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The effect of dilute electrolytes on the formation of non-ionically templated [Si]-MSU-X mesoporous silica molecular sieves

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The effect of adding dilute electrolytes to the synthesis of non-ionically templated [Si]-MSU-X mesostructures has been investigated. An assembly process, $(N^0M^+)(X^-I^0)$, is described that takes into account both the non-ionic template/electrolyte and the silicate/electrolyte interactions. Monovalent cations (H^+, Li^+, Na^+, K^+, Cs^+, NH_4^+) intervene in the template/silicate assembly process directing either the shape or the order of the macro-molecular templating structures to form worm-like and hexagonally ordered pore structures or bimodal mixtures of the two. Anions (F^-, Cl^-, Br^-, I^-, SO_4^{2-}, NO_3^-, OAc^-) interact with the tetraethylorthosilicate (TEOS) silica precursor to effect modifications in the rate of TEOS hydrolysis, the rate of particle nucleation and hence final particle size and the extent of silica cross-linking in the final templated material.

1. Introduction

Significant efforts are being devoted to the preparation of templated mesoporous inorganic frameworks.[1] The recent development of the M41S,[2] SBA-*n*,[3] FSM-16,[4] HMS[5] and MSU-X,[6] -V,[7] -H,[8] -F,[8] -S[9] families of mesoporous silicate materials has made available a number of materials that possess narrow pore diameter distributions and a diverse range of pore and cage symmetries, particle sizes, particle morphologies and chemical compositions.[10] Such materials show potential for application in heterogeneous catalysis, homogeneous catalyst immobilisation, supra-molecular assembly, molecular separations, and optoelectronic technologies.[11]

M41S syntheses[2] rely on charge matching reactions (S^+I^-) between cationically charged organic micelles and anionically charged silicate precursors in alkaline media under hydrothermal reaction conditions. These materials exhibit 2-dimensional hexagonal (MCM-41), 3-dimensional cubic (MCM-48) and lamellar (MCM-50) structures that are solid representations of known surfactant liquid crystal phases.

SBA-*n* synthesis[3] occurs through anion mediation ($S^+X^-I^+$) between cationically charged micelle surfaces (sourced from either quaternary ammonium or polyethylene oxide based surfactants) and cationically charged silicate precursors in very strongly acidic aqueous media, under ambient temperature reaction conditions. The materials formed exhibit 2- and 3-dimensional hexagonal (SBA-2, 3, 8, 15) and cubic (SBA-1, 11, 16) pore architectures. This method can produce materials that exhibit pore symmetries not previously seen in liquid crystals and ultra-large pore structures (SBA-15).[12] The acid templating route can also lead to interesting lowest-energy-surface particle morphologies.[13] Addition of a variety of electrolytes to the highly acidic reaction mixture has recently been shown to modify the macro-morphologies of the SBA-15 materials.[14]

Complementary to the electrostatic routes are the electrically neutral S^0I^0 assembly pathways described by Pinnavaia and co-workers.[5,7–9] These systems assemble mesostructured HMS[5] and MSU-V[7] materials through "weak hydrogen bonding" interactions at the organic/inorganic interfaces of neutral amine assemblies and silicon alkoxides. These reports provided the first indications that macromolecular templating of ordered inorganic structures did not required strong ionic interactions. This suggested that synthetic control over materials design was possible under soft or near biological crystallisation conditions.

Subsequently Pinnavaia *et al.*[6] demonstrated the templating of silica and alumina mesostructures at neutral pH and ambient temperatures in the presence of non-ionic alkyl-polyethylene oxide (PEO) based surfactants or tri-block co-polymers. These so-called MSU-X materials exhibited predominantly 3-dimensional randomly packed "wormhole" channels[6] and large elementary particle sizes. Despite the non-uniformity of the channel packing, the diameters of the channels of MSU-X were nonetheless uniform. This disclosure demonstrated the possibility of forming templated inorganic structures under conditions that might more closely mimic those found in biological systems.

Recent work has demonstrated the great flexibility of the non-ionic templating system. Pore diameters and particle morphologies can be controlled through adjusting the lengths of either the hydrophilic head group or hydrophobic tail of the surfactant molecule,[6] by precise control of the synthesis temperature,[15] by post-synthesis hydrothermal treatment,[16] or by modification of the pH or ionic strength[15,17] of the synthesis medium. The work demonstrated early on[6] has been extended by the Stucky group. They have shown the outstanding potential of the tri-block co-polymers to act as templates[12,14] for the formation of large-pore materials of controlled morphology.[12] Indeed, the great flexibility of the non-ionic surfactant templating system has recently been demonstrated with the formation of both ordered (SBA-11, -12, -15, MSU-F, -H)[18,19] and disordered (MSU-X)[20] mesostructures with controlled particle morphology from sodium silicate solutions.

Surfactant scientists and technologists have long known that electrolytes added to surfactant emulsions can affect the aggregation characteristics of both ionic and non-ionic surfactants.[21] Additionally, sol–gel scientists have shown that electrolytes can modify the rate and extent of silicon alkoxide hydrolysis and condensation.[22] These effects were recently exploited in the MSU-X system by Bagshaw,[17] Pinnavaia *et al.*[9] and Prouzet *et al.*[15] who separately communicated the formation of bimodal pore systems, hexagonally ordered pores and controlled particle morphologies respectively, through various modifications of the ionic strengths of the [Si]-MSU-X synthesis media.

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In the present contribution, detailed investigations of the formation of non-ionically templated [Si]-MSU-X mesostructured silica in the presence of a range of dilute electrolytes are discussed. The results obtained indicate that electrolytes can exert considerable influence over all of the template and silica assembly and condensation processes. The hypothesis is presented that weakly ionic templating systems might provide insights into the interactive roles between weakly ionic biological fluids and hydrogen-bonding templates such as polysaccharides in biomineralisation systems.

2. Experimental

2.1 Synthesis

A number of PEO based surfactants with molecularly diverse structures have been used to assemble MSU-X silicates.[6,15] In the current report, [Si]-MSU-X silicates were prepared exclusively from the commercially available mono-disperse Brij® 97 C_{18} oleyl-$(EO)_{10}$ non-ionic surfactant (Sigma). 50 mL of a 7.5 wt% (0.22 mol L^{-1}) solution of Brij® 97 was prepared in distilled water at 35 ± 2 °C. TEOS (7.6 g) (Aldrich) was then added to the surfactant solution under moderate stirring to a TEOS : surfactant molar ratio of 8 : 1 and stirred for exactly 2 h. At this point an opaque white emulsion was formed between the surfactant and the water immiscible TEOS. The electrolyte, which had been dissolved in a minimum volume of water, was then added at once under moderate stirring to the surfactant/TEOS emulsion such that the concentration was 5 mol% with respect to Si.

Note that in the case of acidification, the acid was added to the surfactant solution to $pH = 3$ before the TEOS addition. During the initial part of the reaction in the low pH systems, the TEOS is acid hydrolysed, the $(R)_x$Si-OH groups are protonated ($(R)_x$Si-OH_2^+) and the TEOS dissolves to form a clear colourless solution.

The synthesis system was then stirred at moderate speed for 48 h. During this aging period, the emulsified or dissolved TEOS undergoes template and electrolyte catalysed hydrolysis and condensation, which leads to the formation of a white precipitate with crystalline appearance. All solid products that formed were recovered by filtration, extensively washed with distilled water and dried at 60 °C in air. The dried samples were then hydrothermally treated to improve the structural cross-linking by dispersing the dried, as-prepared solid in water (1.0 g solid per 30 mL water at neutral pH), sealing in polypropylene bottles and heating under autogenous pressure at 100 °C for 72 h. The hydro-treated products were recovered and dried at 60 °C in air. The occluded surfactant was then removed by calcination in air at 600 °C for 4 h with a temperature ramp of 2 °C min^{-1}.

Note that where HI, NaI and NH_4I electrolytes were employed, product colours varied from dark gold to light yellow indicating the formation of iodine complexes. Where HOAc, NaOAc and NH_4OAc were added, the products ranged from crystalline to poorly condensed silica depending on the specific salt. Where H_3PO_4, Na_3PO_4 and $(NH_4)_3PO_4$ were used, no solid products were formed and the silica remained in solution or emerged as an uncondensed gel.

2.2 Characterisation

XRD patterns of [Si]-MSU-X mesostructures were measured on a Philips PW 1700 series APD diffractometer equipped with an automatic variable divergence slit (sample beam length 12.5 mm) and Co K_α radiation ($\lambda = 0.178896$ nm) using a step-scan mode with a step of 0.03° 2θ and acquisition time of 5 seconds.

^{29}Si MAS NMR spectra were obtained with a Varian Unity 500 spectrometer using a DOTY Scientific multi-nuclear probe and 5 mm zirconia rotors. ^{29}Si resonance frequency, 99.745 MHz; pulse width, 4 μs; recycle delay time, 400 s; spinning speed, 10 kHz; referenced to TMS. The usual notation Q_x is used for the Si speciation, where x denotes the number of Si atoms surrounding a central Si atom bridged by oxygen atoms.

N_2 isotherms were obtained with a Micromeritics ASAP 2010 sorptometer at −196 °C after degassing at 250 °C and 10^{-6} mmHg for at least 4 h. Pore size distributions and pore volumes were calculated using the BJH model. While it has been established that this model is not adequate for accurate quantification of mesopore diameters in the range discussed here,[23] it remains the most readily accessible. In any case, the pore diameter values discussed herein will be precise and self consistent.

Scanning electron micrographs (SEM) were obtained from powdered samples dispersed on carbon tape and gold coated, with a Philips SEM 505 microscope with a LaB_6 filament and low voltage anode operating at 4 keV. Transmission electron micrographs (TEM) were obtained from epoxy imbedded microsectioned samples mounted on carbon-coated copper grids with a Philips EM 450 ST electron microscope operating at 100 keV accelerating voltage.

3. Results

3.1 Alkali metal electrolytes

The ionic strength of the [Si]-MSU-X synthesis system was raised by the addition of various salts of the alkali metals (Li^+, Na^+, K^+, Cs^+). The salts that were used are non-hydrolytic and thus will have no effect on the pH of the synthesis solutions. Thus the template and TEOS could be considered to be non-protonated. Of course, the addition of metal salts will induce the simultaneous action of both cations and anions on the synthesis medium. In order to separate the different effects as much as possible, the cation effect was examined by introducing alkali metal chlorides, while anion effects were investigated by introducing a range of different halide and oxyanions (F^-, Cl^-, Br^-, I^-, SO_4^{2-}, NO_3^-, OAc^-) of sodium.

In standard non-ionic and neutral pH [Si]-MSU-X syntheses, TEOS hydrolysis and subsequent precipitation of the mesostructured silica occurs over a 12–24 h period, with complete condensation achieved after 24–48 h reaction.[6] When electrolytes were added however, it was noted that precipitation of the templated silica product was significantly more rapid,[15] occurring after only 0.1–3 h depending on the specific electrolyte. This observation alone was a fair indication that electrolyte addition can exert a significant influence on the silicate hydrolysis and condensation.

The X-ray diffraction patterns of calcined final products formed in the presence of Na^+ electrolytes, for example NaCl (Fig. 1A), exhibited two major low-angle reflections, along with a number of weaker and broader reflections at higher angles. These reflections were suggestive of the formation of 3-dimensional hexagonal or cubic forms similar to those observed in SBA-n materials.[3,12] The almost equal intensities of the low-angle major reflections however, more strongly suggested either an intimate mixture of different disordered materials or a single material containing more than one unique pore system. The data also indicated some differences between the repeat unit dimensions between different cations. The low intensity nature of the patterns created significant enough ambiguity in identifying the reflections that no attempt at indexing the patterns was made.

N_2 sorption isotherms of calcined samples displayed two well-defined capillary condensation steps in the adsorption branches. Two distinct but less well resolved steps were also observed in the desorption branches. BJH pore size distribution calculations identified two distinct maxima indicating the

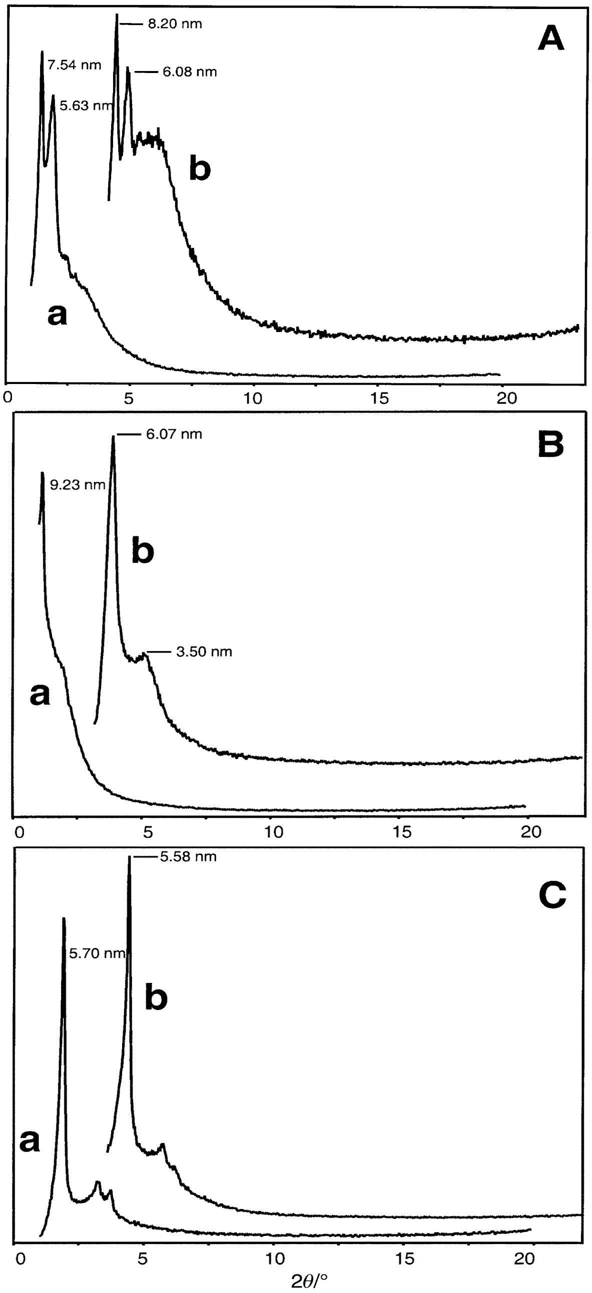


Fig. 1 XRD patterns of hydrothermally treated and calcined Si-MSU-X mesoporous silicas formed through (N^0M^+)/(X^-I^0) assembly: (A) a) NaCl solution, b) NH_4Cl solution, (B) a) NaF, b) NH_4F solution, (C) a) HF, b) HCl solution. Patterns b) are offset for clarity.

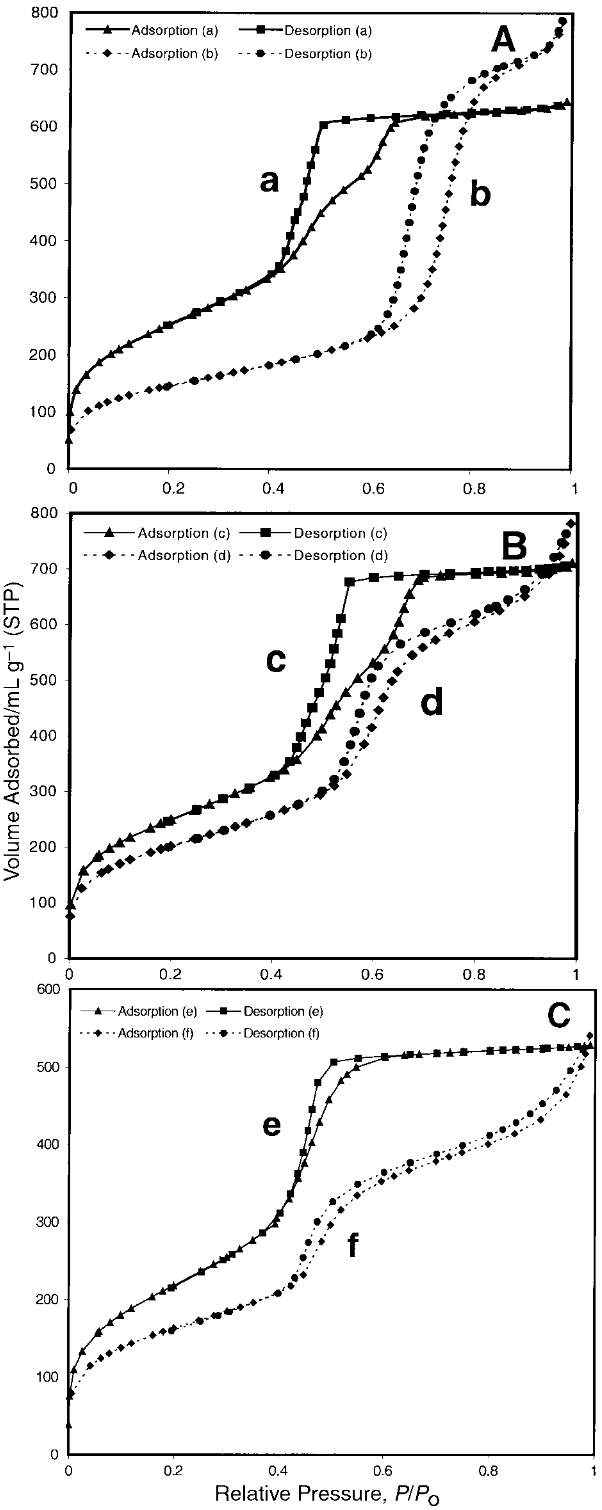


Fig. 2 N_2 adsorption–desorption isotherms of hydrothermally treated and calcined Si-MSU-X mesostructures: (A) Na^+ electrolytes [(a) NaCl, (b) NaF], (B) NH_4^+ electrolytes [(c) NH_4Cl, (d) NH_4F], (C) H^+ electrolytes [(e) HCl, (f) HF].

formation of two distinct mesopore systems possessing different diameters (Fig. 2A). The supposedly bimodal pore systems were most obvious in the isotherms of materials formed in Na^+ electrolyte solutions. The presence of a hysteresis loop might suggest the formation of bottlenecked pores. It is also possible that it is a consequence of the absolute pore sizes and their effect on the nitrogen capillary evaporation thermodynamics.[23] While the formation of the bimodal pore system in the nitrogen isotherms was most notable with Na^+ electrolytes, the other alkali cations produced similar results, albeit with varying lattice regularity and pore diameter fidelity, with the anions exerting a greater influence over the pore diameters than the cations (Table 1). Electrolytes with anions at the extremes of charge density (or the hardness/softness scale[24]), for example F^- (hard) and OAc^- (soft), did not favour the formation of the bimodal pore systems. The anions between these extremes, *e.g.* Cl^-, SO_4^{2-}, NO_3^-, produced materials that exhibited well defined and well separated bimodal pore systems.

The electrolyte effect on the silica bonding within the [Si]-MSU-X lattices was investigated by ^{29}Si MAS NMR. Spectra of as-prepared samples were obtained so that only the electrolyte effect rather than any subsequent hydro treating or calcination would be observed. Selected spectra (Fig. 3A) show strong resonances due to Q_4 and Q_3 Si at chemical shifts around −112 and −100 ppm respectively. Weak Q_2 signals around −91 ppm were observed in samples prepared in the

Table 1 Physico-chemical data of [Si]-MSU-1 samples prepared in the presence of dilute monovalent electrolytes

Electrolyte [Si]-MSU-1	d_{100}	SA/m^2 g^{-1}	Pore diameter/nm	Pore volume/mL g^{-1}	Wall thickness/nm	Q_4/Q_3
No electrolyte	3.0	700	2.4	1.4	0.6	1.02
HF	5.7	580	3.6	0.8	2.1	1.90
HCl	5.6	780	3.2	0.8	2.4	0.78
HBr	5.3	1060	3.0	1.0	2.3	0.72
HNO_3	5.5	890	3.5	1.1	2.0	0.87
H_2SO_4	5.3	790	3.6	0.8	1.7	0.80
HOAc	5.6	870	3.7	1.1	1.9	n.o.
LiCl	9.5, 4.4	615	5.8, 3.6	1.3	3.7	1.07
NaF	9.2	520	8.7	1.2	1.1	1.28
NaCl	7.5, 5.6	900	5.2, 3.4	1.0	2.3	1.01
NaBr	7.9, 5.8	800	5.6, 3.6	1.1	2.3	0.93
$NaNO_3$	7.8, 6.0	725	5.8, 4.5	1.1	2.0	1.14
Na_2SO_4	8.5, 6.0	880	6.2, 3.8	1.2	2.3	1.26
Na(OAc)	8.5, 4.9	900	6.7	1.4	1.8	1.11
KCl	—, 3.7	725	5.5, 4.3	1.3	—	0.96
CsCl	8.9, 4.2	700	4.6, 3.6	1.3	4.3	1.14
NH_4F	6.1, 3.5	720	4.3	1.2	1.8	1.29
NH_4Cl	8.2, 6.1	900	5.5, 3.4	1.1	2.7	1.48
NH_4Br	8.2, 5.5	880	6.5, 3.3	1.1	1.7	0.96
NH_4NO_3	6.1	670	8.0, 5.0	1.0	1.1	1.45
$(NH_4)_2SO_4$	8.5, 6.7	800	7.3, 4.3	1.0	1.2	1.20

presence of "softer" anions, indicating lower levels of silicate condensation in these materials.

The degree of silica cross-linking in the templated lattice is inferred from the Q_4/Q_3 Si ratios, which varied in a consistent manner with changes to the electrolyte anion (Table 1). The Q_4/Q_3 Si ratios of these materials were consistently higher than those observed for neutrally prepared [Si]-MSU-X, indicating that the electrolytes were modifying the degree of silica condensation. The Q_4/Q_3 Si ratios of materials modified by the Li^+, Na^+ and K^+ chlorides were all broadly similar. CsCl however produced a somewhat higher Q_4/Q_3 Si ratio indicating some form of greater hydrolysis activity for this electrolyte. Sodium electrolytes with different counter anions showed a trend of increasing Q_4/Q_3 Si ratio with both increasing anion charge-density or "anion hardness" (*e.g.* NaCl *vs.* NaBr) and the ability of the anion to coordinate to the silicate units (*e.g.* Na_2SO_4 *vs.* NaCl).

TEM images of selected calcined samples strongly suggested the formation of two interrelated pore systems within the single sample. The micrograph of a sample prepared in NaCl solution (Fig. 4A) exhibits regions of both well-defined hexagonal pore order along with non-ordered "wormlike" pores. Comparison of the calculated pore-size data with the TEM images suggested that the hexagonally ordered pores were of slightly smaller pore diameter than the worm-like pores. This observation was new, in that previously reported [Si]-MSU-X materials that were prepared from dilute-acid modified systems[17] also had co-existing regions of hexagonal and worm-like order, but all the observed pores were of the same diameter.

3.2 Ammonium electrolytes

The addition of ammonium electrolytes to the [Si]-MSU-X synthesis medium produced slightly different results to those obtained for alkali metal salt addition. The XRD patterns of calcined samples (*e.g.* NH_4Cl solution (Fig. 1A)) displayed similar multiple reflections to those obtained from sodium electrolyte modified solutions. The reflections at higher angle, however, were not well defined and were observed only as a broad low intensity peak. Based on the alkali metal results, analysis of the XRD data suggested that NH_4^+ electrolyte addition afforded similar mixed pore systems, but with slightly lower overall pore ordering. Indeed, two distinct capillary condensation steps were observed in both the adsorption and desorption branches of the N_2 sorption isotherms of calcined samples (Fig. 2B). Two distinct pore diameters could also be calculated from these isotherms. The separations between the pore diameters for ammonium modified systems were, however, less well defined than in the case of alkali metal electrolyte modification.

^{29}Si MAS NMR spectra indicated that addition of ammonium salts to the synthesis medium produced a greater effect on the hydrolysis and condensation of the silica precursor (Fig. 3B, Table 1) than the alkali metal electrolytes. In the context of the Q_4/Q_3 Si ratios exhibited by other samples, the values for the NH_4^+ modified [Si]-MSU-X silicas were significantly higher than those observed for either materials prepared under neutral conditions or alkali metal electrolyte modified materials. This therefore suggested that the addition of ammonium cations provided a route to increased silica cross-linking.

TEM (Fig. 4B) micrographs showed pore structures that were broadly similar to those observed for alkali metal electrolyte modified materials.

3.3 Dilute acids

Very strong acidification of the non-ionic templating medium has been shown to induce significant pore ordering into materials that would otherwise form with disordered wormhole type structures.[12,25]

The XRD patterns of calcined non-ionically templated materials prepared in solutions acidified by dilute acid (*e.g.* HF, HCl) (Fig. 1C) exhibited at least three reflections that strongly suggested the formation of hexagonally ordered pores. The d_{100} reflections of the various materials were significantly more narrow and intense than materials prepared under neutral non-ionic conditions. The strong intensities of the d_{100} reflections relative to the d_{210} and d_{200} peaks were indicators that the samples did not contain 100% hexagonally ordered pore architectures. The form of the X-ray pattern did however suggest that unique pore diameters were formed.

The solution acidity used here was orders of magnitude lower than those used by Attard *et al.*[25] and also latterly by Stucky *et al.* for the formation of the SBA-*n* family of silicate materials.[12] This would indicate that extreme acid activity is not necessary to exert a significant structure directing effect on the non-ionic surfactant templates. Very highly acidic synthesis systems do appear to be important for complete pore structure control and for the introduction of macro-morphological control.[13] Similar to the M^+ and NH_4^+ modified systems, the degree of structural ordering in H^+ modified systems showed some correlation with different anions. The effect was stronger in the presence of the "harder" acids, *e.g.* HF, HCl, H_2SO_4,

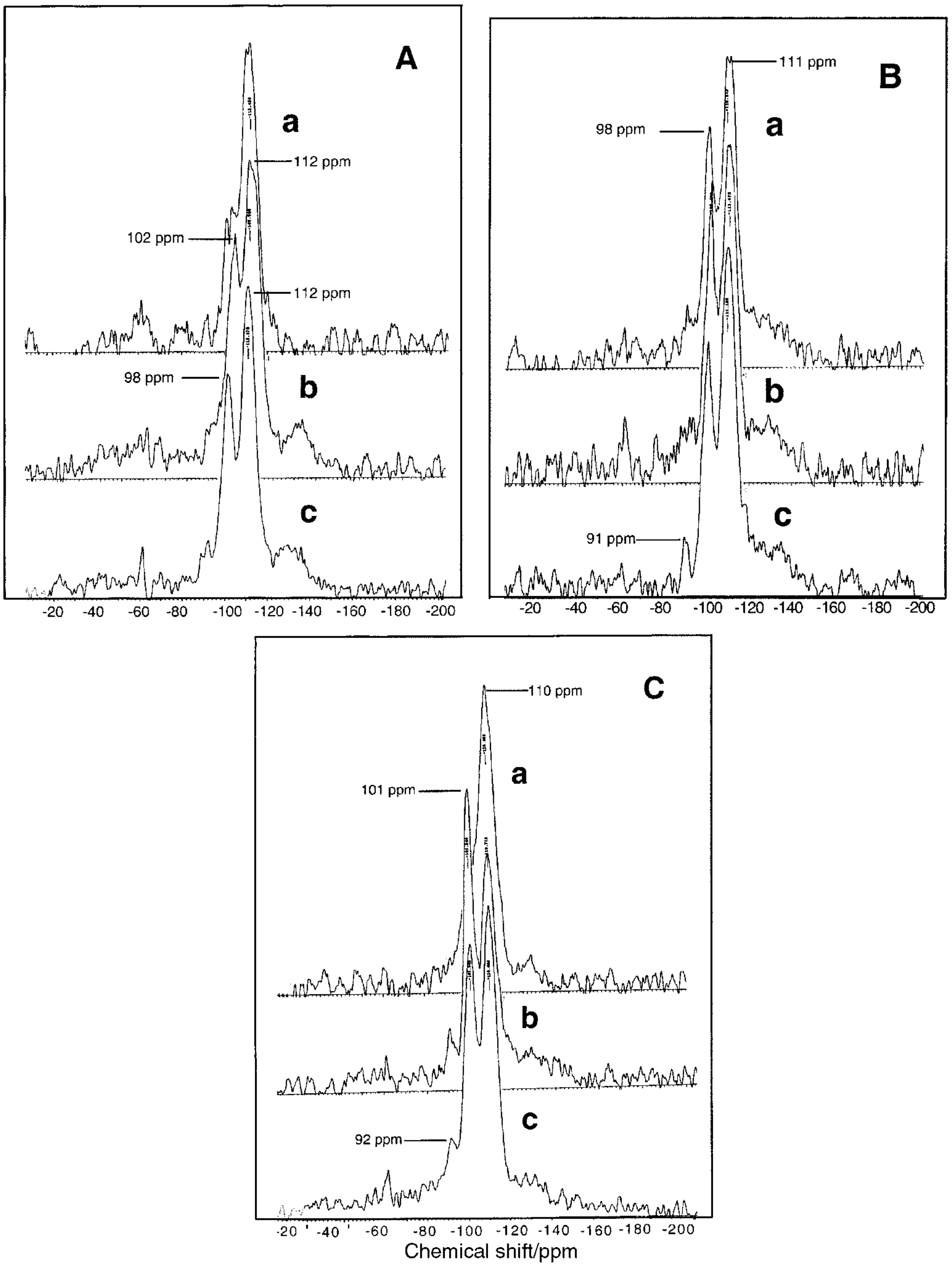


Fig. 3 ^{29}Si MAS NMR spectra of as-prepared Si-MSU-X mesostructures prepared from dilute electrolyte solutions: (A) sodium salts, (B) ammonium salts, (C) acids; (a) Cl$^-$, (b) SO$_4^{2-}$, (c) F$^-$.

than in the presence of the weak or "soft" acids, *e.g.* HOAc. The harder acids induced both greater pore order into the silica structure and more rapid silica hydrolysis and condensation.

N_2 sorption isotherms (Fig. 2C) confirmed the uniformity of the mono-modal hexagonal pore systems. They also showed that the acid modified materials exhibit some pore expansion over materials prepared at neutral pH.[6] Interestingly, the pore diameters of the acid modified materials compared well with the smaller of the two pores found in the bimodal pore systems that were formed in the presence of neutral electrolytes. The pore volumes, however, were smaller than those found for materials prepared under neutral pH electrolyte conditions. The ^{29}Si MAS NMR spectra of as-prepared samples synthesized in acid conditions (Fig. 3C) were significantly different to those of materials formed under neutral pH electrolyte conditions. Low pH syntheses produced spectra that exhibited stronger Q_3 Si resonances, suggesting either lower levels of silica cross-linking or the formation of larger concentrations of surface Si-OH species (Table 1). In agreement with the other electrolyte systems, a correlation also appeared to exist between increasing Q_4/Q_3 Si ratios and the strength of the acid.

TEM images (Fig. 4C) indicated that these materials also possessed mixed wormhole/hexagonal pore assemblies but that the domains of hexagonally ordered pores are much larger than those observed in other systems employed here. In agreement with the N_2 isotherms the pores measured on the TEM images had a unique diameter.

Unlike ionically templated SBA-*n* materials,[3] SEM images of non-ionically templated [Si]-MSU-X materials (not presented), formed here in weakly acidic media, did not show the formation of lowest energy surface particle morphologies.[13] Rather than the intricate tops, ropes, spirals, *etc.,* seen in SBA-*n* type materials,[13,14] the [Si]-MSU-X particles were random aggregations of spherical "crystallites" 2–5 μm in diameter. [Si]-MSU-X materials prepared under neutral pH conditions generally exhibit rectangular monolithic particles in the 100 μm

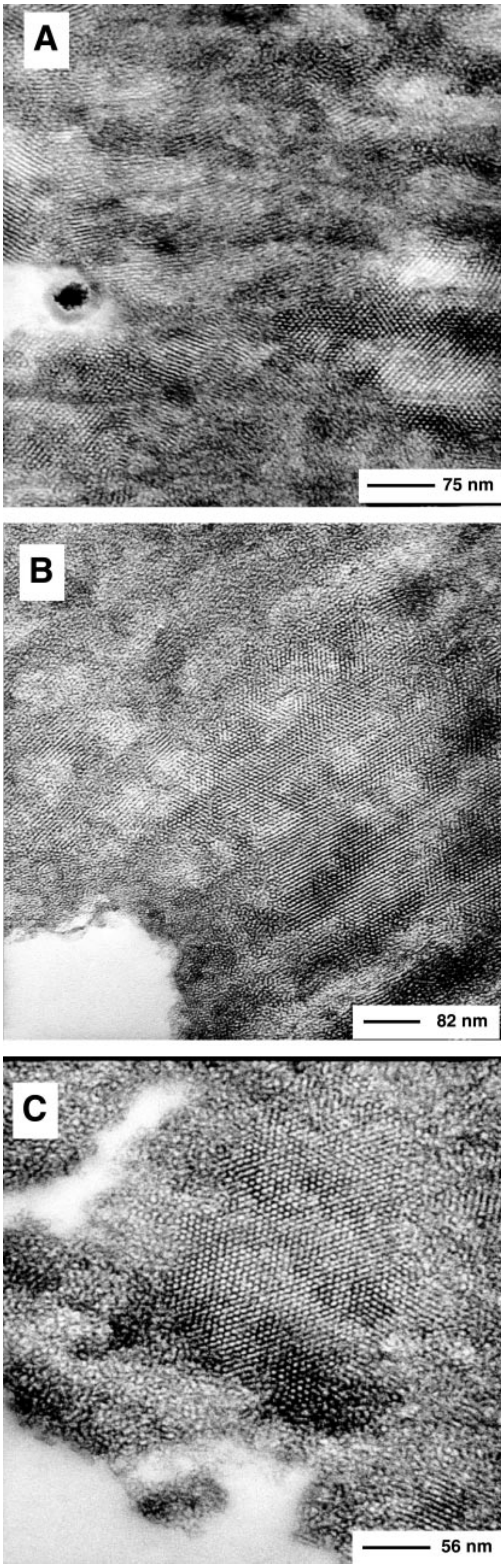


Fig. 4 TEM images of hydrothermally treated and calcined Si-MSU-X mesoporous silicas prepared from dilute electrolyte solutions: (A) NaCl solution, (B) NH_4Cl solution, (C) HF solution.

region, while the aggregated "crystallites" formed 10–50 μm particles here. The observations were in fair agreement with those recently reported by Prouzet *et al.*[26] These workers separated the assembly and condensation stages of [Si]-MSU-X synthesis and prepared spherical materials of controlled dimensions in the presence of NaF electrolyte. The formation here of an acid hydrolysed, soluble and slowly condensing silicate precursor suggests that a similar separation of assembly and condensation processes might be achieved by solution acidification.

3.4 Fluorides

During the course of this study we found that soluble fluoride salts and acids behaved in a slightly different manner to other, softer electrolytes. The addition of fluoride electrolytes to the [Si]-MSU-X synthesis medium caused almost instantaneous hydrolysis of the TEOS and precipitation of a templated silica product at any stage of the synthesis. The synthesis solution also became very viscous owing to the formation of significantly larger numbers of smaller particles. The materials that were produced with neutral fluoride electrolytes exhibited considerable repeat-unit expansion over other materials. This was displayed in the XRD patterns of samples prepared in NaF and NH_4F solution (Fig. 1B), which exhibited d_{100} reflections at very low angles around 1° 2θ. Addition of neutral F^- electrolytes also produced [Si]-MSU-X mesostructures with very large diameters, unique pore systems (Fig. 2A, B, C), high pore volumes (Table 1) and predominantly wormhole pore ordering. Indeed, the pore diameters produced in the presence of NaF were of the same order as those formed in regular SBA-15 materials[12,27] (6.0–9.0 nm). Materials produced in the presence of HF, however, while exhibiting rapid silica precipitation, generally possessed pore structures and diameters the same as those produced by other acids. N_2 sorption isotherms, however, did suggest the formation of significant interparticular porosity (Fig. 2C).

In an interesting observation that agrees well with Prouzet *et al.*,[20,26] the [Si]-MSU-X particles formed in the presence of neutral fluoride salts were significantly smaller than those prepared by any other method. Unlike the materials prepared in the presence of other electrolytes, SEM micrographs (not presented) showed that the fluoride salts produced materials with regular spherical habits.[20,26]

^{29}Si MAS NMR spectra of materials prepared in fluoride media (Fig. 3A, B, C) exhibited, in the cases of NaF and HF but not for NH_4F, very strong Q_4 resonances. The Q_4/Q_3 Si ratios calculated from the spectra were thus significantly greater than the majority of the other materials investigated suggesting increased silica cross-linking and/or low populations of surface Si-OH species.

4. Discussion

4.1 General

The surfaces of non-ionic PEO-based surfactant micelles[21] are not generally considered to be sharp interfaces as with the quaternary ammonium surfactants, but more like a water-rich corona interphase.[28] Within this corona the PEO headgroups are solubilised by the solvent water such that there is a concentration gradient of water from the outer end of the headgroup to the EO–R junction. The water within this region is rendered more nucleophilic than bulk water due to the strong H-bonding interactions between the water and the EO groups. The micellisation of PEO based surfactants is thus intimately controlled by the headgroup/solvent interactions. These interactions can be modified by changes in solvent composition, concentration, temperature, pH and electrolyte concentration.

Prouzet and co-workers[15,20,26] have previously exploited both temperature and NaF modification in the formation of non-ionically templated [Si]-MSU-X materials. These modifications resulted respectively in pore diameter and particle size control. It is noted, however, that the temperature-controlled synthesis method required the use of NaF to effectively catalyse the condensation of both TEOS and sodium silicate silica precursors in order to exploit the micelle size control. It is also noted that the addition of NaF after a considerable period of pre-assembly time, during which the TEOS will be partially template-catalysed, does not result in significant pore order improvement. In terms of the results described here therefore, it would appear that the Prouzet work[15] provides good evidence for the catalytic hydrolysis effect of fluoride ions on the TEOS, but allows no conclusions to be drawn regarding the structure directing effect of Na^+ cations on the flexible R-PEO/TEOS assembly system. New results obtained here and by other workers[8,14,18–20] strongly indicate that there are strong structure directing effects of dissolved cations on the early stages of the non-ionic assembly pathway. They suggest that the time of addition during the synthesis plays a role in the strength or type of structure direction that will occur.

4.2 Acid effect

Several workers, Stucky and Ozin in particular, have demonstrated that very strong reduction of the pH of the synthesis medium can induce the formation of highly ordered silica phases from both cationic and PEO-based templates.[12–14] These higher symmetries, as compared to the wormhole phases, require more ordered micelle packing, implying that acidification increases the micelle packing parameter g in eqn. (1). In the case of the acidification of PEO surfactants, this modification must result from a decrease in the effective headgroup area, a_0, through some form of acid/R-PEO interaction according to:

$$g = V/a_0 l \qquad (1)$$

where V is the total surfactant/solvent volume, a_0 is the effective headgroup area and l is the kinetic surfactant tail length or the curvature elastic energy. Both V and l are assumed constant at any given temperature.

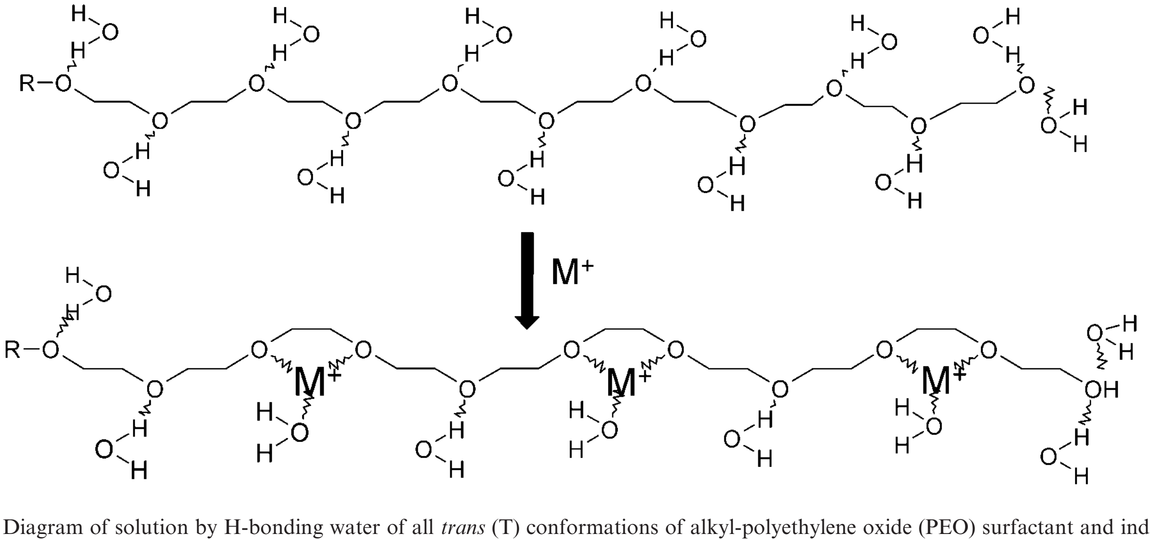
No workers have adequately established that the PEO headgroup actually becomes protonated in the acid synthesis media. The implied packing modification, as reflected in the increases in pore ordering of materials, however, strongly suggests that some form of H_3O^+/EO, or at the very least an H^+/OH (where OH is the PEO surfactant terminal hydroxyl) interaction does occur. Such an interaction with either single or multiple EO or OH groups is required to drive the reduction in effective headgroup area. At this time, no further speculation on the detailed nature of this particular interaction is assumed or described.

The effects of acidification of the synthesis medium on the formation of the silica lattice, however, are twofold. The first is that previously discussed of likely structure direction of the template. The second, perhaps more important, influence is that of the acid catalysed hydrolysis and condensation of the TEOS.[22] This is well established in the literature, which describes the formation of linear oligomeric silicate chains as opposed to the highly branched cluster species formed in alkaline environments. Only worm-like pore structures have been observed in non-ionically templated materials under alkaline pH conditions even if there is a structure directing cation, *e.g.* Na^+, present.[29] This would infer that the specific form of the silica surface propagating around the templating micelles exerts an influence on the symmetry of the final porous structures. This situation is graphically illustrated in the difference in both particle morphologies and available pore symmetries of M41S, SBA-*n* and neutral MSU-X systems.

4.3 Cation effect

The results discussed here along with the very recent disclosures of the highly ordered structures resulting from non-ionic templating of both TEOS and sodium silicate solutions strongly indicate that there is a significant effect of dissolved metal cations on the PEO template assembly pathways.[18–20] These latter reports show that highly ordered pore structures are readily formed from neutralized sodium silicate solutions. The highly symmetrical pores produced from the solutions with high Na^+ concentrations strongly indicate that a cation structure directing effect is operating. The detailed mechanism of this structure direction, however, remains unclear. At this point a mechanism can be speculated, but two separate or perhaps related possibilities are suggested here. It is maintained here that the mechanisms of silicate templating and propagation at the R-PEO interphases are significantly different to those of ionic templates.

An adequate description of the formation of the non-ionically templated silica materials requires a model that describes, at least initially, a ternary PEO/water/silicate complex that forms during the TEOS emulsification phase of the reaction. This complex is formed in the sphere of influence of each surfactant headgroup in the micelle corona and is highly dynamic. The results obtained here indicate that these "complexes" do not form immediately as is thought to be the case in M41S/SBA-*n* synthesis. When the silicate is introduced to the micelle solution it is initially emulsified and therein proceeds to hydrolyse through partially soluble species. It is these partially hydrolysed species that interact with the PEO headgroups forming the flexible ternary "complexes". Addition of the neutral electrolytes to the synthesis system before the complex has been established (*i.e.* before silicate addition)



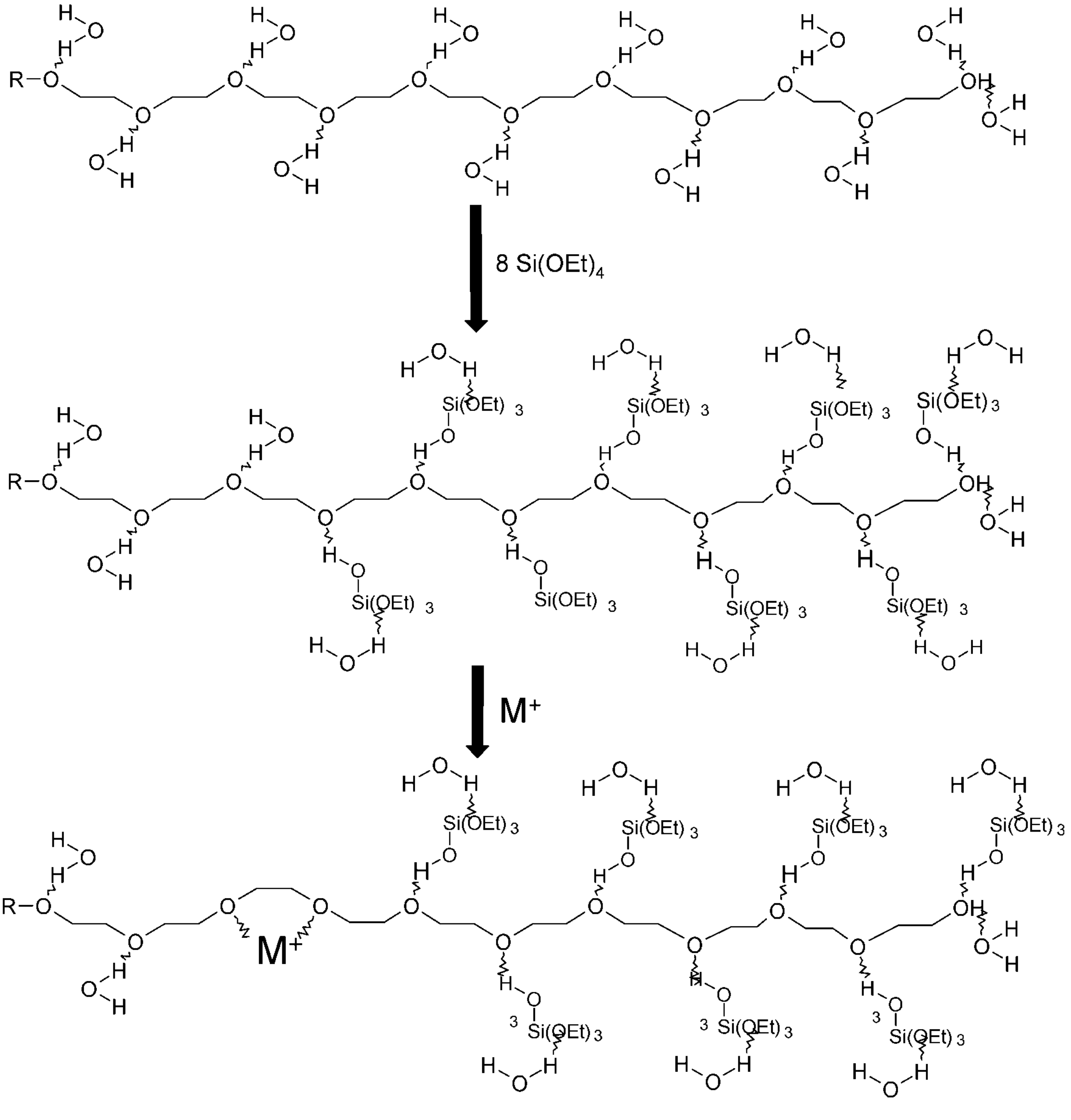
Scheme 1 Diagram of solution by H-bonding water of all *trans* (T) conformations of alkyl-polyethylene oxide (PEO) surfactant and induction of *trans–trans–gauche* (TTG) conformations upon complexation of M^+ cations.

results in the formation of non-templated or only worm-like pore structures (Scheme 1).

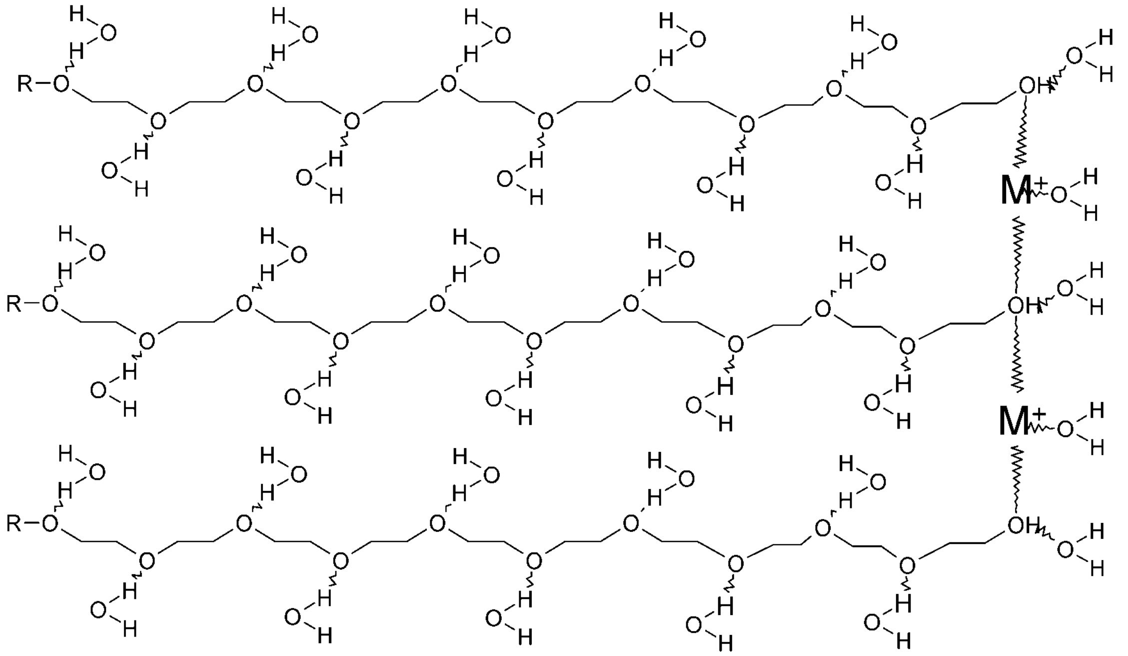
Spectroscopic investigations of PEO-based surfactant interactions with a range of alkali and alkali-earth cations (without any silicate addition) have shown that the metal cations interact with the ethylene oxide functions creating TTGTTG (T = *trans*, G = *gauche*) series of conformations. This creates helical crown ether-like metal–PEO complexes.[30] In the silicate templating environment, this complexation (prior to silicate addition) seemed to cause the H-bonding sites (*i.e.* EO groups) to become unavailable for templating or silicate hydrolysis. This would infer that the H-bonding sites were now directed into the interior of the now helical PEO/M^+ headgroup. This renders the previously nucleophilic EO units no longer available for TEOS coordination and subsequent hydrolysis (Scheme 1). In the absence of a strong hydrolysis catalyst therefore (*e.g.* PEO or H^+), the TEOS will hydrolyse only slowly and not be directed into any specific shape during condensation even where a hard anion is present. The effect is most notable in the cases of Na^+, K^+, NH_4^+, Ca^{2+} and Mg^{2+}, which are all known to interact strongly with the PEO surfactant headgroups, while Li^+ and first row transition metal ions have also been effective.[19]

Where the PEO/water/silicate complex has become established, *i.e.* where TEOS is added and reacted for a short time, the addition of electrolyte has a different effect and ordered rapidly condensed structures are formed. Several possibilities for this modification are possible. A simple explanation is outlined in Scheme 2 where one or two metal cations complex only with the first two or three EO units. This induces *gauche* conformations in the PEO chain that cause the headgroup to form a "kinked" chain, therein reducing the packing parameter, *g*.

A second possibility is that the flexibility of the complex allows the headgroup packing parameter to be modified by the electrolyte cation without disruption of the hydrogen bonding between the PEO headgroups and the growing silicate species. The cations must now interact with the PEO–silicate complex rather than the naked PEO groups. This must occur in a manner that causes the surfactant headgroup area to decrease and subsequently the packing parameter, *g*, to increase without destroying the PEO–silicate interaction. The result is the formation of regions of hexagonal pore symmetry along with regions of regular worm-like disordered pores. A further consequence of this increased packing parameter is a modification in the pore diameters. The data obtained here



Scheme 2 Diagram of complexation and partial hydrolysis of TEOS by PEO surfactant and induction of one G conformation by complexation of M^+ cation after TEOS coordination.



Scheme 3 Diagram of secondary proposal of interaction between M^+ cations linking PEO surfactant headgroups.

and recently elsewhere[18–20] suggest that the hexagonally ordered pores are smaller in diameter than the worm-like pores formed from otherwise identical templates. The cation interaction with the PEO headgroups must therefore also induce molecular conformation changes that reduce the effective templating length of the surfactants.

One might argue that the cations should be homogeneously distributed throughout the templating system and thus creating a homogeneously templated material. It might also be argued that the first cation to interact with the template headgroup induces a conformational structure that prefers to coordinate further cations. In this way, it can be conceived that the cation modified template molecules will not be homogeneously distributed. According to Siew *et al.*[30] a PEO surfactant will coordinate 3–4 alkali or alkali-earth cations for every 10 EO groups. Therefore, 5 mol% cation loading with respect to silica produces 0.4 M^+ per R-$(EO)_{10}$ surfactant molecule. If all the cations are coordinated by the surfactants as 1 : 4 complexes, only 10% of the surfactant molecules will interact fully with the metal cations. Thus can be explained the separation of two distinct pore systems.

A third concept however, is that the cations do not in fact modify the template microstructure, but rather form bridging interactions between terminal OH groups of adjacent templating micelles (Scheme 3). In this way, the cations bind adjacent micelles causing symmetrical structures to be formed over disordered worm-like structures. It is proposed that the number of surfactant molecules modified this way will not be greater than by the former mechanism. This second mechanism also explains most if not all of the chemical observations outlined herein (Scheme 3). While further investigation is required to fully detail the effect of the electrolyte cation on the non-ionic assembly pathway we believe that the recent results showing the non-ionic templating of sodium silicate solutions bare testament to the strong possible effect of metal cations on the templating mechanism.

4.4 Anion effect

The addition of electrolytes by definition also means that both cations and anions will be introduced to the synthesis system. Various anions (X^-) are known to influence the rate and extent of hydrolysis and condensation of the TEOS silica precursor.[17] Anions are proposed to mediate the alkyl ammonium/cationic silicate interaction in the strongly acidic $S^+X^-I^+$ SBA-*n* mesostructure syntheses.[3]

Electrolyte anions are indeed observed to modify, to varying degrees, the silica structure in non-ionically templated [Si]-MSU-X materials. The data indicate that the effect follows the hardness/softness or charge density profile of the specific anions and is most obvious in the cases of H^+, Na^+ or NH_4^+ salts of the hardest anions, fluoride and chloride. Strong nucleophilic attack of the F^- anion, specifically, on the hydrolysing TEOS intermediates is proposed to form a reactive 5-coordinate Si complex. The strongly electron donating ligand causes the alkoxide groups to become strongly reactive to nucleophilic attack of water at the Si–OR bond. In the current case this in turn causes condensation to be so rapid that any cation effects on the PEO/water/silicate complex are overridden leading to the formation of a single diameter, disordered pore system. Furthermore, this very rapid condensation also causes increased particle nucleation and subsequent reduction of the elementary particle size. Further consequences of the addition of F^- are strong internal pore diameter increases that result and the apparent increases in what might be described as textural or interparticular porosity. This behaviour is only observed when fluoride is added to the synthesis medium. These observations are not well explained here, but are very likely to be related to the rapid hydrolysis and condensation of the silicate not allowing the PEO/Na^+/silicate to direct the assembly of the mesostructure.

All anions added to the [Si]-MSU-X synthesis medium, however, modify the rate and extent of TEOS hydrolysis to some degree, with decreasing strength of effect depending on the ionising strength of the anion. Strongly ionising anions (*e.g.* F^-, Cl^-, NO_3^-) increase the rate of silicate hydrolysis and condensation forming highly condensed structures. Poorly ionising electrolytes, such as acetate, cause the hydrolysis of TEOS to be very little improved over the non-ionic state and only disordered systems result. Anions that strongly coordinate with the soluble silicates, such as phosphate, in fact operate to retard the hydrolysis and condensation of silica. This is reflected in the appearance of poorly condensed or gel structures under the reaction conditions described herein.

5. Conclusions

The effects of weakly ionic solutions on [Si]-MSU-X mesostructured silica assembly have been investigated. Bimodal, hexagonal and worm-like pore systems have been prepared from synthesis systems containing weak electrolytes or acids. Cations exert structure-directing effects on a proposed flexible PEO/water/silicate ternary complex leading to modified micelle packing and subsequently modified pore symmetries over materials formed in neutral solutions. Anions modify the rate and extent of TEOS hydrolysis and condensation through the formation of 5-coordinate intermediates of varying strengths. Fluoride is a special case in that it causes not only greatly increased TEOS condensation and smaller particle sizes of spherical morphology, but also increased pore diameters.

In light of the separate cation and anion effects on the silicate assembly observed herein, it may be appropriate to acknowledge this in an assignment of a description of the assembly route. Thus a descriptor such as $(N^0M^+)/(X^-I)$ may more accurately delineate between the cation effect on the template and the anion effect on the TEOS silica precursor. This label encompasses the addition of all electrolyte catalysts, neutral salts, acids and bases.

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