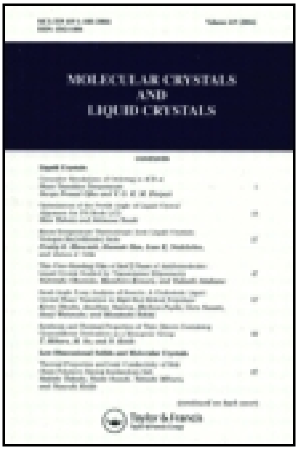

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Amphiphile Diffusion in Cubic Lyotropic Mesophases

Thomas Bull [a] & Björn Lindman [a]

[a] Division of Physical Chemistry 2, Lund Institute of Technology, Chemical Center, P. O. Box 740, S-220 07, Lund, Sweden

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Amphiphile Diffusion in Cubic Lyotropic Mesophases

THOMAS BULL AND BJÖRN LINDMAN

Division of Physical Chemistry 2,
Lund Institute of Technology,
Chemical Center, P. O. Box 740,
S-220 07 Lund, Sweden

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The phase equilibria of systems composed of a surface-active agent and water are usually complex, involving normal solutions, crystalline phases, and a variety of liquid crystalline phases. The most powerful method for investigating the structure of the liquid crystalline phases is X-ray diffraction. (A review on this subject has recently been given by Fontell[1].) While these X-ray studies have led to some generally accepted structural models for several anisotropic mesophases there is still considerable controversy regarding the structure of the optically isotropic cubic mesophases which form in many binary and ternary soap systems. An important reason for this is that for many cubic phases the number of X-ray reflections obtained is insufficient for an unambiguous indexing of the diffraction pattern.

The proposed structures of the cubic phases can be divided into two groups[1], i.e. structures based on net-works of rod-like units over macroscopic distances and structures based on spherical or globular aggregates of small extension. In addition, a combination of these two structural principles has been proposed[2].

It is apparent that independent methods are required for resolving the ambiguities in the interpretation of X-ray diffraction data. In this respect self-diffusion studies should be helpful. In particular we would expect the amphiphile translational mobility over macroscopic distances to be much greater if the amphiphile forms a continuous structure than if it does not.

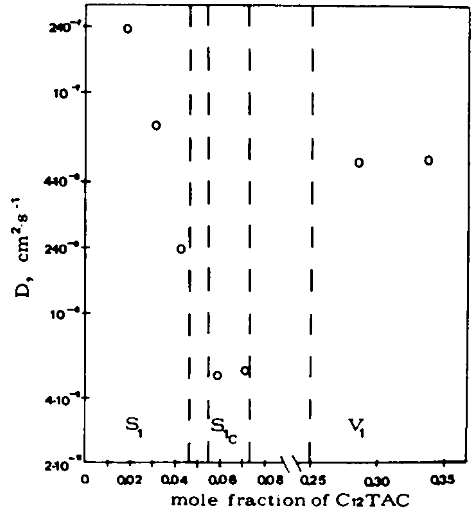

FIGURE 1 Diffusion coefficient, D, of dodecyltrimethyl ammonium chloride ($C_{12}TAC$) at 29°C in the $C_{12}TAC$-D_2O system as a function of the mole fraction of $C_{12}TAC$. S_1 denotes amorphous isotropic solutions and S_{1c} and V_1 optically isotropic mesophases (see text). The phase boundaries were taken from the phase diagram for the $C_{12}TAC$-H_2O system[3].

The binary system dodecyltrimethylammonium chloride ($C_{12}TAC$)-water appears suitable for comparing amphiphile diffusion for different isotropic phases. As shown by Balmbra *et al.*[3] three isotropic phases can be formed at the same temperature, i.e. an amorphous solution and two optically isotropic cubic mesophases.

Figure 1 shows the translational self-diffusion coefficient, D, of $C_{12}TAC$ for some samples composed of $C_{12}TAC$ and D_2O at a temperature of 29±1°C. D was determined using proton NMR[4] with a Bruker BK-322s pulsed NMR spectrometer employing pulsed magnetic field gradients.

In order to cover several orders of magnitude in our measurements, we have assumed that the magnitude of the field gradient times the gradient pulse width ($g\delta$ in Eq. 6 of ref. 4) can be replaced by the area of the gradient pulse as measured by a plot of the current through the gradient coils versus the time. With this assumption we have been able to relate all of our measurements to the diffusion constant for water, which was taken to be $2.5 . 10^{-5}$ cm^2/s (extrapolated from the data reported in ref. 5) at 29°C. Combining the errors in these assumptions and the measurements, we estimate the errors in the D values to be 15-20%.

In Table 1 the approximate proton transverse relaxation times, T_2, are given for some samples composed of $C_{12}TAC$ and D_2O at a temperature of 26±1°C. T_2 was determined using the Gill-Meiboom modification of the Carr-Purcell pulse sequence. Since in the surfactant cation non-equivalent protons are present the transverse relaxation is somewhat non-exponential and the reported T_2 values constitute averages over all the protons. In accordance with what would be expected from the cubic structure of the phases no static dipole-dipole interactions were found.

The samples were prepared by placing weighed amounts of $C_{12}TAC$ and D_2O into test tubes which were sealed off. The samples were stored at elevated temperature for long times with occasional centrifugation to ensure homogenization. The S_{1c} samples were slowly cooled through the transition temperature from amorphous solution to liquid crystalline solution.

In binary systems of water and a surface-active agent cubic mesophases may appear at least at three different places in the phase diagram [1] namely between the micellar aqueous solutions (denoted S_1) and the normal hexagonal phase (middle soap), between the normal hexagonal phase and the lamellar phase (neat soap) and between the lamellar phase and the hexagonal phase of the reversed type. We denote these cubic mesophases S_{1c}, V_1 and V_2, respectively.

In earlier work the model based on spherical units was generally favoured but in recent work especially by Luzzati *et al.*[6-8] and by Fontell[1,9] the continuous network structure is assumed to be correct for the V_1 and V_2 phases. The rod-like network should consist of the amphiphile in the V_1 phase and of water and the polar groups of the amphiphile in the V_2 phase. The S_{1c} phase has been studied to a much smaller extent[2,10]. Tardieu and Luzzati[2] proposed a structure composed of an amphiphile network forming cages in which spherical

TABLE 1

Average proton transverse relaxation time, T_2, at 26°C of optically isotropic samples composed of dodecyltrimethylammonium chloride ($C_{12}TAC$) and heavy water. S_1 denotes amorphous isotropic solutions and S_{1c} and V_1 optically isotropic mesophases (see text).

% by weight of $C_{12}TAC$	phase	T_2, ms
20.0	S_1	351
30.0	S_1	347
37.0	S_1	281
45.0	S_{1c}	84
47.0	S_{1c}	82
50.0	S_{1c}	80
84.0	V_1	46
87.0	V_1	34

aggregates are located but significant arguments can be raised against this structure[1].

It is apparent from Figure 1 that there is a strong and irregular variation of D with the surfactant content. In the S_1 phase, D decreases rapidly with increasing amounts of $C_{12}TAC$. Work on other soaps (see e.g. ref. 11) has shown that this concentration dependence can be well rationalized by taking into account the increasing fraction of aggregated soap with increasing concentration and the decrease in micellar translational mobility, arising from intermicellar interactions with increasing soap concentration.

It is not necessary to assume any changes in the aggregate units in order to explain the decrease in amphiphile translational mobility on going from the micellar solutions to the S_{1c} mesophase. The observations for the S_{1c} phase are, therefore, consistent with an ordered arrangement of micellar-like units. The very low translational mobility compared to the micellar solutions then reflects a low concentration of non-associated surfactant and large interaggregate interactions.

Recent studies by NMR[12] and ESR[13] have shown amphiphile lateral diffusion in similar systems to be relatively fast whereas our D values for the S_{1c} phase indicate that either 1) few continuous amphiphile aggregates extend over macroscopic distances or 2) lateral diffusion within an amphiphile network is somewhat inhibited. The rather long T_2 values for the amphiphile protons tend to favour the former explanation. This interpretation, however, is not consistent with the structural model proposed by Tardieu and Luzzati[2].

Without any fundamental change in the structural building-blocks the amphiphile translational mobility is expected to decrease monotonically with decreasing water content. This is exactly what is observed in the relaxation times reported in Table 1. Since T_2 is predominantly effected by interactions and motions over short distances and it is reasonable to assume that the dipole-dipole interactions which cause relaxation vary only moderately with sample composition it appears that the local motion is more hindered in the V_1 phase than in the S_{1c} phase. In the V_1 phase, D is greater by a factor of 10 than in the S_{1c} phase and also considerably greater than in concentrated micellar solutions. This finding can easily be rationalized by assuming that the V_1 phase contains a continuous network of amphiphile. A network structure is suggested by the location of the phase in the phase diagram (between the hexagonal and lamellar mesophases, see ref. 3) and in general has been favoured in recent X-ray diffraction studies[1,6-9].

Assuming that the amphiphile diffusion over macroscopic distances can be referred to motion within rodlike amphiphile aggregates, we have calculated a diffusion coefficient of about $7 \cdot 10^{-8}$ cm^2/s for motion along the amphiphile rods of the model pictured in ref. 6. This value can be compared to the lateral diffusion coefficient of $1.8 \cdot 10^{-8}$ cm^2/s[13] at 25°C in spin-labeled phosphatidylcholine multilayers. Soap diffusion coefficients at 80°C for different mesophases in the potassium laurate-heavy water system were found to be about $2 \cdot 10^{-6}$ cm^2/s [12,14].

In accordance with previous studies (see e.g. refs. 3 and 14-16) we observed the transverse relaxation time of the isotropic phases to be long (see Table 1) and static dipole-dipole interactions to be absent. This means that in a time short compared to the inverse dipole-dipole interactions the proton-proton vectors take up all directions with respect to the external magnetic field. For the V_1 phase, amphiphile lateral diffusion is rapid enough to average out the dipole-dipole couplings. For structures built up of globular units the averaging process may be due either to lateral diffusion or to rotation of the aggregates.

Partly on the basis of the high resolution NMR spectra of the amphiphile Winsor [17] has recently proposed that the amphiphilic cubic mesophases S_{1c}, V_1 and V_2 are built up of globular units being free to rotate. However, it appears that an averaging out of the direct dipole-dipole interactions can also occur by lateral diffusion and that our diffusion data are not consistent with the structure of the V_1 phase proposed by Winsor [17].

Our preliminary observations on the translational mobility of the surfactant in surfactant-water cubic mesophases suggest a convenient method for distinguishing between structural models which may not easily be discriminated using X-ray diffraction data. If a greater amphiphile translational mobility can be established for a mesophase than for micellar solutions it appears reasonable to assume that a continuous amphiphile network can be present.

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