Structural Characterization of Micellar Aggregates in Sodium Dodecyl Sulfate/Aluminum Nitrate/Urea/Water System in the Synthesis of Mesoporous Alumina

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The mechanism of templated synthesis of ordered mesoporous alumina according to the recipe proposed by Yada et al. (Yada, M.; Machida, M.; Kijima, T. *Chem. Commun.* **1996**, 769) using sodium dodecyl sulfate (SDS) as template, has been investigated by NMR self-diffusion and spin and fluorescence probe techniques. In the precursor solutions urea was found to produce a substantial shortening of the long entangled cylindrical aggregates characteristic of the SDS micellar solutions with aluminum salt in large excess. The formation of mesostructured hexagonal alumina was followed using spin probes incorporated in the SDS aggregates. No structural changes were observed during urea hydrolysis, before the onset of the precipitation. In the precipitate, the presence of the surfactant template is demonstrated as well as its interaction with the aluminum species. Time evolution of this interaction is also observed. Finally, the influence of the composition of the precursor system on the structure and thermal stability of as-synthesized alumina has been studied. It appears that hexagonally structured alumina is formed over a large range of compositions of the starting solution, with the dimension of the unit cell being almost constant. A model of precipitation is proposed that is based on the analogy with the formation of the hexagonal crystalline Al-DS precipitate in the ternary SDS/Al(NO₃)₃/water system.

Introduction

Since the discovery of mesoporous materials of the M41S family,¹ possessing large internal surface areas and narrow pore size distributions, increasing attention has been paid to mesoporous materials of various chemical compositions owing to their potential use as catalysts, molecular sieves, and host materials.^{2–5}

Such mesoporous molecular sieves can be obtained by the calcination of their mesostructured precursors synthesized in the presence of self-assembling amphiphilic compounds. Mesoporous alumina with disordered, but thermally stable, mesostructures, has been synthesized mainly in nonaqueous media starting from aluminum isopropoxide.^{6–8} Inexpensive aluminum salts such as aluminum nitrate or chloride were found to lead to ordered mesostructured alumina.^{9–13} Using a urea-based homogeneous precipitation method the synthesis of hexagonally structured mesoporous alumina was reported, occurring in an aqueous sodium dodecyl sulfate (SDS) micellar solution. However, the sulfate headgroups appear to be embedded in the inorganic walls, resulting in their collapse after removal of the

structure-directing agent. The mechanisms of formation of ordered mesoporous materials were mostly investigated for silica-based materials.¹⁴ In the case of an electrostatic route, the proposed mechanism involves a cooperative organization of the complex between the organic self-assemblies and the inorganic species, driven by electrostatic interactions. Other results^{15,16} suggested that 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. In this case, the micelles act as reservoirs of surfactant.

Sicard et al.¹⁷ have studied the formation mechanism of mesostructured hexagonal alumina in SDS micellar solutions at 60 °C by using a fluorescence probing method. The authors found that in the precursor system the micelles are slightly elongated, and the Al³⁺ counterions bind strongly to the micelle surface. A significant micellar growth was, however, not noticed during urea hydrolysis in the clear isotropic solution, and the organization of organic/inorganic complex into a mesostructured hexagonal material is assumed to occur only during, or immediately before the onset of precipitation.

In our previous papers^{18,19} we have undertaken an in-depth research of the phase behavior of the SDS/Al(NO₃)₃/H₂O system to understand the conditions under which an ordered hexagonal

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Figure 1. Phase diagram (lower-left corner) of the SDS/Al(NO_3)₃/H₂O ternary system. The compositions corresponding to the synthesis mixtures studied are marked with the same numbers as in Table 6. Region I denotes the isotropic micellar solution at low Al³⁺ concentration, II represents the precipitation region, and III is the micellar phase at high Al³⁺ concentration, the "redissolution" area.

alumina structure could be formed. Thus, it is well-known that dilute aqueous solutions of SDS contain small, spherical micelles. Addition of small amounts of trivalent counterions, Al^{3+} (Figure 1, region I) to such a solution does not lead to a significant micelle growth; at a higher Al³⁺ concentration, however (Figure 1, region II), phase separation occurs. One of the phases is a white precipitate consisting of a complex of dodecyl sulfate (DS^{-}) and Al^{3+} with a hexagonal structure. Subsequent addition of the salt results in the complete dissolution of the precipitate to yield a new micellar phase (L_1) , which is highly viscous and contains long, wormlike aggregates (Figure 1, region III). Monte Carlo modeling was performed²⁰ to understand the origins of the two-phase region in the middle of an isotropic phase. Simulation of the interactions between two spherical DS⁻ micelles in the presence of Al(NO₃)₃ has shown that the correlation effect between Al³⁺ counterions strongly adsorbed on the micelle surface results in a purely attractive force that leads to the destabilization of the isotropic micellar phase to form the precipitate. These results are important for understanding the alumina precipitation mechanism, because the composition of the precursor system (without urea) used by Yada^{11,13} for alumina synthesis is placed in the redissolution area.

In the present study we have tried to get a deeper insight into the formation mechanism of hexagonal alumina by using magnetic resonance methods. The report is organized as follows: (i) First, the effect of urea on the micellar aggregation in the redissolution area of the pseudo-ternary SDS/Al(NO₃)₃/ H₂O system is described. These solutions represent the precursors for alumina synthesis. A number of different spectroscopic methods (EPR, fluorescence, FT NMR self-diffusion, ¹H NMR) have been used to characterize the surfactant aggregates in this region and the effect of increasing urea content. (ii) Second, the changes of these aggregates during the synthesis of mesostructured alumina are followed using EPR spectra of spin probes. (iii) Finally, the structural characteristics of mesoporous alumina precipitated from precursors with various molar compositions and their thermal stability are examined using XRD.

Experimental Section

Materials. Sodium dodecyl sulfate (SDS, BDH), aluminum nitrate nonahydrate (Al(NO₃)₃·9H₂O, Acros Organics), and urea (Sigma) were used without further purification. The deuterated water (>99.8%) was purchased from Dr. Glaser AG (Basel).

The fluorescence probe, pyrene (Py, Molecular Probes), and the quencher, 1-decylpyridinium chloride (DPCl, Aldrich), were recrystallized from ethanol. The spin probes used were from the series of x-doxyl stearic acids (5- and 16-DSA,

CHART 1: Chemical Structure of the Spin and Fluorescence Probes^{*a*}



^a DPCl is the quencher used in the dynamic fluorescence method.

SIGMA), and a cationic probe, 4-[*N*,*N*-dimethyl-*N*-(methylene)₁₆]ammonium-2,2,6,6-tetramethylpiperidin-1-oxyl iodide (CAT 16, Molecular Probes). A neutral probe, TEMPO-laurate (C12-NO), prepared as described²¹ was also used. The chemical structures of these probes are presented in Chart 1.

Sample Preparation for the Reference Systems. Samples for the structural characterization of the SDS/Al(NO₃)₃/urea/ water system were prepared by weighing the appropriate amount of each component. The specific spin probes were then added so as to yield a concentration of $(1-2) \times 10^{-4}$ M in the final solution. The procedure used was to evaporate the ethanol solution containing the probe on the walls of a vial under nitrogen gas and then to add the examined solution and let the spin probe dissolve in it. The addition of the fluorescence probe, Py, and the quencher, DPCl, was realized as described in ref 19.

Synthesis of Mesostructured Alumina. The preparation of mesostructured alumina is based on the original recipe described by Yada et al,^{10,11} but various compositions in the starting mixtures have been used. After the complete dissolution of the components, the samples were heated at 80 °C in well-closed vials until the final pH in the range 7.0-7.3 was reached. Thereafter, the aging was realized by keeping the samples at 50 °C for 3 days. Finally, the samples were filtered, washed with water, and dried at room temperature.

For two starting mixtures (Y1 and Y2) with the molar ratios SDS/Al(NO₃)₃/urea/water = 2/1/30/69 and 0.42/1/21/69, respectively, the changes in the surfactant aggregates during the synthesis were followed by measuring the ESR spectra of incorporated spin probes at different stages of the reaction. The first mixture is the precursor system of the Yada synthesis. After the precursor was prepared, under stirring, the spin probe was added as described above, and the ESR measurements were performed in the following stages: (i) in the initial mixture of

reagents, after the dissolution of the components; (ii) in solution, at different times before the onset of precipitation; (iii) for a sample of the precipitate, the reaction being stopped after 6 h, after reaching pH 6.1; (iv) for a sample of the precipitate, the reaction being stopped after about 20 h, with pH 7.3; and finally (v) for a sample of the precipitate, after 20 h heating at 80 °C and further 3 days of aging at 50 °C.

Calcination Procedure. The calcination was performed in air, at a heating rate of 0.3 C min⁻¹. The final temperature selected was either 350 °C, where only the alkyl chain is removed, or 550 °C, where both parts of the surfactant, alkyl chain and sulfate group, are eliminated.¹² The final temperatures were maintained for 3 h before cooling the samples to room temperature.

Ion Exchange. Attempts were made to remove the surfactant from as-synthesized solids by anionic exchange. A 0.1 g sample of the solid (as-synthesized alumina) was stirred with 7 mL of a 50 mM CH₃CO₂Na/EtOH solution at room temperature for 1 h. The product was collected by filtration and washed with ethanol and hot water.

EPR Measurements. The EPR spectra were recorded on a RE1X JEOL spectrometer with 100 kHz field modulation using X-band frequency. An approximate value of the rotational correlation time, $\tau_{\rm C}$, was calculated according to the formula²²

$$\tau_{\rm C} = (6.51 \times 10^{-10}) \Delta H(0) \{ [h(0)/h(-1)]^{1/2} + [h(0)/h(1)]^{1/2} - 2 \} \text{ s} (1)$$

where $\Delta H(0)$ is the line width (in Gauss) of the central line, and h(-1), h(0), and h(1) are the peak-to-peak heights of the M = -1, 0 and +1 derivative lines, respectively. $\tau_{\rm C}$ is connected to the local viscosity, η , by the Debye–Stokes–Einstein equation:

$$\tau_{\rm C} = 4\pi \eta R^3 / 3kT \tag{2}$$

where *R* is the hydrodynamic radius of the tumbling entity. The $\tau_{\rm C}$ values obtained were used to follow, in a qualitative manner, significant changes in the microenvironment of the probes. The order parameter, *S*, is defined as²³ $S = (A_{\parallel} - A_{\perp})/[A_{zz} - (A_{xx} + A_{yy})/2]$, where A_{zz} , A_{xx} , and A_{yy} are the principal elements of the **A** tensor in the absence of molecular motion and A_{\parallel} and A_{\perp} are derived from experimental spectra (see insert in Figure 2). The order parameters *S* were calculated using the following parameters reported for doxyl probes:²⁴ $A_{zz} = 33.5$ G, $A_{xx} = 6.3$ G, and $A_{yy} = 5.8$ G. To correct for the polarity difference between the studied sample and the sample whose A_{zz} , A_{xx} , and A_{yy} values are used, the *S* value calculated above is multiplied with the inverse ratio of the corresponding isotropic nitrogen hfs values, $a_{\rm N}$, calculated as the arithmetical means of the tensor components.²³

Small-Angle X-ray Diffraction. The scattering experiments on as-synthesized and calcined materials were performed on a Kratky compact small-angle system equipped with a position sensitive detector containing 1024 channels of 51.3 μ m width. Cu K α radiation of wavelength 1.542 Å was provided by a Seifert ID300 X generator, operating at 50 kV and 40 mA. A 10 μ m thick Ni filter was used to remove the K $_{\beta}$ radiation. The distance between sample and detector was 277 mm, and the sample to detector volume was kept under vacuum to minimize the background scattering.

Dynamic Fluorescence Measurements. The fluorescence decay curves of pyrene in the absence and in the presence of a quencher were recorded by the single photon counting technique,



Figure 2. ESR spectra of 5-DSA in SDS/Al(NO_3)₃/water/urea mixtures with increasing urea content. Samples are denominated as in Table 1, where the corresponding compositions are given: (a) S; (b)SA; (c) SAU2; (d) SAU 4; (e) SAU6.

the experimental setup being described in detail earlier.¹⁹ The wavelengths for excitation and emission were $\lambda_{ex} = 325$ nm and $\lambda_{em} = 394$ nm, respectively.

NMR Self-Diffusion Measurements. The experiments were carried out on a Bruker DMX200 spectrometer, operating at the ¹H resonance frequency of 200 MHz. The self-diffusion coefficients of the surfactant, water and urea were measured using the Fourier transform pulsed field gradient stimulated spin—echo (FT-SPGSE) technique.²⁵ For all the samples, the echo intensities decayed monoexponentially.

Results

1. Structural Characterization of Precursor SDS/Al(NO₃)₃/ Water/Urea Micellar Solutions. This part is devoted to the description of the effect of urea on the SDS aggregates. The spherical micelles from the isotropic micellar solution of the SDS/water binary system²⁶ and the wormlike aggregates obtained in the case of the pseudoternary SDS/Al(NO₃)₃/H₂O system¹⁸ have been chosen as references.

i. EPR Measurements. The effects of increasing urea content have been followed on a series of samples starting from a SDS/ water sample (S, Table 1) and from a SDS/Al(NO₃)₃/water solution (SA, Table 1), in which the concentrations of the components were those used in the alumina synthesis reaction mixture (see below). Three spin probes (5-DSA, 16-DSA, and C12-NO) were used to report on local viscosity (τ_c) and order parameter (*S*) in different regions of the surfactant aggregates.

The ESR line shapes of amphiphilic spin probes strongly depend on their dynamics. When dissolved in surfactant aggregates and aligned with the surfactant molecules, their local motion is dominated by the rapid rotation around the long molecular axis, resulting in anisotropic effects. Superimposed motions are the tumbling of the entire aggregate and the lateral diffusion of the probe molecule over the aggregate surface.

The rotational correlation time of the aggregate tumbling (see eq 2) is smaller than 5×10^{-8} s for micelles with R < 20-24 Å at 20 °C in water. Such micelles give rise to motionally

TABLE 1: ESR Parameters of Spin Probe Spectra in SDS/Al(NO₃)₃/Urea/Water Solutions

| | composition (mol·kg ⁻¹) | | | | 5-I | DSA | | 16-DSA | C12-NO |
|--------|-------------------------------------|-----------------------------------|------------------|------|--|----------------|------|----------------------------------|----------------------------|
| sample | SDS | Al(NO ₃) ₃ | H ₂ O | urea | $\overline{A_{\parallel}(\mathrm{G})}$ | $A_{\perp}(G)$ | S | $10^{10} \tau_{\rm C} ({\rm s})$ | $10^{10} \tau_{\rm C}$ (s) |
| S | 0.42 | 0 | 69 | 0 | | | | 5.0 | 2.5 |
| SA | 0.42 | 1 | 69 | 0 | | | | 9.6 | 4.2 |
| SAU1 | 0.42 | 1 | 69 | 2.3 | | | | 11.8 | 6.2 |
| SAU2 | 0.42 | 1 | 69 | 4.5 | | | | 12.0 | 7.5 |
| SAU4 | 0.42 | 1 | 69 | 9.0 | 24.9 | 10.3 | 0.53 | 12.7 | 8.7 |
| SAU6 | 0.42 | 1 | 69 | 13.5 | 25.8 | 10.1 | 0.57 | 13.5 | 8.8 |
| SAU8 | 0.42 | 1 | 69 | 18.0 | 25.9 | 10.4 | 0.55 | 14.7 | 8.7 |
| SAU13 | 0.42 | 1 | 69 | 30.0 | 26.3 | 8.9 | 0.65 | | 10.0 |

narrowed three-line spectra. In a similar way, lateral diffusion contributes to averaging of anisotropic features if the translational diffusion coefficient on the aggregate surface, $D > 3 \times 10^{-11} \text{ m}^2/\text{s.}^{27,28}$

The ESR spectrum of 5-DSA in sample S containing small, spherical micelles, consists of three asymmetric, rather broad lines (Figure 2a), characteristic of averaging of the anisotropic components of the A and g tensors, but with the probe tumbling at the limit of rapid toward slow motion. This happens when the rotational correlation time of the probe, τ_c , is higher than 10^{-9} s. In this case τ_c cannot be correctly calculated with eq 1. The same type of ESR spectrum was found in solution SA (Figure 2b), where the SDS aggregates are long, entangled cylinders ("wormlike" aggregates¹⁸). However, increasing quantities of urea gradually change the spectrum of 5-DSA in the SAU series (see Table 1), so that starting from sample SAU4 only the local, anisotropic motion determines the line shape (Figure 2d,e). In these cases an order degree, S, could be measured. This type of ESR spectrum could arise from three different structures:²⁷ (1) discoidal micelle (oblate ellipsoid) large enough so that tumbling is slow on the ESR time scale; (2) rodlike micelle (prolate ellipsoid), if the lateral diffusion is by some reason too slow; (3) spherical micelle with R > 20 Å. Unfortunately, none of these possibilities can be completely discarded. Urea, included in the solvation sphere, may increase the aggregate hydrodynamic radius to some extent or increase the lateral diffusion coefficient so as to slow the lateral diffusion rate below the threshold of ESR time-window.

The neutral spin probe, C12-NO, which is included in SDS micelles with the nitroxide group close to the micelle interface, has an isotropic motion in both S and SA samples (Figure 3a and b). In the SAU series (see Table 1), in a similar way with the 5-DSA probe, the motion becomes more and more anisotropic (for this probe the anisotropy is reflected in the decreasing height of the three lines from low to high field²⁹); i.e., only the local rotation of the probe around the long axis remains rapid, and there is no contribution from micelle tumbling and lateral diffusion (Figure 3c,d).

The ESR spectrum of 16-DSA (not shown) is isotropic in all samples. The high τ_c value, given in Table 1, reflects the local viscosity increase within the aggregate core, where the nitroxide moiety of this probe is supposed to reside, with aluminum nitrate addition sample (SA), which continues with urea addition, in the SAU series. It shows that structural modifications in the aggregates also take place, along with dimensional and geometrical changes.

ii. NMR Surfactant Self-Diffusion. The experimental selfdiffusion coefficients of the surfactant in different SDS/Al- $(NO_3)_3$ /urea/H₂O solutions are presented in Table 2. As the overall concentration of the surfactant is much higher than the critical micellar concentration (cmc), the contribution of the free monomer to the observed self-diffusion coefficient can be neglected, and consequently, the measured diffusion reflects the



Figure 3. ESR spectra of C12-NO in $SDS/Al(NO_3)_3$ /water/urea mixtures with increasing urea content; samples are denominated as in Table 1, where the corresponding compositions are given: (a) SA; (b) SAU2; (c) SAU4; (d) SAU6.

| ABLE 2: Results of | ¹ H NMR | Measurements |
|---------------------------|--------------------|--------------|
|---------------------------|--------------------|--------------|

| | co | mposition (| | W | | | | |
|--------|------|-----------------------------------|--------|-------|-----------------------------|----------------------|------|------|
| sample | SDS | Al(NO ₃) ₃ | H_2O | urea | $\phi_{\mathrm{agg}}{}^{b}$ | $(m^2 \cdot s^{-1})$ | р | (Hz) |
| 1 | 0.5 | 0 | 69.0 | 0 | 0.0498 | 4.45 | _ | 13.7 |
| 2 | 0.5 | 0.56 | 69.0 | 0 | 0.0498 | 0.26 | 28.5 | 50.8 |
| 3 | 0.42 | 0.89 | 69.0 | 4.57 | 0.0717 | 0.28 | 21.0 | 41.8 |
| 4 | 0.37 | 0.82 | 69.0 | 8.57 | 0.0560 | 1.46 | 13.5 | 22.0 |
| 5 | 0.44 | 0.97 | 69.0 | 15.62 | 0.0558 | 2.50 | 5.8 | 16.3 |

 ${}^{a}D_{obs}$, surfactant self-diffusion coefficient; *W*, the line width; *p*, the calculated axes ratio. b Volume fraction of the aggregates.

diffusion of the micelle itself. Addition of Al³⁺ in large concentration (Figure 1, region III) to an aqueous SDS solution results in a very strong *decrease* of D_{obs} (Table 2). This reflects the micelle growth induced by the excess of Al salt, leading to long, wormlike aggregates.¹⁸ Subsequent addition of urea to these wormlike micellar solutions produces a significant increase of $D_{\rm obs}$ (which is also reflected in the dramatic macroscopic viscosity decrease). The enhanced mobility of the aggregates as the system takes up urea, may partly be due to a dilution effect, but the order of magnitude increase in D_{obs} can only be explained by a significant reduction of aggregate sizes. This fact can be roughly quantified by estimating the axial ratio, p, of the elongated micelles, following a numerical procedure described in detail in ref 30. As expected, the calculated p values (shown in Table 2) decrease as the urea concentration increases. By this procedure, the micelles were found to be still elongated even at the highest urea/SDS molar ratio (35:1) as the assump-



Figure 4. ¹H NMR spectra of dodecyl sulfate in SDS/Al(NO₃)₃/water/ urea mixtures with increasing urea content. Samples are numbered as in Table 2: (a) 2; (b) 3; (c) 4; (d) 5. The spectra were recorded by pulsed FT technique at 200 MHz.

tion of spherical aggregates resulted in an un-physically large hydrodynamic radius.

iii. NMR Relaxation of Surfactant. The ¹H NMR spectra of the surfactant in elongated aggregates present in various SDS/ Al(NO₃)₃/H₂O/urea mixtures are displayed in Figure 4. The corresponding line widths, defined as the width at the half-height of the main NMR alkyl chain signal of the surfactant, are presented in Table 2. Without urea the spectra exhibit a non-Lorentzian band shape, with the alkyl and terminal methyl NMR proton bands highly overlapped (Figure 4a). This type of spectrum represents the typical relaxation observed in wormlike aggregates.³¹ As a result of urea addition, the two bands become narrower and their shape changes toward a Lorentzian shape (see Figure 4d). The large, 50 Hz, line width in the absence of urea, which corresponds to long cylinder-like aggregates, decreases gradually with the urea content, reaching a value of 16.3 Hz at the highest urea content. This value is still higher than the one recorded for spherical micelles in the binary surfactant/water system (\sim 14 Hz). Although the line width does not have a direct and simple physical meaning, the observed line narrowing clearly points to the decrease of the mean aggregate length.³¹

iv. NMR Solvent Self-Diffusion. The observed self-diffusion coefficients of water and urea are presented in Table 3. The addition of the aluminum salt to water/urea mixtures leads to a marked decrease in urea self-diffusion, probably due to formation of a complex involving urea and Al^{3+} or NO_3^{-} . Formation of such complexes would influence not only the electrostatic interactions between the charged species but also the presence of urea molecules near to the polar—apolar interface. The characterization of these complexes is, however, beyond the aim of the present paper.

The reduced diffusion coefficients of the solvent, D/D_0 , defined as the ratio of the self-diffusion coefficients in the presence and in the absence of the aggregates, are also shown in Table 3. The fraction *f* of solvent molecules bound to the charged headgroups was estimated from³²

$$D = fD_{\rm mic} + A(1 - f)D_0 \tag{3}$$

Here D_{mic} is the diffusion coefficient of the aggregates and *A* represents the obstruction factor. Thus, the hydration number (i.e., the number of water molecules bound per surfactant) was found to decrease from 12 in the absence of urea to 7 when

urea is present. The binding of urea is, however, calculated with high uncertainty due to the low fraction of "bound" urea. Nevertheless, one can estimate that about one to three urea molecules are bound to each surfactant headgroup. This finding is in line with ESR observation of local viscosity increase with urea addition and with the proposed mechanism for urea action, suggesting that urea replaces some of the water molecules in the solvation sphere of the polar headgroup of the amphiphile.^{33–35}

v. Dynamic Fluorescence Quenching. The quenched fluorescence decay of pyrene in the SDS/Al(NO₃)₃/urea/water solutions, was analyzed within two models, depending on how the mean length of the aggregates, $L_{\rm mic}$, relates to the diffusion length $L_{\rm diff}$. Here

$$L_{\rm diff} = \sqrt{\pi D/k_0} \tag{4}$$

where *D* is the mutual diffusion coefficient of the probe and quencher and k_0 represents the deactivation rate constant of the excited probe in the absence of quenchers.

Model I describes the fluorescence decay for the excited probe-quencher pair solubilized in aggregates when $L_{\rm mic} \gg 2L_{\rm diff}$:^{36,37}

$$\ln F(t)/F(0) = -k_0 t - B_0 c_0 \{\exp(B_1 t) \operatorname{erf}(B_1 t)^{1/2} - 1 + 2(B_1 t/\pi)^{1/2} \}$$
(5)

The two parameters, B_0 and B_1 , are given by

$$B_0 = \left(\frac{3D}{k_q R}\right) \qquad B_1 = \left(\frac{2k_q R}{3}\right)^2 \frac{1}{D} \tag{6}$$

where k_q is the first-order quenching rate constant in the reaction volume of length 4R/3 surrounding the excited probe and c_0 is the quencher concentration expressed as molecules per unit length.

When $L_{\rm mic} \leq 2L_{\rm diff}$, the fluorescence decay data can be analyzed, within the framework of Infelta–Tachiya-type equation (model II)^{38,39}

$$F(t) = F(0) \exp(-A_2 t + A_3(\exp(-A_4 t) - 1))$$
(7)

where A_i parameters are explicitly

$$A_2 = k_0$$
 $A_3 = n$ $A_4 = 4\Gamma_1^2 D/L^2$ (8)

n is the average number of quenchers per micelle, and Γ_1 depends on the quenching rate constant, k_q , and the encounter radius of excited probe and quencher.

In a recent study of the SDS/Al(NO₃)₃/water system with excess Al salt (Figure 1, region III), large wormlike aggregates have been identified with a number of experimental techniques.¹⁸ The fluorescence quenching data carried out in the SDS/Al-(NO₃)₃/water system with excess Al salt (Figure 1, region III) have shown that the statistical parameter χ^2 can be reliably used as a criterion to discriminate between the two models and implicitly to evaluate the mean length of the aggregates as compared with the diffusion length, L_{diff} .¹⁹

Both models have been applied to fit the fluorescence quenching curves of pyrene measured in selected SDS/Al/urea/ water mixtures (urea were added in DS⁻ wormlike micelles solutions) (Table 4). In the solution with a moderate quantity of urea (2.68 mol kg⁻¹), both models give approximately the same value of χ^2 , implying a decrease in the mean aggregate length to $2L_{\text{diff.}}$ By further addition of urea, model II gives more

TABLE 3: Reduced Self-Diffusion Coefficient of Urea and Water, D/D₀, and the Obstruction Factor, A

| | composition (| mol∙kg ^{−1}) | | $10^9 D_{\rm obs}({\rm H_2O})$ | | $10^9 D_{\rm obs}({\rm urea})$ | D/D_0 | | | |
|------|-----------------------------------|------------------------|-------|--------------------------------|----------------------|--------------------------------|------------------|------|-------|--|
| SDS | Al(NO ₃) ₃ | H ₂ O | urea | $\phi_{\mathrm{agg}}{}^a$ | $(m^2 \cdot s^{-1})$ | $(m^2 \cdot s^{-1})$ | H ₂ O | urea | Α | |
| 0 | 0 | 69.0 | 6.81 | | 1.67 | 0.92 | | | | |
| 0 | 0 | 69.0 | 3.62 | | 1.77 | 1.00 | | | | |
| 0 | 0.79 | 69.0 | 8.33 | | 1.14 | 0.21 | | | | |
| 0 | 0.93 | 69.0 | 14.18 | | 0.96 | 0.17 | | | | |
| 0 | 0.89 | 69.0 | 4.60 | | 1.19 | 0.22 | | | | |
| 0.42 | 0.89 | 69.0 | 4.57 | 0.072 | 1.08 | 0.18 | 0.91 | 0.67 | 0.955 | |
| 0.37 | 0.82 | 69.0 | 8.57 | 0.056 | 1.04 | 0.20 | 0.93 | 0.83 | 0.964 | |
| 0.44 | 0.97 | 69.0 | 15.62 | 0.056 | 0.86 | 0.19 | 0.92 | 0.95 | 0.964 | |

^a Volume fraction of the aggregates.

TABLE 4: TRFQ Data^a

| composition (molar ratio) | | | 10 ³ [SDS] | 10 ³ [DPC1] | model I | | | | model II | |
|---------------------------|-----------------------------------|-----------------------|-----------------------|------------------------|---------------------|---|---|----------------------|------------|----------------------|
| SDS | Al(NO ₃) ₃ | H ₂ O | urea | (M/kg) | (M/kg) | $\overline{k_q^{\ b} (10^8 \text{ s}^{-1})}$ | $D^b (10^{-10} \text{ m}^2 \text{ s}^{-1})$ | $\chi^{2 c}$ | Ν | $\chi^{2 c}$ |
| 0.25 | 0.57 | 0 | 69.0 | 183 | 0.4 1.4 1.8 | 1.2 ± 0.1 1.2 ± 0.1 1.3 ± 0.1 | 3.9 ± 0.2 4.3 ± 0.2 4.5 ± 0.2 | 1.20 | | 3.27 |
| 0.35 0.41 0.42 | 1.08 0.89 0.97 | 2.68 4.56 14.71 | 69.0 69.0 69.0 | 211 237 183 | 0.42 0.87 0.7 | 0.72 ± 0.2 | 0.64 ± 0.2 | 1.06 1.30 1.96 | 220 218 | 1.09 1.10 1.49 |

^{*a*} Quenching rate constant, k_q , and mutual diffusion coefficient, *D*, from the one-dimensional quenching model and the apparent mean aggregation numbers, *N*, from the Infelta–Tachiya type equation. ^{*b*} A hydrophobic radius of the cylinder of 17 Å was considered.⁴⁰ ^{*c*} Reduced χ^2 .

TABLE 5: ESR Parameters of the Spin Probes in the Initial Solution (Molar Ratio SDS/Al(NO3)3/Water/Urea = 0.42/1/69/21),during Reaction and in the As-Synthesized Alumina

| treatment | | | | | | | |
|--|---|------------|------------|--|------|-----------------------|--|
| state | temp/time | pH final | spin probe | $10^{10} \tau_{\rm C} ({\rm s})$ | S | $2A_{zz}$ (G) | observations |
| initial sol precipitate precipitate precipitate | 80 °C/6 h 80 °C/15 h 50 °C/3 days | 6.1 7.3 | 5-DSA | | 0.60 | 60.0 64.8 6 4.8 | |
| initial sol precipitate precipitate precipitate | 80 °C/6 h 80 °C/15 h 50 °C/3 days | 6.1 7.3 | 16-DSA | $16.2 \\ \sim 25 \\ \sim 25 \\ \sim 25 \\ \sim 25$ | | | outside "fast motion" regime idem idem |
| initial sol precipitate precipitate precipitate | 80 °C/6 h 80 °C/12 h 50 °C/3 days | 6.1 7.3 | CAT 16 | | | 42.2 50.0 | anisotropic features anisotropic features |
| initial sol precipitate precipitate precipitate | 80 °C/6 h 80 °C/12 h 50 °C/3 days | 6.1 7.3 | C12-NO | 8.6 10.0 15.0 15.5 | | | $egin{array}{llllllllllllllllllllllllllllllllllll$ |

reliable statistics than model I. At the highest urea content (14.71 mol kg⁻¹), the residuals obtained from model I clearly deviate from an even distribution and the corresponding χ^2 is higher than the value found for model II. These facts imply that the mean length of the wormlike micelles decreases to values lower than L_{diff} , so the quenching process is no longer dominated by diffusion.

An average number of quenchers per micelle, n (and consequently a mean aggregation number, N), can be obtained only for the shortest micelles found at the highest urea content (see Table 4) when model II applies. However, we consider that the result is uncertain, owing to the expected polydispersity in aggregate sizes and the given aggregation number should only be seen as a minimum estimated value. By fitting this last curve with the classical Infelta–Tachiya model for probe–quencher pairs solubilized exclusively in monodisperse spherical micelles, the quencher exit rate found, k_- , of $6.9 \times 10^5 \text{ s}^{-1}$ was much higher than expected for DS⁻ spherical micelles ($(0.3-0.7) \times 10^5 \text{ s}^{-1}$),¹⁹ implying that the micelles are still elongated.

2. ESR of Spin Probes during Alumina Synthesis. The EPR studies aimed at characterizing the aggregates during the formation of mesostructured alumina are reported. The measurements were performed at different stages of synthesis (for details see the Experimental Section), and the relevant parameters of the ESR spectra are collected in Table 5. In the following, only the spectra of the probes in the sample Y2, with the molar ratios $Al(NO_3)_3/SDS/urea/water = 1/0.42/21/69$ will be discussed in a detail, the values for sample Y1 being almost identical.

The ESR spectra of the starting solution show that the spin probes are included in surfactant aggregates. The shape and the parameters of the ESR spectrum of 5-DSA report on a high degree of ordering of the surfactant chains in the interface region and on absence of rapid aggregate tumbling and/or lateral diffusion (see the discussion in the section devoted to precursor systems (Figure 5a)). Heating for 4 h to 80 °C does not change significantly the spectrum. We have also measured carefully a sample heated at 60 °C over 40 h, to evidence any possible changes in the aggregate geometry as the solution composition changes during urea hydrolysis, before precipitation. At pH \sim



Figure 5. ESR spectra of 5-DSA during alumina synthesis: (a) initial solution, Y2, molar ratio SDS/Al(NO₃)₃/water/urea = 0.42/1/69/21; (b) precipitate after 6 h at 80 °C, pH = 6.1; (c) precipitate after 15 h at 80 °C, pH = 7.3; (d) precipitate after aging (c) at 50° C for 3 days. The trace enhancing the small peak at high field was recorded with a higher modulation amplitude (2–3 G) as compared to the complete spectrum (1 G).

5 the spectrum of the bulk showed immobilization of the radical. Filtration showed that the signal was associated with very fine solid particles. Thus no significant structural changes take place with the surfactant aggregates in solution before the onset of precipitation.

After 6 h at 80 °C, when pH 6.1 is attained and precipitation has started, the spin probe 5-DSA appears partly immobilized in the precipitate (Figure 5b). After 15 h of reaction, when pH 7.3 is attained and the precipitation is complete, the spectrum of 5-DSA in precipitate indicates complete immobilization of the probe (Figure 5c). Changes during aging were not evidenced (Figure 5d).

The spectrum (not shown) of a probe with the radical moiety located in the core region of the micelles (16-DSA) indicates a strong increase in local viscosity during alumina precipitation, but the probe maintains a fairly high degree of mobility in the as-synthesized alumina (Table 5). This is considered as strong evidence that the measured data refer to probes in surfactant aggregates in the mesoporous frame.

For the CAT 16 probe, the peculiar line shape—resembling the 5-DSA spectra—observed in the precipitate first formed (6 h reaction at 80 °C) (Figure 6b) and which is maintained in the final stage (Figure 6c), indicates a tilt angle of the radical moiety (piperidine cycle) vs the long molecular axis. This way the nitrogen p_{π} orbital (of the free electron) becomes approximately parallel with the long molecular axis, which is the preferred rotational axis, as in doxyl stearic acid probes. This probe is anchored at the interface with the quaternary nitrogen atom and exposes the piperidine cycle outside the organic phase. The observed tilt of the cycle indicates certain constraints on the probe geometry at the organic/inorganic interface, when the alumina precipitate is formed (Scheme 1).

A small change in the tilt angle between the long molecular axis and the nitroxide moiety, causing a change in the relative amplitudes of the three derivative line (see ref 41 for a similar change of spectrum, simulated by a small change of the tilt angle) (Figure 7c,d) is evidenced also by the $C_{12}NO$ probe in the precipitate, but only after 12 h of reaction.

This neutral probe is supposed to be included deeper in the SDS aggregate than the charged CAT 16 (especially because



Figure 6. ESR spectra of CAT 16 during alumina synthesis: (a) initial solution, molar ratios SDS/Al(NO₃)₃/water/urea = 0.42/1/69/21; (b) precipitate after 6 h at 80 °C, pH = 6.1; (c) precipitate after 12 h at 80 °C. The traces enhancing the small peak at high field were recorded with a higher modulation amplitude (2–3 G) as compared to the complete spectra (1 G).





^a Changes of radical geometry during alumina precipitation are suggested.

in CAT 16 the radical moiety is positioned in front of the charged quaternary ammonium group, which will be anchored at the water interface) Such a relative radial positioning was well established in aggregates of nonionic block-copolymers (Pluronics).⁴² In support of this statement, the probe maintains a fairly high mobility in the final solid. Therefore the evolution observed is an indication of structural changes continuing during the precipitation of alumina and affecting deeper regions of the template.

3. Influence of Composition on the Structure of As-Synthesized Alumina. A number of syntheses have been carried out, starting from different ratios of the components, to evidence the effect of the aggregate size and shape in the precursor system on the structure of the product. In all compositions the water/ urea molar ratio was maintained constant and the Al salt content was higher than 5 wt %, ensuring the stability of the solution as a single micellar phase (i.e., Figure 1, region III).

All these syntheses led to ordered materials, whose typical X-ray diffractograms are presented in Figure 8. The XRD patterns of as-synthesized alumina exhibited two or three Bragg peaks. Their relative positions on the scattering vector axis, q,



Figure 7. ESR spectra of C12-NO during alumina synthesis: (a) initial solution, molar ratios SDS/Al(NO₃)₃/water/urea = 0.42/1/69/21; (b) precipitate after 6 h at 80 °C, pH = 6.1; (c) precipitate after 12 h at 80 °C; (d) precipitate after aging (c) at 50 °C for 3 days.



Figure 8. XRD powder diffraction patterns of as-synthesized alumina obtained from precursors with the SDS/Al(NO₃)₃/water/urea molar ratios: (a) 0.26/1.1/69/31, final pH = 7.3; (b) 2/1/69/30, final pH = 7.2. The aluminum-based solids were allowed to age 3 days at 50 °C.

followed in all cases the ratios $1:\sqrt{3}:2$, implying that hexagonal structures were formed. The absence of the third diffraction peak, corresponding to a (200) reflection was noticed in a few syntheses of concentrated surfactant systems. It can be inferred that the absence of the third peak indicated the formation of a less ordered material.

Regarding the aging effect, the 3 days of aging at 50 °C had a rather limited effect as the dimension of the unit cell remained unchanged and only a slight enhancement of the Bragg peaks was observed in case of less ordered materials.

The dimensions of the unit cells, *a*, calculated from the position of (100) reflection are shown in Table 6. Its value is approximately 40 Å, with a slight dependence on the composition of the precursor system. The hexagonal framework always collapsed during calcination. The disappearance of the morphology took place even in those cases when, to prevent the removal of the SO₄^{2–} group from the inorganic frame, a low calcination

TABLE 6: Position of the First Diffraction Peak, d_{100} , and the Unit Cell Dimension, a, of As-Synthesized Alumina

| | co | mposition (m | olar rati | o) | | | |
|-----|------|-----------------------------------|-----------|------|-----|----------------------|---------------------|
| no. | SDS | Al(NO ₃) ₃ | H_2O | urea | pН | $d_{100}({\rm \AA})$ | $a^{a}(\text{\AA})$ |
| 1 | 0.24 | 0.69 | 69 | 31 | 7.8 | 33.5 | 38.6 |
| 2 | 0.26 | 1.09 | 69 | 31 | 6.4 | 38.4 | 44.3 |
| 3 | 0.26 | 1.09 | 69 | 31 | 7.3 | 35.6 | 41.1 |
| Y2 | 0.42 | 1 | 69 | 21 | 7.2 | 34.8 | 40.1 |
| 4 | 0.54 | 2.1 | 69 | 31 | 7.2 | 32.7 | 37.7 |
| 5 | 0.61 | 1.69 | 69 | 31 | 7.5 | 35.3 | 40.7 |
| 6 | 1.23 | 0.83 | 69 | 31 | 7.3 | 35.0 | 40.4 |
| 7 | 1.23 | 0.83 | 69 | 31 | 6.4 | 36.4 | 42.0 |
| 8 | 1.88 | 2.12 | 69 | 31 | 6.1 | 38.2 | 44.1 |
| Y1 | 2 | 1 | 69 | 30 | 7.2 | 33.5 | 38.6 |

^{*a*} The standard deviation for *a* is 1 Å.

temperature (350 $^{\circ}$ C) was used. A similar result, the collapse of the hexagonal framework, was also obtained in the case of surfactant removal by ionic exchange.

Discussion

The effect of urea on the aggregate structure in the redissolution area of the pseudoternary SDS/Al(NO₃)₃/H₂O system (Figure 1, region III) was investigated by several spectroscopic methods and all results agree that addition of urea produces a very significant reduction of the length of the wormlike aggregates.

During synthesis (heating) no changes in the aggregate shapes are observed in solution, before the formation of the precipitate. Thus, we do not see any intermediate structure between the starting aggregates and the precipitate. This result tends to support the mechanism of formation of the mesostructured hexagonal alumina proposed by Sicard et al. on the basis of fluorescence measurements.¹⁷

In the precipitate, 5-DSA is strongly immobilized by electrostatic interaction with positively charged aluminum oligomeric species. The immobilization degree (described by 2A_{zz} value) increases from the precipitate first formed (~ 6 h) to the final precipitate (pH \sim 7.3 and \sim 15 h). This interaction reflects the DS⁻ binding to alumina precursors. It should be remarked that in the hexagonal $DS-Al^{3+}$ crystalline phase (Figure 1, region II) 5-DSA maintains rapid lateral diffusion, presumably because its counterion is also free to move. The cationic probe CAT 16, appears to have the piperidine ring tilted vs the long molecular axis (Scheme 1) in the precipitate, as soon as it is formed, as a result of steric or specific interaction with aluminum species. A similar, but smaller change in tilt angle is found with the neutral probe C12-NO, not immediately after precipitation, but after about 6 h. This effect is due to the formation and the development of the layer of the alumina on the surface of the surfactant template, during reaction. 16-DSA, located in the hydrocarbon core of SDS retains isotropic rotation mobility, but with reduced rate, in connection with the viscosity increase in the core of the template.

However, the question of how the complex between the inorganic polymers and the surfactant micelles evolve toward a hexagonal structure is not elucidated. Earlier results concerning the pseudoternary SDS/Al(NO₃)₃/water system¹⁸ may offer some clues for understanding the formation of hexagonal alumina. Thus, it was observed that concentrations of Al³⁺ lower than those used in the syntheses do not stabilize the SDS micellar solutions and lead to the precipitation of the surfactant (Figure 1, region II). Intriguingly, the precipitate has a hexagonal structure with the dimension of the unit cell of 44 Å,¹⁸ which is only slightly higher than those of the as-synthesized hexagonal

aluminas (~40 Å). These observations suggest that the arrangement of the surfactant/inorganic species complex into the hexagonal pattern may occur in the same way as the formation of the insoluble hexagonal DS^--Al^{3+} complex in the SDA/ $Al(NO_3)_3/H_2O$ system.

We therefore propose the following model for the formation of hexagonal meso-structured alumina: the starting SDS/Al-(NO₃)₃/water/urea mixture is stabilized by the high content of Al³⁺. Then, whereas the pH increases as a result of urea decomposition, the content of the charged hydroxoaluminum species becomes significant at the expense of Al³⁺. The decrease in Al³⁺ content leads to destabilization of the micellar phase, and DS⁻ starts to precipitate, forming, together with Al species, an ordered hexagonal structure. Subsequent increase of pH would have as the only result the condensation of the polyions of aluminum contained in the precipitate, with the preservation of the hexagonal arrangement. This mechanism does not exclude the formation of alumina without a hexagonal framework as a result of the electrostatic interaction between the micelles in solution and the inorganic polymeric species.

Concluding Remarks

The present study has shown, in the first part, the progressive decrease of the mean length of the wormlike micelles in the ternary $SDS/Al(NO_3)_3/H_2O$ system under the influence of added urea.

The use of the nitroxide spin probes located in different regions of the micelles allowed the investigation of the complex formed by the growing inorganic polymer and dodecyl sulfate aggregates during synthesis. No structural changes were observed for the aggregates in solution before the onset of precipitation. In the precipitate, the presence of the surfactant template is demonstrated as well as its interaction with the aluminum species at the interface. An evolution of this interaction in time is also observed.

Finally, the ability of the SDS/Al(NO₃)₃/water/urea system to produce mesostructured alumina over a large domain of concentrations was demonstrated. The structure and the topology of the final product was fixed and did not depend on the size of the aggregates in the precursor systems. The thermal stability of the as-synthesized alumina was, however, poor and the removal of the surfactant has always led to the collapsing of the hexagonal framework.

A tentative explanation of the precipitation mechanism is proposed, by analogy with the destabilization of the micellar solutions in the SDS/Al(NO₃)₃/water system and formation of a hexagonal Al^{3+} -DS⁻ precipitate when the Al^{3+} concentration drops below a certain value.

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