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# Fluorescence Probing Investigations of the Mechanism of Formation of Organized Mesoporous Silica

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Spectrofluorometry (pyrene and dipyrrenylpropane emission spectra) and time-resolved fluorescence quenching have been used to study the effect of addition of a large excess of sodium hydroxide and sodium silicate on the properties of micelles of cetyltrimethylammonium bromide and chloride (CTAB and CTAC). The systems investigated had overall compositions similar to those used when preparing organized mesoporous silica. Our purpose was to test whether the surfactant counterions are effectively exchanged by silicate ions and micelles grow in the presence of silica. The results show the CTAC or CTAB micelle micropolarity is not affected by the presence of the additives. The pyrene lifetime measurements with the CTAB systems indicate that only a small fraction of micelle-bound bromide ions, about 16%, is exchanged by hydroxyl and silicate ions even when they are largely in excess. The presence of the two additives was found to increase very little the micelle aggregation number in CTAB- and CTAC-containing systems, indicating that there is hardly any micelle growth under the experimental conditions used. Last the micelle microviscosity is also little modified by the effect of the additives. These results call for a reexamination of some of the assumptions underlying models used to describe the synthesis of these extremely interesting materials.

## Introduction

A new family of mesoporous molecular sieves with regular and constant pore diameters in the range 1.5–10 nm, designated as M41S, was synthesized in 1992.<sup>1,2</sup> The solids were prepared by hydrothermal transformation of alkaline silicate or aluminosilicate gels in the presence of quaternary ammonium surfactants  $C_nH_{2n+1}(CH_3)_3N^+$  with different counterions ( $Cl^-$ ,  $Br^-$ ,  $OH^-$ ) and  $n = 8$ –18. Depending on the conditions of synthesis, the solids obtained consist of a hexagonal phase (MCM-41), a cubic phase (MCM-48), or a lamellar phase (MCM-50).

Although low-density silica phases prepared in the presence of surfactants had been patented in 1971,<sup>3,4</sup> the exciting characteristics of these materials (larger pore diameter and specific surface area up to 1000 m<sup>2</sup>/g) were evidenced by the Mobil group and generated an intense interest. Since then, extensive investigations were devoted to the mechanism of formation of these materials.<sup>2,5–10</sup>

The liquid crystal templating (LCT) mechanism in which surfactant liquid crystal mesophases are assumed to act as organic templates was first proposed.<sup>1,2,8</sup> Later on, these authors and others provided evidence that no preexisting LC phase is required for the formation of these materials.<sup>7,9,10</sup> Several studies were performed using in situ probing spectroscopies to elucidate the mechanism of formation of these materials.<sup>6,10–14</sup> One of the main contribution was that of Stucky and co-workers<sup>10</sup> who proposed that these mesostructures result from a cooperative organization process involving electrostatic interactions between the positively charged quaternary ammonium micelles ( $S^+$ ) and the negatively charged silicate or aluminosilicate framework ( $I^-$ ). According to these authors,<sup>10</sup> prior to silicate addition, the molecularly dispersed surfactant is in dynamic equilibrium with spherical and/or cylindrical micelles. Upon addition of silica, the multicharged silicate species displace the original surfactant counterions ( $Cl^-$ ,  $Br^-$ ) to form organic–inorganic ion pairs, which reorganize first into a silica-tropic mesophase followed by silica cross-linking. The nature of the formed mesophase is controlled by the multidentate interaction via the interface packing density. Ionic exchange between surfactant counterions and silicate polyanions seems to be the key point in the proposed mechanism. Micelle growth in the presence of silica is also often assumed.

Fluorescence probing has been extensively used to characterize surfactant-containing systems.<sup>15,16</sup> Indeed the

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(1) Kresge, C. T.; Leonowicz, M. E.; Roth, W. J.; Vartuli, J. C.; Beck, J. S. *Nature* **1992**, *359*, 710.

(2) Beck, J. S.; Vartuli, J. C.; Roth, W. J.; Leonowicz, M. E.; Kresge, C. T.; Schmitt, K. D.; Chu, C. T. W.; Olson, D. H.; Sheppard, E. W.; McCullen, S. B.; Higgins, J. B.; Schlenker, J. L. *J. Am. Chem. Soc.* **1992**, *114*, 10834.

(3) Chiola, V.; Ritsko, J. E.; Vanderpool, C. D. U.S. Patent 3356725, 1971.

(4) Di Renzo, F.; Cambon, H.; Dutartre, R. *Microporous Mater.* **1997**, *10*, 283.

(5) Monnier, A.; Schüth, F.; Huo, Q.; Kumar, D.; Margolese, D.; Maxwell, R. S.; Stucky, G. D.; Krishnamurty, M.; Petroff, P.; Firouzi, A.; Janicke, M.; Chmelka, B. F. *Science* **1993**, *261*, 1299.

(6) Chen, C. Y.; Burkett, S. L.; Li, H. X.; Davis, M. E. *Microporous Mater.* **1993**, *2*, 27.

(7) Huo, Q.; Margolese, D.; Ciesla, U.; Demuth, D. G.; Feng, P.; Gier, T. E.; Sieger, P.; Firouzi, A.; Chmelka, B. F.; Schüth, F.; Stucky, G. D. *Chem. Mater.* **1994**, *6*, 1176.

(8) Vartuli, J. C.; Kresge, C. T.; Leonowicz, M. E.; Chu, A. S.; McCullen, S. B.; Johnson, I. D.; Sheppard, E. W. *Chem. Mater.* **1994**, *6*, 2070.

(9) Beck, J. S.; Vartuli, J. C.; Kennedy, G. J.; Kresge, C. T.; Roth, W. J.; Schramm, S. E. *Chem. Mater.* **1994**, *6*, 1816.

(10) Firouzi, A.; Kumar, D.; Bull, L. M.; Besier, T.; Sieger, P.; Huo, Q.; Walker, S. A.; Zasadzinski, J. A.; Glinka, C.; Nicol, J.; Margolese, D.; Stucky, G. D.; Chmelka, B. F. *Science* **1995**, *267*, 1138.

(11) Lee, Y. S.; Surjadi, D.; Rathman, J. F. *Langmuir* **1996**, *12*, 6202.

(12) Firouzi, A.; Atef, F.; Oertli, A. G.; Stucky, G. D.; Chmelka, B. F. *J. Am. Chem. Soc.* **1997**, *119*, 3596.

(13) Calabro, D. C.; Valyocsik, E. W.; Ryan, F. X. *Microporous Mater.* **1996**, *7*, 243.

(14) Galarneau, A.; Di Renzo, F.; Fajula, F.; Mollo, L.; Fubini, B.; Ottaviani, M. F. *J. Colloid Interface Sci.* **1998**, *201*, 105.

(15) Thomas, J. K. *Acc. Chem. Res.* **1977**, *10*, 133.

use of appropriate probes permits one to obtain information on the micropolarity and microviscosity sensed by these probes in surfactant aggregates. Also time-resolved fluorescence quenching permits the determination of the surfactant aggregation numbers in these aggregates.<sup>15,16</sup> Besides, fluorescence lifetime measurements can be used to study the exchange between two different counterions (bromide and silicate, for instance) if one of the ions (bromide) is a quencher of the fluorescence of the probe used (pyrene).<sup>17,18</sup>

These various possibilities have been used in the study described below. This study concerns surfactant/NaOH/silica systems similar to those which lead to organized mesoporous silica by lowering of the pH. The lifetime of the fluorescent probe pyrene was measured in micellar solutions of cetyltrimethylammonium bromide (CTAB) and of cetyltrimethylammonium chloride (CTAC) alone and in the presence of NaOH and sodium silicate. The micelle microviscosity and micropolarity and the surfactant aggregation number were determined in the same systems. Experiments were also performed by lowering the pH of the systems either by adding hydrochloric acid or by replacing part of the sodium hydroxide by sodium chloride. The results show little exchange of the micelle-bound bromide counterions by the added hydroxide and/or silicate ions even in the presence of a large excess of the latter. Also addition of a large excess of NaOH and sodium silicate was found to have hardly any effect on the micelle size.

### Experimental Section

The CTAB and CTAC were purchased from Aldrich or Fluka and purified by several recrystallizations from ethanol/ethyl acetate mixtures. The samples of pyrene, dipyranylpropane, and cetylpyridinium chloride (CPyC, quencher of the pyrene fluorescence) were the same as described previously.<sup>19–21</sup> Water glass (Fluka; ~27% SiO<sub>2</sub>, ~14% NaOH; density 1.39) was used as source of silica. (It is realized that the species contained in this solution are numerous and complex. Silicate anion or sodium silicate are used below as shortcuts.) Stock solutions of NaOH (5.0 M), NaCl (5.0 M), sodium silicate (6.25 M in SiO<sub>2</sub>), CTAB (0.25 M), and CTAC (0.5 M) were used for preparing the solutions investigated. Pyrene and dipyranylpropane were introduced into the stock surfactant solutions at concentrations such that upon surfactant dilution to 0.100 M, their final concentrations were about 1.5 and 0.5 mM, respectively.

All systems involving CTAB were thoroughly degassed to remove molecular oxygen, which is a strong quencher of the pyrene fluorescence. Indeed these systems were the ones where the exchange of bromide ions was investigated and the presence of oxygen would have reduced the accuracy of the experiments. The CTAC systems were air-saturated as the experiments were performed to investigate changes of micelle size.

The fluorescence emission spectra of micelle-solubilized probes were recorded using a Hitachi F4010 spectrofluorometer. The spectra of micelle-solubilized pyrene yielded the value of the intensity ratio  $I_1/I_3$  which gives a measure of the micelle micropolarity.<sup>15,16</sup> The dipyranylpropane spectra were used to determine the value of the ratio  $I_M/I_E$  of the intensities of the monomer and excimer forms of this probe. The product of this ratio by the lifetime of the dipyranylpropane excimer,  $\tau_E$ , is

proportional to the viscosity of the probe environment.<sup>21,22</sup> Below it is taken as a measure of the microviscosity of the micelles solubilizing dipyranylpropane.

The lifetimes of the dipyranylpropane excimer and of pyrene were measured using a single photon counting apparatus.<sup>19–21</sup> The same apparatus was used for recording the fluorescence decay curves of micelle-solubilized pyrene in the presence of CPyC. The decay curves were analyzed to yield the micelle aggregation number.<sup>19–21</sup> All the experiments were performed at 30 °C, which corresponds to the temperature used for synthesizing organized mesoporous silica. The pH values were measured using a Tacussel pH-meter type TS60/N-1.

### Results and Discussion

The experiments were performed at a fixed concentration of 0.1 M CTAB or CTAC in pure water and upon additions of first NaOH then SiO<sub>2</sub> water glass in order to reach levels of these two components comparable to those found in the surfactant + sodium silicate mixtures used for a typical preparation of organized mesoporous silica.<sup>23</sup> Precipitation occurred upon direct addition of sodium silicate to the surfactant solutions in the absence of NaOH owing to the low pH (about 8 before addition), thereby preventing the study of these systems. The polarity ratio  $I_1/I_3$ , the pyrene lifetime  $\tau$ , the micelle aggregation number  $N$  (number of surfactants per micelle),<sup>19,20</sup> the micelle microviscosity, and the pH of the solution were measured. The results for the CTAB-containing and CTAC-containing systems are summarized in Table 1. It is important to note that all the reported measurements but one (system 12) concerned clear solutions where the silica polymerization had not started. Thus these results really refer to systems which are the precursors of those leading to organized mesoporous silica. The aspect of systems 1–12 in Table 1 did not change even after they remained for 2 days in the fluorescence cells used for the measurements. The systems can therefore be considered to be in a state of thermodynamic equilibrium.

**Micelle Micropolarity.** Considering first the values of the polarity ratio  $I_1/I_3$ , it is seen that additions of NaOH, or NaOH + SiO<sub>2</sub>, or NaCl have no influence on the polarity sensed by pyrene solubilized in the initial CTAB or CTAC micelles. This result is not too surprising as the polarity sensed by pyrene is essentially that of the micelle palisade layer<sup>16</sup> and depends little on the counterion nature. This is clearly seen when comparing the  $I_1/I_3$  values for the CTAB and CTAC solutions in the absence of additives.

**Bromide Ion Exchange.** The values of the pyrene lifetime  $\tau$  in deaerated solutions of CTAB and CTAC (systems 1 and 5 in Table 1) are very different, 165 vs 342 ns, owing to the efficient dynamic quenching of the pyrene fluorescence by the micelle-bound bromide ions, micelle-bound chloride ions having no quenching effect.<sup>17,18</sup> Micelle-bound hydroxyl ions also have no quenching effect on the pyrene fluorescence since  $\tau$  has nearly the same value in solutions of CTAC and of cetyltrimethylammonium hydroxide (CTAOH).<sup>24</sup> The  $\tau$  value for system 7 in Table 1 shows that the same holds for the silicate anions. Indeed, the  $\tau$  values in deaerated solutions of CTAC and of CTAC + NaOH + sodium silicate (systems 5 and 7 in Table 1) are identical (342 ns) whereas any quenching by silicate anions would have resulted in a lower value of  $\tau$  in system 7, provided chloride/silicate exchange took place (such exchange does take place, see below). The quenching of the pyrene fluorescence by the bromide ions can thus

(16) Zana, R. In *Surfactant Solutions. New Methods of Investigation*; Zana, R., Ed.; M. Dekker Inc.: New York, 1987; Chapter 5 and references therein.

(17) Abuin, E.; Lissi, E.; Bianchi, N.; Miola, L.; Quina, F. H. *J. Phys. Chem.* **1983**, *97*, 5166.

(18) Abuin, E.; Lissi, E. *J. Colloid Interface Sci.* **1991**, *143*, 97.

(19) Alargova, R. G.; Kochijashky, I. I.; Zana, R. *Langmuir* **1998**, *14*, 1575.

(20) Alargova, R. G.; Kochijashky, I. I.; Sierra, M. L.; Zana, R. *Langmuir* **1998**, *14*, 5412.

(21) Zana, R.; In, M.; Lévy, H.; Duportail, G. *Langmuir* **1997**, *13*, 5552.

(22) Turley, W. D.; Offen, H. W. *J. Phys. Chem.* **1985**, *89*, 2933.

(23) Voegtlin, A. C.; Matijasic, A.; Patarin, J.; Sauerland, C.; Grillet, Y.; Huve, L. *Microporous Mater.* **1997**, *10*, 137.

(24) Lianos, P.; Zana, R. *J. Phys. Chem.* **1983**, *87*, 1289.

**Table 1. Systems CTAB/SiO<sub>2</sub>/NaOH and CTAC/SiO<sub>2</sub>/NaOH/NaCl: Values of the Pyrene Fluorescence Intensity Ratio  $I_1/I_3$  (Micropolarity), Pyrene Fluorescence Lifetime  $\tau$ , Micelle Aggregation Number  $N$ ,  $\tau_E I_M/I_E$  (Microviscosity), and pH**

system <sup>a</sup>	number	$I_1/I_3$	$\tau$ (ns)	$N$	$\tau_E I_M/I_E$ (ns)	pH
0.100 M CTAB	1 <sup>b</sup>	1.346	165	145	572	8.3
0.100 M CTAB	2 <sup>b</sup>	1.345	177	149	569	13.6
0.500 M NaOH						
0.100 M CTAB	3 <sup>b</sup>	1.346	180	161	650	12.9
0.500 M NaOH						
0.675 M SiO <sub>2</sub>						
0.100 M CTAB	4 <sup>b</sup>	1.35	205	254	676	8.4
1.00 M NaCl						
0.100 M CTAC	5	1.384	155	103	372	7.0
			342 <sup>b</sup>	101 <sup>b</sup>		
0.100 M CTAC	6	1.36	165	105.6	373	13.6
0.500 M NaOH						
0.100 M CTAC	7	1.36	190	113	414	13.2
0.500 M NaOH			342 <sup>b</sup>	116 <sup>b</sup>		
0.500 M SiO <sub>2</sub>						
0.100 M CTAC	8	1.353	175	154	476	12.6
0.200 M NaOH						
0.300 M NaCl						
0.500 M SiO <sub>2</sub>						
0.100 M CTAC	9	1.355	177	157		12.1
0.100 M NaOH						
0.400 M NaCl						
0.500 M SiO <sub>2</sub>						
0.100 M CTAC	10	1.36	172	152		11.6
0.500 M NaCl						
0.500 M SiO <sub>2</sub>						
0.100 M CTAC	11	1.36	175	143		12.5
0.500 M NaOH						
0.300 M HCl						
0.500 M SiO <sub>2</sub>						
(equivalent to 8)						
0.100 M CTAC	12	1.34	171	148		11.6
0.500 M NaOH						
0.492 M HCl						
0.500 M SiO <sub>2</sub>						
(equivalent to 10)						

<sup>a</sup> For SiO<sub>2</sub>-containing systems, the total NaOH content is equal to that listed in the table plus that coming for the water glass (~0.3 times the SiO<sub>2</sub> concentration). <sup>b</sup> Values for deaerated solutions.

be used to detect a possible exchange of micelle-bound bromide ions by added hydroxyl or silicate anions (or by any nonquenching counterion for that matter). Indeed, when such an exchange occurs, the concentration of micelle-bound bromide ion decreases and the pyrene lifetime increases from the value  $\tau(\text{Br}) = 165$  ns in the absence of exchange to  $\tau(\text{Cl}) = 342$  ns in the case of complete exchange upon addition of hydroxyl, silicate, or chloride ions. The difference between the lifetime values in CTAB solutions with and without additive can be used to estimate the fraction of exchanged micelle-bound bromide ions  $f(\text{Br})$ . Indeed, one can write

$$1/\tau(\text{Br}) = 1/\tau_0 + k_{Q,\text{Br}}[\text{Br}]_0 \quad (1)$$

where  $\tau_0$  is the pyrene fluorescence lifetime in the absence of any quencher,  $k_{Q,\text{Br}}$  is the rate constant for the quenching of pyrene by micelle-bound bromide ions, and  $[\text{Br}]_0$  is the concentration of micelle-bound bromide ions.  $\tau_0$  is equal to  $\tau(\text{Cl})$ . Upon addition of a nonquenching anion ( $\text{Cl}^-$ ,  $\text{OH}^-$ , silicate), part of the bound bromide ions are exchanged and their concentration is decreased to  $[\text{Br}]_1$ . The pyrene lifetime becomes

$$1/\tau = 1/\tau(\text{Cl}) + k_{Q,\text{Br}}[\text{Br}]_1 \quad (2)$$

The fraction of exchanged bromide ions thus is written as

$$f(\text{Br}) = ([\text{Br}]_0 - [\text{Br}]_1)/([\text{Br}]_0) = [1/\tau(\text{Br}) - 1/\tau]/[1/\tau(\text{Br}) - 1/\tau(\text{Cl})] \quad (3)$$

where  $\tau$  is the pyrene lifetime in the system after introduction of quenching ions that can partly replace bromide ions at the micelle surface. Conversely,  $f(\text{Br})$  closely represents the fraction of added ions bound to CTAB micelles, referred to the initial concentration of micelle-bound bromide ions.

Table 1 shows a slight increase of  $\tau$  upon addition of 0.5 M NaOH to 0.1 M CTAB, corresponding to  $f(\text{Br}) = 0.13$ . The subsequent addition of 0.675 M SiO<sub>2</sub> produces a further small increase of  $\tau$ , leading to  $f(\text{Br}) = 0.16$ . Thus, even in the very unlikely situation where this exchange represents a substitution of bromide ions only by added silicate anions (no bound  $\text{OH}^-$ ), these results indicate that the exchange is small since it involves less than one out of six bromide ions bound to the micelle surface. This is far from the assumption made in the current models of formation of organized mesoporous silica which imply that silicate anions substitute nearly all surfactant counterions. Recall that the degree of binding of bromide ions to CTAB micelles in the absence of additive is about 80%.<sup>25</sup> The degree of  $\text{OH}^-$  binding to CTAC micelle is of about 30%.<sup>24</sup> It is thus likely that the overall degree of binding in the CTAB + NaOH systems is lower than that in pure CTAB solutions. The same is likely to be true upon addition of SiO<sub>2</sub>.

The result for system 4 in Table 1 shows that the exchange of bromide ions by chloride ions can be substantial and result in a larger increase of value of  $\tau$ . Thus the presence of 1.0 M NaCl is seen to increase  $\tau$  much more than 0.5 M NaOH + 0.675 M SiO<sub>2</sub>. In this case,  $f(\text{Br}) = 0.38$ . Our results can be taken as indicating that the silicate anions used are less efficient than chloride ions in displacing micelle-bound bromide ions from the micelle surface. This means that under the experimental conditions used, chloride ions are more strongly bound to the surface of CTA micelles than silicate ions, but less than bromide ions since most bromide ions remain bound even in the presence of a large excess of chloride ions. This last conclusion confirms those reached in previous reports.<sup>17,18</sup> Nevertheless, since our results indicate that some bromide ions are exchanged for hydroxyl and silicate anions, even more chloride ions will be exchanged by these two ions.

The CTAC-containing systems were generally air-saturated. The values of the pyrene lifetimes are then seen to be system-dependent. This is so because pyrene is quenched by the molecular oxygen solubilized in the system and the efficiency of this quenching depends much on the microviscosity of the system.<sup>21,26</sup> Higher microviscosity will result in larger lifetime as is indeed observed. When oxygen is removed, the lifetime value becomes nearly independent of the system (see results for deaerated systems 5 and 7, Table 1).

**Micelle Aggregation Number  $N$ .** The value of  $N$  is seen to be significantly larger for CTAB than for CTAC, thereby confirming previous reports.<sup>27,28</sup> This is the result of the larger binding of bromide than of chloride ions to the CTA micelle surface.<sup>17,18</sup> However the variations of  $N$  upon addition of NaOH and of NaOH + silica are qualitatively similar for the CTAB and CTAC solutions. Thus the addition of 0.5 M NaOH brings about a very

(25) Zana, R. J. *Colloid Interface Sci.* **1980**, *78*, 330.

(26) Regev, O.; Zana, R. J. *Colloid Interface Sci.*, in press.

(27) Malliaris, A.; Lang, J.; Zana, R. J. *Chem. Soc., Faraday Trans. 1* **1986**, *82*, 109.

(28) Zana, R.; Muto, Y.; Esumi, K.; Meguro, K. J. *Colloid Interface Sci.* **1988**, *123*, 502.



small increase of  $N$  which is likely the result of two antagonistic effects: (i) A decrease of  $N$  due to the exchange of a small part of micelle-bound bromide ions by added hydroxyl ions. Indeed, the value of  $N$  for CTAOH micelles is much lower than that for CTAB micelles, about 51<sup>24</sup> versus 150 at 0.1 M. (ii) An increase of  $N$  associated to the increased ionic strength of the system due to the added NaOH.<sup>29</sup> The effect of the subsequent addition of silicate anions is to bring about an additional small increase of  $N$  with both CTAB and CTAC, which can be explained in the same manner as the effect of NaOH additions. Our results are in agreement with the rheological studies of CTAC solutions which showed no change of micelle size in the presence of silicate anions up to a surfactant concentration of about 0.18 M.<sup>11</sup>

In the experiments discussed thus far the pH was above or equal to 13. The effect of a pH lowering was investigated using the surfactant CTAC. The results for systems 7 and 8 in Table 1 show that an increase of  $N$  from 113 to 154 as the pH is decreased from 13.2 to 12.6 by replacing part of NaOH by NaCl (this is equivalent to neutralizing part of the excess NaOH by HCl, as is done when lowering the pH to induce the formation of mesoporous silica). Further substitution of NaOH by NaCl resulted in a lower pH of 11.6, but in no further change of  $N$  (systems 9 and 10). We also repeated some experiments by adding HCl to systems containing NaOH, under very strong stirring (systems 11 and 12). This procedure led in system 12 to the formation of a very small amount of precipitate, corresponding to a poorly organized mesoporous silica as confirmed by X-ray diffraction analysis. Nevertheless, these measurements yielded the same value of  $N$  as the previous ones.

The main point in these  $N$  values is of course the fact that there is only a very small increase of aggregation number, from 103 to 113, upon addition of silicate anions. A somewhat larger increase of  $N$ , from 113 to 152, is observed upon decreasing the pH (systems 7 and 10). But such  $N$  values correspond to only slightly elongated micelles. Thus the assumption that very elongated micelles form upon silicate ion binding is not tenable in view of the present results, at least at this stage of the system. Nevertheless, since organization does occur and leads to organized mesoporous silica, our results suggest that this organization must take place at a later stage, at a pH lower than 11.6, when the polymerization of silica has already started in the system.

**Microviscosity.** Table 1 shows similar variation of microviscosity upon addition of NaOH and then of sodium silicate. The effect of NaOH additions is negligible. That of the subsequent addition of sodium silicate is significant. Two points are noteworthy. First the microviscosity appears to increase with the micelle size, in agreement with previous reports.<sup>21,30–32</sup> Second, the microviscosity of the CTAB-containing system is always larger than that of CTAC-containing systems in the presence of the same

additives (NaOH and sodium silicate). This result further confirms that the silicate anions have not replaced all surfactant counterions at the micelle surface. Indeed if this were so, the same microviscosity would be measured for the two systems.

### Concluding Remarks

The present study involved strongly alkaline surfactant/sodium silicate systems where the silica was not polymerized. The measurements conclusively showed that the introduction of hydroxyl and silicate anions into micellar solutions of CTAB resulted only in the exchange of a small fraction of micelle-bound bromide ions by the added ions. Also, additions of NaOH and sodium silicate did not bring about a significant change of micelle size or shape. These two conclusions do not support what is sometimes postulated in the mechanisms of mesoporous silica formation. The *templating effect of the surfactant* so often invoked in these mechanisms is probably not relevant, except in experiments such as those of Attard et al.<sup>33</sup> who used systems containing up to 50% nonionic surfactant and where LC phases were present. However in a large number of reported studies, the surfactant content is far too low for LC phases to be present or to form upon addition of silicate and templating cannot be involved as already pointed out<sup>10</sup> and as demonstrated by our results. Nevertheless since it has been unambiguously shown that the presence of surfactant is necessary for the formation of organized mesoporous silica, it is probably more correct to talk of *surfactant-assisted mesoporous silica formation*.

The question which then arises in view of our results concerns the step where the surfactant/silica interactions take place, resulting in the organization of the system and in the formation of organized mesoporous silica. We have seen above that the neutralization of part of the excess alkalinity of the system results in a significant increase of micelle size (see  $N$  values for systems 7 and 10) associated to the progressive substitution of the hydroxyl ions by chloride ions, at constant ionic strength. A further decrease of pH may result in further growth. However these larger values of  $N$  still correspond to micelles which are small compared to the length of the pores in the final material. We feel that the most important step in the process is the formation of prepolymers of silica in regions of the system where, upon addition of HCl, there is locally a large excess of HCl which induces the polymerization of the silicate anions, leading to colloidal silica particles. The interaction of these prepolymers with surfactant micelles may be responsible for micelle growth and subsequent reorganization of the silica/micelle complexes. The coupling of these processes to further silica polymerization in the complexes may ultimately lead to the mesoporous silica. At this stage of the study we cannot exclude that interactions may occur between free (as opposed to micellized) surfactant ions and silicate anions, with the micelles acting as reservoirs of surfactant ions, as suggested by Huo et al.<sup>7</sup>

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(29) Lianos, P.; Zana, R. *J. Phys. Chem.* **1980**, *84*, 3339.

(30) Miyagishi, S.; Asakawa, T.; Nishida, M. *J. Colloid Interface Sci.* **1987**, *115*, 199.

(31) Miyagishi, S.; Akasoh, W.; Hashimoto, T.; Asakawa, T. *J. Colloid Interface Sci.* **1996**, *184*, 527.

(32) Miyagishi, S.; Kurimoto, H.; Asakawa, T. *Langmuir* **1995**, *11*, 2951.

(33) Attard, G. S.; Glyde, J. C.; Goltner, C. G. *Nature* **1995**, *378*, 366.