Evidence for supramolecular organization of alkane and surfactant molecules in the process of forming mesoporous silica

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Investigations of the pore expansion in mesoporous silica in the presence of n-alkanes suggest a cooperative organization of the surfactant and alkane molecules, involving additivity of chain lengths.

The discovery of mesoporous silica by Beck *et al.*[1] involving an unusual combination of supramolecular cationic surfactant aggregates and anionic silicate species is a fine example of cooperative organization. The formation of supramolecular aggregates here is favoured by the hydrophobic interactions between the surfactant chains. Such an organization of ionic organic and inorganic molecular species to produce periodic arrays can be understood on the basis of the model of Stucky and coworkers.[2,3] The pore size in mesoporous silica can be expanded by the addition of various organic molecules, in particular 1,3,5-trimethylbenzene (TMB), the hydrophobic solvation interactions of the aromatic molecules playing the key role.[1,2] We have investigated the systematics in the pore size expansion when normal alkanes, C_nH_{2n+2}, are employed as solubilizing agents, with the expectation that the study may throw light on the nature of the supramolecular organization of the different species involved in the process.

By employing hexadecyltrimethylammonium bromide as the surfactant (SA), we have prepared mesoporous silicas starting with gels of the composition $SiO_2 : Na_2O : SA : alkane : H_2O$ (1 : 0.08 : 0.16 : 0.16 : 63) prepared from the appropriate quantities of tetraethylorthosilicate, NaOH, SA, alkane and distilled water. The molar ratio of the surfactant and the alkane was kept at 1 : 1, since this ratio was optimal for obtaining the maximum possible pore size with a given alkane just as in the case of TMB.[2] The gels were subjected to hydrothermal treatment at 363 K for 24 h. The solids obtained were examined by powder X-ray diffraction (XRD) and transmission electron microscopy.

Fig. 1 shows the XRD patterns of some mesoporous silica samples prepared with the n-alkanes as the solubilizing agents along with the pattern of the sample prepared in the absence of any solubilizing agent. The d_{100} value of 39 Å found in the absence of a solubilizing agent suggests that the surfactant molecule in the micelle is fully extended as in Fig. 2(a). The d_{100} spacing (corresponding to the reflection peak) shows a progressive increase with the increase in the chain length of the alkane, reaching a value of *ca.* 74 Å with $C_{14}H_{30}$. In Fig. 3 the observed d_{100} values are plotted against the number of carbon atoms, n, of the alkane. There is some increase in the d_{100} value up to n = 8, but a significant increase from n = 9 to 15. The X-ray lines are somewhat broad suggesting the presence of
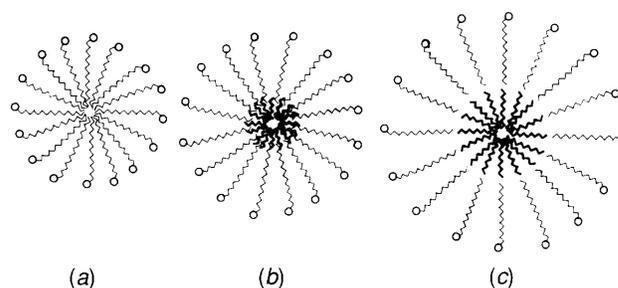

Fig. 2 Schematic drawings of a micelle of surfactant molecules (*a*) in the absence of a solubilizing agent and (*b*), (*c*) in the presence of normal alkanes as solubilizing agents. The alkane molecules at the centre of the micelle are represented by thicker lines.
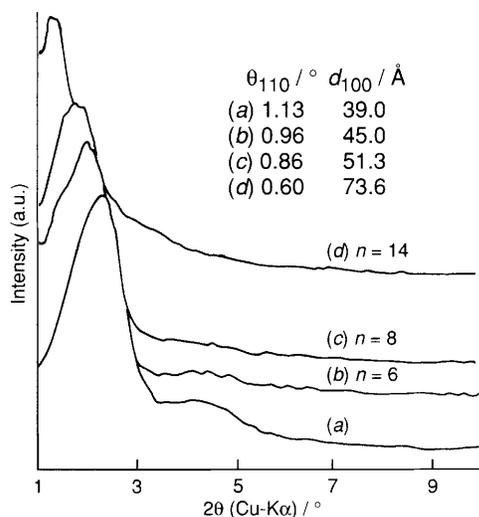

	θ_{110} / °	d_{100} / Å
(a)	1.13	39.0
(b)	0.96	45.0
(c)	0.86	51.3
(d)	0.60	73.6

Fig. 1 X-Ray diffraction patterns of mesoporous silica formed with a cationic surfactant (*a*) in the absence of a solubilizing agent and (*b*)–(*d*) in the presence of normal alkanes, C_nH_{2n+2} (with 1 : 1 molar ratio of the surfactant and the alkane). The n values are indicated beside the diffraction profiles.
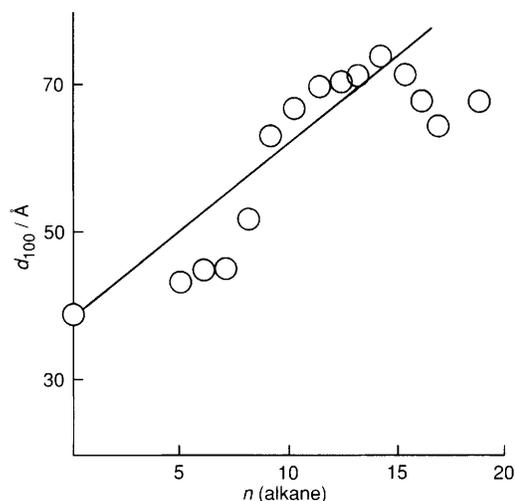

Fig. 3 Plot of the observed d_{100} values of mesoporous silica against the number of carbon atoms, n, of the alkane. The straight line is that expected if the lengths of the alkane chain and surfactant tail were to be additive in forming the micelle template for the formation of mesoporous silica.

disorder or variability in structure, but the TEM images confirm the systematic nature of the increase in pore size with chain length of the alkane. Fig. 4 shows the TEM image of mesoporous silica obtained by using n-$C_{10}H_{22}$. The variation of d_{100} with n can be understood with reference to the theoretical line (shown in Fig. 3) representing the d_{100} values expected if there were additivity of the chain lengths of the alkane and the surfactant molecule in forming the initial micelle.

The d_{100} values found for alkanes with $n = 5$–8 fall well below the theoretical line in Fig. 2, suggesting that the entire chain length of the alkane is not involved in increasing the size of the micelle. Thus, hexane with a chain length of 6.4 Å would be expected to increase the d_{100} by about 12.8 Å if the entire chain length were to contribute to the formation of the micelle, giving d_{100} of $39 + 12.8 = 51.8$ Å, whereas the observed d_{100}

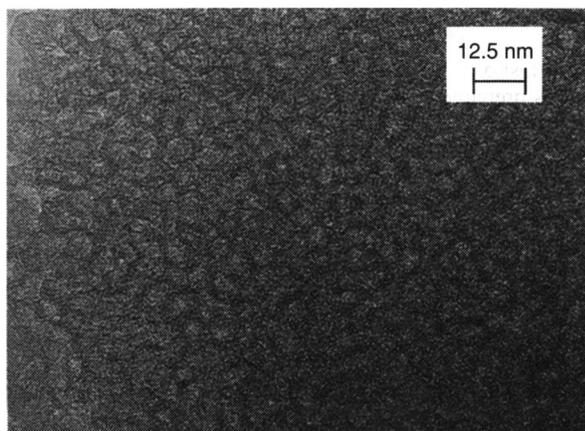**Fig. 4** TEM image of mesoporous silica obtained by using n-$C_{10}H_{22}$ as the solubilizing agent. The pore size is *ca.* 66 Å.

value is 45.0 Å. The micelles formed with the $n = 5$–8 alkanes and the surfactant molecules can be described as molecular dispersions of the solubilizing agent between the tails of the surfactant molecules as depicted in Fig. 2(*b*). With the higher alkanes ($n = 9$–15), on the other hand, the increase in d_{100} is close to that expected on the basis of the chain length of the alkanes and accordingly the observed d_{100} values are close to the theoretical line in Fig. 3. For example, with $C_{14}H_{30}$ (chain length of 16.6 Å), the expected increase in d_{100} would be 33.2 Å, predicting a d_{100} value of $39 + 33.2 = 72.2$ Å; the observed d_{100} of 73.6 Å is quite close to this value. Alkanes with $n > 15$ do not show such additivity (*e.g.* d_{110} with $n = 16$ is 66.9 Å) suggesting that the chains may not be rigid. The behaviour of the $n = 9$–15 alkanes is best described by Fig. 2(*c*) where the alkane molecules form a core which is then surrounded by a layer of the cationic surfactant molecules, with a one-to-one alignment of the alkane chain and the surfactant tail. Such a cooperative organization arising from hydrophobic interaction is noteworthy, lending credence to the expectation that the structure-directing effect of organic molecules may make it possible to design inorganic solids.[4]

References

1 J. S. Beck, J. C. Vartuli, W. J. Roth, M. E. Leonowicz, C. T. Kresge, K. D. Schmitt, C. T. W. Chu, D. H. Olson, E. W. Sheppard, S. B. McCullen, J. B. Higgins and J. L. Schlenker, *J. Am. Chem. Soc.*, 1992, **114**, 10834.
2 Q. Huo, D. I. Margolese, U. Ciesla, D. G. Demuth, P. Feng, T. E. Gier, P. Sieger, A. Firouzi, B. F. Chmelka, F. Schuth and G. D. Stucky, *Chem. Mater.*, 1994, **6**, 1176.
3 A. Firouzi, D. Kumar, L. M. Bull, T. Besier, P. Sieger, Q. Huo, S. A. Walker, J. A. Zasadzinski, C. Glinka, J. Nicol, D. Margolese, G. D. Stucky and B. F. Chmelka, *Science*, 1995, **267**, 1138.
4 M. E. Davies, *CHEMTECH*, 1994, 22.