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Lamellar liquid crystals of zwitterionic surfactants with hydrocarbon and polyisobutylene chains

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Lamellar liquid crystals of zwitterionic surfactants with hydrocarbon and polyisobutylene chains

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Surfactants from either polyisobutylene or alkylsuccinic anhydrides derivatized with diethanolamine in a 1:1 molar ratio with hydrocarbon and polyisobutylene chains of similar length formed lamellar liquid crystals *in situ* and also with added water. The repeat distance between layers was determined using low angle X-ray diffraction (LAXD), and the water penetration into the hydrocarbon space in the lamellar structure was calculated.

The results revealed a significantly increased repeat distance for the polyisobutylene chain surfactants compared to the alkyl analogues. The water penetration was significantly greater for a surfactant with a decyl chain compared to the one with a dodecyl chain and was intermediate for the polyisobutylene based surfactant.

1. Introduction

The structure of lyotropic liquid crystals has been extensively investigated after Ekwall's [1] pioneering research in the area. Both the structure and dynamics of such systems are by now reasonably well described [2–10]. For a long time, the investigations were concentrated on systems in the which the mesogenic compound was in water, but the early discovery by Moucharafich [11] showed that liquid crystals could also be formed with polar organic substances, by replacing water, and a long series of publications [12–18] has followed this introduction.

In this article we introduce liquid crystals formed by surfactants in which the alkyl chain is replaced by a polyisobutylene polymer. The repeat distance in a lamellar liquid crystal was significantly changed when the alkyl chain was replaced by a polyisobutylene chain of similar length.

2. Experimental

2.1. *Materials*

The polyisobutylene-substituted succinic anhydride (PS) of average molecular weight 500 (Ex. Exxon Chemicals, U.S.A.) was derivatized by reacting PS and diethanolamine in equimolar quantities at ~60°C in a hexane medium. Hexane was removed by distillation [19–21].

Similarly, the decyl-, dodecyl- and tetradecyl-succinic anhydrides (Humfry Chemicals, U.S.A.) were derivatized with diethanolamine at ~80°C [21].

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2.2. *Low angle X-ray diffraction*

The interlayer spacings of liquid crystalline phases were determined by low angle X-ray diffraction (Siemens Crystalloflex 4) with a Tennelec detector system (PSD 100). The path length was 50 cm and 0·7 mm capillaries with 0·01 mm walls were used. The measurements were made at 40 kV, 30 mA and room temperature (22·5°C).

3. Results

The repeat distances for the lamellar liquid crystals of the three surfactants are given in figure 1. The alkyl chain-based surfactants with decyl and dodecyl chains displayed a linear dependence on the water to surfactant volume ratio with repeat distances in the 30–45 Å range, while the polyisobutylene chain variety gave an initial value of 51·5 Å, with an initial increase to 71 Å. The surfactant with a C_{14} alkyl chain was crystalline and did not accept water.

Infrared spectra of octylamine, octanoic acid and the diethanolamine derivative of dodecylsuccinic anhydride are given in figure 2. The absorbances, important for this investigation, are found in table 1 and show that ionization of some carboxylic groups ($1552·5\,\mathrm{cm}^{-1}$) occurs and also that there is a hydrogen bond between the ionized and non-ionized carboxylic groups ($1959·8\,\mathrm{cm}^{-1}$).

4. Discussion

The repeat distances in figure 1 provide significant information about the structures present. In the first instance, the interlayer spacings without water may be compared to the lengths of the fully extended hydrocarbon chains. The chains of the two shorter surfactants (C_{10} and C_{12}) in the fully extended form should cover a length of 12·9 and 15·4 Å, respectively [22]. With the remainder of the surfactant covering approximately 6 Å, a repeat distance of 38 and 43 Å would be expected for fully extended chains. The

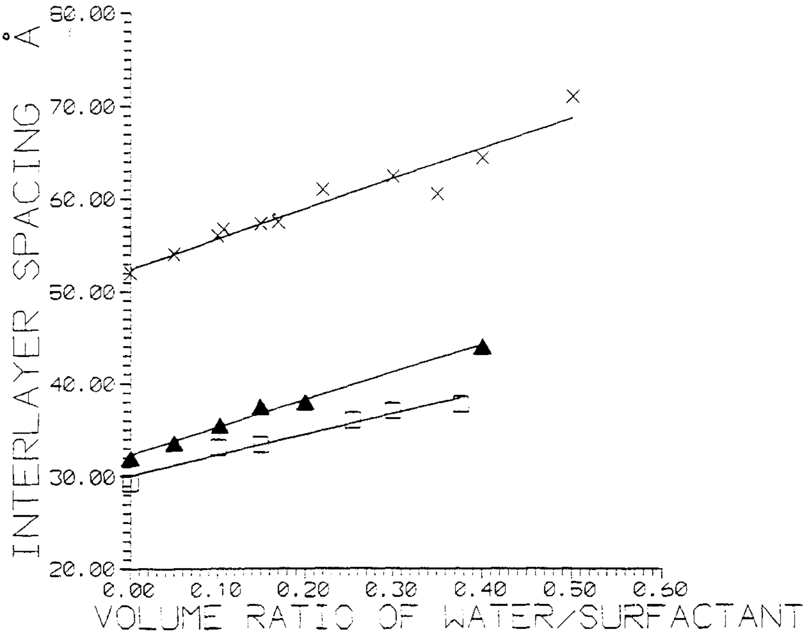


Figure 1. Interlayer spacings for the (□) decyl; (▲) dodecyl and (×) polyisobutylene surfactant.

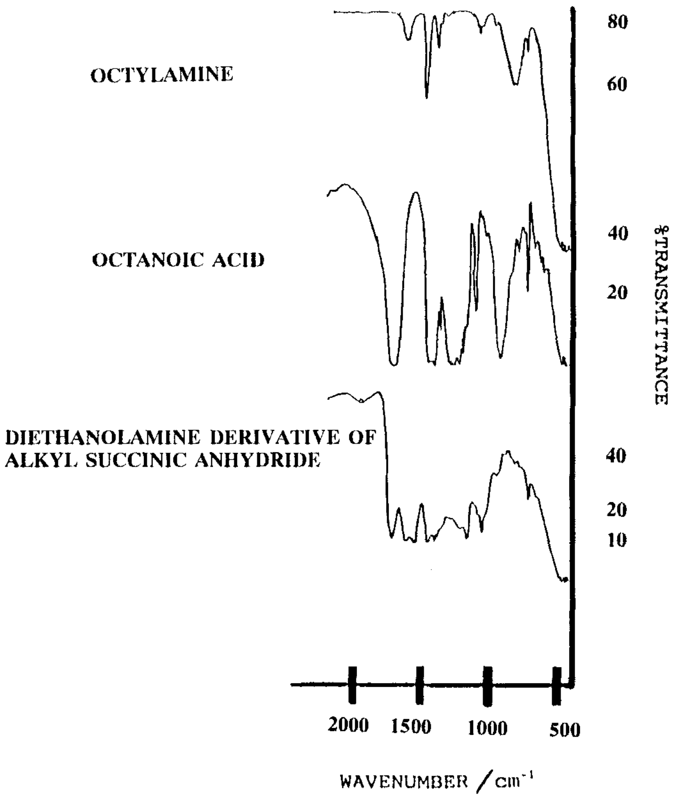


Figure 2. Infrared spectra of octylamine, octanoic acid and the diethanolamine derivative of alkylsuccinic anhydride (C_{12}).

Table 1. Vibration frequencies for the alkylsuccinic anhydride surfactant carboxylic group.

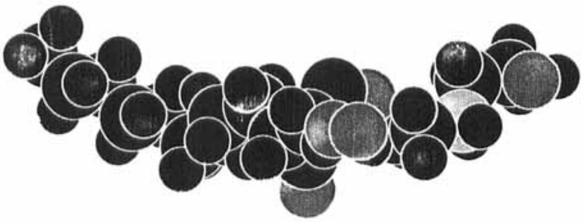
Vibration frequency	Form of vibration
937·5	Out-of-plane deformation vibration
1552·5	Anti-symmetric stretching vibration of an ionized carboxylate group
1959·8	Carboxylic acid –OH group H-bonded to an ionized carboxylate group or iminium group

experimental results of 30 Å (79 per cent) and 32 Å (74 per cent) indicate a considerable disorder in the hydrocarbon chains. The shortening due to disorder may be quantifed in terms of a number of *trans*-carbon–carbon bonds being changed to *cis*-conformations. Simple geometry of the hydrocarbon chain reveals a reduction in chain length of approximately 1·5 Å for such a change. Hence, the shortening of 8–11 Å corresponds to a change of approximately 5 and 7 *trans*- to *cis*-conformations. Such a number is large for C_{10} and C_{12} hydrocarbon chains and the magnitudes certainly merit discussion as to the underlying cause.

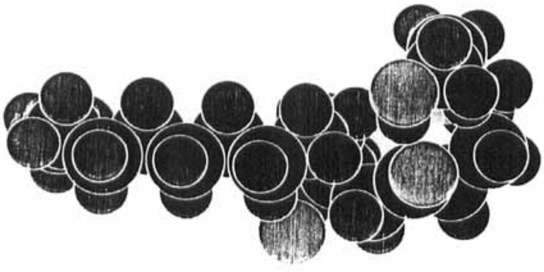
Without further experimental evidence, we attribute the cause of the chain disorder to the lateral space requirements due to the conformation of the head group of the surfactants. This conformation depends on the relative degree of protonation of the carboxylic and the imino groups. The infrared spectra, shown in figure 2, provide information about the ionization state of the carboxylic group. The disappearance of the out-of-plane deformation vibration at 937·5 cm^{-1} revealed that no carboxylic group *dimers* with internal hydrogen bonds were present. Furthermore, the absorption at 1552·5 cm^{-1} which is from the anti-symmetric stretching vibration of an ionized carboxylate group showed this group to have been formed. In addition, the absorption at 1959·8 cm^{-1} arises from a carboxylic acid OH group hydrogen bonded to an ionized carboxylate group or an iminium group [23].

Given this information, the possibility that the long chains of the head group could be arranged in parallel with the extended conformation shown in figure 3 (*a*), is virtually ruled out and the most probable conformation is with the head group coiled, figure 3 (*b*). The latter conformation permits the iminium group to be adjacent to the ionized carboxylate group and also allows a hydrogen bond between the ionized and non-ionized carboxylate groups. Whichever of these two bonds is the predominant one in the lamellar liquid crystal, the influence of the curled conformation, causing a disorder of the long hydrocarbon chain, is the decisive factor for the small interlayer spacing. A cross-sectional area of the head group, which is double that of the hydrocarbon, leads to a pronounced reduction of the chain order, as well as of the interlayer spacing. Hence, the interlayer spacing values obtained are realistic.

On the other hand, the interlayer spacing for the surfactant with the polyisobutylene chain was different. An experimental interlayer spacing of 52 Å leaves 8 Å for the polar part of the molecule after the length of the polyisobutylene chain has been taken into account. 8 Å corresponds approximately to an extended chain of six carbon atoms, a reasonable value for the conformation according to figure 4.



(*a*)



(*b*)

Figure 3. (*a*) Diethanolamine derivative of alkylsucccinic anhydride. 'Linear' conformation. (*b*) Diethanolamine derivative of alkylsuccinic anhydride. 'Curled' conformation.

Figure 4. Surfactant comprising polyisobutylene (C_{14}) chains. Liquid crystalline packing conformation.

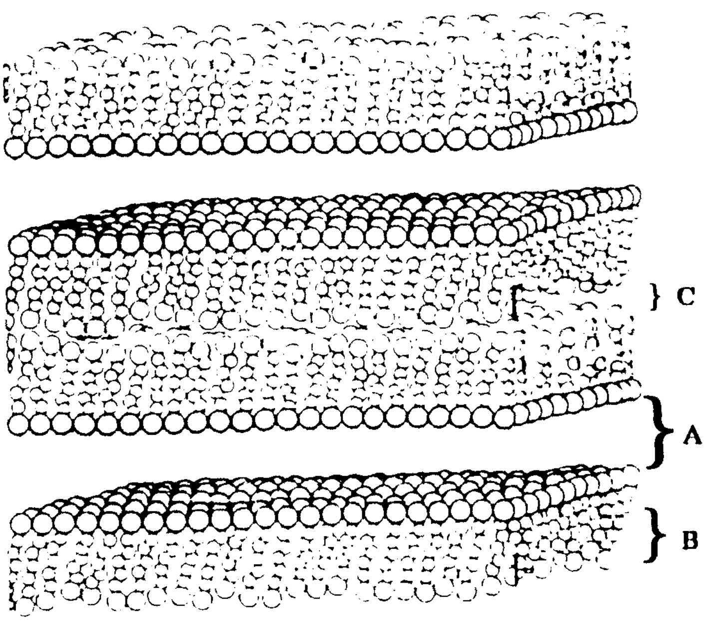


Figure 5. General view of a lamellar liquid crystal. A, layers of water molecules and polar groups; B, hydrocarbon chains; C, methyl group layers and space between them.

The variation of interlayer spacing with water content is a measure of the degree to which the water penetrates the hydrocarbon chain region B, figure 5. This fraction penetrating the amphiphile layer may be calculated from straight geometry. The variation of interlayer spacing with added water is

$$d = d_0(1+R)/(1+\alpha R) \qquad (1)$$

in which d is interlayer spacing, d_0 is its value at zero solvent content, R is the volume ratio of water to amphiphile and α is the volume fraction of water penetrating into the B region, figure 5. The α values from the experimental results in figure 1 are given in table 2 where PIB is polyisobutylene.

These values of the interlayer spacings are accurate to within ±1 Å (90 per cent confidence); this is a fact that should be taken into consideration when discussing the α

Table 2. Interlayer spacings and penetration values.

Surfactant	*R*	*d*	α
C_{10}	0	29·3	—
	0·036	32·6	−0·37
	0·051	32·3	0·22
	0·101	33·1	0·33
	0·150	33·4	0·46
	0·254	36·0	0·32
	0·300	37·0	0·30
	0·376	37·7	0·36
C_{12}	0	32·0	—
	0·050	33·7	−0·06
	0·101	35·7	−0·13
	0·150	37·8	−0·18
	0·199	38·1	0·04
	0·394	43·8	0·05
PIB	0	52·0	—
	0·050	54·0	0·22
	0·100	56·0	0·21
	0·108	56·5	0·18
	0·150	57·0	0·33
	0·170	57·1	0·39
	0·220	61·5	0·22
	0·298	62·0	0·29
	0·350	60·0	0·49
	0·398	64·2	0·33
	0·498	70·9	0·19

values in table 2. Hence, it may be concluded that the penetration of water into the hydrocarbon chain zone B of the polyisobutylene surfactant is significant. Furthermore, the fact that the penetration values show a moderate increase with the water content indicates a limited conformational change of the head group due to the presence of water.

The surfactants with the aliphatic chains present a different picture; the α values, despite their lack of precision, show a trend. Increased amounts of water resulted in an increase in the α values, especially in the case of the C_{10} surfactant. It is tempting to interpret these values as differences in water penetration only, but this is unlikely to be the case. Instead, the determining factor is probably conformational changes of the head group. In the absence of water, the conformation shown in figure 3 (*b*) is the most likely to be present, on the basis of the X-ray and IR results.

With this structure in mind, and given that the α values are related both to head group conformational change and to water penetration, the following description is proposed. Initial addition of water relaxes the strong hydrogen bonds between the ionized carboxylate group, the carboxylic acid group and the iminium ion, as has been demonstrated earlier [23]. This relaxation of structure results in a conformational change from the curled version of figure 3 (*b*) to the linear version of figure 3 (*a*). An increase in interlayer spacing takes place as a result of the more extended conformation. Under these conditions, application of formula (1) leads to anomalously low values of α and extension of the hydrocarbon chain results in a negative α value.

The magnitude of the interlayer spacing increase from head group conformational change may be estimated. A transition of shape from that in figure 3 (*b*) to (*a*) results in an increase of the order of 1·5 Å, when the polar chains are packed in parallel. In addition, an increase in interlayer spacing is expected through the reduced disorder of the hydrocarbon chain, when the area per head group is reduced upon a conformational change from figure 3 (*b*) to (*a*).

The initial increase in interlayer spacing of the two hydrocarbon chain surfactants was followed by a slower increase, see figure 1. This reduced increase in interlayer spacing is expected when the head groups are in a parallel packing mode according to figure 3 (*a*). The water now has access to the space between head groups which become transversely more and more separated as the water content increases. Such a change is reflected in the positive penetration for high water values.

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