
<td>0.276</td>
<td>0.035</td>
</tr>
<tr>
<td>P25B76 TJGS/3100/48</td>
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<td>1.67</td>
<td>1.67</td>
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<td>6.26</td>
<td>0.399</td>
<td>0.267</td>
<td>0.267</td>
<td>0.067</td>
</tr>
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</table>
## Appendix 2

### Silica Compositions

#### Brij 78

<table>
<thead>
<tr>
<th>Sample Label and Lab Book Reference</th>
<th>TMOS /g</th>
<th>Pluronic P123 /g</th>
<th>0.5 M HCl(aq) /g</th>
<th>Brij 78 /g</th>
<th>Total mass /g</th>
<th>Mass fraction TMOS</th>
<th>Mass fraction Pluronic P123</th>
<th>Mass fraction 0.5 M HCl(aq)</th>
<th>Mass fraction Brij 78</th>
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<tbody>
<tr>
<td>P13B78 TJGS/3100/97</td>
<td>2.50</td>
<td>1.67</td>
<td>1.67</td>
<td>0.21</td>
<td>6.05</td>
<td>0.413</td>
<td>0.276</td>
<td>0.276</td>
<td>0.035</td>
</tr>
<tr>
<td>P25B78 TJGS/3100/85</td>
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<td>1.67</td>
<td>1.67</td>
<td>0.42</td>
<td>6.26</td>
<td>0.399</td>
<td>0.267</td>
<td>0.267</td>
<td>0.067</td>
</tr>
<tr>
<td>P38B78 TJGS/3100/98</td>
<td>2.50</td>
<td>1.67</td>
<td>1.67</td>
<td>0.63</td>
<td>6.47</td>
<td>0.386</td>
<td>0.258</td>
<td>0.258</td>
<td>0.097</td>
</tr>
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<td>1.67</td>
<td>1.67</td>
<td>0.84</td>
<td>6.68</td>
<td>0.374</td>
<td>0.250</td>
<td>0.250</td>
<td>0.126</td>
</tr>
<tr>
<td>P1B78 TJGS/3100/99</td>
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<td>7.51</td>
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</table>

#### Brij 78 – 50wt% surfactant

<table>
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<th>TMOS /g</th>
<th>Pluronic P123 /g</th>
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<th>Brij 78 /g</th>
<th>Total mass /g</th>
<th>Mass fraction TMOS</th>
<th>Mass fraction Pluronic P123</th>
<th>Mass fraction 0.5 M HCl(aq)</th>
<th>Mass fraction Brij 78</th>
</tr>
</thead>
<tbody>
<tr>
<td>P13B78C TJGS/3100/105</td>
<td>2.50</td>
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<tr>
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<td>1.67</td>
<td>0.33</td>
<td>5.83</td>
<td>0.429</td>
<td>0.228</td>
<td>0.286</td>
<td>0.057</td>
</tr>
<tr>
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<td>1.67</td>
<td>0.45</td>
<td>5.83</td>
<td>0.429</td>
<td>0.208</td>
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<td>P50B78C TJGS/3100/108</td>
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#### 2,2 dimethoxy propane

<table>
<thead>
<tr>
<th>Sample Label and Lab Book Reference</th>
<th>TMOS /g</th>
<th>Pluronic P123 /g</th>
<th>0.5 M HCl(aq) /g</th>
<th>2, 2 Dimethoxy propane /g</th>
<th>Total mass /g</th>
<th>Mass fraction TMOS</th>
<th>Mass fraction Pluronic P123</th>
<th>Mass fraction 0.5 M HCl(aq)</th>
<th>Mass fraction butanediol</th>
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<tbody>
<tr>
<td>P25DMP TJGS/3100/50</td>
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<td>1.67</td>
<td>1.67</td>
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#### Pluronic F127 with cosolvents

<table>
<thead>
<tr>
<th>Sample Label and Lab Book Reference</th>
<th>F127: TMOS by mass</th>
<th>TMOS /g</th>
<th>Pluronic F127 /g</th>
<th>0.5 M HCl(aq) /g</th>
<th>Total mass /g</th>
<th>Mole ratio of Water: TMOS</th>
<th>Mass fraction Pluronic F127</th>
<th>Mass fraction 0.5 M HCl(aq)</th>
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## 1,3,5 trimethyl benzene

<table>
<thead>
<tr>
<th>Sample Label and Lab Book Reference</th>
<th>TMOS /g</th>
<th>Pluronic F127 /g</th>
<th>0.5 M HCl(aq) /g</th>
<th>1,3,5 trimethyl benzene /g</th>
<th>Total mass /g</th>
<th>Mass fraction TMOS</th>
<th>Mass fraction Pluronic F127</th>
<th>Mass fraction 0.5 M HCl(aq)</th>
<th>Mass fraction 1,3,5 trimethyl benzene</th>
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<tr>
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<td>0.437</td>
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<td>0.250</td>
<td>0.063</td>
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<tr>
<td>F38TMB TJGS/3100/103</td>
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<td>1.43</td>
<td>0.54</td>
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<td>0.242</td>
<td>0.242</td>
<td>0.092</td>
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<tr>
<td>F50TMB TJGS/3100/90</td>
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<td>0.118</td>
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<tr>
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<td>1.43</td>
<td>1.43</td>
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<td>0.211</td>
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</table>

## 1-decanol

<table>
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<tr>
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<th>Pluronic F127 /g</th>
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<th>Decanol /g</th>
<th>Total mass /g</th>
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<th>Mass fraction Pluronic F127</th>
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## Brij 72

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<tr>
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<th>TMOS /g</th>
<th>Pluronic F127 /g</th>
<th>0.5 M HCl(aq) /g</th>
<th>Brij 72 /g</th>
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<th>Mass fraction TMOS</th>
<th>Mass fraction Pluronic F127</th>
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<td>1.43</td>
<td>1.43</td>
<td>0.36</td>
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<tr>
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<td>0.54</td>
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<td>F1B72 TJGS/3100/101</td>
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## Brij 76

<table>
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<th>TMOS /g</th>
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<th>0.5 M HCl(aq) /g</th>
<th>Brij 76 /g</th>
<th>Total mass /g</th>
<th>Mass fraction TMOS</th>
<th>Mass fraction Pluronic F127</th>
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## Brij 78

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<tr>
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<th>TMOS /g</th>
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<th>0.5 M HCl(aq) /g</th>
<th>Brij 76 /g</th>
<th>Total mass /g</th>
<th>Mass fraction TMOS</th>
<th>Mass fraction Pluronic F127</th>
<th>Mass fraction 0.5 M HCl(aq)</th>
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<td>0.36</td>
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<td>0.437</td>
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<td>0.235</td>
<td>0.235</td>
<td>0.118</td>
</tr>
</tbody>
</table>
Appendix 3

Surface area model for \(H_i\) materials

By considering an \(H_i\) material as an infinitely sized particle with smooth pores of uniform size and separation it is possible to obtain a theoretical surface area and pore volume for the material. If the fundamental unit is considered:

- Pore radius = \(r\)
- Pore separation = \(a\)
- Tube length = \(l\)
- Density of the material = \(\rho\)

**Fundamental unit**

(dashed triangle)

Surface area of fundamental unit = \(\pi l\)

Area occupied by material (shaded area) = \(\frac{1}{2}a^2 \sin 60 - \frac{1}{2} \pi r^2\)

Mass of material = \(\frac{1}{2} \rho \left( \frac{\sqrt{3}}{2} a^2 - \pi r^2 \right)\)

Specific surface area of fundamental unit,

\[
S_f = \frac{\text{Surface area}}{\text{mass}} = \frac{4\pi r}{\rho(\sqrt{3}a^2 - 2\pi r^2)} \tag{1}
\]

Specific pore volume of fundamental unit,

\[
V_f = \frac{\text{Pore volume}}{\text{mass}} = \frac{2\pi r^2}{\rho(\sqrt{3}a^2 - 2\pi r^2)} \tag{2}
\]
The specific surface area of an H\textsubscript{1} material is dependent on the density ($\rho$) of the material, the distance between the pores ($a$) and the radius of the pores ($r$).

The model does not take into account some of the properties that were observed for the real materials:

- The surface area is not just due to the hexagonal pore structure but also has a contribution from the micropores within the samples.
- The pore size distribution is not taken into account as the pore diameter is fixed.
- The pore walls were not totally smooth, roughness of the pore walls adds to the experimental surface area.
- Defects in the pore structure also affect the surface area.
- The external surface area of the particles was not accounted for, but this is not a significant contribution for particles larger than 100 nm.

By plotting $S_f$ against pore diameter and wall thickness for silica it was possible to see how the surface area varies as a function of pore size and wall thickness (figure 3a).

From this plot it is observed that surface area is strongly dependant on the wall thickness for a fixed pore diameter, particularly for walls < 4 nm thick, there is a rapid increase in surface area as the wall thickness decreases. For a fixed wall thickness, as the pore diameter is increased the surface area increases to a maximum value then decreases gradually as the pore diameter is increased further. The pore diameter where this maxima occurs is dependent on the wall thickness. The greater the wall thickness the greater the pore diameter for this maxima. Also the maxima becomes less pronounced with a smaller decrease in surface area. By plotting $V_f$ against pore diameter and wall thickness for silica it was possible to see how the pore volume varies as a function of pore size and wall thickness (figure 3b). From this plot it is observed that, as with surface area, the pore volume increases with decreasing wall thickness for a fixed pore diameter. The pore volume also increases with increasing pore diameter for a fixed wall thickness.
Figure 3a The variation in theoretical surface area, calculated from equation (1), with changing wall thickness and pore diameter for mesoporous H₃ silica.

Figure 3b The variation in theoretical pore volume, calculated from equation (2), with changing wall thickness and pore diameter for mesoporous H₃ silica.
In summary, the model proposed here was a useful guide to predicting the relative magnitudes of surface areas and pore volumes for 2-d hexagonal (H\textsubscript{1}) mesoporous materials. However, factors such as microporosity, pore wall roughness, width of the pore size distribution and external surface were not accounted for by the model, and as a result the absolute surface areas calculated from the model are lower than the experimental values. The model shows that surface area increases with decreasing wall thickness, but for a fixed wall thickness the surface area passed through a maximum value as the pore diameter is increased, where as the pore volume increases with increasing pore diameter and decreasing wall thickness.