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Structure of the lamellar and L_2 phases in the system sodium n-octylbenzene sulfonate/n-pentanol/water

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Résumé. — La structure de la phase isotrope L_2 apparaissant dans le système octylbenzène sulfonate de sodium/n-pentanol/eau est discutée à partir de résultats obtenus en diffusion centrale des rayons X. Ces résultats sont compatibles avec une structure locale lamellaire où une partie de l'alcool serait rejetée de la structure lamellaire. La longueur de corrélation d'une telle structure est à peu près dix fois plus faible que dans le cristal liquide lamellaire.

Abstract. — The structure of the isotropic phase L_2 occurring in the ternary system sodium octylbenzene sulfonate/n-pentanol/water is discussed on the basis of small angle X-ray scattering data. Experimental results are consistent with a local lamellar structure with a fraction of the alcohol expelled from the lamellar regions. The correlation length of this structure is about ten times smaller than is found in lamellar liquid crystals.

1. Introduction.

The structure of isotropic phases occurring in ternary systems composed of water/surfactant/alcohol is still being debated. Many models have been proposed. For example Ekwall [1] described the L_2 phase as water closed aggregates while Scriven suggested a bicontinuous structure [2].

The aim of this paper is to present the main results of X-ray investigations into the ternary system sodium octylbenzene sulfonate (OBS)/n-pentanol/water and to show that they are in good agreement with a theory developed by Parodi [3]. This theory, based on the elasticity of a lamellar liquid crystal, predicts a lamellar-type structure for L_2 .

Such a structure was suggested by Larsson [4], but the systematic study of the evolution of L_2 as a function of the water volume fraction allows us to extend this model. It is shown that a fraction of the alcohol is expelled from the lamellar structure. The lamellar volume fraction decreases when the ratio pentanol/OBS increases.

2. Results.

This study of the lamellar and L_2 phases is essentially based on X-ray measurements. The experimental procedure was described in a previous paper [5]. As was mentioned in that paper, small-

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angle X-ray diffraction spectra of the L_2 phase show a maximum. The position of this maximum depends strongly on the water volume fraction. If this maximum can be attributed to a repeat distance in the material, the behaviour of the L_2 and the lamellar phases appears very similar.

We thus studied the evolution of the liquid crystal when the water volume fraction ϕ_w increases at constant alcohol/OBS ratios (Fig. 1). The same investigation was carried out into the isotropic phase.

Fig. 1. — Schematic representation of the isotropic (L_1 , L_2) and lamellar (LLC) zones of the OBS/water/pentanol system at 25 °C. The lines are at constant pentanol/OBS ratio. These ratios are respectively 1.5 (1); 2.6 (2); 4.4 (3); 5.9 (4); 7 (5); 13.3 (6).

2.1 THE LAMELLAR PHASE. — Figure 2 shows the variation of the inverse of the interlamellar distance *versus* ϕ_w . The structure appears to be an expanding one [1] i.e. the repeat distance d can be represented by $1/d = (1 - \phi_w)/d_a$ where d_a is the thickness of the alcohol plus surfactant layer. It must be pointed out that the experimental points are located on the same straight line for all alcohol/OBS ratios. This means that the thickness of the amphiphile layer is practically independent of this ratio.

A study of the influence of the length of the alcohol on the lamellar structure shows that this thickness is proportional to the sum of the molecular lengths of the alcohol and OBS.

2.2 THE PHASE L_2 . — The same type of investigation was carried out into the L_2 phase. The variation of the scattering vector corresponding to the maximum with respect to ϕ_w is shown on figure 2. Here again, s varies linearly with ϕ_w in most of the diagram. In that respect the behaviour of the L_2 phase is similar to the behaviour of the lamellar phase. But the intersection with the ϕ_w axis, instead of being at $\phi_w = 1$, is now at a smaller value.

These experimental results suggest the following extension to the model proposed by Larsson. The phase L_2 has a local lamellar structure but part of the alcohol is expelled from it. In other words, the system becomes inhomogeneous. If ϕ_1 is the volume fraction of the lamellar structure, the thickness of the water is given by $d_w = d(\phi_w/\phi_1)$ where $d = d_a + d_w$. Then the linear function which gives the variation of the position of the maximum of the X-ray pattern with the volume fraction of the water is :

$$s = \frac{1}{d_a} \left(1 - \frac{\phi_w}{\phi_1} \right)$$

where ϕ_1 is the volume fraction of lamellar structure ⁽¹⁾.

⁽¹⁾ Let us note that the data are not compatible with a reversed hexagonal structure (where $s \sim \phi_w^{1/2}$) also proposed by Larsson.

Fig. 2. — Variation of the scattering vector corresponding to the maximum intensity in the small-angle X-ray diffraction patterns *versus* the water volume fraction. The numbers refer to the lines drawn in figure 1. In the lamellar liquid crystal, all the points are on the same curve. In the phase L_2 the intersection of the extrapolated lines gives the volume ratio of lamellar structure ϕ_l .

ϕ_l is given by the intersection of the curve $s = f(\phi_w)$ with the ϕ_w axis and d_a is given by the intersection of this curve with the s axis.

Table I gives the main parameters of the L_2 phase obtained from this model. The variations of d_a , when the ratio alcohol/OBS increases, are not significant compared to the accuracy of the experimental data. One can see that d_a is slightly larger than it is in the lamellar phase. In the LLC d_a is equal to $20.5 \pm 0.5 \text{ \AA}$ while in L_2 $d_a = 24 \pm 0.5 \text{ \AA}$. At present we are not able to explain this variation.

The broadening of the diffraction peak can be explained in terms of the short correlation length of the L_2 lamellar structure. An order of magnitude estimate of the ratio of the correlation

Table I. — *Parameters of the L_2 -phase assuming a local lamellar structure. The numbers in parentheses refer to the lines drawn on figure 1. The quantity of alcohol expelled from the lamellar structure increases when the overall [OBS]/[pentanol] ratio increases. d_a is the thickness of the amphiphile layer.*

[OBS]/[pentanol] ratio		lamellar volume fraction	$d_a \text{ \AA}$
Total	in the lamellar structure		
5.9 (4)	5.2	0.94	24.3
7.0 (5)	4.2	0.80	23.6
13.3 (6)	3.3	0.47	24.1

length in the lamellar liquid crystal to that in L_2 can be obtained by comparison of the half-widths of the diffraction peaks using Scherrer's formula for example [6]. It is about ten times smaller in the L_2 phase. In the water-rich corner of the L_2 phase, the behaviour changes. The maximum in the X-ray diagram remains constant as ϕ_w changes. This is still unexplained.

3. Conclusions.

The X-ray data for the lamellar liquid crystalline phase have been analysed on the basis of a purely steric model of water and lipidic lamellae. These swell as the volume fraction of water increases, the thickness of the amphiphile double layer (alcohol plus surfactant) remaining practically constant.

The results over a large region of the L_2 phase diagram are also consistent with a lamellar structure, but with a much shorter correlation length. This was expected from the analysis of Parodi. In contrast to the liquid crystal phase, a fraction of the alcohol is expelled from these lamellar regions. This fraction increases as the pentanol/OBS ratio increases. Such behaviour is somewhat at variance with the lamellar structure proposed by Larsson. As for the liquid crystal, the thickness of the amphiphile layer is constant. In the water-rich corner (where s is not a linear function of ϕ_w) and the alcohol-rich corner, L_2 has a different behaviour. Investigations into these regions are in progress. Preliminary results for the quaternary system obtained by addition of decane seem to indicate that here again [7] the validity of the water sphere model is dubious.

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