

Formation of mesoporous silicates using Triton XN surfactants in the presence of concentrated mineral acids

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Mesoporous silicates have been prepared from synthesis mixtures with different acid contents using Triton XN surfactants with short poly(ethylene oxide) (PEO) chains. At very high acid contents, even Triton X45 ($n_{\text{EO}}=5.0$) with a very low cloud point, gives mesoporous solids. Triton X114 ($n_{\text{EO}}=8.0$) and Triton X100 ($n_{\text{EO}}=10.0$) give high quality (HQ) products within a well-defined range of acid contents. HQ products give sharper XRD peaks and narrower pore size distributions than low quality (LQ) products. We attribute the formation of the HQ products to the altered organisation of the surfactant and the formation of hydrogen-bonded adducts with the PEO chains. The N_2 adsorption-desorption parameters of the solids obtained by calcining silica-Triton XN mesophases are governed by the hydrophilicity of the surfactant, which in turn depends on the length of the PEO chains and on the acid content. Increased hydrophilicity leads to a decrease in the surface area, pore volume and pore diameter of the products.

Introduction

Mesoporous silica molecular sieves can be prepared *via* various synthetic routes using a variety of surfactants.¹⁻⁶ The routes can be classified according to the nature of the interactions which lead to the formation of hybrid organic-inorganic materials. Charge matching is thought to be crucial in synthesis involving cationic quaternary ammonium surfactants both in basic (S^+I^- pathway) and acidic ($\text{S}^+\text{X}^-\text{I}^+$ pathway) media, and leads to hexagonal, cubic or lamellar mesophases. Mesostructured materials can be synthesised using neutral amines, by virtue of the hydrogen bonding of silica species and amino groups (S^0I^0 pathway, HMS silicates).^{2,7,8} Nonionic poly(ethylene oxide) (PEO) surfactants are also efficient templates for supramolecular assembly leading to materials with disordered tubular pore systems (MSU silicates). Thus, Bagshaw and co-workers used different nonionic surfactants for direct gel synthesis of mesoporous silica and alumina molecular sieves with d_{100} ranging from 4.1 to 6.3 nm.^{6,9} The advantages of nonionic surfactants over neutral long-chain amines and quaternary ammonium compounds are their low cost, low toxicity and biodegradability.¹⁰⁻¹²

Studies of the formation mechanism of mesoporous silicates made using neutral PEO surfactants have focused on the role of interactions between the surfactant EO group, bound water, tetraethylorthosilicate (TEOS) and the silica species formed during the hydrolysis of the latter. Hydrogen bonding plays a key role both during the micellization of the surfactant and in the interactions between PEO chains and the silica species. However, Bagshaw *et al.* noted the poor correlation between the length of the chains (the hydrophilic part) and the pore diameter of the products.⁶ A solution method has been used to synthesise mesoporous silicates through neutral templating with PEO surfactants.¹³ Fluoride anions were present in the synthesis mixture to promote crystallization of silica-surfactant mesophases. The temperature of the synthesis has been shown to direct the pore size of the products. However, no mesostructured phases were obtained above the cloud point of the surfactant.

We have used PEO surfactants to prepare mesoporous

silicates from aqueous solutions in the presence of concentrated mineral acids. Products of different structures and with different thermal stabilities have been prepared from cationic surfactants in the presence of concentrated acids,^{7,14} and Yang *et al.* synthesised mesoporous silica spheres under quiescent acidic conditions.¹⁵ Inorganic acids have also been shown to improve the long-range ordering of mesoporous MCM-41 silica.¹⁶ Zhao and co-workers used nonionic triblock and star diblock copolymers in acidic media (2 M HCl) to synthesise mesoporous silicates with pore sizes in the 20–100 Å range and different pore arrangements,^{17,18} and suggested that the formation of silica-surfactant mesocomposites from the silica species and nonionic alkyl PEO surfactants occurs through the (S^0H^+)(X^-I^+) pathway.

We have used Triton XN surfactants ($N=45, 100$ and 114) with relatively short PEO chains to obtain mesoporous silicates over a broad range of acid concentrations and found that the acidity of the starting solutions controls the quality of the mesostructured products. Thus, depending on the length of the PEO chains, we have obtained high quality (HQ) solids with sharp X-ray diffraction (XRD) peaks, high surface areas and relatively narrow pore size distribution. By variation of the synthesis conditions through changing the concentration of the acid and the source of silica, we show that this effect is due to the altered organisation of the organic component in response to the acid content of the starting mixture. Previous attempts to synthesise mesoporous composites with Triton XN surfactants *via* the gel method afforded only low quality (LQ) products with broad XRD peaks and much lower surface areas than for MCM-41 silicates.⁶ Triton X100 was recently used to synthesise mesoporous silicates using sodium silicate over a wide range of pH.^{19,20} Relatively stable products were obtained only at a pH of above 6 and their pore diameter increased from 1.5 to 2.5 nm upon raising the pH and the concentration of sodium. However, only poorly organized mesostructures with low thermal stability were formed at pH values below 5–6. We also show that the addition of a large amount of inorganic acids (well above the amount used by others¹⁸) makes it possible to synthesise mesoporous products from PEO surfactants with cloud points below ambient temperature.

Experimental

Synthesis

In a typical synthesis procedure, an aqueous solution of the surfactant and an inorganic acid (HCl or H₂SO₄, both from BDH) was prepared at ambient temperature and magnetically stirred for 1 h. Tetraethyl orthosilicate (TEOS, Aldrich, 98% pure) was then added dropwise under stirring. The precipitates were collected after 48 h, washed with distilled water until the pH of the washing liquid was 4.0–5.0, and dried at 50–60 °C overnight. Triton XN [*N*=45 (Sigma), 100 and 114 (Aldrich)], and Igepal (CA520, CO520, CA720 and CO720, Aldrich) were used as surfactants. A solution of sodium silicate (14% NaOH, 27% SiO₂, Aldrich) was used as an alternative source of silica in some syntheses. The typical composition of the synthesis mixtures was 1.00 SiO₂:*n* surfactant:*m* HA:225 H₂O, with *n*=0.10–0.40 and *m*=4.0–37.0 for both HCl and H₂SO₄. The products were calcined at 500 °C for 16 h in air.

X-Ray diffraction (XRD)

The XRD patterns were recorded using a Philips 1710 powder diffractometer with Cu-K α radiation (40 kV, 40 mA), 0.020° step size and 1.0 s counting time per step.

Solid-state NMR

Solid-state ²⁹Si magic-angle-spinning (MAS) NMR spectra were recorded at 79.44 MHz (9.4 T field) using a Chemagnetics CMX-400 spectrometer and zirconia rotors 7.5 mm in diameter spun in nitrogen at 3.2 kHz. $\pi/3$ pulses of 4.5 μ s duration were used and 64 scans were acquired with a recycle delay of 600 s. ²⁹Si chemical shifts are quoted in ppm from external TMS. ¹³C CP/MAS NMR spectra were recorded at 100.56 MHz using zirconia rotors 4 mm in diameter spun in nitrogen at 4 kHz. The ¹H $\pi/2$ pulse length was 3.6 μ s.

Thermogravimetric analysis (TGA)

Thermogravimetric analysis was carried out using a Polymer Laboratories TGA 1500 instrument under a flow of nitrogen in the 20–800 °C temperature range at a heating rate of 10 °C min⁻¹. Although there was no further weight loss after 600 °C, the value at 800 °C is quoted. TGA data were found to be in excellent agreement with the results of CHN analysis.

N₂ adsorption

N₂ adsorption–desorption isotherms were measured using the volumetric method with a Coulter SA3100 sorptometer at –196 °C. Calcined samples were dried at 120 °C before analysis and then kept for 8 h at 200 °C under vacuum. The surface area was calculated using the BET method on the basis of the adsorption branch in partial pressure (*p/p*₀) over the range 0.05–0.20. The pore volume was determined from the amount of N₂ adsorbed at *p/p*₀=0.99. Calculation of the pore size was performed using the Horvath–Kawazoe method.²¹

Results

Synthesis and XRD

In contrast to the gel method using nonionic surfactant templates, the addition of TEOS to dilute solutions of Triton XN (*N*=100 and 114) does not promote crystallization of silica–organic mesophases, so that mineral acids must be added to the synthesis mixture. White products were formed after periods of 1–2 min to 2 h, depending on the acid content and the length of the PEO chain.

The different solubility of the surfactants is caused by the different lengths of the hydrophilic part of the Triton XN

chains (*N*=45, 100 and 114; *n*_{EO}=5, 10, and 8, respectively). Thus, at ambient temperatures Triton X100 and Triton X114 form micellar solutions (cloud points of 65 and 25 °C, respectively),^{11,12} while Triton X45 (cloud point <0 °C) is insoluble in water and forms white emulsions composed of pure surfactant in equilibrium with the solvent, and surfactant micelles containing a large amount of water. The surfactant concentration in the synthesis mixtures was 2.0–2.5 wt%, above the CMC,¹² thus indicating that the template is in the micellar form. The surfactant : SiO₂ ratios (henceforth referred to as *s/S*) were varied in the 0.05–0.40 range. A typical synthetic procedure used *s/S*=0.20, corresponding to an excess of surfactant over the whole range of acid contents. Synthesis mixtures with lower *s/S* gave colloidal solutions containing substantial amounts of colloidal silica.

The XRD patterns of the as-synthesized materials obtained from the mixture 0.20 Triton X114 : 1.00 TEOS : *n* HCl : 223.5 H₂O (*n*=4.0–37.0) and of their calcined forms are shown in Fig. 1. Thermally stable silica–Triton X114 mesoporous products can be synthesised over the whole range of HCl contents. The single XRD peak indicates the presence of a tubular pore system. Analysis of XRD patterns enabled us to distinguish solids with different degrees of ordering depending on the HCl content. Thus, HQ products with sharp XRD peaks are formed when HCl : TEOS = 11.0–17.0. Solids synthesised outside this range give less intense and much broader peaks, indicating a lower degree of mesoscopic organisation. For synthesis mixtures containing H₂SO₄ instead of HCl, HQ products are produced when H₂SO₄ : TEOS = 13.0–24.0 (Table 1). As with HCl, synthesis mixtures with H₂SO₄ : TEOS < 13.0 and H₂SO₄ : TEOS > 24.0 promote the formation of solids with broad XRD peaks.

The different quality of the products obtained at different acid contents is reflected in the XRD patterns of the as-synthesised and calcined materials. Thus, as-synthesised HQ Triton X114–silica mesocomposites give sharp peaks with FWHM \approx (0.16–0.18°) 2θ . Calcination broadens the peak to (0.30–0.32°) 2θ . For LQ products obtained at HCl : TEOS below 13.0 or above 24.0, the peak is substantially wider (at least 0.62° 2θ) which, along with a much lower intensity of the XRD pattern, indicates a much smaller particle size and lower degree of mesoscopic organisation.

The range of acid contents producing HQ mesophases depends on the nature of the surfactant (*e.g.* the number of ethylene oxide units in the hydrophilic part) (Table 1). Thus, HQ Triton X100–silica mesocomposites were obtained at HCl : TEOS \leq 4.0 or H₂SO₄ : TEOS = 4.0–9.3. Solids synthesised at higher acid contents give broad XRD peaks. Formation of the products with different degrees of ordering, depending on the acid content in the synthesis mixture, has also been observed when TEOS was substituted by a solution of sodium silicate.

The behaviour of Triton X45 in the synthesis is different from that of Triton X114 and Triton X100. Despite the cloud point of Triton X45 being below ambient temperature, a relatively low acid content (HCl : SiO₂ = 4.0–13.0) promotes the formation of well-organised solids (Fig. 2a). However, the products are not thermally stable. On the other hand, materials formed at high acid contents are thermally stable but give broad XRD peaks (Fig. 2b). It is clear that the acid content influences the behaviour of the surfactant. Thus, white milky emulsions of Triton X45 are formed at low HCl contents (due to a low cloud point temperature), and clear template solutions are obtained at high acidity, indicating that the presence of large quantities of acids increases the cloud point of the surfactant.

The pore dimensions *d*₁₀₀ (37.5–41.5 Å for as-synthesised and 33.5–38.0 Å for calcined products) are much smaller than those reported for silicates made from Triton X100 and Triton X114 (61.0–62.0 Å)⁶ *via* the gel method. For syntheses in acidic

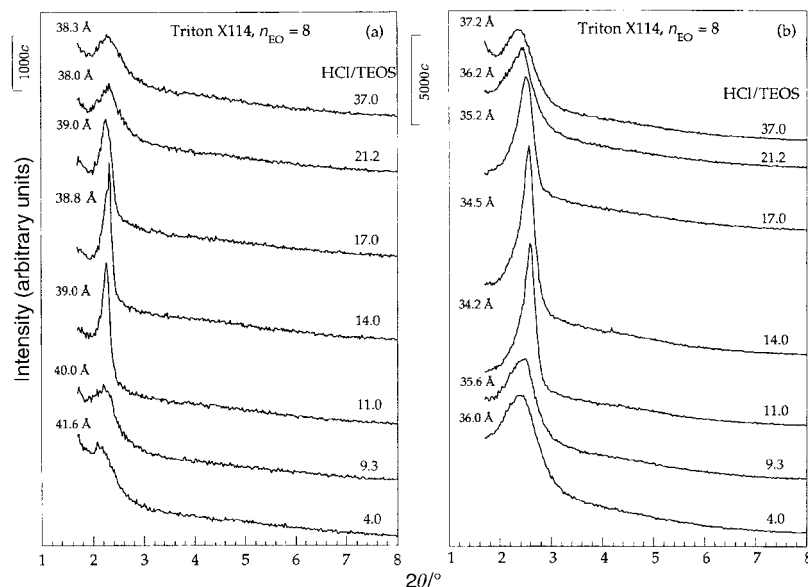


Fig. 1 XRD patterns of silica-surfactant mesophases synthesized from starting mixtures: 0.20 Triton X114 : 1.00 TEOS : n HCl : 225 H₂O: (a) as-synthesised; (b) calcined.

solutions, the d -spacing of the products is primarily determined by the size of the hydrophobic part of the surfactant micelles, and is practically independent of the length of PEO chains. Thus, using Igepal CO720 and Igepal CO520, in which the hydrophobe contains just one extra CH₂ group, increases the d -spacing by 2.0–3.0 Å in comparison to Triton XN.

A comparison of the XRD patterns of silicates obtained *via* the acidic nonionic templating pathway with those of MCM-41 shows a lower degree of ordering, as higher angle reflections, typical of the well-ordered hexagonal pore system of MCM-41,^{7,14} are not resolved. The same has been observed for MSU silicates^{6,13} and for HMS materials synthesised in the presence of neutral long-chain amines.² HQ silicates obtained from Triton X100 and Triton X114 in the presence of inorganic acids are more organised than MSU or HMS materials, as the single XRD peak is much sharper. This is unexpected, considering that in acid-free media Triton XN gives less well ordered materials than those prepared from Tergitol, Igepal RC and Pluronic.⁶ LQ silicates show comparable ordering to that of MSU made without the addition of inorganic acids and calcined HMS silicates synthesised using neutral amines.

XRD studies of Triton XN-silica mesocomposites synthesised in acidic media at ambient temperatures indicate the formation of solids with different degrees of mesoscopic organisation depending on the acid content and the length of the hydrophilic part of the surfactant. In order to estimate the origin of this effect, the composition and structure of the mesophases were analysed using thermogravimetry and solid-state NMR.

Thermogravimetric analysis

Typically, TG curves of silica-Triton XN mesophases reveal three thermal events: (i) the loss of physisorbed water; (ii) the

loss of intra-channel water; and (iii) the decomposition of the template. The weight loss during the second step is substantially larger for materials synthesised from Triton X45 at low acidity than from other surfactants, indicating a much higher water content. The total weight loss of the silica-Triton XN products gradually decreases with increased acid content for both HCl and H₂SO₄ (Fig. 3). An increase of the mesophase quality is observed at certain values of total weight loss.

Mesocomposites containing a surfactant with longer PEO chains show lower total weight losses at the same acid content. Thus, the s/S ratio in the LQ solids synthesised at HCl : TEOS = 37.0 is 0.160 for the Triton X45-silica mesophase ($n_{EO}=5$), while products synthesised in the presence of Triton X114 ($n_{EO}=8$) and Triton X100 ($n_{EO}=10$) have s/S of 0.0872 and 0.0611, respectively. For Triton X114, the HQ products have $s/S=0.100$ – 0.135 . Solids with lower or higher s/S ratios show a much lower degree of mesoscopic organisation. For Triton X100 with longer hydrophilic PEO chains, the HQ products have $s/S=0.097$ – 0.115 .

²⁹Si MAS NMR

The ²⁹Si MAS NMR spectra of silica-Triton XN mesophases consist of three resonances corresponding to Q₂ (–90 to –92 ppm), Q₃ (–101 to –103 ppm) and Q₄ (–109 to –111 ppm) silicate species²² (Fig. 4). The degree of condensation of the silica network increases with increasing acid content in the synthesis mixture, reflected in the decreased (Q₂+Q₃)/Q₄ ratio (Table 2). Calcined products give broad and poorly resolved spectra showing an increased population of Q₄ sites.

Comparison of the ²⁹Si MAS NMR spectra of Triton XN-silica mesocomposites with those reported for MCM-41 (obtained *via* the S⁺I[–] and S⁺X[–]I⁺ pathways) and HMS silicates synthesised at ambient temperature, suggests that the

Table 1 Ranges of formation of “high quality” silica-surfactant mesophases

Acid	Range studied, H _n A : SiO ₂	Range of HQ solids		
		Triton X114, $n_{EO}=8$		Triton X100, $n_{EO}=10$
		TEOS	Na _x SiO _y	TEOS
HCl	4.0–37.0	11.0–17.0	10.0–21.0	4.0
H ₂ SO ₄	4.0–37.0	13.0–24.0	17.0–30.0	4.0–9.3

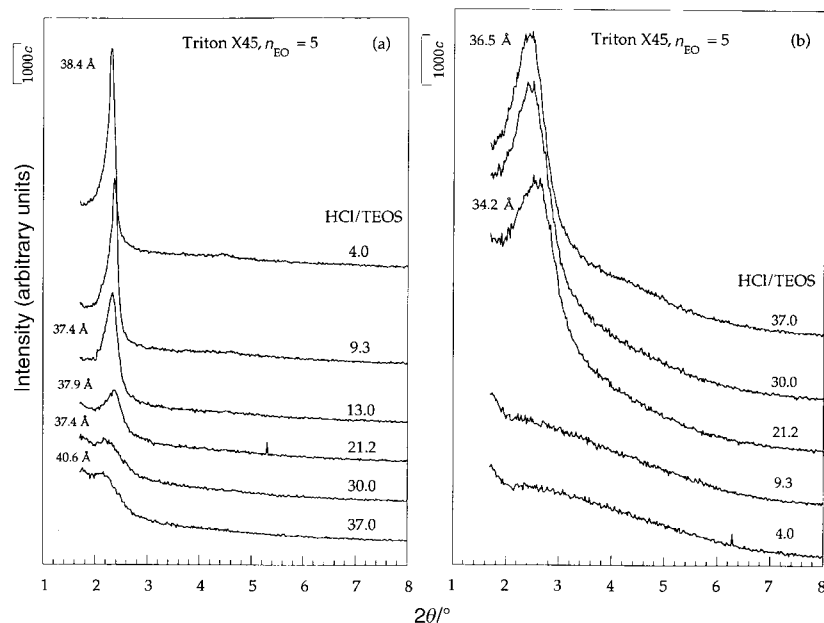


Fig. 2 XRD patterns of silica-surfactant mesophases synthesized from the starting mixture: 0.30 Triton X45 : 1.00 TEOS : n HCl : 225 H₂O: (a) as-synthesised; (b) calcined.

degree of condensation of the silica network is similar to that in MCM-41, but lower than in HMS silicates.^{7,8,14} This conclusion is supported by the ²⁹Si spectra of the calcined materials. ²⁹Si solid-state NMR and TGA were used to estimate the composition of the mesocomposites. The average number of EO units per Q_n ($n=2$ and 3) silicate unit, \bar{n}_{EO} , in HQ

mesophases made with Triton X100 and Triton X114 and from either TEOS or Na_xSiO₃, in the presence of either acid, is in the 1.85–2.05 range. LQ products synthesised in the presence of high acid contents have $\bar{n}_{EO} < 1.60$, while products prepared with acid contents lower than those required to obtain HQ mesophases have $\bar{n}_{EO} > 2.30$ (Table 2). These results suggest that the arrangement of surfactant PEO chains within the silica walls in the products depends on the acid content of the starting mixture.

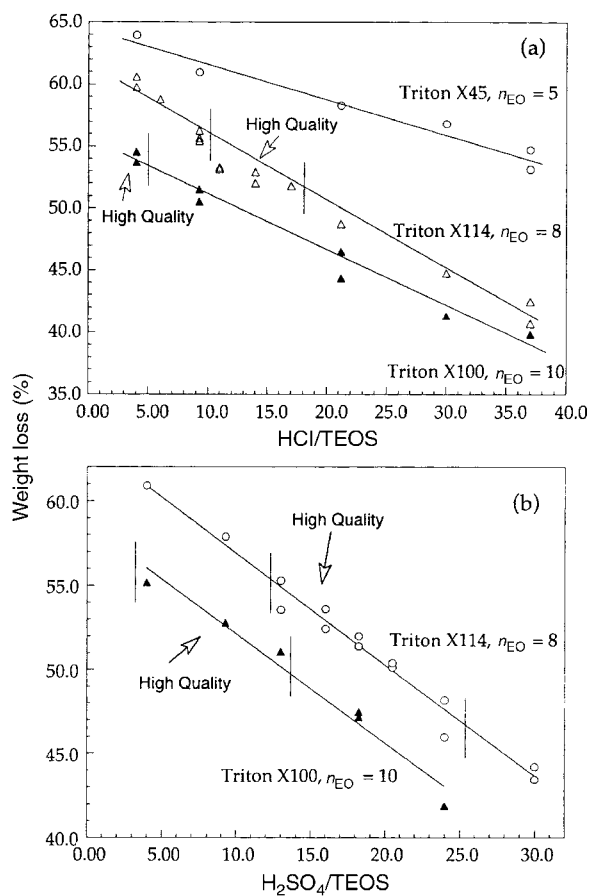


Fig. 3 Dependence of total weight loss of silica-surfactant mesophases synthesized from the starting mixtures 0.20 Triton XN : 1.00 TEOS : m HA : 225 H₂O: (a) HA = HCl; (b) HA = H₂SO₄.

¹³C CP/MAS NMR

¹³C CP/MAS spectra (not shown) of mesocomposites obtained at different acid contents are similar and contain three main peaks attributable to three different segments of the surfactant molecules. The peak at 32.6 ppm is assigned to the C atoms of the aliphatic part of the surfactant [the (CH₃)₃CCH₂C(CH₃)₂ group]. The broad asymmetric resonance at 70.5 ppm comes from the carbon atoms in different (–CH₂CH₂–O) units. A very broad peak centred at ca. 150 ppm corresponds to the phenyl groups. All the ¹³C CP/MAS NMR lines in the spectra of Triton X114 contained within the silica mesophases are much

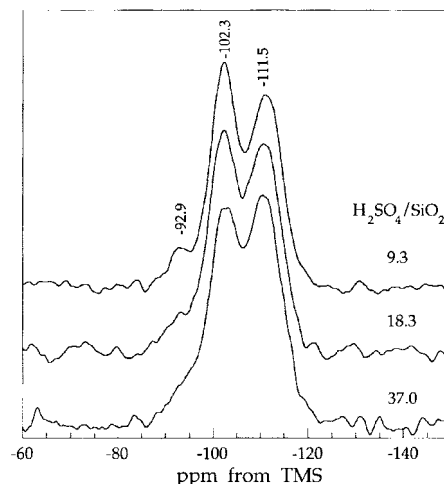


Fig. 4 ²⁹Si MAS NMR spectra of silica-Triton X114 mesocomposites prepared in the presence of different acid contents.

Table 2 Composition and degree of condensation of silica–Triton *XN* mesophases (from ^{29}Si MAS NMR)^a

Surfactant	n_{EO}	Acid	SiO_2	Acid : SiO_2	Surfactant : SiO_2	$(\text{Q}_2 + \text{Q}_3)/\text{Q}_4$	\bar{n}_{EO}
Triton X100	10	HCl	TEOS	4.0*	0.1040	1.019	2.05
				9.3	0.0942	0.984	1.90
				37.0	0.0547	0.897	1.16
		H ₂ SO ₄	TEOS	4.0	0.1055	1.155	2.00
				9.3*	0.0949	1.014	1.89
				24.0	0.0627	0.894	1.33
Triton X114	8	HCl	TEOS	4.0	0.1510	1.028	2.40
				11.0*	0.1075	0.854	1.90
				37.0	0.0783	0.667	1.59
				4.0	0.1582	1.076	2.44
				11.0*	0.1140	1.001	1.84
				30.0	0.0761	0.914	1.28
		H ₂ SO ₄	Na _x SiO _y	9.3	0.1496	1.143	2.24
				18.3*	0.1163	1.036	1.83
				37.0	0.0752	0.964	1.23
				4.0	0.2275	0.929	2.36
				37.0	0.1204	0.780	1.63
Triton X45	5	HCl	TEOS				

^a n_{EO} is the number of ethylene oxide units in the surfactant; \bar{n}_{EO} is the average number of ethylene oxide units per Q_n ($n=2, 3$) silica site; * denotes HQ mesophases.

broader and much less well resolved than those in the solution spectrum.²³ The largest broadening is observed for the peaks corresponding to EO units and phenyl groups, indicating the most severe motional hindering of these groups in the solid state.

N₂ adsorption–desorption

N₂ adsorption–desorption isotherms of solids produced by calcining silica–Triton *XN* mesophases are typical of materials with the “wormlike” pore arrangement.^{2,6,7,9} Adsorption parameters are listed in Table 3. The evidence for framework-confined mesoporosity is the adsorption–desorption step at $p/p_0=0.10$ – 0.35 . Unlike mesoporous HMS silicates, in which there is a substantial contribution from textural mesopores, in most cases no hysteresis step at $p/p_0>0.60$ is observed for solids obtained from Triton *XN*–silica mesocomposites.

Analysis of the N₂ adsorption–desorption isotherms and pore size distributions in LQ silicates made from the mesophases synthesised at HCl : TEOS = 37.0 (Fig. 5a) reveals the increase in the pore diameters with the decreasing number of EO units in the hydrophilic part of the molecule. Thus, the values of D_{av} in solids prepared from Triton X45–SiO₂ and

Triton X100–SiO₂ are 24.5 and 17.5 Å, respectively. Although the values of S_{BET} and V_{ads} for LQ silicates are high, the pore size distribution is not well defined (especially for Triton X100–SiO₂ mesophases) (Fig. 5b). An increase in the number of EO units in the surfactant also results in a decrease in the surface area and the adsorbed volume.

N₂ adsorption–desorption isotherms of HQ silicates synthesised from Triton X114–SiO₂ and Triton X100–SiO₂ are given in Fig. 6a. The adsorption step in the isotherms is steeper and occurs at larger values of p/p_0 than for the LQ materials. As a result, the pore size distribution becomes narrower and the average pore diameter is larger than in LQ solids synthesised in the presence of the highest acid content (Fig. 6b). As in the LQ materials, the average pore diameter decreases with increasing PEO chain length, and the values of D_{av} in the calcined products made using Triton X100 and Triton X114 are 19.6 and 21.3 Å, respectively.

Comparison of the adsorption parameters of silicates obtained at different acid contents in the synthesis mixtures containing Triton X100 or Triton X114 indicates a decrease in both S_{BET} and V_{ads} with increasing acid content in the synthesis mixtures. This has been observed for materials synthesised in

Table 3 N₂ adsorption–desorption parameters of mesoporous silicates^a

Surfactant	n_{EO}	HCl : SiO_2	SiO_2	$S_{\text{BET}}/\text{m}^2 \text{g}^{-1}$	$V_{\text{ads}}/\text{ml g}^{-1}$	$D_{\text{av}}(\text{HK})/\text{Å}$	$d/\text{Å}$	$(d-D_{\text{av}})/\text{Å}$		
(a) Synthesised in the presence of HCl										
Triton X45	5	37.0	TEOS	1275	0.796	24.5	36.7	12.2		
Triton X114	8	4.0	TEOS	1423	0.858	23.3	36.4	13.1		
		6.0	TEOS	1347	0.774	22.6	36.2	13.6		
		8.0	TEOS	1294	0.701	21.2	36.5	15.3		
		14.0*	TEOS	1278	0.622	21.3	34.5	13.2		
		11.0*	Na ₂ SiO ₃	1356	0.731	21.8	35.0	13.2		
		37.0	TEOS	1110	0.533	19.6	37.2	17.6		
Triton X100	10	37.9	Na ₂ SiO ₃	1164	0.571	19.7	36.9	17.2		
		4.0*	TEOS	1174	0.576	19.6	35.2	15.6		
		37.0	TEOS	862	0.398	17.5	35.6	18.1		
(b) Synthesised in the presence of H ₂ SO ₄										
Triton X114	8	4.0	TEOS	1472	0.860	23.6	36.8	13.2		
		9.3	TEOS	1373	0.716	21.5	35.6	14.1		
		9.3	Na ₂ SiO ₃	1261	0.620	20.0	34.7	14.7		
		13.0*	TEOS	1334	0.491	21.3	33.9	12.6		
		18.3*	Na ₂ SiO ₃	1230	0.619	21.2	33.7	12.5		
		30.0	TEOS	969	0.511	19.2	37.7	18.5		
		38.6	Na ₂ SiO ₃	975	0.475	19.7	37.4	17.7		
		Triton X100	10	4.0*	TEOS	1298	0.643	19.6	35.6	16.0
				9.3*	TEOS	1210	0.581	19.6	35.0	15.4
				24.0	TEOS	954	0.455	17.3	37.1	19.8

^a* denotes HQ products.

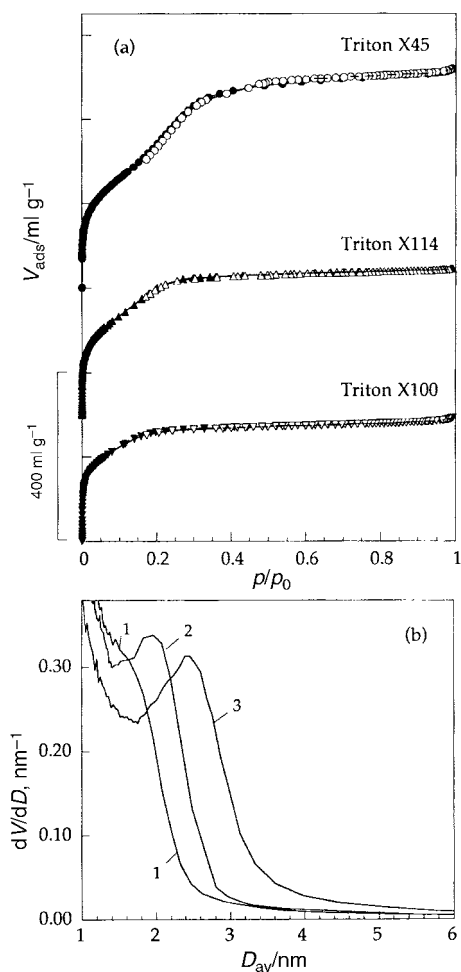


Fig. 5 (a) N_2 adsorption–desorption isotherms of LQ mesoporous silicates obtained from Triton XN -silica. (b) Horvath–Kawazoe pore size distributions determined from N_2 adsorption isotherms for calcined LQ silicates obtained from the mesophases containing: (1) Triton X100; (2) Triton X114; (3) Triton X45.

the presence of either acid and from different sources of silica (TEOS and Na_2SiO_3) (Table 3). The pore size distribution in HQ products synthesised at particular acid:SiO₂ ratios is narrower than in LQ solids obtained at either higher or lower acid:SiO₂ ratios (as for the Triton X114-silica mesocomposites).

Adsorption–desorption isotherms enable the estimation of the wall thickness of the tubular pores from the d -spacing and the average pore diameter obtained by the Horvath–Kawazoe method.²¹ For a tubular pore system, the average wall thickness (W_{av}) is obtained by subtracting D_{av} from the d -spacing.¹³ LQ solids obtained from SiO₂–Triton XN ($N=100, 114$) mesocomposites synthesised with HCl:TEOS=37.0 have $W_{av}=18.0$ Å. HQ silicates have much thinner walls. Thus, the values of W_{av} for mesocomposites made using Triton X100 and Triton X114 are 15.7 and 13.0 Å, respectively. LQ solids obtained from SiO₂–Triton X114 in the presence of low acid contents have slightly thicker walls ($W_{av}=14.0$ Å). Solids obtained in the presence of Triton X45 with a much shorter PEO chain give a much smaller value of 12.2 Å.

Generally, the values of S_{BET} and V_{ads} and the average pore diameter decrease with the increasing hydrophilicity of the surfactant. This is observed both for the changes in hydrophilicity caused by lengthening the PEO chains and by increasing the acid content in the synthesis mixtures. On the other hand, an increase in the hydrophilicity of the surfactant produces solids with thicker walls.

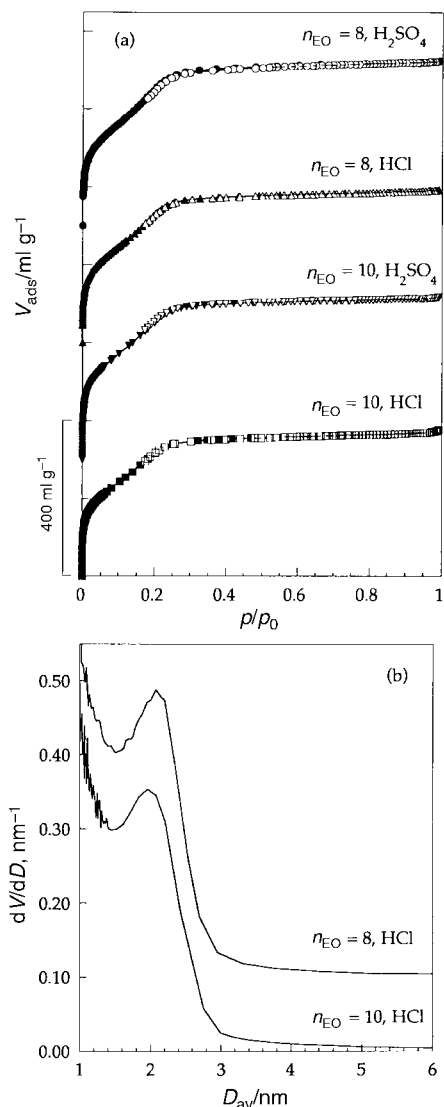


Fig. 6 (a) N_2 adsorption–desorption isotherms of HQ products synthesised from Triton XN -silica ($N=100, 114$); n_{EO} denotes the number of EO-units in the surfactant. (b) Horvath–Kawazoe pore size distributions determined from N_2 adsorption isotherms for HQ silicates.

Formation of silica–Triton X114 mesophases

The kinetics of the reaction have been studied in order to establish the mechanism of formation of products with different degrees of ordering in the presence of different acid contents. The experiments were performed using surfactants with PEO chains of various lengths and different sources of silica over a range of acid contents.

Increasing the acid content in the synthesis mixture containing TEOS increases the rate of formation of mesostructured solids, as evidenced by the reduction in the formation time for mesostructured solids (henceforth referred to as “crystallization time”). This is observed for both Triton X100 and Triton X114. It is clear that lengthening the PEO chains leads to a decrease in the reaction rate at relatively low acid contents (Fig. 7). Acid contents above HA:TEOS=20.0 reduce the mesophase formation time to less than 2 min for both surfactants.

When comparing the crystallization rates of mixtures containing HCl and H₂SO₄ we cannot assume a complete dissociation of H₂SO₄, as its concentration in the solution is very high. It is more accurate to consider only the first step of H₂SO₄ dissociation and compare the molar contents of the

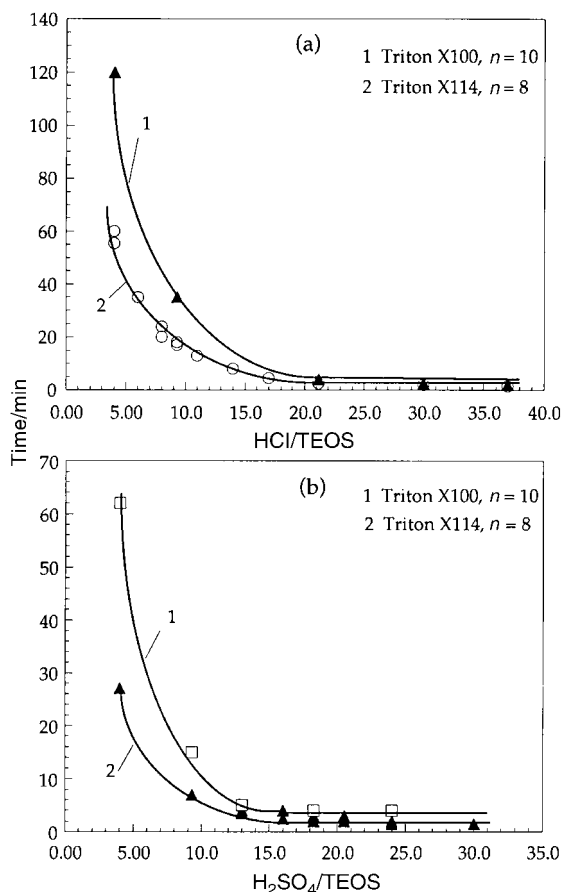


Fig. 7 Crystallization times for silica-Triton XN products with different acid contents in the starting mixtures containing: (a) HCl; (b) H₂SO₄.

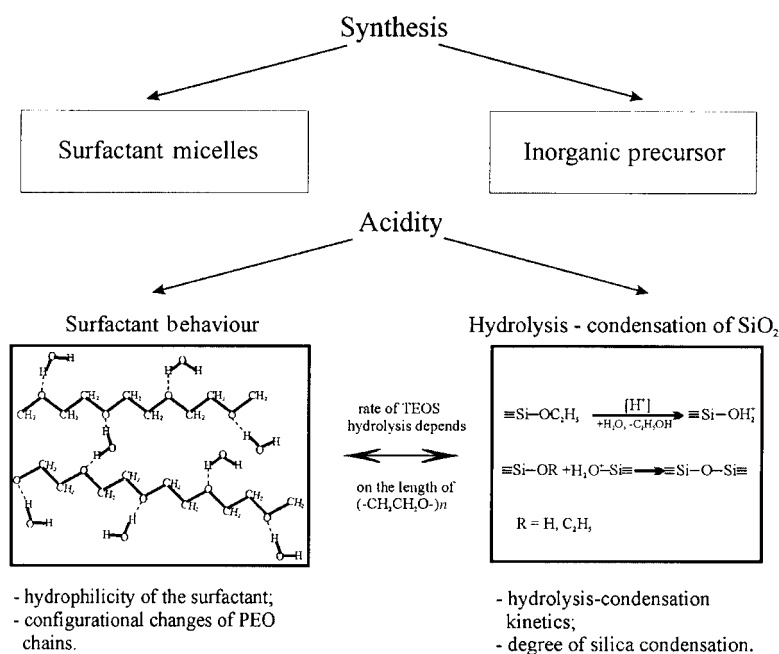
acids. This suggests that the rate of mesocomposite formation is higher in solutions containing H₂SO₄.

The formation of the mesocomposites is clearly a complex process governed by factors related both to the surfactant behaviour and the condensation chemistry of silica. However, the reason for the formation of silicates with different degrees of ordering at different acid contents is still unclear. The rate of

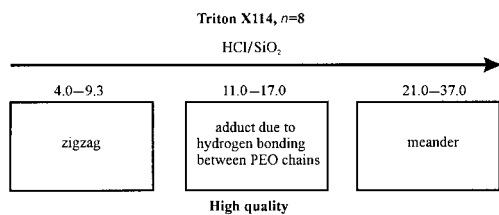
crystallization increases gradually with increasing acid content. In this case, it could be assumed that the nature of the effect in question is purely kinetic, *i.e.* that the acid content determines the rate of the hydrolysis-condensation of TEOS, and a particular acid content guarantees slow kinetics for TEOS hydrolysis-condensation, thus leading to solids with an improved mesoscopic ordering. However, this is at variance with the experimental results. First, the materials synthesised in the presence of Triton X114 and the lowest acid content (and thus with the lowest crystallization rate) are poorly ordered. Second, HQ solids have also been synthesised under a different kinetic regime using sodium silicate as the source of silica. In this case the crystallization time is reduced significantly while HQ products are obtained with acid contents close to those giving HQ mesophases in the presence of TEOS. The dependence of the crystallization time on the acid content can therefore be related to TEOS as a particular source of silica and its hydrolysis-condensation chemistry.

To obtain further insights into the mechanism of the reaction, we have examined the structure of intermediates collected during the course of the synthesis of HQ and LQ solids. HQ products were obtained from the synthesis mixtures with the composition 1.0 TEOS:0.20 Triton X114:11.0 HCl:223.5 H₂O. LQ solids were synthesised at higher acid content (HCl:TEOS=36.0). During HQ synthesis the solids collected 1 h after addition of TEOS give a sharp XRD peak characteristic of HQ mesophases. The d_{100} spacing decreases during the course of the reaction from 42.1 Å after 1 h to 39.6 Å after 12–48 h. Solids obtained in the presence of a much higher acid content give a broad XRD peak after just 15 min of synthesis, and no HQ products are obtained at any stage of the reaction.

The surfactant content of HQ solids decreases as the reaction proceeds. Thus, after 1 h of the reaction $s/S=0.187$, decreasing to 0.135 after 8 h and to 0.127 after 96 h. At the same time, the degree of condensation of the inorganic component increases as the $(Q_2+Q_3)/Q_4$ ratio decreases from 1.34 after 1 h to 0.90 after 48 h. Combining this with the XRD results leads us to suggest that during the synthesis of HQ mesocomposites the inorganic precursor reacts with the pre-organised organic template to form a well-ordered tubular mesophase containing a large amount of the surfactant. These products react with the soluble inorganic precursor species, subsequently leading to an



Scheme 1 Acidic synthesis of Triton XN-silica mesocomposites.



Scheme 2 Synthesis of HQ silica-Triton X114 mesophases.

increase in the relative contribution of the inorganic component and its degree of condensation.

Unlike in HQ materials, the amount of surfactant in the LQ solids made in the presence of much higher acid contents is unchanged. This can be attributed to very fast hydrolysis and condensation of TEOS at high acidity. As a result, there is no clear trend in the degree of silica condensation with the $(Q_2 + Q_3)/Q_4$ ratio in the 0.79–1.00 range. In this case, the disordered tubular structure remains virtually unchanged during the course of the synthesis.

Discussion

The formation of mesostructured silica-surfactant hybrids can be seen as an organisation of hydrophobic and hydrophilic components into a biphasic composite.¹⁴ Three different interactions must therefore be considered: inorganic-organic, organic-organic, and inorganic-inorganic. The structure of the products is very sensitive to the balance of thermodynamic and kinetic forces within the system, and changes in both the organic and inorganic components can give rise to a particular organisation of the products.²⁴

Neutral polyethylene oxide surfactants promote the formation of silica-surfactant mesophases *via* hydrogen bonding between the neutral surfactant headgroups and the neutral inorganic precursor. The presence of high quantities of acid in

the synthesis mixtures can affect both the surfactant behaviour and the hydrolysis-condensation of the silica species (Scheme 1).

It is clear that the hydrolysis-condensation of silica is affected by changes in the acid content. First, ²⁹Si MAS NMR shows that the acid content in the starting mixture controls the degree of condensation of the silica walls formed around the surfactant arrays. Second, the rate of crystallization of silica-Triton XN mesophases ($N=100$ and 114) from mixtures containing TEOS increases with the acid content. The rate of crystallization also depends on the length of PEO chains in the surfactant. The more hydrophilic Triton X100 shows slower kinetics of mesophase formation compared to Triton X114. This suggests that the hydrolysis-condensation of TEOS is directed to the surfactant-inorganic interface. Clearly, the energy barrier of the transfer of the surfactant from liquid to solid state is lower for the more hydrophobic Triton X114 than for Triton X100. Therefore, products containing surfactant with smaller PEO chains are formed faster.

The substitution of TEOS by a dilute solution of sodium silicate resulted in much faster precipitation, indicating that, in this case, the crystallization is limited by the rate of binding of the silica species to the surfactant associates and the rate of silica condensation. However, the fact that HQ products are obtained both from TEOS and Na_xSiO_y under different kinetic regimes shows that the kinetics of hydrolysis-condensation of the inorganic precursor are not primarily responsible for the sharp increase in the crystallinity of products obtained within a particular range of acid content.

The addition of large quantities of acids to the starting mixtures induces changes in the behaviour of the surfactant. These are easily noticeable for Triton X45 with a short PEO chain ($n_{\text{EO}}=5$). The milky emulsions formed by this surfactant at low acid content become clear when the acidity is increased to $\text{HCl}:\text{surfactant}:\text{TEOS}=37.0:0.20:1.00$. As a result, Triton X45 in the presence of high acid contents gives products

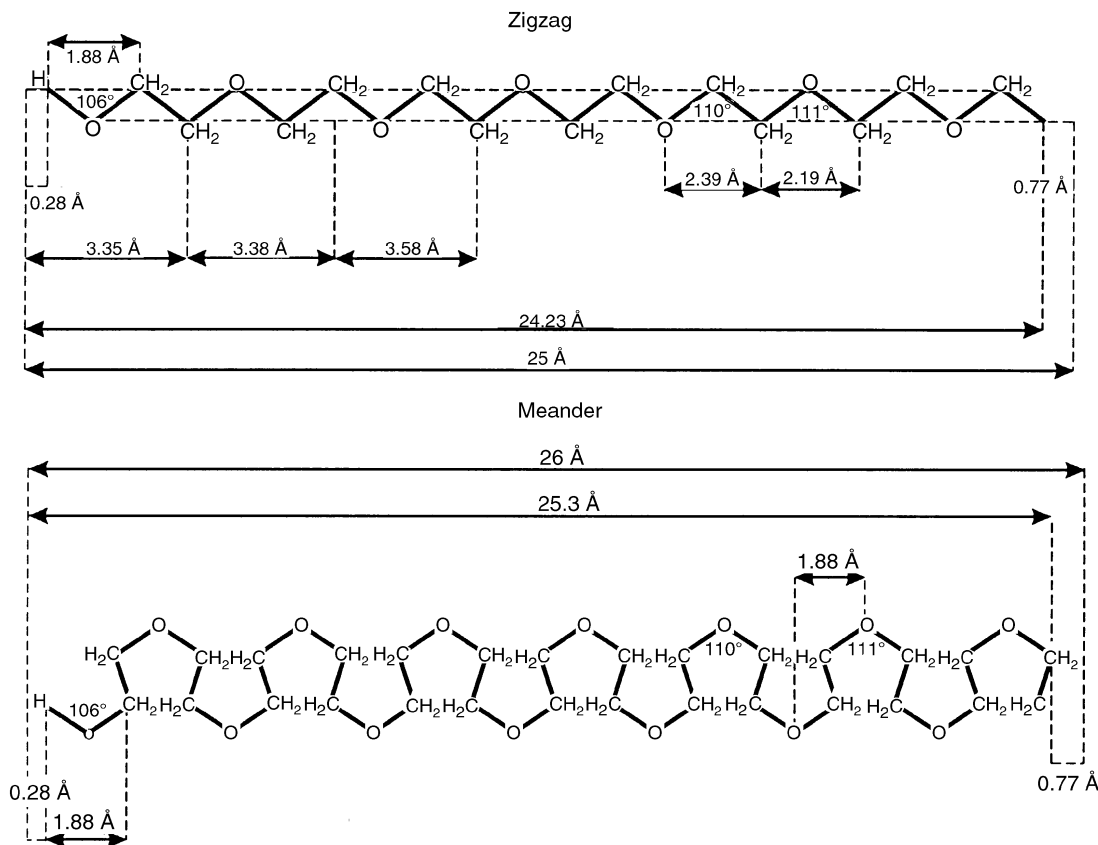


Fig. 8 Zigzag and meander conformations of the PEO chains.

analogous to those from Triton X114 and Triton X100 ($n_{EO}=8$ or 10, respectively), even though the cloud point of this surfactant is very low. We assume that the high acidity of the synthesis mixtures enhances the hydrogen bonding between the PEO chains and, as a result, leads to increasing surfactant hydrophilicity and to preferential micellar organisation. It can be assumed that Triton X114 and Triton X100 are more hydrophilic in acidic media, because of the increased number of hydrogen bonds formed by the PEO chains and protonation of the terminal OH groups with the possible formation of oxonium salts.¹⁰



We submit that the formation of HQ products from Triton X100 and Triton X114 within certain ranges of acid contents can be explained in terms of changes in the organisation of PEO chains. Crystallization of HQ mesophases is probably related to the formation, *via* hydrogen bonding, of a PEO interchain adduct, which is stable within a particular range of acid contents for each surfactant. Outside this range the adduct is not formed, because of insufficiently attractive ($C_{acid} < C_{opt}$) or excessively repulsive ($C_{acid} > C_{opt}$) interactions between the PEO chains, involving water molecules, H_3O^+ and acid anions. As a result, only poorly ordered products are formed. The formation of a hydrogen bonded adduct may be related to the configurational changes of the PEO chains in solution (Scheme 2). The configuration of PEO is known to change from a *zigzag* to a *meander* above $n_{EO}=9$ (Fig. 8).¹² For Triton X114 with $n_{EO}=8$, the *zigzag* configuration is dominant at low acid contents, while the *meander* configuration is probably more stable at high acidity, due to the increased hydrophilicity of the surfactant. It seems therefore that the formation of the hydrogen-bonded adduct is related to the *zigzag*-to-*meander* transformation of the PEO chains. For the more hydrophilic Triton X100 the transformation occurs (and the *meander* configuration is adopted) at a lower acid content than for Triton X114.

This conclusion is further confirmed by the influence of the acid anions on the stability of the HQ products. Thus, H_2SO_4 promotes the formation of well-organised mesocomposites at a much wider range of concentrations than HCl, since HSO_4^- anions are themselves capable of participating in hydrogen bonding and can additionally stabilise the adduct. The mechanism of formation of the hydrogen-bonded adduct is unclear. The adduct governs the degree of organisation of the product of the synthesis during its early stages, as high quality products with a low degree of silica condensation have been obtained 40–60 min after the addition of TEOS to an acidic solution of the surfactant. However, we do not know whether the adduct appears prior to the addition of the inorganic precursor or is formed as a result of fast conformational changes in the PEO chains caused by the addition of the source of silica.

Analysis of the wall thickness of the mesophases formed at different acid contents suggests that HQ mesophases are

additionally stabilised in comparison with LQ products. Thus, HQ products have thinner pore walls than LQ products. In this case, the presence of the hydrogen-bonded adduct can contribute to the formation of stable mesoporous solids with thinner pore walls than in case of the synthesis of LQ products with a lower degree of organisation of the PEO chains.

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