

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/231673503>

# Study of the Mechanism of Formation of a Mesostructured Hexagonal Alumina by Means of Fluorescence Probing Techniques

ARTICLE *in* LANGMUIR · DECEMBER 2001

Impact Factor: 4.46 · DOI: 10.1021/la011268m

---

CITATIONS

20

---

READS

14

4 AUTHORS, INCLUDING:



Lorette Sicard

Paris Diderot University

38 PUBLICATIONS 347 CITATIONS

SEE PROFILE



Bénédicte Lebeau

Université de Haute-Alsace

172 PUBLICATIONS 5,202 CITATIONS

SEE PROFILE

# Study of the Mechanism of Formation of a Mesostructured Hexagonal Alumina by Means of Fluorescence Probing Techniques

Lorette Sicard,<sup>†</sup> Bénédicte Lebeau,<sup>†</sup> Joël Patarin,<sup>†</sup> and Raoul Zana<sup>\*,‡</sup>

Laboratoire de Matériaux Minéraux (UPRES-A-7016, CNRS), E.N.S.C.Mu.,  
Université de Haute-Alsace, 3 rue A. Werner, 68093 Mulhouse-Cedex, France,  
and Institut C. Sadron (CNRS-ULP), 6 rue Boussingault, 67000 Strasbourg, France

Received August 10, 2001. In Final Form: October 4, 2001

The formation of mesostructured hexagonal alumina from aluminum nitrate in micellar solutions of sodium dodecyl sulfate (SDS) in a water/urea mixture as reported by Yada et al. (*Inorg. Chem.* **1997**, *36*, 5565) has been investigated by means of fluorescence probing (spectrofluorometry and time-resolved fluorescence), using pyrene and dipyrrenylpropane as fluorescent probes. The investigations involved mainly the reference systems 0.60 M SDS and 0.60 M SDS/9.1 M urea, and the precursor system 0.60 M SDS/9.1 M urea/0.30 M Al(NO<sub>3</sub>)<sub>3</sub>, at a temperature of 60 °C. In a first step, the micelle aggregation number, the micelle microviscosity, and the pyrene fluorescence lifetime were determined in the initial state of these systems, i.e., before the start of the polymerization process that leads to the mesostructured material. The effects of substitution of Al(NO<sub>3</sub>)<sub>3</sub> by AlCl<sub>3</sub> or NaNO<sub>3</sub> and of a change of the concentrations of SDS and Al(NO<sub>3</sub>)<sub>3</sub> were also investigated. The micelles present in the precursor system were found to have an aggregation number of 105, which indicated a slightly elongated shape, and an ionization degree around 0.12, indicating a strong binding of Al<sup>3+</sup> ions to the micelle surface. The bound Al<sup>3+</sup> ions were shown to carry to the micelle surface a small amount of nitrate ions, to the extent of about 5 mol % with respect to SDS. The bound nitrate ions strongly quenched the pyrene fluorescence. Similar results were obtained for the dilute precursor system 0.10 M SDS/9.1 M urea/0.30 M Al(NO<sub>3</sub>)<sub>3</sub> and for the corresponding reference systems. In a second step the systems were studied as a function of the aging time (time spent at 60 °C). The microviscosity of the micelles in the precursor system increased with the aging time. This result, together with the variation of the time after which a precipitate was visually observed in the system with the SDS concentration, strongly supports a mechanism where the main locus for polymerization is the micelle surface. The pyrene lifetime increased with the aging time revealing a release of nitrate ions that is associated to the polymerization of the bound aluminum species that decreases their electrical charge. However the micelle aggregation number remained unaffected by the polymerization. It appears that the transformation of the complex formed by the growing alumina polymers and the dodecyl sulfate micelles into an organized material takes place just before or during the precipitation of the organized solid. This behavior is similar to that noted for the formation of organized mesoporous silica even though qualitative differences exist in the precursor systems for silica and alumina used in our investigations. A model is presented that explains the various observations.

## Introduction

Mesoporous materials of the M41S family present a regular arrangement of mesopores that gives them a large surface area and a narrow mesopore size distribution.<sup>1</sup> In the case of mesoporous alumina, these properties are of great interest for applications in catalysis. However the studies concerning the synthesis of alumina materials are few compared to those of siliceous materials.

The first syntheses of mesostructured alumina were reported by Huo et al.<sup>2,3</sup> with mono- and didodecyl phosphate and dodecylbenzenesulfonate surfactants. The structure of the produced materials was lamellar. The majority of the other syntheses carried out in the presence of anionic surfactants led to disordered structures,<sup>4–6</sup> revealed by the presence of a broad single diffraction peak at low angle, or to alumina whose structure was not

elucidated.<sup>7,8</sup> The use of nonionic<sup>6,9–12</sup> or cationic<sup>13–15</sup> surfactants was also found to lead to the formation of disordered<sup>6,9–15</sup> or to lamellar<sup>13</sup> mesostructures. Yada et al.<sup>16–19</sup> synthesized the only mesostructured alumina with a hexagonal structure reported so far, using sodium

<sup>†</sup> Université de Haute-Alsace.

<sup>‡</sup> Institut C. Sadron (CNRS-ULP).

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

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

(3) Huo, Q.; Margolese, D. I.; Ciesla, U.; Feng, P.; Gier, T. E.; Sieger, P.; Leon, R.; Petroff, P. M.; Schuth, F.; Stucky, G. D. *Nature* **1994**, *368*, 317.

(4) Stein, A.; Holland, B. T. *J. Porous Mater.* **1996**, *3*, 83.

(5) Holland, B. T.; Isbester, P. K.; Munson, E. J.; Stein, A. *Mater. Res. Bull.* **1999**, *34*, 471.

(6) Vaudry, F.; Khodabandeh, S.; Davis, M. E. *Chem. Mater.* **1996**, *8*, 1451.

(7) Liu, X.; Wei, Y.; Jin, D.; Shih, W. H. *Mater. Lett.* **2000**, *42*, 143.

(8) Valange, S.; Guth, J. L.; Kolenda, F.; Lacombe, S.; Gabelica, Z. *Microporous Mesoporous Mater.* **2000**, *35–36*, 597.

(9) Bagshaw, S. A.; Pinnavaia, T. J. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1102.

(10) Zhang, W.; Pinnavaia, T. J. *Chem. Commun.* **1998**, 1185.

(11) Yang, P.; Zhao, D.; Margolese, D. I.; Chmelka, B. F.; Stucky, G. D. *Chem. Mater.* **1999**, *10*, 2813.

(12) Neeraj; Eswaramoorthy, M. *Proc.—Indian Acad. Sci., Chem. Sci.* **1998**, *110*, 143.

(13) Acosta, S.; Ayral, A.; Guizard, C.; Cot, L. *J. Sol-Gel Sci. Technol.* **1996**, *8*, 195.

(14) Cabrera, S.; El Haskouri, J.; Alamo, J.; Beltrán, A.; Beltrán, D.; Mendioroz, S.; Marcos, M. D.; Amorós, P. *Adv. Mater.* **1999**, *5*, 379.

(15) Cabrera, S.; El Haskouri, J.; Guillem, C.; Latorre, J.; Beltrán-Porter, A.; Beltrán-Porter, D.; Marcos, M. D.; Amorós, P. *Solid State Sci.* **2000**, *2*, 405.

(16) Yada, M.; Machida, M.; Kijima, T. *Chem. Commun.* **1996**, 769.

(17) Yada, M.; Hiyoshi, H.; Ohe, K.; Machida, M.; Kijima, T. *Inorg. Chem.* **1997**, *36*, 5565.

dodecyl sulfate (SDS) in the presence of urea acting as pH modifier. However, the calcination of the materials led to a collapse of their structure. The sulfate headgroups appear to be too embedded in the inorganic walls. This would result in sintering upon calcination. Yada et al.<sup>20,21</sup> showed that the addition of yttrium with a molar ratio Y/Al = 0.18 in the final product stabilized the structure and permitted the extraction of the surfactant with sodium acetate without altering the structure. They also reported that the material that precipitates first has a lamellar structure and that a structural transition occurs at a pH between 6 and 7.<sup>16,17</sup> This transition can be inhibited by co-incorporation of an alcohol or didodecyltrimethylammonium bromide.<sup>19</sup> Finally, a wide variety of morphologies were obtained by varying the urea concentration.<sup>17</sup> Recently the system used by Yada et al. was further investigated.<sup>22,23</sup> Contrary to what was previously reported, no layered intermediate was observed.<sup>22</sup> The materials exhibited a hexagonal symmetry as clearly indicated by the presence of the (100), (110), and (200) X-ray diffraction peaks. Transmission electron micrographs confirmed the hexagonal structure of the pore channels. Scanning electron micrographs showed a worm-like morphology that characterizes MCM-41-type materials.<sup>24</sup> Elemental analysis indicated an incorporation of dodecyl sulfate anions (DS<sup>-</sup>) with a molar ratio [DS<sup>-</sup>]/[Al] close to 0.25–0.3.<sup>23</sup> No sodium or nitrogen atoms were detected in the produced material.<sup>23</sup> A thermal analysis study of this material indicated a strong interaction between the sulfate headgroup of SDS and the alumina framework.<sup>23</sup>

The mechanisms of formation of ordered mesoporous materials were mostly investigated for silica-based materials.<sup>25</sup> A mechanism that involves a cooperative organization of the organic and inorganic species driven by the electrostatic interactions between the cationic surfactant micelles and the inorganic framework was postulated.<sup>26</sup> A key assumption in this mechanism is that the surfactant counterions bound to the spherical or cylindrical micelles are exchanged by the added silicate species. The polymerization of the latter would lead to a rearrangement into a hexagonal structure. However, this mechanism was not supported by the results of recent fluorescence probing studies of systems made of alkaline cetyltrimethylammonium bromide (CTAB) and water glass (silica source) that are precursors of MCM-41-type siliceous materials.<sup>27,28</sup> Indeed, these studies showed that there is very little exchange of the micelle-bound bromide counterions

at the micelle surface by silicate species present in the added water glass. Also, no growth of the micelles occurred upon addition of water glass to the alkaline CTAB solution and the micelles remained quasi-spherical until precipitation of the mesostructured silica occurred. These results led to the postulate that the silicate species polymerize in the bulk phase and that the growing polymers bind free surfactant ions until precipitation of the organized polymer/surfactant complex takes place. The micelles simply act as reservoirs of surfactant. Nevertheless, one cannot discard the possibility that the mechanism of formation of mesostructured silica depends on the conditions in which the material is synthesized, particularly the nature and concentration of the surfactant and also the nature of the silica source.

Thus, fluorescence probing techniques can provide extremely important information on the mechanism of formation of mesostructured materials. We therefore decided to apply these techniques to study the mechanism of formation of mesostructured hexagonal alumina. This paper reports the results of these investigations. Recall that fluorescent probe techniques probe the systems in situ. They permit one to determine the size, shape, and microviscosity of micelles.<sup>29</sup> In systems where one ionic species is a quencher of the probe fluorescence, these techniques also permit one to follow ion exchange that may occur at the micelle surface during the formation of the organized material.<sup>27,28</sup> The synthesis of mesostructured hexagonal alumina was performed by heating the precursor system 0.60 M SDS/9.1 M urea/0.30 M Al(NO<sub>3</sub>)<sub>3</sub> for a sufficient time (aging time) at 60 °C. This composition is very close to that used by Yada et al.<sup>16</sup> The decomposition of urea brings about an increase of the pH of the system from 3.5 to 5.5 that results in the precipitation of mesostructured hexagonal alumina. At the outset it is recalled that the anionic dodecyl sulfate micelles in the precursor systems strongly bind Al<sup>3+</sup> ions.<sup>22,30</sup> Thus the initial situation in this system is *qualitatively* different from that in the precursor system of mesostructured silica. There the binding of silicate species by the micelles was shown to be very small.<sup>27,28</sup> In the first part of this study the dodecyl sulfate micelles in the precursor system and in the reference systems 0.60 M SDS and 0.60 M SDS/9.1 M urea were fully characterized. For the sake of comparison, systems where AlCl<sub>3</sub> or NaNO<sub>3</sub> replaced Al(NO<sub>3</sub>)<sub>3</sub> were also investigated. These studies revealed that some nitrate ions are carried to the micelle surface by the bound Al<sup>3+</sup> ions and quench the pyrene fluorescence. This result increased the interest of using fluorescence probing techniques for the investigation of the system of Yada et al.<sup>16–19</sup> A dilute precursor system with a SDS concentration of 0.10 M was also investigated. In this system the Al/SDS concentration ratio is close to that in the final material (see above). In the second part of the study the variations of micellar properties in the reference and precursor systems were determined as a function of the aging time, at 60 °C. The results obtained in this investigation indicate that as the pH increases, the inorganic cations polymerize at the micelle surface. The micelles are little affected during most of the aging process that leads to the formation of the mesostructured hexagonal alumina. Precipitation of the organized material occurs when the molecular weight of the inorganic polymer/surfactant complex is large enough.

(18) Yada, M.; Hiyoshi, H.; Machida, M.; Kijima, T. *J. Porous Mater.* **1998**, *5*, 133.

(19) Yada, M.; Kitamura, H.; Machida, M.; Kijima, T. *Langmuir* **1997**, *13*, 5252.

(20) Yada, M.; Ohya, M.; Machida, M.; Kijima, T. *Chem. Commun.* **1998**, 1941.

(21) Yada, M.; Kitamura, H.; Machida, M.; Kijima, T. *Inorg. Chem.* **1998**, *37*, 7, 5470.

(22) Sicard, L.; Frasc, J.; Soulard, M.; Lebeau, B.; Patarin, J.; Davey, T.; Zana, R.; Kolenda, F. *Microporous Mesoporous Mater.* **2001**, *44–45*, 25.

(23) Sicard, L.; Llewellyn, P. L.; Patarin, J.; Kolenda, F. *Microporous Mesoporous Mater.* **2001**, *44–45*, 195.

(24) Ozin, G. A.; Kresge, C. T.; Yang, H. In *Mesoporous Molecular Sieves, Studies in Surface Science and Catalysis 117*; Bonnevot, L., B  land, F., Danumah, C., Giasson, S., Kaliaguine, S., Eds.; Elsevier Science B.V., Amsterdam, 1998; p 119.

(25) Ying, J. Y.; Mehnert, C. P.; Wong, M. S. *Angew. Chem., Int. Ed.* **1999**, *38*, 56.

(26) 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. I.; Stucky, G. D.; Chmelka, B. F. *Science* **1995**, *267*, 1138.

(27) Zana, R.; Frasc, J.; Soulard, M.; Lebeau, B.; Patarin, J. *Langmuir* **1999**, *15*, 2603.

(28) Frasc, J.; Lebeau, B.; Soulard, M.; Patarin, J.; Zana, R. *Langmuir* **2000**, *16*, 9049.

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

(30) Alargova, R. G.; Petkov, D.; Petsev, I.; Broze, G.; Mehreteab, A. *Langmuir* **1995**, *11*, 1530.

## Experimental Section

**Materials.** Aluminum nitrate nonahydrate (Carlo Erba) and anhydrous aluminum chloride (Merck) were used as aluminum sources. Sodium nitrate (Fluka) was used as a source of nitrate in some experiments. SDS was purchased from Serva and urea from Sigma.

Dipyrenylpropane, used as fluorescent probe in microviscosity studies, was purchased from Molecular Probes (Eugene, OR). Pyrene and the quencher dodecylpyridinium chloride (DPC) were the same as in previous studies.<sup>28,31,32</sup> The pyrene and dipyrenylpropane concentrations in the different systems were about 4 and 0.6  $\mu\text{M}$ , respectively. The DPC concentration was adjusted depending on the system used.

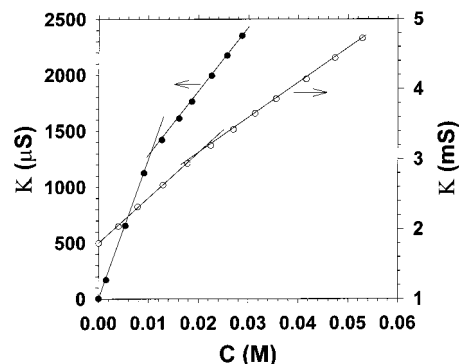
### Synthesis of the Mesoporous Hexagonal Alumina.

The mesoporous material precipitated out after maintaining the precursor system at 60 °C for a sufficient time. This temperature is lower than that used by Yada et al., 80 °C.<sup>16</sup> Indeed, the fluorescence apparatuses used did not operate well above 65 °C. Also this lower temperature much increased the time during which the system remained clear and transparent, providing a better resolution of the polymerization process. We checked by X-ray diffraction (XRD) and chemical analysis that the mesoporous solids obtained at 60 and 80 °C are identical.

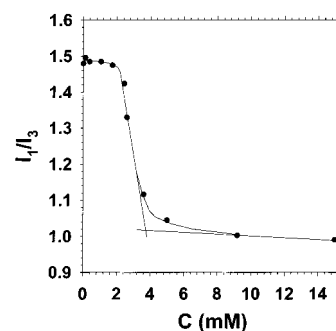
The reactive systems for fluorescence studies were prepared as is now described. An appropriate amount of a stock solution of pyrene in ethanol was introduced into a volumetric flask in order that the final pyrene concentration was around 4  $\mu\text{M}$ . This solution was spread over the flask wall while the ethanol was evaporated in a gentle stream of air. SDS and urea were weighted in the flask in order to have the appropriate concentrations, and some water was added. Dissolution of the pyrene, SDS, and part of the urea was achieved by stirring overnight at room temperature. Solid aluminum nitrate nonahydrate was then introduced, and full dissolution was rapidly obtained at 40 °C, yielding a clear and transparent solution. Whenever necessary, an appropriate amount of an aqueous stock solution of quencher (DPC) was added to the solution at the same time as the aluminum nitrate. For the microviscosity experiments, the pyrene solution in ethanol was replaced by a stock solution of dipyrenylpropane in tetrahydrofuran. The solvent was not evaporated because the dissolution of solid dipyrenylpropane in the solution would take a very long time. The amount of added tetrahydrofuran represented less than one part per thousand of the solution volume. It did not influence the micellar properties and the course of the reaction. The system was stirred overnight at 30 °C. Temperature was then raised to 60 °C. Systems where  $\text{Al}(\text{NO}_3)_3$  was replaced by  $\text{AlCl}_3$  or  $\text{NaNO}_3$  were similarly prepared.

**Methods.** The micelle aggregation numbers and pyrene fluorescence lifetimes (reciprocal of the fluorescence decay rate) were determined by time-resolved fluorescence.<sup>27,28,31,32</sup> The fluorescence decay curves were recorded in the absence of DPC in lifetime measurements and in the presence of DPC in measurements of aggregation numbers, using a single photon counting apparatus operated at 335 nm for the excitation of the pyrene fluorescence and 381 nm for the fluorescence emission.<sup>27,28,31,32</sup> The lifetime of the dipyrenylpropane excimer,  $\tau_E$ , was measured with the same apparatus using an excitation wavelength of 335 nm and recording the decay curve at above 450 nm. The fluorescence emission spectra of dipyrenylpropane were recorded in the range 350–550 nm with a Hitachi F4010 spectrofluorometer using an excitation wavelength of 346 nm. The intensities of the monomer emission,  $I_M$ , at about 378 nm and of the excimer emission,  $I_E$ , at about 480 nm were used to calculate the quantity  $Q = \tau_E(I_M/I_E)$  that is proportional to the microviscosity sensed by dipyrenylpropane in the micellar environment.<sup>33–35</sup> This quantity is simply referred to as microviscosity.

The investigated system was introduced in the fluorescence cell and deaerated by three or four successive freeze–pump–



**Figure 1.** Variation of the electrical conductivity  $K$  of SDS solutions with the surfactant concentration  $C$  in water (●) and in water/9.1 M urea (○) at 60 °C.



**Figure 2.** Variation of the  $I_1/I_3$  ratio with the SDS concentration in water/9.1 M urea/0.30 M  $\text{Al}(\text{NO}_3)_3$  at 60 °C.

thaw cycles prior to fluorescence measurements. The cell was then filled with pure nitrogen at atmospheric pressure in order to avoid a boiling of the system when the temperature was raised to 60 °C. All measurements reported below were performed at  $60 \pm 0.3$  °C.

The critical micelle concentration (cmc) of SDS in water and in water/9.1 M urea was determined by the electrical conductivity method. The conductivity was measured using a Wayne-Kerr automatic precision bridge B905. The cmc of SDS in water/9.1 M urea/0.30 M  $\text{Al}(\text{NO}_3)_3$  was obtained from the plot of the pyrene polarity index  $I_1/I_3$  (ratio of the intensity of the first and third vibronic peaks in the fluorescence emission spectrum of pyrene) against the SDS concentration.<sup>29,36</sup> The emission spectra were recorded using the Hitachi F4010 spectrofluorometer operated at an excitation wavelength of 335 nm.

## Results and Discussion

**Reference and Precursor Systems.** This section reports results of studies that aimed at characterizing the micelles in the reference and in the precursor systems, at 60 °C. The measurements were performed immediately after raising the temperature of the systems to 60 °C.

Figures 1 and 2 show the variations of the electrical conductivity  $K$  and of the pyrene fluorescence intensity ratio ( $I_1/I_3$ ) with the surfactant concentration  $C$  at 60 °C in various systems. The values of the cmc obtained from these plots are 10.5, 21.0, and 3.5 mM in water, water/9.1 M urea, and water/9.1 M urea/0.30 M  $\text{Al}(\text{NO}_3)_3$ , respectively. The values of the micelle aggregation number  $N$ , of the microviscosity  $Q$ , and of the pyrene fluorescence lifetime  $\tau$  in the reference and precursor systems and in other systems are listed in Table 1.

The results in Figure 1 permit an estimation of the value of the ionization degree  $\alpha$  of the dodecyl sulfate micelles in water and water/9.1 M urea. Approximate

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

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

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

(34) Turley, W. D.; Offen, H. W. *J. Phys. Chem.* **1986**, *90*, 1967.

(35) Miyagishi, S.; Suzuki, H.; Asakawa, T. *Langmuir* **1996**, *12*, 2900.

(36) Kalyanasundaram, K.; Thomas, J. K. *J. Am. Chem. Soc.* **1977**, *99*, 2039.



**Table 1. Micelle Aggregation Number (*N*), Pyrene Fluorescence Lifetime (*τ*), and Microviscosity (*Q*) in Deaerated Reference and Precursor Systems**

	composition	<i>N</i> <sup>a</sup>	<i>τ</i> <sup>a</sup> (ns)	<i>Q</i> (ns)
1	0.60 M SDS	74 (83 ± 15)	310 (107)	36
2	0.60 M SDS/9.1 M urea	53 (56 ± 5)	280 (164)	53
3	0.60 M SDS/9.1 M urea/0.30 M Al(NO <sub>3</sub> ) <sub>3</sub>	104 (107 ± 10)	176 (120)	59
4	0.60 M SDS/0.30 M Al(NO <sub>3</sub> ) <sub>3</sub>		261 <sup>b</sup>	
5	0.60 M SDS/9.1 M urea/0.30 M AlCl <sub>3</sub>	112	278	
6	0.60 M SDS/0.90 M NaNO <sub>3</sub>		293	
7	0.60 M SDS/9.1 M urea/0.90 M NaNO <sub>3</sub>		231	
8	0.10 M SDS	50	296	40
9	0.10 M SDS/9.1 M urea	30	270	46
10	0.10 M SDS/9.1 M urea/0.30 M Al(NO <sub>3</sub> ) <sub>3</sub>	95	161	56
11	0.10 M SDS/9.1 M urea/0.30 M AlCl <sub>3</sub>		273	

<sup>a</sup> Values in parentheses are for aerated systems. <sup>b</sup> Value obtained by extrapolation (see text).

values of  $\alpha$  can be obtained from the expression:  $\alpha = (dK/dC)_{C > \text{cmc}} / (dK/dC)_{C < \text{cmc}}$ .<sup>37</sup> However this method generally yields values of  $\alpha$  that are too large, the more ionized the micelles, the larger the error, because it underestimates the micelle contribution to the conductivity of the system.<sup>38</sup> In the present study the values of  $\alpha$  have been obtained using the method of Evans<sup>39</sup> which accounts more correctly for the micelle contribution. This method makes use of the equation

$$10^3 \frac{dK}{dC} \Big|_{C > \text{cmc}} = N^{2/3} \alpha^2 \left[ 10^3 \frac{dK}{dC} \Big|_{C < \text{cmc}} - \lambda_X \right] + \alpha \lambda_X \quad (1)$$

In eq 1  $\lambda_X$  is the equivalent conductivity of the counterion. By use of the values of *N* listed in Table 1, the calculations yielded  $\alpha = 0.28$  and  $0.44$  for SDS micelles in water and in water/9.1 M urea, respectively. These values are close to those reported for SDS in the same two systems at 25 °C (0.30 and 0.46, respectively).<sup>40</sup>

The fluorescence results reported in Figure 2 do not permit one to obtain the value of  $\alpha$  in water/9.1 M urea/0.30 M Al(NO<sub>3</sub>)<sub>3</sub>. However this value can be estimated by comparing the cmc and *N* data for X(DS)<sub>2</sub> surfactant solutions, where X is a divalent metal ion, and for the precursor systems. Thus, cmc values around 4.5 equiv/L, aggregation numbers around 90 at the cmc, and micelle ionization degrees of about 0.12 have been reported for several X(DS)<sub>2</sub> surfactants (X = Mg<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>).<sup>41,42</sup> The cmc and *N* values are very close to those found for the precursor systems even though these systems contain trivalent Al<sup>3+</sup> ions. In fact we have obtained the value *N* = 95 for the dilute precursor system 0.1 M SDS/9.1 M urea/0.3 M Al(NO<sub>3</sub>)<sub>3</sub> (Table 1, line 10), where the SDS concentration is closer to the cmc value. Since both precursor systems and X(DS)<sub>2</sub> solutions involve micelles of dodecyl sulfate ions, it is likely that the values of  $\alpha$  in X(DS)<sub>2</sub> solutions and in the precursor system are very close and around 0.12. Such a low value of  $\alpha$  indicates that the micelles in the precursor system are nearly neutralized by bound Al<sup>3+</sup> ions, despite the high concentration of urea that tends to increase the micelle ionization (see preceding paragraph). Our results thus lend support to the prediction that the binding of multivalent cations such as Al<sup>3+</sup> by anionic micelles should be very strong.<sup>30</sup>

The variations of the cmc, *N*, and *Q* in going from water to water/9.1 M urea and water/9.1 M urea/0.30 M Al(NO<sub>3</sub>)<sub>3</sub> are in agreement with reported results for other ionic surfactants. Addition of urea is known to increase the cmc, decrease *N*, and increase the microviscosity.<sup>40,43–47</sup> There has been discussion in the literature as to whether urea affects the micelle properties by an indirect mechanism (change of the chemical potential of the surfactant in the free state) and/or by a direct mechanism (urea penetration in the micelle palisade layer). Strong evidence for the direct mechanism has been reported.<sup>40,43–47</sup> In particular, the increase of microviscosity has been interpreted as reflecting micelle/urea interactions at the micelle surface that support the direct mechanism.<sup>40,43,45</sup> Nevertheless, an alternative explanation can be given based on the decrease of micelle aggregation number in the presence of urea (see Table 1). Indeed as *N* decreases the micelle size comes closer to that of the dipyrrenylpropane molecule. The motion of the probe is then increasingly hindered and the probe reports a higher microviscosity. It is likely that the indirect mechanism is also operative in the water/9.1 M urea mixture used in the present study in view of the high content of urea (about 50 wt %), in addition to the direct mechanism.

The addition of Al(NO<sub>3</sub>)<sub>3</sub> brings about a drastic decrease of cmc, from 21 to about 3.5 mM, a large increase of *N*, and an increase of microviscosity (see Table 1). Such a behavior is due to the fact that anionic micelles bind multivalent cations more strongly than univalent cations, thus resulting in a lower cmc and a larger *N*.<sup>30,41,42</sup> The observed increase of micelle microviscosity is in agreement with reports that show that for a given surfactant the micelle microviscosity increases with the micelle size.<sup>48,49</sup> This increase reflects the tighter packing of the surfactant in the micelles as the *N* increases and the resulting hindrance brought to the motion of the probe.

The values of *N* in Table 1 provide information on the shape of the micelles in the various systems. The values of *N* in the two reference systems 0.60 M SDS and 0.60 M SDS/9.1 M urea are close to 55–60. This value corresponds to the maximum spherical micelle that a surfactant with a dodecyl chain can form in water.<sup>37</sup> Thus,

(43) Ruiz, C. C. *Colloids Surf., A* **1995**, 273, 1033; **1999**, 147, 349.

(44) Shen, X. H.; Belletete, M.; Durocher, G. *J. Phys. Chem. B* **1997**, 101, 8212.

(45) Hao, J. C.; Wang, T. T.; Shi, S.; Lu, R. H.; Wang, H. Q. *Langmuir* **1997**, 13, 1897.

(46) Florenzano, F. H.; Dossantos, L. G.; Cuicov, I. M.; Scarpa, M. V.; Chaimovich, H.; Politi, M. J. *Langmuir* **1996**, 12, 1166.

(47) Asakawa, T.; Hashikawa, M.; Amada, K.; Miyagishi, S. *Langmuir* **1995**, 11, 2376.

(48) Miyagishi, S.; Kurimoto, H.; Asakawa, T. *Langmuir* **1995**, 11, 2951 and references therein.

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

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

(38) Sugihara, G.; Nakamura, A.; Nakashima, T.; Araki, Y.; Okano, T.; Fujiwara, M. *Colloid Polym. Sci.* **1997**, 275, 790.

(39) Evans, H. C. *J. Chem. Soc.* **1956**, 579.

(40) Abuin, E. B.; Lissi, E. A.; Aspee, A.; Gonzalez, F. D., and Varas, J. M. *J. Colloid Interface Sci.* **1997**, 186, 332.

(41) Baumuller, W.; Hoffman, H.; Ulbricht, W.; Tondre, C.; Zana, R. *J. Colloid Interface Sci.* **1978**, 64, 418.

(42) Satake, I.; Iwamatsu, I.; Hosokawa, S.; Matuura, R. *Bull. Chem. Soc. Jpn.* **1963**, 36, 204.

to a first approximation, the micelles of SDS at 60 °C in the two reference systems are spherical or nearly spherical. The aggregation number in the precursor system 0.60 M SDS/9.1 M urea/0.30 M  $\text{Al}(\text{NO}_3)_3$  is almost twice as large as those in the reference systems. The corresponding micelles are therefore slightly elongated. To a first approximation the axial ratio of these elongated micelles can be taken as the ratio of measured aggregation number/aggregation number of the maximum spherical micelle, i.e.,  $104/57 \approx 1.8$ . Note that for the 0.60 M SDS solution in water at 25 °C,  $N = 125$ .<sup>50</sup> Thus the micelles in the 0.60 M SDS solution are nearly spherical at 60 °C but slightly elongated at 25 °C. It is also noteworthy that the effect of the addition of  $\text{Al}(\text{NO}_3)_3$  on the aggregation number of SDS micelles seen in Table 1 is much reduced by the presence of the high content of urea. Indeed, the micelle aggregation number was found to be 250 in the system 0.60 M SDS/0.097 M  $\text{Al}(\text{NO}_3)_3$ , i.e., a much larger value than that found in the precursor system (104, see Table 1), even though the  $\text{Al}(\text{NO}_3)_3$  concentration was much lower. In the absence of urea, concentrations of  $\text{Al}(\text{NO}_3)_3$  larger than about 0.1 M resulted in the formation of a precipitate.

Turning to the values of the pyrene fluorescence lifetime  $\tau$ , lines 1 and 2 in Table 1 show that the lifetime in deaerated samples decreases slightly in going from 0.60 M SDS to 0.60 M SDS/9.1 M urea. This effect is not due to a weak quenching of the pyrene fluorescence by the urea that may be present in the micelle palisade layer or at the micelle surface. Indeed in the absence of SDS the pyrene lifetime at 60 °C was found to increase from 169 to 181 ns in going from water to water/9.1 M urea, both deaerated. The decrease of lifetime in the presence of urea appears to be due to an increased exposure of the micelle-solubilized pyrene to water. Indeed the addition of urea brings about a decrease of micelle aggregation number, from 74 to 53 (Table 1). It is known<sup>51</sup> that for a given surfactant the surface area per surfactant at the micelle surface increases as the aggregation number decreases. The lower value of  $N$  in the presence of urea corresponds to a more open structure of the micelle that favors contacts between water and pyrene at the micelle surface and reduces the fluorescence lifetime. The lifetime in the precursor system is *much shorter* than in the 0.60 M SDS/9.1 M urea reference system and also much shorter than that expected assuming that urea and  $\text{Al}^{3+}$  ions affect the lifetime independently. Thus, in separate experiments performed in the absence of urea, the lifetime of micelle-solubilized pyrene was found to decrease upon addition of  $\text{Al}(\text{NO}_3)_3$ . Precipitation occurred at above 0.5 equiv of  $\text{Al}^{3+}$ /equiv of SDS. The data were plotted as  $1/\tau$  against the  $\text{Al}(\text{NO}_3)_3$  concentration and linearly extrapolated to 1.5 equiv/equiv (value in the precursor system), yielding a lifetime of 261 ns. Combining this value to the lifetimes of micelle-solubilized pyrene in the reference systems 0.60 M SDS and 0.60 M SDS/9.1 M urea yielded a value of 240 ns for the lifetime expected in the precursor system, on the assumption that the effects of urea and  $\text{Al}(\text{NO}_3)_3$  are additive. The fact that this value is significantly larger than the experimental one, 176 ns, indicates that another quenching process must be operative in the precursor system. Most likely this quenching is due to some nitrate ions accompanying the bound  $\text{Al}^{3+}$  ions at the micelle surface. The more open structure of the dodecyl sulfate micelles in the presence of urea (see above) very much amplifies this quenching with respect to the system in the

absence of urea, where the micelle structure is more compact. This is also clearly seen by comparing the results in lines 6 and 7 in Table 1.

Two additional series of results give further support to the assumed quenching of pyrene by nitrate ions that are bound together with  $\text{Al}^{3+}$  ions to the micelle surface. First the pyrene lifetime was measured in the full precursor system when the 0.30 M  $\text{Al}(\text{NO}_3)_3$  was replaced by 0.30 M  $\text{AlCl}_3$ . The micelle aggregation number was found to be 112 (Table 1, line 5), a value very close to that in the precursor system, whereas the lifetime was 278 ns, a value very close to that in the 0.60 M SDS/9.1 M urea system (compare lines 2, 3, and 5 in Table 1). These results clearly support the conclusion that some nitrate ions are carried to the dodecyl sulfate micelle surface by the bound  $\text{Al}^{3+}$  ions and quench the pyrene fluorescence. Experiments performed in water showed that nitrate ions quench the pyrene fluorescence. For instance the values of the pyrene lifetime in water/9.1 M urea and water/9.1 M urea/0.30 M  $\text{Al}(\text{NO}_3)_3$  were 181 and 14 ns, respectively, in the absence of SDS. In the second series of experiments the 0.30 M  $\text{Al}(\text{NO}_3)_3$  present in the precursor system was replaced by 0.90 M  $\text{NaNO}_3$ . The lifetime was found to be 231 ns instead of 176 ns (lines 3 and 7 in Table 1), indicating a weaker quenching than that seen in the presence of  $\text{Al}^{3+}$  ions. Likewise, the lifetime in the 0.60 M SDS/0.90 M  $\text{NaNO}_3$  system was found to be 293 ns as compared to 310 ns in 0.60 M SDS (lines 1 and 6 in Table 1) and 261 ns in 0.60 M SDS/0.30 M  $\text{Al}(\text{NO}_3)_3$  (extrapolated value, see above). Thus, the amount of nitrate ions that can come close to the micelle surface and quench the pyrene fluorescence is much smaller when sodium ions replace aluminum ions, mainly because the former are less bound than  $\text{Al}^{3+}$  ions to dodecyl sulfate micelles. Calculations based on the values of the lifetimes in the different systems showed that the concentration of nitrate ions at the micelle surface is about three times larger in the presence of  $\text{Al}^{3+}$  ions than the concentrations obtained with  $\text{Na}^+$  ions. This is the main reason for the loss of quenching efficiency when replacing  $\text{Al}(\text{NO}_3)_3$  by  $\text{NaNO}_3$  in the precursor system. The fraction of nitrate ions bound to the micelle surface in the presence of  $\text{Al}^{3+}$  ions in the precursor system has been estimated on the basis of the values of the pyrene lifetime in water/9.1 M urea, water/9.1 M urea/0.30 M  $\text{Al}(\text{NO}_3)_3$ , and in the precursor system. It has been found to be about 3.5% with respect to the concentration of the nitrate ion in the precursor system and 5% with respect to the SDS concentration.

The micelles present in the system 0.10 M SDS/9.1 M urea/0.30 M  $\text{Al}(\text{NO}_3)_3$  (referred to as *dilute* precursor system) and in the corresponding reference systems 0.10 M SDS and 0.10 M SDS/9.1 M urea were also characterized. The SDS/ $\text{Al}$  molar concentration ratio in the dilute precursor system is close to that in the mesostructured material that precipitates out after sufficient aging of the system. It is noteworthy that the material obtained with the dilute precursor system is similar to the one obtained with the 0.60 M SDS-containing precursor system. The results are summarized in Table 1, lines 8–11. With respect to the more concentrated reference and precursor systems, the aggregation numbers and lifetimes are smaller, and the changes of microviscosity in going from water to water/9.1 M urea and water/9.1 M urea/0.30 M  $\text{Al}(\text{NO}_3)_3$  are qualitatively similar. The quenching effect due to the nitrate ions is also present and disappears completely when replacing  $\text{Al}(\text{NO}_3)_3$  by  $\text{AlCl}_3$  (lines 10 and 11 in Table 1).

Last, it must be pointed out that the variations of lifetime in going from 0.60 M SDS to 0.60 M SDS/9.1 M

(50) Lang, J.; Zana, R. Unpublished results.

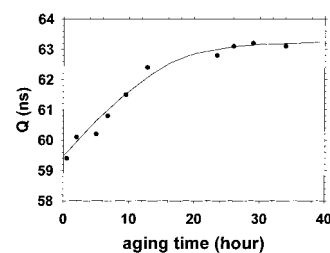
(51) Tanford, C. *J. Phys. Chem.* **1972**, *76*, 3020.

urea and 0.60 M SDS/9.1 M urea/0.30 M  $\text{Al}(\text{NO}_3)_3$  are very different in aerated systems with respect to deaerated systems whereas the aggregation numbers are the same in the two types of systems. The results listed in Table 1 (lines 1 to 3) show that the pyrene lifetime increases from 107 to 164 ns in going from 0.60 M SDS to 0.60 M SDS/9.1 M urea, instead of the small decrease noted in deaerated systems, then decreases to 120 ns in going to the 0.60 M SDS/9.1 M urea/0.30 M  $\text{Al}(\text{NO}_3)_3$  system. The strong quenching of pyrene by the molecular oxygen ( $\text{O}_2$ ) dissolved in the systems is responsible for these different behaviors. In the aerated 0.60 M SDS system, pyrene is very efficiently quenched by  $\text{O}_2$ . In going to the aerated 0.6 M SDS/9.1 M urea system, several effects may decrease the efficiency of the quenching. First, as seen above, the microviscosity is increased. Second urea may reduce the concentration of  $\text{O}_2$  dissolved within the micelle or at the micelle surface by increasing the partition of  $\text{O}_2$  in favor of the intermicellar solution. Third, the urea present at the micelle surface may reduce contacts between pyrene and  $\text{O}_2$ . The low value of the lifetime in the precursor system is then due to the nitrate ions accompanying the bound  $\text{Al}^{3+}$  ions and/or to a decrease of the amount of urea present at the micelle surface. Obviously, the presence of  $\text{O}_2$  greatly complicates the explanation of the behavior of the pyrene lifetime. This by itself would have been sufficient to warrant a full removal of the oxygen from the investigated systems, as was done in the present study. Another reason for doing so is that the air initially dissolved in the system was spontaneously and progressively released at 60 °C, resulting in a significant increase of the pyrene lifetime that is unrelated to the polymerization process. Last the accuracy of measurements of aggregation numbers is much diminished when the probe lifetime is short, as is the case in the presence of  $\text{O}_2$ .<sup>29</sup>

In summary, the micelles present in the precursor system 0.60 M SDS/9.1 M urea/0.30 M  $\text{Al}(\text{NO}_3)_3$  at 60 °C have an aggregation number of 104 and a slightly elongated shape and are nearly fully neutralized by bound  $\text{Al}^{3+}$  ions. The micelles in the more dilute precursor system (with 0.10 M instead of 0.60 M SDS) have very similar properties. In both systems some nitrate ions are brought to the micelle surface by the bound  $\text{Al}^{3+}$  ions and strongly quench the pyrene fluorescence. Thus measurements of lifetime can be used to monitor possible changes of concentration of nitrate ions at the micelle surface associated with the polymerization of alumina species.

**Effect of the Aging of the Systems on the Micellar Properties.** The reference and the precursor systems (lines 1–3 and 10 in Table 1) have been studied as a function of aging time (time spent at 60 °C). For each system the time zero of the aging process was the moment at which the temperature of the system reached 60 °C.

As expected, the micelle aggregation number and microviscosity and the pyrene fluorescence lifetime remained constant in the 0.60 M SDS and 0.6 M SDS/9.1 M urea reference systems where no polymerization occurs. The micelle aggregation number did not change in the 0.60 M SDS/9.1 M urea/0.30 M  $\text{Al}(\text{NO}_3)_3$  precursor system (reactive medium). Consequently, the micelles retained their slightly elongated shape until precipitation occurred, after about 40 h. The microviscosity increased progressively from  $Q = 59$  to 63 ns during the first 35 h as shown in Figure 3. A larger increase occurred at aging times larger than 35 h with systems that were still clear as judged with the naked eye. However it was found that these systems scattered light (see below). This may have affected the measured value of the ratio  $I_M/I_E$  to which the



**Figure 3.** Variation of the microviscosity  $Q$  in the precursor system 0.60 M SDS/9.1 M urea/0.30 M  $\text{Al}(\text{NO}_3)_3$  with the aging time of the system at 60 °C.

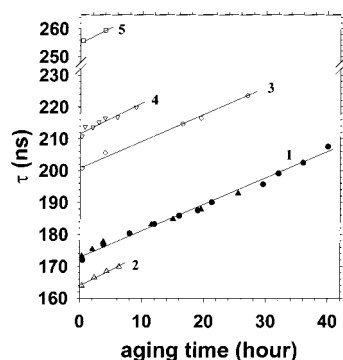
microviscosity is proportional and these results were therefore discarded. The observed increase of microviscosity is an indication that a polymerization of aluminum species is taking place at the surface of the dodecyl sulfate micelles. Indeed, it has been reported that the microviscosity sensed by fluorescent probes in polymer/surfactant complexes is always larger than that obtained in free micelles.<sup>52</sup>

A mechanism that assumes a polymerization of charged aluminum species at the micelle surface is also supported by the observed increase of the time  $t_{\text{prec}}$  required for the visual observation of a precipitate in the precursor system, from about 8 h to 40 h upon increasing the SDS concentration from 0.10 to 0.60 M. The reasoning is as follows. The polymerization involves the reaction of  $\text{Al}^{3+}$  ions with hydroxyl ions produced by the decomposition of urea. The amount of micelle-bound  $\text{Al}^{3+}$  ions increases, whereas that of free  $\text{Al}^{3+}$  ions decreases upon increasing SDS concentration. The amount of hydroxyl ions produced per unit time is constant. If it is assumed that the polymerization involves the bound  $\text{Al}^{3+}$  ions, this constant amount of hydroxyl ions produced per unit time will react with more bound aluminum species as the SDS concentration is increased. The growth of the produced polymers with time will thus be slower and the time required for precipitation will be longer, as is experimentally observed. Obviously the assumption that the polymerization involves the free  $\text{Al}^{3+}$  ions would lead to predict a decrease of  $t_{\text{prec}}$  upon increasing SDS concentration. Indeed the concentration of free  $\text{Al}^{3+}$  ions would then be decreased and the constant amount of hydroxyl ions produced per unit time would make the polymers grow faster and the precipitation would occur earlier. Note that the values of  $t_{\text{prec}}$  varied slightly from run to run (for instance, for the concentrated precursor system  $t_{\text{prec}}$  varied between 35 and 45 h). Such small variations are expected. Indeed, the advancement of the polymerization depends somehow on the treatment applied to the precursor system before heating it to 60 °C (mainly the stirring and degassing described in the Experimental Section). Urea probably starts decomposing during this treatment to an extent that is difficult to control. This effect affects the value of  $t_{\text{prec}}$ . It also affects, but only very slightly, the values of the quantities measured at time zero and also makes it impossible to correlate the time dependence of these quantities to that of the pH.

The variation of  $t_{\text{prec}}$  with the  $\text{Al}(\text{NO}_3)_3$  concentration in 0.60 M SDS/9.1 M urea/ $x$  M  $\text{Al}(\text{NO}_3)_3$  systems was also investigated. The time  $t_{\text{prec}}$  increased significantly with the  $\text{Al}(\text{NO}_3)_3$  concentration, with values of about 6, 10, 30, and 40 h for  $x = 0.08, 0.15, 0.22$ , and 0.30 M, respectively. However this variation did not permit a choice between micelle surface and bulk phase polymerization. Indeed as

(52) Anthony, O.; Zana, R. *Langmuir* **1996**, *12*, 1967 and references therein.





**Figure 4.** Variation of the pyrene fluorescence lifetime with the aging time at 60 °C in the precursor system 0.60 M SDS/9.1 M urea/0.30 M  $\text{Al}(\text{NO}_3)_3$  (● and ▲ represent two separate runs), in the dilute precursor system 0.10 M SDS/9.1 M urea/0.30 M  $\text{Al}(\text{NO}_3)_3$  (△), and in the systems 0.60 M SDS/9.1 M urea/ $x$  M  $\text{Al}(\text{NO}_3)_3$  with  $x = 0.08$  (□), 0.15 (▽), and 0.22 M (○).

the  $\text{Al}(\text{NO}_3)_3$  concentration is decreased, the concentrations of both the free and bound  $\text{Al}^{3+}$  ions decrease and the effect on  $t_{\text{prec}}$  is qualitatively the same, whichever the locus of polymerization.

The most important effect associated to the aging of the system is the nearly linear increase of the value of the fluorescence lifetime  $\tau$  with the aging time, represented in Figure 4. This increase was observed reproducibly in several independent runs for the precursor systems, and the different  $\tau$  vs time plots were shifted one with respect to another by only 2–3 ns (compare the two runs in curve 1, Figure 4). The increase of  $\tau$  with time is significant in all cases. It can only be due to a decrease of the concentration of nitrate ions at the micelle surface. This decrease however does not appear to be due to a change of the micelle structure associated to a release of interfacial urea since the micelle aggregation number remained constant. More likely, it is linked to a decrease of the positive charge of the aluminum species bound to the micelle surface due to the polymerization. Two explanations can be given to this change of charge. In the first one, micelle-bound  $\text{Al}^{3+}$  ions are assumed to react with hydroxyl ions produced by the decomposition of urea, resulting in complex oxygenated ions of lower charge. Our preceding results concerning the systems with  $\text{NaNO}_3$  and  $\text{Al}(\text{NO}_3)_3$  (lines 3 and 7 in Table 1) lead to predict that some nitrate ions will be released from the micelle surface if the electrical charge of the bound counterions decreases. The second explanation assumes that a part of micelle-bound aluminum species leaves the micelle surface and polymerizes in the bulk. The resulting polymers interact with free dodecyl sulfate ions forming complexes that grow in size until precipitation occurs. In this case, the micelles would only be reservoirs of dodecyl sulfate ions, similar to what was postulated in the mechanism of formation of silica-based mesoporous materials.<sup>27,28</sup> However, the micelle aggregation number should decrease if alumina species leave the micelle surface. Such a decrease was not observed with the 0.60 M SDS/9.1 M urea/0.30 M  $\text{Al}(\text{NO}_3)_3$  precursor system, and therefore it appears this mechanism should be discarded.

However, it may be argued that the decrease of  $N$  was not observed because the SDS concentration in the precursor system was in large excess with respect to that required for the formation of the mesostructured material (about 0.1 M, see above). The micellar properties in such a system would be affected only little by the loss of a small fraction of the surfactant bound to the growing polymers. Indeed the time-resolved fluorescence quenching tech-

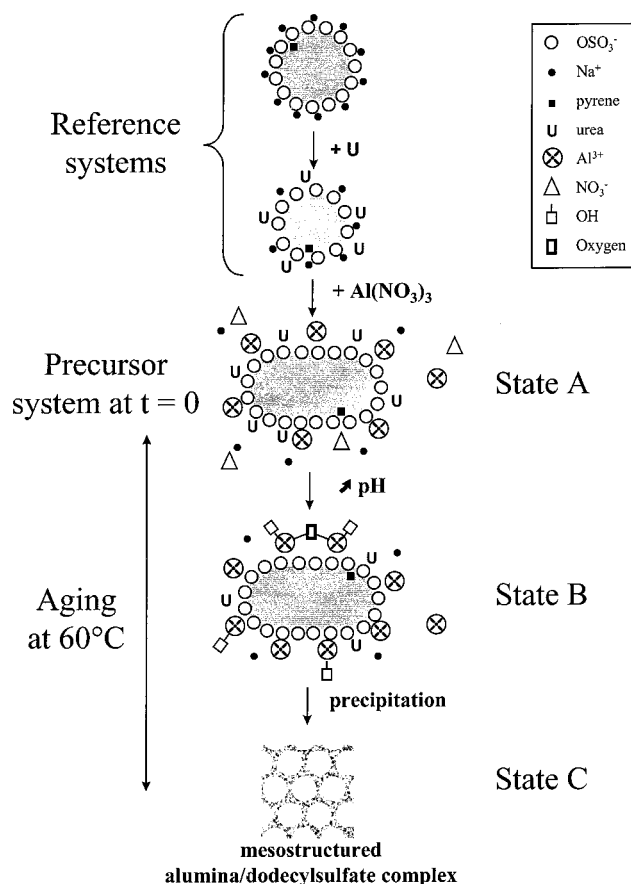
nique would then measure an average aggregation number that is heavily weighted in favor of the most important component, that is, the free micelles. The above experiments were therefore repeated with the dilute precursor system with a SDS concentration of 0.1 M (see curve 2, Figure 4). The precipitation of the organized material occurred after a time  $t_{\text{prec}} = 6\text{--}8$  h as compared to about 40 h for the more concentrated precursor system. The micelle aggregation number in the dilute precursor system remained constant at 95, and the fluorescence lifetime increased from about 164 to 170 ns (see Figure 4). The microviscosity increased very slightly, from 56.0 ns at  $t = 0.5$  h to 56.9 ns at  $t = 5.5$  h. Just before the visual observation of a precipitate at  $t = 7$  h,  $Q$  increased to 58.5 ns and continued to increase after precipitation began. To gain more insight in this effect, turbidity measurements were carried out on the dilute precursor system. These experiments showed the same trend: the intensity of scattered light remained low and nearly constant until about 1 h before precipitation was visually detected ( $t_{\text{prec}} = 8$  h in this experiment). This behavior is in line with the constancy of the micelle aggregation number measured by fluorescence quenching. Thus no large particles are formed in the system undergoing polymerization up to a time close to  $t_{\text{prec}}$ . One is thus led to conclude that the growth of the inorganic polymers to large sizes also occurs rather shortly before precipitation of the complex. Also, the second mechanism discussed in the preceding paragraph can be now safely discarded.

The aging of precursor systems of composition 0.60 M SDS/9.1 M urea/ $x$  M  $\text{Al}(\text{NO}_3)_3$ , where  $x = 0.08, 0.15$ , and 0.22 M was also investigated (see curves 3–5, Figure 4). The variations of the pyrene lifetime with the aging time of the system were all nearly linear and with about the same slope irrespective of the  $\text{Al}(\text{NO}_3)_3$  concentration. The increase of the value of the pyrene fluorescence lifetime at  $t = 0$  seen in Figure 4 is directly related to the concentration of micelle-bound  $\text{Al}^{3+}$  ions and, thus, to the concentration of nitrate ions that they carry to the micelle surface. The lower the concentration of  $\text{Al}^{3+}$ , the lower the nitrate ion concentration and the weaker the quenching of the pyrene fluorescence.

No effect of aging on the pyrene lifetime was found when using the precursor system with  $\text{AlCl}_3$  instead of  $\text{Al}(\text{NO}_3)_3$ .

**Mechanism of Formation of Mesostructured Alumina in SDS/Urea/Aluminum Salt Systems.** The precursor system 0.60 M SDS/9.1 M urea/0.30 M  $\text{Al}(\text{NO}_3)_3$  at aging time zero contains dodecyl sulfate micelles that are slightly elongated (axial ratio  $\approx 1.8$ ), with an aggregation number of about 104. The micelle charge is low due to a strong binding of  $\text{Al}^{3+}$  ions resulting in an apparent ionization degree of about 0.12. The bound  $\text{Al}^{3+}$  ions carry a small number of nitrate ions to the micelle surface. Three facts suggest that the polymerization most likely occurs at the micelle surface. First, the concentration of  $\text{Al}^{3+}$  ions at the micelle surface is much larger than that in the bulk phase. Second the micelle microviscosity increases with the aging time. Third, the time required for precipitation of the mesostructured alumina increases with the SDS concentration. A scheme of the mechanism proposed for the formation of the mesostructured alumina is given in Figure 5. In the precursor system in the initial state A ( $t = 0$  h), the dodecyl sulfate micelles are surrounded by bound aluminum cations, some urea molecules, and a few nitrate anions, responsible for the quenching of the pyrene fluorescence. The decomposition of urea is accompanied by the formation of hydroxyl ions, and the pH increases gradually from 3.5 at time zero to 5.5 at the end of the process. The increase of the pH initiates the formation of





**Figure 5.** Scheme of the mechanism proposed for the formation of the mesostructured hexagonal alumina showing the reference and precursor systems, the effect of aging, and the formation of the mesostructured material. In this scheme, the headgroups and ions are shown in numbers five times smaller than the measured values.

charged complex oxygenated aluminum species that can start polymerizing (state B). The growing polymeric species remain completely or partially bound to the negatively charged micelles via electrostatic interactions between their residual positive charge and the negatively charged sulfate headgroups at the micelle surface. On the contrary, the initially bound nitrate ions progressively leave the micelles because the positive charge per aluminum bound on the polymer decreases as polymerization proceeds. This brings about the observed increase of the pyrene fluorescence lifetime. The growing inorganic polymers may bind several micelles, and micelle cross-linking by inorganic polymers may occur. Nevertheless, both light scattering and time-resolved fluorescence studies indicate that most of the growth of the inorganic polymer and of the polymer/surfactant micelle complexes takes place shortly before precipitation occurs. The complexes precipitate out once their size becomes sufficiently large. Their organization into a mesostructured hexagonal material (state C) occurs during or shortly before precipitation. It is likely that this precipitation involves a near complete neutralization of the micelle charge by the residual charge on the polymers. Indeed, the material that precipitates out does not contain sodium and nitrate ions.

To this point the constancy of the micelle aggregation number throughout the aging process, a behavior that is surprising at first sight, has not been discussed in terms of the postulated mechanism of polymerization at the micelle surface. A possible explanation is as follows. It is first recalled that for each experimental run the reported

micelle aggregation numbers correspond to systems that were completely clear (no precipitate visually observed). The  $N$  values at the longest aging time were always obtained just before or very shortly after visual observation of a very small amount of precipitate. Indeed the fluorescence quenching method used in this work does not permit measurements of aggregation number in systems that are macroscopically heterogeneous (mixture of solid and solution) and/or mixed (slightly elongated free micelles and bound micelles that may be cylindrical). Thus, only a very small part of the surfactant was consumed for the formation of this small amount of precipitate. This explains that even at times only slightly longer than  $t_{\text{prec}}$  the micelle aggregation number did not change. Also, it is likely that polymerization does not proceed in a uniform manner. All growing inorganic polymers do not have the same molecular weight. Among these polymers, those having the highest molecular weight are also those giving rise to the largest polymer/micelle complexes and precipitating first. Since the measurements of aggregation numbers were stopped at this point (presence of the first visible precipitate), it is not surprising that the micelle aggregation number did not change. Furthermore, it is known that for polyelectrolyte/oppositely charged surfactant systems, the lower the polymer molecular weight, the weaker the polymer/micelle interaction<sup>53,54</sup> and the smaller the modification of micellar properties due to the interaction. In the case of alumina polymer/SDS micelle complexes, small alumina polymers are not expected to modify the micelle aggregation number more than the species from which they originate, that is,  $\text{Al}^{3+}$  ions and charged complex oxygenated aluminum species. It is also known that the polyelectrolyte/oppositely charged surfactant complexes that precipitate out are often mesostructured.<sup>55–58</sup> Thus the consideration of the aging precursor system provides an explanation of the near constancy of the micelle aggregation number and the formation of a mesostructured precipitated solid.

## Conclusions

The mechanism of formation of mesostructured hexagonal alumina in a micellar solution of SDS micelles in a water/9.1 M urea mixture has been investigated at 60 °C by fluorescence probing methods. The micelles in the initial precursor systems have been characterized (size, microviscosity, amount of bound  $\text{Al}^{3+}$ , and nitrate ions). The polymerization process has been initiated by keeping the systems at 60 °C until a solid mesostructured material precipitated out. This polymerization is caused by the hydroxyl ions formed upon decomposition of urea and occurs at the surface of the dodecyl sulfate micelles. As the polymerization progressed, the micelle size hardly changed, but the pyrene fluorescence lifetime increased. This last effect reflects the release of the micelle-bound nitrate ions that are strong quenchers of the pyrene fluorescence. The organization of the complex formed by the growing inorganic alumina polymer and dodecyl sulfate micelles must occur just before the precipitation of the solid material takes place. This part of the

(53) Liu, J.; Takisawa, N.; Shirahama, K.; Abe, H.; Sakamoto, K. *J. Phys. Chem. B* **1997**, *101*, 7520.

(54) Liu, J.; Shirahama, K.; Miyajima, T.; Kwak, J. C. T. *Colloid Polym. Sci.* **1998**, *276*, 40.

(55) Antonietti, M.; Conrad, J.; Thünemann, A. *Macromolecules* **1994**, *27*, 6007.

(56) Thünemann, A.; Lochhaas, K. H. *Langmuir* **1999**, *15*, 6724.

(57) Sokolov, E. L.; Yeh, F.; Khokhlov, A.; Chu, B. *Langmuir* **1996**, *12*, 6229.

(58) Zhou, S.; Burger, C.; Yeh, F.; Chu, B. *Macromolecules* **1998**, *31*, 8157.

mechanism of formation of organized mesostructured alumina is similar to that proposed for the formation of organized silica, even though the precursor systems differ much, with the polymerizing species bound to the micelles in the case of alumina and free in the case of silica. However the approach of the systems on the basis of polyelectrolytes interacting with oppositely charged micelles permits one to understand all of the observed behaviors.

**Acknowledgment.** This work was supported in part by the Institut Français du Pétrole (IFP, France) and by the Centre National de la Recherche Scientifique (CNRS, France) through the PhD work of L. Sicard and the GDR program No. 690. Special thanks to F. Kolenda (IFP) for fruitful discussions.

LA011268M