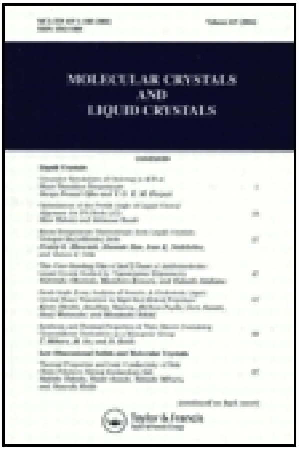

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The Lamellar Phase of Nonionic Surfactants: The Interplay Between Headgroup Hydration and Mobility

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The Lamellar Phase of Nonionic Surfactants: The Interplay Between Headgroup Hydration and Mobility

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Variable temperature measurements (288–303°K) of the inter-lamellar spacing in conjunction with order parameters derived for the α-carbon segment of the alkyl chain of $C_{12}(EO)_4$ in the lamellar phase show an inter-dependence of headgroup hydration and the dynamic structure of the bilayers. Different behaviors observed for samples containing less than 30% (w/w) of water compared to those at higher hydrations and are a result of either absence or presence of "bulk" water respectively for the two situations.

INTRODUCTION

The wide importance of the surfactant phase behavior has been the subject of numerous studies.[1–4] In particular, the temperature dependent properties of non-ionic surfactant association behavior has attracted great interest e.g., the hydration properties of a series of polyoxyethylene surfactants have been studied extensively by Tiddy *et al.*[5,6] Surfactants of this type may be written in the general form $C_n(EO)_m$ where n is the number of carbon atoms in the hydrophobic chain and m is the number of oxyethylene groups in the hydrophilic headgroup. Their results showed that the properties depend sensitively on composition, temperature and the chemical structure of the surfactant. The dynamics of their lamellar phases have been the subject of investigation[7–11] as a result of their ability to incorporate relatively large amounts of solubilized materials.

It is thought that the interaction between the EO groups and water is responsible for the complex temperature dependent phase behavior. Interactions between the polar headgroup in layered structures have been studied[12–15] with surfactant adsorbed on mica sheets. Hydration forces between the surfactant layers were derived from measurements of water vapor pressures[16] and ^2H and ^{17}O NMR properties[17–20] in lamellar liquid crystals. Similarly, ^{13}C and ^1H relaxation times have been used to study[21,22] the configurational flexibility of the surfactant hydrophobic chains. Head group conformational mobility has also been discussed[11] using order parameters derived from selectively deuterated surfactant analogues.

As part of a program to investigate the behavior of amphiphiles in lamellar liquid crystals, experiments have been performed using analogue of $C_{12}(EO)_4$ deuterated selectively at the carbon position on the alkyl chain adjacent to the headgroup chain. This compound, α-$C_{12}(EO)_4$-d_2, allows study of the processes occurring or affecting the water-hydrocarbon chain interface. In this respect, these studies complement those which focussed on the chain dynamics in the bilayer and headgroup as well as those concerning the aqueous component and its interaction with the surfactant.

EXPERIMENTAL

Materials

Tetraoxyethylene n-dodecyl ether, $C_{12}(EO)_4$, (Nikko Chemical Co., Japan) was >98% pure in terms of headgroup chain length as determined by gas chromatography. α-$C_{12}(EO)_4$-d_2 was synthesized as described elsewhere[11] and was >98% pure. Water was deionized and double distilled using an all glass apparatus.

Sample Preparation

A stock surfactant solution was prepared containing 5% (w/w) of α-$C_{12}(EO)_4$-d_2 dissolved in $C_{12}(EO)_4$. Samples with different weight ratio of water/surfactant were prepared by weighting the components directly into N.M.R. tubes (10 mm o.d.), thoroughly mixed with a vortex mixer and then centrifuged. This procedure was repeated several times until a homogeneous phase, as viewed with polarized light, was produced.

N.M.R. Spectroscopy

^2H N.M.R. spectra were obtained using a spectrometer (I.B.M. NR/AF-250) operating in the Fourier Transform mode and a resonance frequency of 38.398 MHz for deuterium. Measurements were made in the temperature range of 273–323°K (Bruker VTU-1000 temperature control unit) with a stability of better than ±1.0°K.

Low Angle X-Ray Diffraction

Bubble free samples were introduced into special thin walled capillary glass tubes (0.7 mm diameter) and both ends of the tube sealed. The sample tube was mounted to a brass plate with a hole (2 mm diameter) in the beam. Measurements were performed using Ni filtered copper K_α radiation (λ = 1.54 nm) with reflections recorded on a position sensitive detector (Tennelec PSD-1100). Typical acquisition times (1024 Channels, MCA (Canberra) data acquisition system) were a few minutes. The temperature of the sample was controlled by water circulating through the sample chamber from a temperature controlled reservoir. A temperature sensor mounted close to the sample was used to monitor the temperature and showed variation of ±0.5°K during the time of operation at a set temperature.

RESULTS

A partial phase diagram (Figure 1) of lamellar liquid crystal region was determined for the purpose of this study. The lamellar phase region is similar but somewhat narrower comparing to that obtained by Tiddy[5] for the same system. When the composition was just outside the phase boundary, it may initially look like one phase, however, a phase separation occurred after longer period of storage. This was also confirmed from ^{2}H-NMR which showed an isotropic central peak in addition to the doublet of characteristic powder pattern of anisotropic mesophase.

Quadrupolar splittings for the α-position of $C_{12}(EO)_4$ were obtained for lamellar phase samples (Figure 2) with water contents in the range 20–55% (w/w) from 273 to 323°K and are presented in Table I. Values between 8 and 15 KHz are observed depending upon the temperature and composition which are in agreement with the previously observed[9] values obtained using perdeuterated surfactant. Plots of these splittings as a function of temperature (Figure 2) reveal a monotonic decrease with increasing temperature for water contents less than 30% (w/w). In the case of samples with water contents greater than 30%, the splitting passes through a maximum value, the position of which is shifted to higher temperature with increasing water contents.

The compositional dependencies of the quadrupolar splitting of the α-position are presented (Figure 3) at different temperatures. Below a water weight fraction of 30%, the variation with composition changes from increasing with increasing water content for temperature above 293°K to decrease with increasing water content for temperature below 283°K. Above 30% (w/w) of water in sample, the splitting decreases with increasing water composition; the rate of this decrease was similar for temperatures in the range 298 to 323°K but at low temperatures, the rate of decrease becomes larger the lower the temperature.

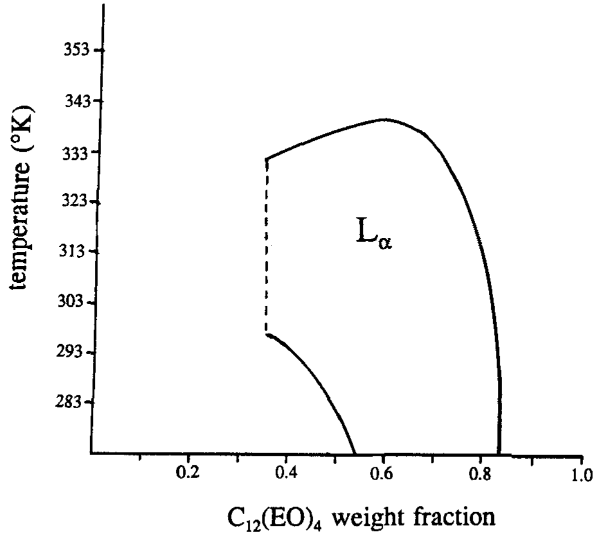

FIGURE 1 Partial phase diagram of the lamellar liquid crystal region (Lα) of $C_{12}(EO)_4$-H_2O system in the temperature range 273 to 343°K.

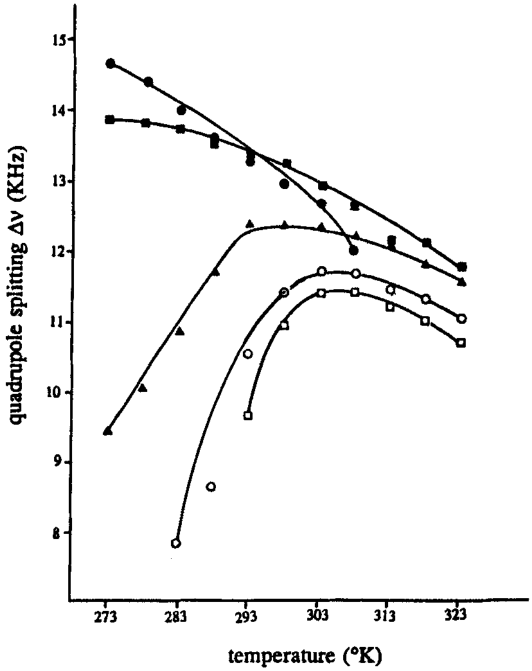

FIGURE 2 Quadrupole splittings of α-position of $C_{12}(EO)_4$ as a function of temperature at various $C_{12}(EO_4)/H_2O$ ratios: ●, 80/20; ■, 70/30; ▲, 60/40; ○, 50/50; □, 45/55.

The interlayer spacings of the lamellar liquid crystal (Figure 4) show a linear increase with increasing water/surfactant weight ratio. The slope of the plots increases with temperature up to 298°K becoming temperature independent above this temperature. Extrapolation of the data to infinite dilution shows the intercept of decrease by ca. 8% with increasing temperature in the range 288 to 298°K.

DISCUSSION

The interlayer spacing of the lamellar liquid crystal measured as a function of solvent content can usually[4, 23, 24] be expressed as

$$d_s = d \times \phi_s^n \tag{1}$$

where d_s is the thickness of the solvent layer, d is the total interlayer distance and ϕ_s is the volume fraction of the solvent. The value of exponent n varies with the degree of penetration of the solvent into the bilayers formed by the amphiphile. A value of $n = 1$ indicates no solvent penetration whereas $n = 0$ shows complete penetration.

In case of non-penetration i.e., $n = 1$

$$d_s = d \times \phi_s \tag{2}$$

TABLE I

Quadrupole splitting (Hz) of the α-position of $C_{12}(EO)4$ at various $C_{12}(EO)_4/H_2O$ weight ratio at different temperatures

T(°K)	$C_{12}(EO)_4/H_2O$ (wt/wt)				
	80/20	70/30	60/40	50/50	45/55
273	14,672	13,891	9,471	-	-
278	14,428	13,768	10,095	-	-
283	13,964	13,708	10,815	7,849	-
288	13,500	13,561	11,717	8,666	-
293	13,354	13,256	12,426	10,522	9,679
298	12,975	13,232	12,389	11,474	10,998
303	12,670	12,914	12,353	11,730	11,449
308	12,048	12,658	12,291	11,706	11,401
313	-	12,451	12,157	11,498	11,205
318	-	12,194	11,852	11,303	11,059
323	-	11,791	11,656	11,058	10,754

- : two phase

The total interlayer distance can be divided into two parts; namely, the solvent layer thickness, d_s, and the bilayer thickness, d_a. Thus,

$$d = d_a + d_s \tag{3}$$

from Equations (2) and (3) it follows that

$$d_a = d \times \phi_a \tag{4}$$

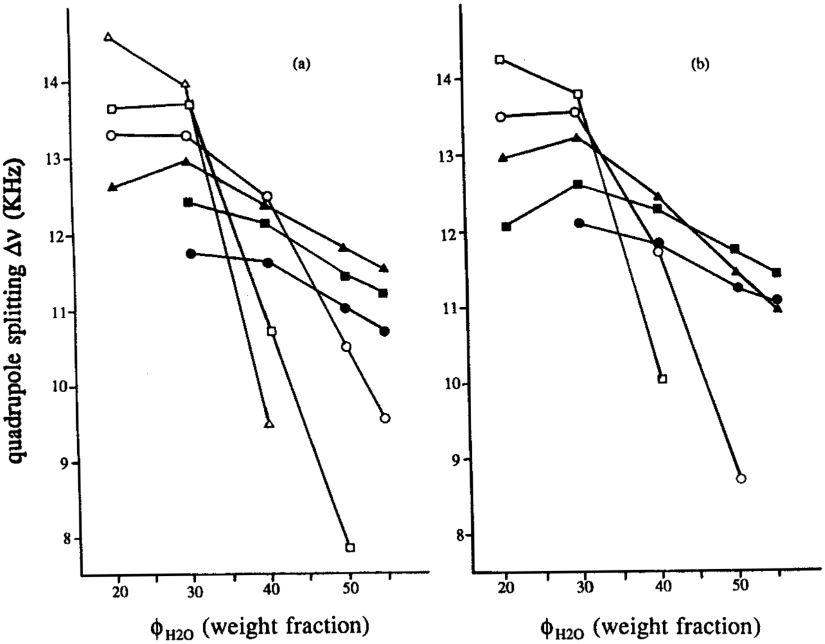

FIGURE 3 Quadrupole splittings of α-position of $C_{12}(EO)_4$ as a function of water weight fraction at variable temperature (°K) for water-$C_{12}(EO)_4$ mixtures: (a) △, 273; □, 283; ○, 293; ▲, 303; ■, 313; ●, 323. (b) □, 278; ○, 288; ▲, 298; ■, 308; ●, 318.

where ϕ_a is the volume fraction of the amphiphile. Substitution of Equations (2) and (4) into (3) gives

$$\begin{aligned} d &= d_a + d_a \frac{\phi_s}{\phi_a} \\ &= d_a + d_a \frac{\phi_s}{(1 - \phi_s)} \end{aligned} \tag{5}$$

If some solvent penetration of the bilayers occurs i.e., Equation (2) no longer holds, providing the bilayer structure is not affected, Equation (1) can be re-written as

$$d_s = d \times \phi_s \times n \tag{6}$$

where n is the fraction of solvent that stays in the solvent layer. Then,

$$d = d_a + n \times d_a \times \frac{\phi_s}{(1 - \phi_s)} \tag{7}$$

A plot of the interlayer spacing, therefore, against $\phi_s/(1 - \phi_s)$ should yield a straight line with an intercept d_a and slope equal to $n \times d_a$. A value of n smaller

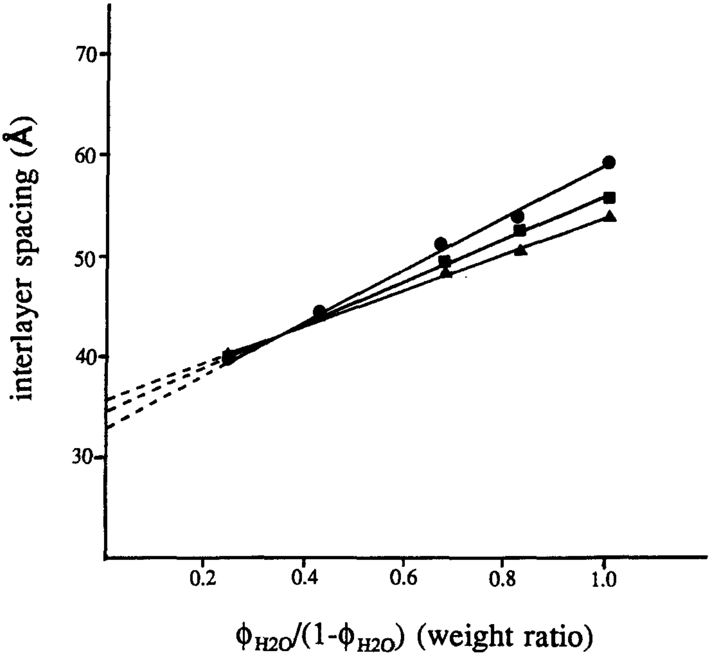

FIGURE 4 Interlayer spacing as a function of water weight ratio for $C_{12}(EO)_4$-H_2O system at variable temperature (°K): ●, 298, 303 and 308; ■, 293; ▲, 288.

than one implies that a penetration of solvent has occurred and the interlayer spacings is reduced. In this situation, the fraction of solvent that penetrates into bilayer can be expressed as

$$\begin{aligned} P(\%) &= (1 - n) \\ &= \frac{(d_{\text{cal}} - d_{\text{exp}})}{(d_{\text{cal}} - d_a)} \times 100\% \end{aligned} \tag{8}$$

Here d_{cal} is the interlayer spacing calculated by assuming no penetration and d_{exp} is the experimentally observed value from small angle X-ray diffraction. Table II presents the percentage of water penetrated into surfactant bilayer calculated from Equation 8 and Figure 3.

It can be seen (Figure 4) that in the temperature range 288 to 298°K that these plots not only have different slopes but also different d_a values. If it is assumed that the penetrated solvent had not affected the bilayer structure only the slopes should have changed for different penetrations. The extrapolated value d_a at infinite dilution, however, should not have been affected. One possibility for this phenomenon could be a result of changes of temperature. However, increasing temperature, in principle, should decrease the order of surfactant chain which was in contrary to the plot of Figure 2. These results, therefore, indicate that penetration of the water into the surfactant bilayer does perturb its structure.

TABLE II

The percentage of water penetrated into lamellar bilayer

Temperature (°K)	% of water penetrated
298, 303 and 308	20
293	37
288	49

In general, increasing temperature will cause dehydration of a nonionic surfactant[5,6] and reduce the amount of penetration of water between the surfactant molecules. If it is assumed that the effect of penetrated solvent is proportional its volume fraction, the extrapolated value of d_a will be same as that of the unpenetrated bilayer; this was not observed (Figure 4). It appears, therefore, that the effect of water on the bilayer structure has an optimum set of conditions. At low temperature (<298°K) the penetration of solvent is not only higher but also causes a decrease in the bilayer thickness. The apparent disordering of the bilayer can be the result of the effects of increased hydration or an increasing angle of tilt between the axis defining the normal of amphiphilic chains and director, or both.

In the temperature range 298 to 308°K, the interlayer spacing does not change either because the degree of water penetration is unchanged or the bilayer structure is insensitive to temperature or, if not, these two effects cancel each other. Some tentative support to the second possibility comes from the observation (Figure 2) of a decreasing order parameter at the α-methylene position as the temperature increased in this range.

A maximum in the order parameter was observed (Figure 2) with increasing temperature at high (>40%) water content. From a thermodynamic point of view, increasing temperature will increase the entropy in the system and a monotonic decreasing order parameter would be expected. However, to the contrary, in the low temperature range (<293°K) the order parameter shows an increase with increasing temperature. It is known[25] that the value of the order parameter depends upon the molecular packing in lamellar phase; in particular, it increases with decrease in the area available to each surfactant molecule in the bilayer interface. Dehydration of the surfactant headgroups will reduce the area/molecule of the surfactant in the bilayer leading to an increase in the order parameter for segments in the interface such as α-methylene studied here. This is supported by the low angle X-ray observations (Figure 4) of the system in this temperature range that show increasing d-spacings for a given water content with increasing temperature in the range 288 to 298°K.

For lower water content samples (≤30% w/w), the order parameter does not pass through a maximum and decreases monotonically with increasing temperature. At these concentrations, the amount of water bound to the headgroups is smaller

TABLE III

The no of water molecules penetrated per $C_{12}(EO)_4$ molecules at different temperature

$C_{12}(EO)_4/H_2O$ (wt/wt)	80/20	70/30	60/40	50/50	45/55
(no. of $H_2O)/C_{12}(EO)_4$	5.02	8.62	13.4	20.1	24.6
	(no of water penetrated)/$C_{12}(EO)_4$				
298, 303 and 308 (°K)	1.04	1.72	2.68	4.02	4.92
293 (°K)	1.85	3.18	4.95	7.43	9.10
288 (°K)	2.46	4.22	6.56	9.84	12.0

than that required to fulfill the maximum possible solvation i.e. ca. 9 moles H_2O/mole surfactant. This can be seen from a calculation that assumes, to a first approximation, that structural changes in the bilayer can be neglected. Calculation of the amount of water penetrated into the bilayer, r, leads to values (Table III) as high as 12.0 moles H_2O/mole of surfactant for highest water content sample at the lowest observation temperature (288°K) down to ca. 1.0 mole H_2O/mole of surfactant for the lowest water content at the highest temperature (>298°K). The bilayer distance used here included the contribution of the oxyethylene polar head groups. With such a long EO-chain, it is reasonable to consider the penetrated water as the hydration water of the surfactant. This should be equal to the r-value calculated from a combination of vapor pressure and N.M.R. measurements obtained previously (Tiddy) when the water content is high. At 298°K, a value for r of 4.94 is obtained in good agreement the value of 5 given the previous work[17] for a sample containing 24.6 moles H_2O/mole of surfactant.

At each composition, it should also be noted that at 288°K the amount of penetrated water represents 50% of the total water in the sample across the whole composition range. The general increase in r value with decreasing temperature may be thought of in terms of an increase in the number of water molecules being influenced sufficiently by the headgroup chains to become regarded as hydrated rather than being "free" or like bulk water in physical properties. For compositions containing less than 30% (w/w) of water, all of the water molecules are essentially bound to the EO groups and no "free" fraction exists. A loss of dynamic motion or loss of conformational freedom in the EO chains at low temperatures leads to the observed increased order in the bilayer/water interfacial region.

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