

Figure 4. Effects of changing mole percent of TiO_2 in the Ti-Al binary oxides upon the specific photocatalytic activity of TiO_2 species for the photocatalyzed isomerization of *cis*-2-butene (--O--) and photocatalyzed hydrogenation of propene with water. (The specific photocatalytic activity of TiO_2 species was given by dividing the yields of photoformed products by the content of TiO_2 in the used catalysts. --O--, catalyst was calcined at 773 K; --O--, catalyst was calcined at 773 K.)

of alumina to TiO_2 component leads to an enhancement of activity. As seen in Figure 4, photocatalytic activity of the Ti-Al binary oxide calcined at 973 K is higher than that of calcined at 773 K. Although the details are unclear at present, it was found that the optimum calcination temperature of the oxides was around 973 K, and even after the calcination at this temperature all TiO_2 species in the Ti-Al binary oxides were found to keep the anatase form, in contrast with the pure anatase type TiO_2 which easily change into rutile by the calcination at around 923 K.

From these results the following conclusions are possible. The Ti–Al oxide catalyst consists of surface layers in which TiO_2 species are surrounded by Al_2O_3 carrier acting as cocatalyst, these structure resulting in the enhancement of the activity of TiO_2 species. In this situation, the photon energy absorbed by the oxide is utilized for the reaction with high efficiency due to the less efficient radiationless energy transfer on the surface with coordinatively unsaturated surface ions.¹⁰ On the other hand, the

ions in saturated or high coordination have a larger number of bonds to the oxide and couple more strongly with the phonon transitions of the lattice, providing a high probability of radiationless decay.^{2c,4,11,12} It is of interest to point out that, even with catalysts having a much lower content of alumina, such surface layers seem to be formed on some special parts of the catalyst, by considering the facts that in this region a peculiar enhancement is observed and the results obtained by XPS indicate the enhancement of Al₂O₃ on the surfaces. Of course, such a peculiar enhancement in the photocatalytic activity would also be explicable by assuming Al_2O_3 to act as an impurity of the trapping sites in TiO₂. Thus, the present work not only provides useful information on the nature and properties of the Ti-Al binary oxide catalysts but also shows the significant enhancement of photocatalytic activity of TiO₂ species located in the Al₂O₃ carrier matrix as cocatalyst in the Ti-Al binary oxides. Details of this system will be clarified in the near future by means of photoluminescence spectroscopy, because the preliminary experiments indicate that the Ti-Al binary oxides exhibit a photoluminescence at around 450 nm, which depends upon the composition of the catalysts.

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Registry No. Al_2O_3 , 1344-28-1; TiO₂, 13463-67-7; H₂O, 7732-18-5; propene, 115-07-1; *cis*-2-butene, 590-18-1; aluminum titanium oxide, 37220-25-0; ethane, 74-84-0; methane, 74-82-8.

(10) Although it is difficult to determine the exact efficiency (quantum yield) of photons absorbed by the catalysts because of difficulty to determine the number of photons absorbed, their relative efficiencies were estimated by considering the reflectance spectra of catalysts and the yields of products. These values are given in Table I and Figure 1.

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Size and Shape of Micelles in the Ternary System *n*-Dodecylbetaine/Water/1-Pentanol

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The phase diagram of the system *n*-dodecylbetaine/water/1-pentanol is first presented. The use of several experimental techniques, namely (principally) small-angle X-ray scattering and fluorescence probe studies, allows us to obtain the size and the shape of the micelles in the L_1 phase. It is shown that the most probable shape corresponds to elongated aggregates, the self-consistency of the results leading to exclude the other shapes.

Introduction

The phase diagrams of systems involving ionic surfactants alcohol and brine have the same characteristic structure,^{1,2} especially in the water-rich region. It can be thought that this behavior is principally due to the presence of salt and, therefore, to the screening effect of the salt on electrostatic interactions. It is thus not surprising to obtain a very similar phase diagram when

dealing with a zwitterionic surfactant. Such a phase diagram is first presented in the case of *n*-dodecylbetaine.

Evolution of the shape of the aggregates when alcohol is added to binary solution is beginning to be known in the case of ionic surfactants diluted in water or brine. The aim of this paper is

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Figure 1. Phase diagram of the system n-dodecylbetaine/water/pentanol.

to present results obtained with a zwitterionic surfactant, since only a few results have been reported so far with such surfactants in the presence of alcohol.

The study of the shape of aggregates obtained by small-angle X-ray scattering (SAXS) often leads to questionable results. For instance, if the maximum of the scattering vector is too low (that is the resolution is too low), polydisperse spheres, prolate or oblate ellipsoids, can satisfactorily fit the experimental data. We show here that even if our resolution is a mean resolution (in contrast with high resolution as defined by Cabane³), the knowledge of the surfactant aggregation number obtained by another technique (a fluorescence probing method) leads us to suggest a possible shape for the micelles in the L_1 phase.

Phase Diagram

About 220 solutions were prepared, most of them being located in the water-rich region (volume fraction of water >90%). These solutions were held in a thermostated bath at 25 ± 0.1 °C. The phases were characterized by microscopic observation between crossed polarizers. Small-angle X-ray scattering measurements were also done in order to confirm the structure of the lamellar phase.

General Feature. The phase diagram of the ternary system n-dodecylbetaine/water/pentanol is represented in Figure 1. There are two isotropic phases L_1 and L_2 and one mesomorphic phase located between these two phases. The mesomorphic phase is a lamellar liquid crystal (CL). Its extension is large, and it joins the two binary axes water/betaine and alcohol/betaine. The L₂ phase also occupies a great fraction of the phase diagram. The solubility of betaine in alcohol is large (close to 70%) and decreases when water is added. The L_1 phase region is smaller than the others. The solubility limit of betaine in water is close to 50 wt%.

Water-Rich Region. The water-rich corner (Figure 2) of the phase diagram presents a characteristic aspect¹ which also can be seen in systems involving ionic surfactants and brine.² The two main features are (i) in these diagrams the phase boundaries are straight lines and (ii) the lamellar and L2 regions have a large extension to the water corner.

The lamellar phase, characterized by static birefringence, is stable up to 96.5 wt% water. In the more concentrated regions, an X-ray study allows us to obtain the thickness d_a of the hydrophobic lamella; one finds $d_a = 25$ Å. Thus, in the extreme limit of dilution, the repetition distance of the hydrophobic lamella would be of the order of 700 Å. The stability of such a structure is discussed elsewhere.4

The very diluted phase L_2 is called L_2^* . Indeed, this phase is connected to the L_2 phase, but its behavior is quite different. While



Figure 2. Enlargement of Figure 1 in the water-rich region.

TABLE I: Microanalysis Results

	С	Н	0	Ν	-
% theoretical with 1 H_2O	66.34	12.2	16.58	4.87	
% theoretical with $1/3$ H ₂ O % obtained	69.45	12.15	13.3	5.06	
expt 1	69.91	12.10	13.92	4.57	
expt 2	70.05	12.19	13.71	4.72	
mean value	69.98	12.145	13.815	4.645	

 L_2 is always isotropic, L_2^* is isotropic at rest and birefringent under shear.⁵ Apart from these monophasic domains, one finds the corresponding diphasic and triphasic domains CL/L₂*, CL/L₁,

Note that along the diphasic domain CL/L_1 there is a triphasic region where two isotropic phases and the lamellar phase coexist. This involves the existence of a critical point located on the boundary of the L_1 phase. This critical point has not been yet exactly located, but one can estimate that the corresponding pentanol concentration is about 3-4 wt%. We note that L_1^* is one of the isotropic phases which appears in the corresponding diphasic region.

Material and Methods

Material. n-Dodecylbetaine (C12H25N+(CH3)2CH2COO-) was synthesized according to the method given by Beckett and Woodward⁶ and by Tori and Nakagawa.⁷ Dodecyldimethylamine (Fluka) was treated with sodium monochloroacetate (Fluka) and purified as in ref 8. Moreover, in order to eliminate all of the sodium chloride, ion-exchange resins (Duolite MB 5101 and MB 6300 V) were used.

The purity of *n*-dodecylbetaine has been verified by NMR and micro analysis. The final product contained one water molecule for three surfactant molecules (Table I).

Fluorescence Probing Method. The single-photon-counting method⁹ was used for the fluorescence decay data collection as in other studies.¹⁰ The surfactant aggregation number N was obtained from the analysis of the decay curve using a nonlinear weighted least-squares procedure.¹⁰ The measurements were performed using pyrene excimer formation. The method is described in detail in ref 10. The probe distribution is assumed to follow Poisson statistics, which is valid if there is equiprobability for the micelles to be occupied by the probe. Low probe concentrations are used to agree with this assumption. On the other

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Figure 3. Shell model for a spherical micelle. $\rho_0 = 0.333 \text{ e}/\text{Å}^3$ is the electron density of water.

hand, the residence time of the quencher in the micelle is larger than the probe fluorescence lifetime; we then have the case of an "immobile quencher". At least it is shown that¹¹ the polydispersity does not affect the mean value of the aggregation number. Pyrene (Aldrich, 99%) was extensively zone-refined, and the [pyrene]/ [micelle] molar concentration ratio was kept close to unity. All solutions were thoroughly degassed prior to measurement by 3-4 freeze-pump-thaw cycles.

Small-Angle X-ray Scattering. The experimental method is described in a previous paper.¹² The measurements are done at fixed count on a low-angle GDPA 30 goniometer (CGR, France). The tube is a microfocus with a copper anticathode ($\lambda = 1.54$ Å). The collimation corresponds to a beam of infinite height. The experimental data were not desmeared. The theoretical curves are convoluted before comparison with the experimental ones. The explored scattering vector domain is 4×10^{-3} Å⁻¹ < s < 7 × 10⁻² \AA^{-1} (s = 2 sin θ/λ = $Q/2\pi$, 0.025 $\text{\AA}^{-1} < Q < 0.44^{-1}$ Å). The resolution in the real space is then³ π/Qm , that is, of the order of 7 Å. The intensity is normalized to one electron of the sample, and the solvent and the container contribution is subtracted from the signal of the sample as in ref 12.

These experimental data will be compared to the form factor calculated for various shapes:^{12,13} spheres and revolution spheroids (oblate and prolate). In these models the micelles are considered as made of two concentric shells: a hydrophobic core of uniform electron density ρ_{par} and a polar shell of electron density ρ_{pol} (Figure 3). The core includes the C_{12} chain, while the other part of the molecule of betaine (namely, $N^+(CH_3)_2CH_2COO^-$) is located in the polar region. In the case of ellipsoids the thickness of the polar region is assumed to be constant. These theoretical form factors are fitted with the experimental curves. We used a generalized least-squares procedure where the adjustable parameters are the axial ratio of the micelle (for the ellipsoidal model) and the electron densities of the paraffinic core and the polar shell. The obtained values for these electron densities must be close to the theoretical ones calculated by using the partial volume of every constituent. The self-consistency of the results is always controlled: volume of the core, volume of the polar region compatible with a plausible hydration. We consider that the uncertainty in the normalized intensity is low; thus, we do not introduce any scale factor in the fitting procedure.

Light Scattering. The experimental apparatus is classical (AMTEC spectrophotometer). It allows to measure both intensity and quasi-elastic light scattering (QELS). Static and dynamic measurements can be done with the same sample at the same

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TABLE II: Surfactant Aggregation Number Measured in Binary Solutions as a Function of the Temperature

solution, % TA	temp, °C	N	solution, % TA	temp, °C	N
2.7 2.7 2.7 2.7 2.7 5	15 25 35 45 25	82 79 76 71 82	10 10 10 10 20	15 25 45 60 25	81 77 73 63 77
η(cp) ηs 8 6	⊡ Binary © ●	3% 5% 10%		· • •	
4 -		°/			
0	/ @0- ^Q -@ ^{Q4}	, , , , , , , , , , , , , , , , , , ,	10	spheric model	\mathbf{D}_{w} $\times 10^{2}$

Figure 4. Variation of the relative viscosity as a function of $1 - \phi_w$ where ϕ_{w} is the volume fraction of water. Each curve corresponds to a different surfactant concentration: \Box , 3; O, 5; and \bullet , 10 wt%. ϕ_w is varied by addition of alcohol to the binary surfactant + water systems.

place. The sample is illuminated with an argon ion laser ($\lambda =$ 4880 Å), and the incident beam is focused on the micellar solution. The accessible angular domain is $10^{\circ} \le 2\theta \le 150^{\circ}$, that is, 3.0 $\times 10^{-4}$ Å⁻¹ < Q < 3.3 $\times 10^{-3}$ Å⁻¹. In the QELS configuration, the Fourier transform of the autocorrelation function is calculated by a spectrum analyzer (Rockland).

Results and Discussion

Binary System. The explored concentrations in surfactant varies from 2 to 20 wt%. In this concentration range the surfactant aggregation number remains constant. At 25 °C the mean value is N = 79, which is in agreement with literature^{8,14} (Table II). As for the other zwitterionic surfactants,¹⁵ the increase of the surfactant concentration does not result in a growth of the size of the micelles but in an increase of their number. It can moreover be seen that when the temperature is increased N decreases.

The knowledge of the aggregation number can yet allow us to evaluate the shape of the micelles using elementary steric considerations. Indeed, the hydrophobic chains of betaine can be considered as behaving like liquid paraffins³ penetrated little by water as in ionic micelles.^{16,17} Then we can obtain, using partial molar volume, the volume of the core. The corresponding core radius calculated in the spherical shape hypothesis is 18 Å, which is to be compared to the length of the hydrophobic chain, namely 17 Å.¹⁸ These values are compatible with a spherical or qua-

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Figure 5. Fit of experimental data (\bullet) with the form factor of a prolate ellipsoid for a binary solution: the betaine concentration is 10 wt%. The interaction peak can be seen at $s \approx 8 \times 10^{-3} \text{ Å}^{-1}$. The intensities are normalized to one electron of the sample.



Figure 6. Fit of the same experimental data (\bullet) as that in Figure 5 with the form factor of polydisperse spheres (the polydispersity is here 20%) and using a hard-sphere potential. The mean radius of the sphere is 26 Å.

si-spherical model. This is confirmed by viscosity measurements. One obtains values following the classical Einstein law at least up to a volume fraction of micelles equal to 10% (Figure 4).

X-ray experiments allow us to obtain a more precise description of these aggregates. The model for the shape is either a sphere or ellipsoids of revolution. The adjustable parameters, in the case of binary systems, are the electron density of the polar region, the minor axis of the ellipsoid, and the polar thickness which is assumed to be constant in all points of the micelle as surfactant concentration is varied. The self-consistency of the results was always controled, especially the volume of the paraffinic region which must be compatible with the volume of N hydrophobic chains (we consider here the chain with 12 carbon atoms), N being the aggregation number obtained from quenching data.

Two models seem to agree: prolate ellipsoids (Figure 5) and polydisperse spheres (Figure 6). In the case of the spherical model, the interactions are taken into account by using a hardsphere potential¹⁹ since in that case the observed intensity can be written as the product of the form factor P(s) and the structure factor S(s). The peak appearing at $s \approx 0.008 \text{ Å}^{-1}$ is the interaction peak while the maximum found at $s \approx 0.02 \text{ Å}^{-1}$ is due to the form factor (related to the polar shell). The experimental data are fitted, in the case of ellipsoidal objects, over a range from $s \approx 0.014$ to 0.07 Å^{-1} . The lower limit is chosen in order to eliminate the region perturbed by the interactions. The upper one is higher than the one commonly seen, for instance in neutron experiments (namely, $s \approx 0.03 \text{ Å}^{-1}$ or $Q \approx 0.2 \text{ Å}^{-1}$). The use of this range in s introduces

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Figure 7. Aggregation number N as a function of $1 - \phi_w$. The same procedure is followed as in Figure 4.

a hard constraint owing to the sensitivity of the scattering in this region to the shape of the micelles. Indeed, it is in this region that undulations of the form factor of monodisperse spheres appear while ellipsoids give a monotonic decrease. The resolution is not too far from high resolution as defined by Cabane.³ Measurements are not done at higher scattering vectors because the intensity is very small in this region and, owing to the low power of our laboratory source (in contrast with a synchrotron source for instance), the statistical errors are too high. In solutions containing 5 or 10 wt% surfactant, the axial ratio for prolate ellipsoids is of the order of 1.65, which gives 2×26 Å for the minor axis of the whole particle and 2×43 Å for the major axis. Such a deformation does not affect viscosity measurements. The semiminor axis can be found equal to 26 Å though the molecule's extented length is 23 Å, the 3 Å corresponding to the hydration water.

It must be noted that the fits with oblate ellipsoids give volumes of the paraffinic core which are not compatible with the measured aggregation numbers: this volume is of the order of 50% or 60% of the volume of prolate objects.

All these measures were completed by light-scattering experiments. In the whole concentration range, the mean hydrodynamic radius is found constant and equal to 30 Å. This value seems a little too high in the hypothesis of spherical objects. Indeed, the length of the molecule of betaine can be crudely obtained from the length of the hydrophobic chain, the bond lengths, and the covalent radius of the atoms included in the polar region (namely, $-N^+(CH_3)_2CH_2COO^-$). One finds as said above a total length of about 23 Å. The excess would correspond to water of hydration and here would correspond to a thickness of 7 Å which seems quite high. On the other hand, in the spherical hypothesis, X-ray results give a radius of 26 Å, and even if it is not the same radius which is measured with the two techniques, the discrepancy seems too large. Finally, if one uses the values obtained with SAXS in the ellipsoidal hypothesis and one calculates the corresponding hydrodynamic radius,²⁰ one finds $R_{\rm H} = 30$ Å which seems to confirm the deformation of the aggregates. The constancy of $R_{\rm H}$ over all the studied concentration range allows us to consider that the dynamic scattering is not sensitive to the interactions.

Finally, a last sign seems to be in favor of nonspherical objects; it is the concentration invariance of the measured aggregation number. Indeed,²¹ the width of the distribution in N can be related to the variation of the average aggregation number with the volume fraction of micelles. If this variation is very low, the standard deviation must be low, too.

Ternary System. The results on aggregation numbers and viscosity are given in Figures 4, 7, and 8. It can be seen that addition of alcohol to binary solutions leads to an increase of the

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Figure 8. Effect of addition of alcohol on the surfactant aggregation number when starting from binary solutions (surfactant concentration: \blacksquare , 2; O, 5; \bullet , 10 wt%). ϕ_A is the volume fraction of alcohol.

aggregation number. But, even near the phase boundary, this aggregation number remains relatively low. We do not expect a very large growth in size (giant micelles).

Figures 4 and 7, where the evolution of η and N is shown as a function of $1 - \phi_w$ (ϕ_w is the volume fraction of water) when alcohol is added to binary solutions, show that, even for a little amount of alcohol, η quickly deviates from the straight line. Recall that for spheres a linear increase of η versus $\phi = 1 - \phi_w$ should be observed according to the relation $\eta = \eta_s (1 + 2.5\phi)$. The results shown in Figure 4 seem to indicate that when alcohol is added to the binary surfactant + water systems, either intermicellar interactions increase and/or micelles remain no longer spherical or quasi-spherical. However, for volume fraction of objects up to 15%, N seems to remain quasi-constant while η still increases (although this increase is lower). This last behavior can be explained by the fact the true N values are in fact larger than the ones reported in Figure 7. Indeed, intermicellar exchange of the probe has been observed in the fluorescence experiments for the systems containing alcohol. Such intermicellar exchanges are due to either fragmentation-coagulation or collisions with tem-porary merging of the micelles.^{10b} In the case of collisions the reported N values are true values. In the case of fragmentation-coagulation N is obtained only under a given assumption, 10b and if this assumption is not valid, the N values obtained from fluorescence experiments are then underestimated. Although the exchange process observed here for zwitterionic surfactants might mainly be due to collisions, the fragmenation-coagulation process cannot be ruled out.

The shape and the size of the aggregates are obtained more precisely by small-angle X-ray scattering.

The adjustable parameters are the same as for binary solutions. But there is a new unknown, the partition coefficient of alcohol between the micelles and the water. It is determined by using a two-pseudophase model.²² the micelles and the water. The resulting values for the alcohol-to-surfactant molar ratio y in the aggregates are given in Table III. Another parameter is the distribution of the alcohol in the micelles, that is, the proportion of alcohol located in the core and the palisade layer, which affects the two electron densities $\rho_{\rm pol}$ and $\rho_{\rm par}$.

TABLE III: Parameters of Prolate Ellipsoids in the Ternary System n-Dodecylbetaine/Water/Pentanol^a

system							
$\overline{C_{\text{TA}}} \times 10^2, \text{ g/g}$	$C_{\rm A} \times 10^2, {\rm g/g}$	N	N*	ν	у	$\rho_{\rm par}$	$ ho_{ m pol}$
2	0	80	80	1.65	0	0.276	0.350
1.98	1	140	140	4.5	0.781	0.272	0.348
1.97	1.5	160	160	5.5	1.15	0.273	0.336
1.96	1.75	172	172	6	1.32	0.273	0.332
1.96	1.9	190	200	6.5	1.4	0.272	0.333
5	0	82	80	1.65	0	0.276	0.352
4.95	1	120	120	4.2	0.448	0.270	0.347
4.9	2	166	165	5.5	0.91	0.272	0.346
4.83	3.5	250	250	6.75	1.62	0.270	0.340
10	0	81	80	1.65	0	0.276	0.348
9.8	2	154	155	4.8	0.526	0.273	0.346
9.6	4	202	200	6.4	1.08	0.271	0.342
9.5	5	218	210	6	1.37	0.270	0.341
9.45	5.5	214	210	5.5	1.53	0.270	0.350

^aN is the measured aggregation number, N^* is the aggregation number used in the fitting procedure, ν is the axial ratio of the whole particle, and γ is the molar ratio of alcohol to surfactant in the aggregate. In the ternary solutions, the small half-axis of the core is taken equal to 12 Å and the polar thickness is assumed to be constant and found to be 12 Å. ρ_{par} and ρ_{pol} are respectively the electron densities of the paraffinic core and the polar shell $(e/Å^3)$.



Figure 9. Fit of experimental data (\bullet) with the form factor of a prolate ellipsoid. $C_{\text{betaine}} = 9.8 \text{ wt\%}$; $C_{\text{alcohol}} = 2 \text{ wt\%}$.



Figure 10. Fit of the same experimental data (\bullet) as that in Figure 9 with oblate ellipsoid. The volume of the core is incompatible with the aggregation number.

Two shapes for the micelles are tested, namely, oblate and prolate ellipsoids. (The aggregation number is incompatible with spherical aggregates.) As it is shown in Figures 9 and 10, the experimental curves can be fitted with both models. Nevertheless, the volume of the paraffinic core obtained from the oblate model is incompatible with the surfactant aggregation number measured by fluorescence, while the prolate model is self-consistent. It thus

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seems that an oblate shape must be ruled out. Table III gives the values of the parameters giving the best fits. The electron densities given in the table are obtained from fits. The obtained values must be close to the theoretical ones calculated by using the partial volumes of the constituents of the core or the polar region of the micelle. It can be observed, on the experimental data, that the maximum located at $s \approx 0.02$ Å⁻¹ has disappeared. This is due to the decrease of the electron density of the polar region (and thus of the contrast between this region and the water), owing to the location of the alcohol in this region. The axial ratio of the whole particle, for instance, for the most concentrated binary solution, is found to be 4.2 if 2 wt% alcohol is added. This seems to agree with the viscosity measurements: addition of a little amount of alcohol to binary solutions induces a break in the variation of η . It is reasonable to think that oblate aggregates with small ellipticity must not give such a behavior.

For the most concentrated solutions, for which the aggregation number seems to reach a limit, the experimental data can be fitted by using the measured aggregation numbers. Moreover, if one considers that the aggregation number is underestimated, it seems that oblate objects are still incompatible. Indeed, if one overestimates the N value of, for instance, 25%, prolate ellipsoids also give satisfying results.

In the studied range of concentration, the axial ratio of the aggregate reaches a value of about 7, which gives a total length of 350 Å if the smallest dimension is equal to 50 Å. (The volume fraction of micelles here is of the order of 15%.)

Conclusion

Combination of several experimental techniques, and especially small-angle X-ray scattering and fluorescence probe study, allows us to obtain the size and the shape of the micelles in ternary systems involving alcohol. Although in the binary solutions one cannot affirm whether or not the aggregates are deformed, in ternary systems the oblate shape seems to be ruled out, while prolate ellipsoids lead to self-consistent results. It must be emphasized that it is the knowledge of the aggregation number and the fact that our experiments are mean-resolution experiments (and not low-resolution ones) which allow us to be almost sure that the aggregates are elongated, even in binary systems. The phase diagram of the n-dodecylbetaine is very similar to those obtained with ionic surfactants, alcohol and brine. The trend in the micellar sizes and shapes with the change in alcohol concentration can thus be useful in the study of the structure and the stability of the isotropic and ordered phases found in all these systems.

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Synthesis and Structural Characterization of a Lithium Galloslicate with the Zeolite **ABW Framework**

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The syntheses and characterization of gallo- and aluminogallosilicates with the zeolite ABW framework, LiGa_xAl_{1-x}SiO₄·H₂O with x = 0, 0.5, and 1.0, are described. The structure of the hydrated gallosilicate, x = 1.0, has been determined at 19 and 298 K by full profile analyses of time-of-flight and monochromatic powder neutron diffraction data, respectively. The framework geometries are similar to that described earlier for hydrated aluminosilicate zeolite Li-A(BW). There is complete ordering of silicon and gallium in the framework. Lithium cations are found at only a single, fully occupied site that is coordinated by three framework oxygen atoms and by the sorbed water molecule in a near-regular tetrahedral arrangement. Despite there being only partial D for H exchange in the sample, the positions and occupancies of the two protons of the sorbed water molecule were successfully determined and refined. The orientation of the water molecules is such that both protons are involved in hydrogen-bonded linkages to framework oxygen atoms, although the distances involved are relatively long and the connections are therefore weak. The relatively long mean Si-O bond lengths of 1.647 (5) Å (19 K) and 1.634 (5) Å (298 K) are considered to reflect the combination of a direct influence of the lithium cations, the acuteness of the Si-O-Ga angles, and the direct effect of Ga substitution. Condensed δ -Eucryptite phases, LiMSiO₄, M = Al, and Ga, derived from the ABW materials by air calcination are orthorhombic, space group $Pna2_1$ or Pnam, with a = 10.055 (3) Å, b = 6.636(2) Å, and c = 4.968 (2) Å [M = Ga] and a = 9.901 (3) Å, b = 6.594 (2) Å, and c = 4.940 (1) Å [M = Al], and are probably closely related structurally to the zeolite ABW framework.

Introduction

Barrer and White in 1951 discovered two zeolitic products in crystallizations from the (Li₂O)-(Al₂O₃)-(SiO₂)-(H₂O) system.^{1,2} The structure of the first of these lithium aluminosilicate zeolites, termed Li-A(BW), was determined by Kerr in 1974^3 from powder X-ray diffraction data. The ABW framework⁴ consists of 4-, 6-, and 8-membered rings, the last defining channels that run parallel

to the crystallographic c direction of the orthorhombic unit cell. Kerr's structural results have been substantiated by a recent single-crystal X-ray diffraction study.⁵ Solid-state nuclear magnetic resonance (NMR) measurements have also been reported.6

We have been investigating the scope and structural consequences of framework gallium substitution in zeolite structures.⁷⁻¹²

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