^{14}N NMR Study of Surfactant Mesophases in the Synthesis of Mesoporous Silicates

Allan Steel,[a] Stuart W. Carr[b] and Michael W. Anderson*[a]

[a] *Department of Chemistry, UMIST, P.O. Box 88, Manchester, UK M60 1QD*

[b] *Unilever Research, Port Sunlight Laboratories, Quarry Road East, Bebington, Merseyside, UK L63 3JW*

Surfactant mesophase formation during the synthesis of M41S, the mesoporous material, has been studied using ^{14}N nuclear magnetic resonance spectroscopy. Siliceous gels producing M41S materials displaying hexagonal and lamellar powder X-ray diffraction patterns have been observed to contain hexagonal mesophases which revert to an isotropic solution after heating while X-ray diffraction shows the silicate to be ordered.

Recently there has been much interest in the discovery that surfactants can template the synthesis of highly ordered mesoporous silicates. Two similar approaches employ either monomeric silicates[1,2] or layered silicates[3] as source material to build a honeycomb framework with 16–100 Å uniform channels. The pore dimensions can be controlled by appropriate choice of templating agent. A liquid-crystal template mechanism has been proposed in which surfactant molecules in the reaction gel form mesophases about which silicon atoms arrange. The final product is a silicate skeleton which contains voids that mimic these mesophases. Hitherto, no definite proof of mesophase formation within the reaction scheme has been reported. In this communication we report the first direct observations of surfactant mesophases within M41S gels using ^{14}N NMR spectroscopy and suggest a new mechanism of formation.

^{14}N NMR spectra were recorded on a Bruker MSL400 solid-state spectrometer using a static probe operating at 28.913 MHz. Chemical shifts are referenced to aqueous ammonium chloride solution. Spectra were recorded with 6 μs, 30°, radiofrequency pulses and a repetition time of 0.2 s. X-Ray diffractograms were recorded on a Scintag XPS2000 powder diffractometer using Cu-Kα radiation with continuous scanning at 1° min^{-1} from 1–10° 2θ. Lamellar reaction gels were prepared from cetyltrimethylammonium chloride (CTMACl), sodium hydroxide, tetraethylorthosilicate (TEOS) and water as described elsewhere.[4] Hexagonal reaction gels were prepared from cetyltrimethylammonium chloride, tetrabutylammonium (TBA) silicate, fumed silica and water.[4] Gels were placed into teflon-lined bottles and heated for 3 d at 90 °C. The nature of the final product depended upon the proportion of tetraethylorthosilicate contained in the reaction gel.

Fig. 1 shows the ^{14}N spectra of a range of surfactant mesophases of the cetyltrimethylammonium chloride–water system recorded at 90 °C. A full range of mesophases was observed at different surfactant concentrations. The appearance of these spectra easily distinguishes the mesophase type. Each mesophase possesses a characteristic quadrupole splitting, Δ, (lamellar $\Delta = 23\,000$ Hz, cubic $\Delta = 0$ Hz, hexagonal $\Delta = 10\,500$ Hz). For a surfactant in isotropic solution $\Delta = 0$ Hz. All signals were also observed at room temp. with the exception of the lamellar phase, which only forms above 40 °C.

Fig. 2(*a*) shows the ^{14}N NMR spectra of a siliceous gel which produced an M41S material with hexagonal symmetry, MCM-41, after heating at 90 °C for 3 d. This spectra exhibits three peaks, a central signal at +791 Hz and two broad signals at +5905 and −4556 Hz. The signal at 791 Hz corresponds to the surfactant molecules present in isotropic solution with the other two signals being the powder pattern for the hexagonal mesophase. The sample was then heated in the spectrometer at 90 °C for 15 min and allowed to cool back to room temp. and a spectrum recorded. The signals due to the hexagonal mesophase had disappeared while the intensity of the central narrow signal had increased after the sample had been heated. The bulk material from which this gel sample was taken was then heated in an oven at 90 °C for 3 d. The ^{14}N spectrum of the product consisted of one peak at +791 Hz and was unchanged from the spectrum of the sample that had been heated for 15 min.

Fig. 3(*a*) shows the X-ray powder diffraction pattern of the sample that was heated at 90 °C in the NMR spectrometer. The material is ordered after only 15 min heating. The reflections can be indexed to a two-dimensional hexagonal cell.

Fig. 2(*b*) shows the ^{14}N NMR spectrum of a siliceous gel that forms an M41S material with lamellar symmetry. Again cetyltrimethylammonium chloride is the template molecule for this mixture. This spectrum is very similar to that for the gel which produced the hexagonal M41S [Fig. 2(*a*)]. This gel also contains surfactant present as isotropic solution and hexagonal mesophase. After heating this sample *in situ* at 90 °C for 15 min and cooling to room temp. the hexagonal mesophase disappeared. This was accompanied by a large increase in signal intensity from the isotropic solution. At no stage could a signal corresponding to a lamellar surfactant be detected. Fig. 3(*b*) shows the X-ray powder diffraction pattern of the product displaying lamellar symmetry after the bulk gel was heated for 3 d at 90 °C.

In aqueous solution the lamellar mesophase is not observed below 40 °C. Therefore, ^{14}N NMR spectra were recorded at 45 °C on all gels. In no instance was a lamellar mesophase observed.

The ^{14}N NMR spectra shown here provide direct evidence that surfactant mesophases are present in M41S synthesis gels prior to organisation of the silicate phase. In gels producing hexagonal and lamellar products only hexagonal surfactant mesophase is observed. This is unexpected for two reasons: firstly the water–surfactant concentration is too low to sustain

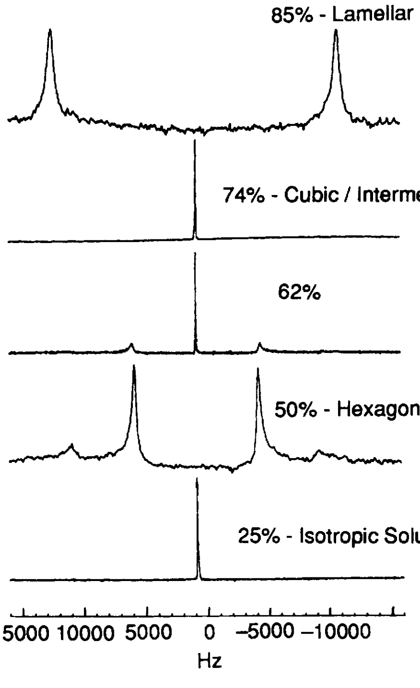


Fig. 1 ^{14}N NMR spectra of the cetyltrimethylammonium chloride–H_2O system at 90 °C and various mass percent surfactant concentrations. Frequency shift measured from aqueous ammonium chloride.

any mesophase formation in a pure water–surfactant mix;[5] second the formation of a hexagonal mesophase in a gel that forms a lamellar product is inconsistent with the different liquid-crystal templating mechanisms proposed by Mobil scientists[1,2] and Monnier *et al.*[6]

Two different liquid-crystal template mechanisms have been proposed: (*i*) Mobil scientists[1,2] suggest that there is an intimate relationship between the symmetry of the mesophases and that of the final product. Thus a lamellar material would be expected to form around a lamellar mesophase and a hexagonal material around a hexagonal mesophase; (*ii*) Monnier *et al.*[6] suggest that initially the surfactant is present as the lamellar phase regardless of the final product. This lamellar mesophase transforms as the silicate network grows.

Inagaki *et al.*[3] have produced an ordered silicate mesoporous material templated around surfactant molecules. The silica source for this compound is kanemite, a layered silicate, and very low concentrations of surfactants are employed during the synthesis. The X-ray diffraction patterns and transition electron micrographs show this material to be very similar to M41S. In order to explain the formation of their compound, Inagaki *et al.*[3] suggest that layered silicates intercalate surfactant molecules which then organise into hexagonal mesophases as the silicate sheets pucker and condense. This could be considered as a third possible mechanism because of the similarities between this mesoporous material and M41S.

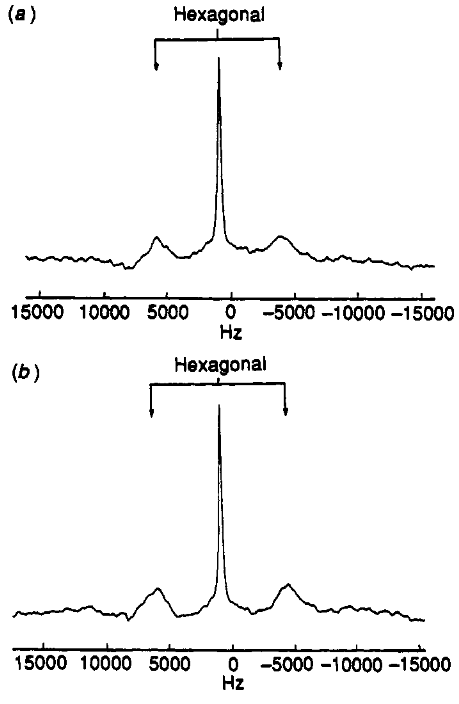
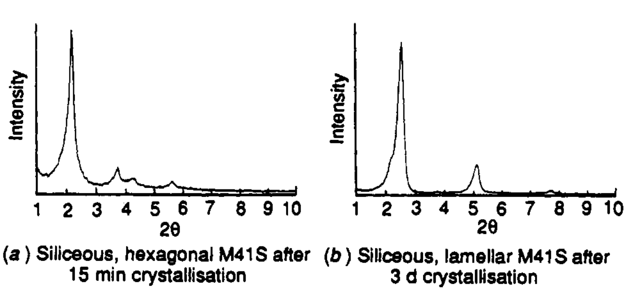
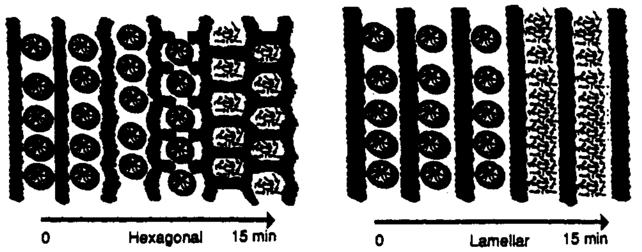


Fig. 2 ^{14}N NMR spectra of (*a*) siliceous M41S gel with composition 1 fumed SiO_2 : 0.25 CTMACl : 0.25 TBA silicate : 24.9 H_2O. The product after heating at 90 °C for 3 d displayed hexagonal symmetry. (*b*) siliceous M41S gel with composition 1 TEOS : 0.38 CTMACl : 0.46 NaOH : 60.2 H_2O. The product after heating at 90 °C for 3 d displayed lamellar symmetry. Frequency shift measured from aqueous ammonium chloride for both spectra.



(*a*) Siliceous, hexagonal M41S after 15 min crystallisation (*b*) Siliceous, lamellar M41S after 3 d crystallisation

Fig. 3 X-Ray diffraction patterns of (*a*) silica gel from Fig. 2(*a*) after heating for 15 min at 90 °C in the NMR spectrometer. (*b*) silica gel from Fig. 2(*b*) after it had been heated in an oven at 90 °C for 3 d.



Scheme 1 Formation of hexagonal and lamellar M41S.

We suggest the following modified liquid-crystal templating mechanism. As the silicate source is introduced into the reaction gel it dissolves into the aqueous regions around the surfactant molecules and promotes organisation of the hexagonal mesophase. The silicate first becomes ordered into layers between which the hexagonal mesophases are sandwiched. Further ordering of the silicate results in the layers puckering, closing together and growing into hexagonal channels. This transformation occurs after *ca.* 15 min and is accompanied by the surfactant reverting to an isotropic solution. Formation of M41S with hexagonal pores is illustrated in Scheme 1. In a reaction gel containing a higher silicate to surfactant ratio the silicate again forms into layers with hexagonal mesophases intercalated between them. In this situation the silicate layers are necessarily thicker and are not able to pucker. Consequently, the resultant product maintains a lamellar arrangement of silicate layers. Again the surfactant reverts to isotropic solution as the silicate condenses into the final product. Scheme 1 also shows the formation of lamellar M41S materials.

We would like to thank Unilever Research and SERC for financial support. We also wish to thank G. J. T. Tiddy for helpful discussions.

Received, 2nd March 1994; Com. 4/01280A

Footnote

† *Note added at proof*: Since submission we have become aware of a related article by Chen *et al.*, (*Microporous Mater.*, 1993, **2**, 27). The findings of that paper do not alter our conclusions in this independent study.

References

1 J. S. Beck, J. C. Vartuli, W. J. Roth, M. E. Leonowicz, C. T. Kregse, K. D. Schmitt, C. T.-W. Chu, D. H. Olson, E. W. Sheppard, S. B. McCullen, J. B. Higgins and J. L. Schenkler, *J. Am. Chem. Soc.*, 1992, **114**, 10834.
2 C. T. Kregse, M. E. Leonowicz, W. J. Roth, J. C. Vartuli and J. S. Beck, *Nature*, 1992, **359**, 710.
3 S. Inagaki, Y. Fukushima and K. Kuroda, *J. Chem. Soc., Chem. Commun.*, 1993.
4 C. T. Kresge, M. E. Leonowicz, J. Wieslaw and J. Roth, *US Pat.* 5,098,684, 1992.
5 E. S. Blackmore and G. J. T. Tiddy, *Liquid Crystals*, 1989, **8**, 131.
6 A. Monnier, F. Schuth, Q. Huo, D. Kumar, D. Margolese, R. S. Maxwell, G. D. Stucky, M. Krishnamurty, P. Petroff, A. Firouzi, M. Janicke and B. F. Chmelka, *Science*, 1993, **261**, 1299.