A Lamellar Liquid Crystal with a Vegetable Oil

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ABSTRACT: The molecular arrangement was studied in the sodium octanoate and cetyltrimethylammonium bromide (CTAB) system, a lamellar liquid crystal, before and after the addition of a vegetable oil [refined, bleached and deodorized (RBD) palm olein] by means of small-angle x-ray diffraction and optical microscopy. Results from the small-angle x-ray showed the RBD palm olein molecules to be partitioned between the nonpolar methyl group layers for both systems. The water molecules, located between the polar head groups, showed less penetrating tendency into the layered structure of cationic surfactant than into the anionic one, both before and after addition of RBD palm olein.
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KEY WORDS: Cetyltrimethylammonium bromide, optical microscopy, RBD palm olein, small-angle x-ray diffraction, sodium octanoate.

In our previous paper (1), we were concerned with the effect of a Malaysian vegetable oil or refined, bleached and deodorized (RBD) palm olein on the lamellar liquid crystalline structure of water combined with sodium octanoate/octanoic acid, 3:2, or with cetyltrimethylammionium bromide (CTAB)/hexanol, 7:3, and we observed the optical patterns between crossed polarizers in a microscope. The results indicated that some dislocation or perturbation exists after addition of RBD palm olein, which disrupts the molecular arrangement in the structure but retains its lamellar structure. This result merits a determination of the molecular arrangement in the lamellar liquid crystalline before and after addition of this vegetable oil. In this report, we present results of small-angle x-ray diffraction (SAXS) as developed by Luzatti and co-workers (2,3). This technique complements optical observations (4), can be used to determine the interlayer spacing in the lamellar liquid crystalline and provides information about location and partition of molecules between different parts of the lamellar structure (5–8). The lamellar liquid crystalline structure has a large solubilization ability due to its dual properties (hydrophilic and lipophilic) and a high degree of order (9). Solubilization of a compound by such structures has been studied extensively (10–12), reflecting its importance in industrial applications.

EXPERIMENTAL PROCEDURES

Materials. The surfactants and hexanol for the preparation of the lamellar liquid crystalline structure were purchased from Sigma Chemical Co. (St. Louis, MO) and were of highest purity (>99%). The RBD palm olein was obtained from the Malaysian Palm Oil Research Institute (PORIM) (Bang, Selangor, Malaysia), and its fatty acid content was analyzed by gas–liquid chromatography (Table 1). The iodine number based on the hydrocarbon content was 58.4.

Preparation of sample. Liquid crystal samples for the x-ray studies were prepared as follows. First, the surfactants were combined with hexanol at a water content of the sample varying from 30 to 40%. The samples were mixed by repeated centrifugation in a sealed 7-mm sample tube, vortexed and allowed to equilibrate to 30 ± 0.2°C for five days. Next, the RBD palm olein was added to the samples, and the water content was adjusted to 30–40%. The mixed samples were then checked by cross polarizers, optical microscopy and SAXS to establish their phase behavior.

SAXS. The small-angle x-ray measurements were obtained with a Rigaku-Denki (Tokyo, Japan) Small-Angle Scattering Goniometer Model 1 with a Philips 1120/90 X-ray Generator (40 kV and 40 mA). Nickel-filtered copper radiation was used, and the diameter of the ring was determined by a double-beam recording Microdensitometer Mk IIIC (Joyce, Loebl & Co. Ltd., London, England).

TABLE 1
Fatty Acid Compositions of Refined, Bleached and Deodorized Palm Olein

Fatty acids		Percentage
Lauric	C12:0	0.2
Myristic	C14:0	1.0
Palmitic	C16:0	39.8
Stearic	C18:0	4.4
Oleic	C18:1	42.5
Linoleic	C18:2	11.2
Others		0.9

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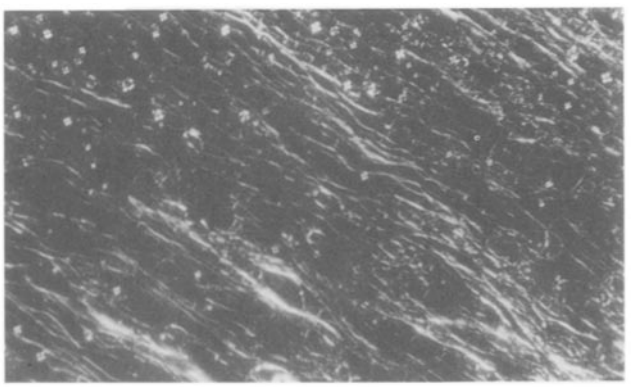
RESULTS

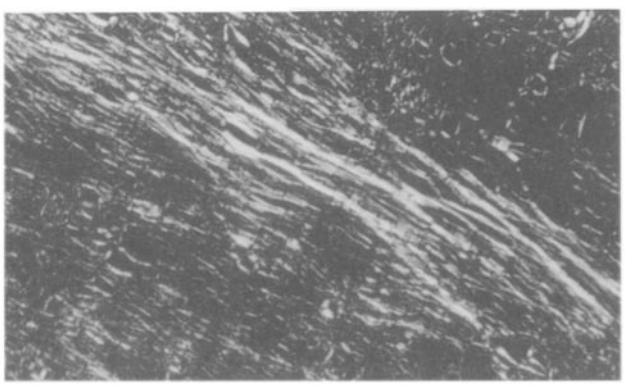
The typical lamellar liquid crystalline structure used in this investigation was formed by the addition to water of the ionic surfactant/cosurfactant mixture over a concentration range of 30–40 wt%. The overall lamellar liquid crystalline structure was maintained after the addition of RBD palm olein to the structure. This behavior is illustrated by the optical pattern of CTAB systems in Figures 1 and 2. The small-angle x-ray photograms (Fig. 3) reveal the anisotropic properties by the difference in intensity of the rings for different orientations. This behavior is typical of a lamellar liquid structure (13).

The calculated interlayer spacings from the small-angle x-ray diffractogram patterns were plotted against water ratio in the range of 30–40 wt%, corresponding to the weight ratios of 0.4–0.67. The interlayer spacing of the cationic CTAB/hexanol/water lamellar liquid crystal increased from 38.2 to 44.5 Å in the interval used (Fig. 4).

Addition of 5 wt% RBD palm olein to CTAB + hexanol increased the interlayer spacing slightly by 1 Å when the water content was maintained at 40 to 40%. Subsequent addition of 10 wt% RBD palm olein further increased the interlayer spacing from 41.1 to 46.4 A with retained dependence on the water content.

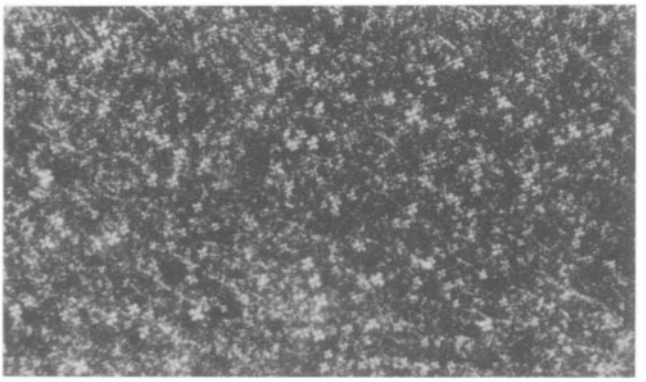


(a)

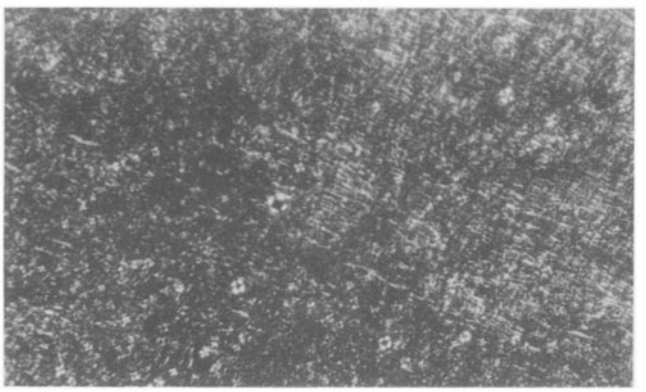


(b)

FIG. 1. Optical patterns of cetyltrimethylammonium bromide/hexanol (7:3) at (a) 30% and (b) 40% water.



(a)



(b)

FIG. 2. Optical patterns of cetyltrimethylammonium bromide/hexanol (7:3) after addition of 5% refined, bleached and deodorized palm olein at (a) 30% and (b) 40% water.

The behavior for the anionic surfactant sodium octanoate/octanoic acid/water before and after addition of RBD palm olein is shown in Figure 5. The interlayer spacing of the lamellar liquid crystalline structure, prior to the addition of RBD palm olein, increased from 27.7 to 30.9 Å with increased water content. Upon addition of 5 wt% oil, based on the amphiphile combination, the interlayer spacing increased from 28.0 to 31.9 Å with increased water content.

DISCUSSION

The results provide information about the molecule arrangement in the lamellar liquid crystal containing RBD palm olein, with two features of interest. First, the geometrical dimensions in the lamellar structure (Fig. 6) are obtained and, second, the results furnish information about the amount of water penetrating from zone A to zone B (Fig. 6). Both features are based on the change of interlayer spacings with water content.

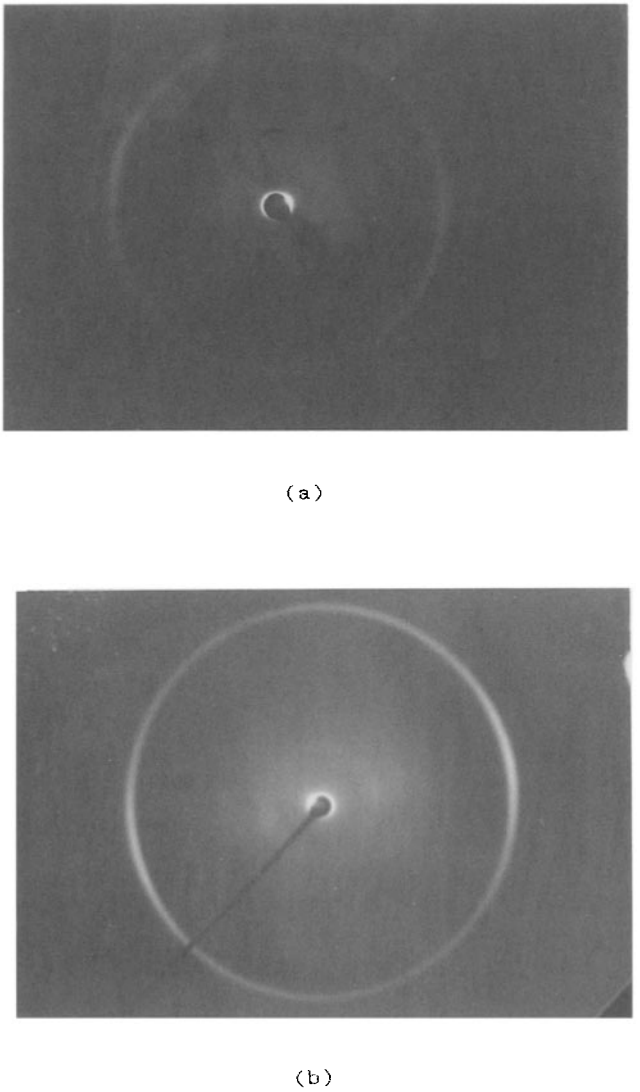


FIG. 3. X-ray photograms of (a) cationic and (b) anionic systems.

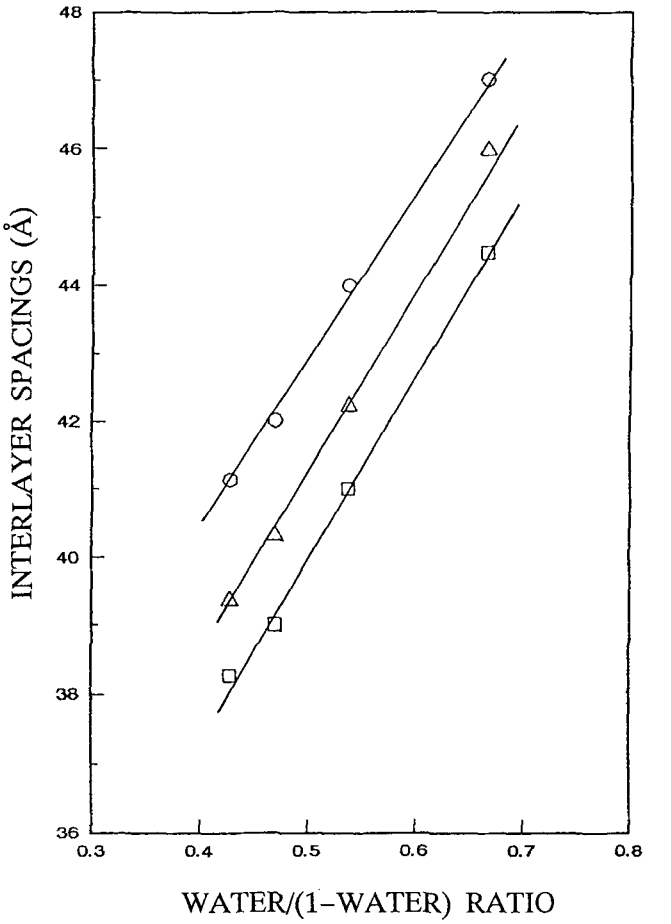


FIG. 4. Variation of interlayer spacing with water fraction for the cationic systems: □, cetyltrimethylammonium bromide (CTAB); △, CTAB + 5% refined, bleached and deodorized (RBD); ○, CTAB + 10% RBD.

Discussion of the influence of palm oil is not meaningful until the conditions are clarified in the lamellar liquid crystal without the oil. The comparison (Fig. 6 and Table 2) shows the interlayer spacing extrapolated to zero water, which is a measure for the extension of the amphiphilic part of the structure, d_o (Fig. 7). The values, 25.2 Å for the cationic system (Table 2) and 21.8 Å for the anionic one, are informative when compared to distances of 28.8 and 19.8 Å, respectively, calculated for maximally extended chains. The cationic combination shows a lower value than that of fully extended chains, which is expected because of disorder with gauche conformation along the chains.

The anionic structure, on the other hand, gave an extrapolated spacing in excess of the value calculated maximally extended chains. Such a result may only be explained by some of the amphiphile chains being located in the space between the terminal methyl group layers, C (Fig. 6). A 10% increase of the interlayer spacing would translate to approximately 20% of the acid molecules being in the C layer (Fig. 6), assuming that the more hydrophilic soap molecules are all anchored at the A/B interface (Fig. 6).

The interlayer spacings of both surfactants are plotted together in Figure 7 and show a significant difference in the slopes for the two surfactants. The lamellar liquid crystal of the cationic surfactant exhibits a value twice that of its anionic counterpart. The thickness of the amphiphilic layer is obtained by extrapolation of the interlayer spacings in Figures 4 and 5 to zero water contents (5). The values are given together with the values of the slope for the straight lines (Table 2).

The table shows a regular increase of the extrapolated values of the interlayer spacing, d_o, except for the composition after the addition of RBD palm olein in the anionic system. The extrapolated value is the same as for the lamellar liquid crystal of the anionic sodium octanoate system. However, the slopes of the cationic systems are steeper than those of the anionics. The slope also indicates the same value for all the cationic systems.

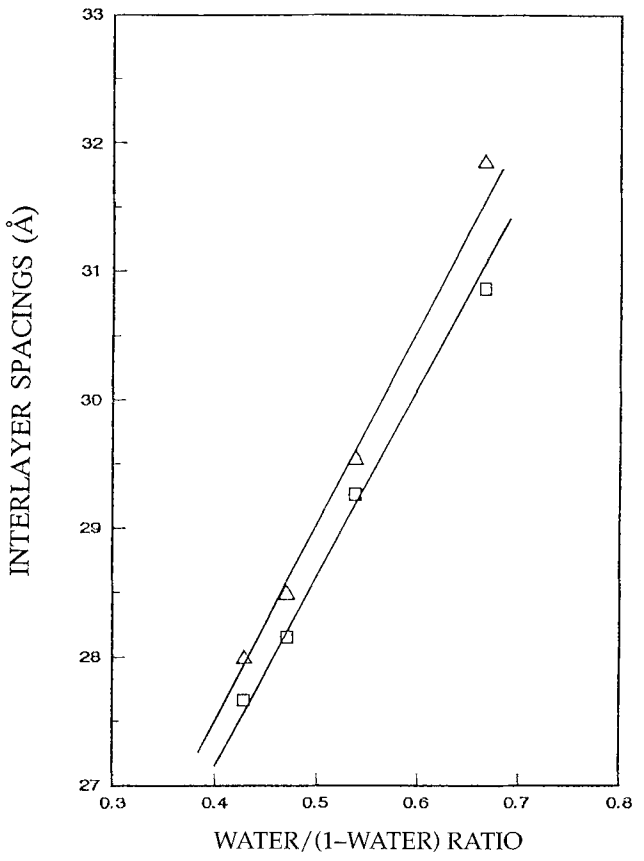


FIG. 5. Variation of interlayer spacing with water fraction for the anionic systems: □, sodium octanoate; △, sodium octanoate + 5% refined, bleached and deodorized.

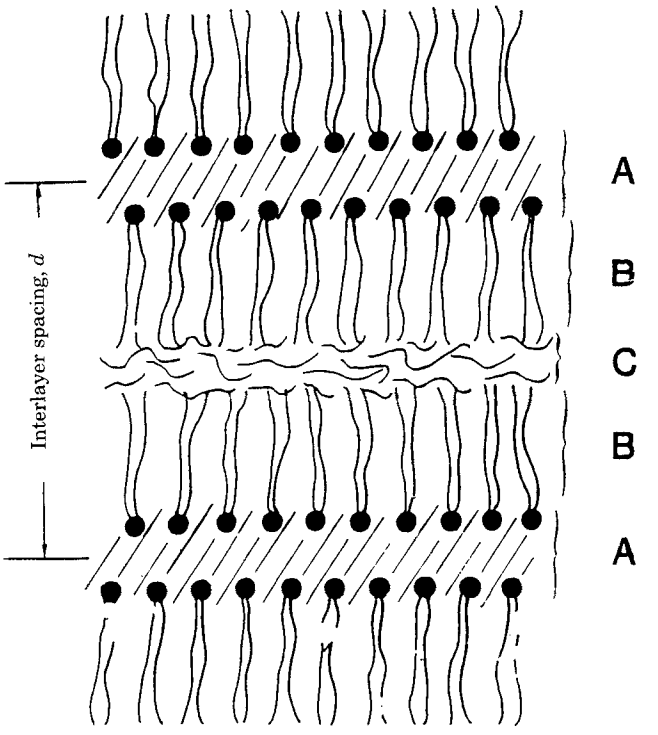


FIG. 6. The structure of a lamellar liquid crystal may be divided into three zones: (A) the water layer and the polar layer; (B) the methylene groups of the hydrocarbon chain; and (C) the terminal methyl group layers and the space between them.

Furthermore, the results demonstrate that lamellar liquid crystalline structures are formed with RBD palm olein over the range of 30–40% water content. This is evident by the optical patterns and x-ray diffractograms. The result also reveals that water, partitioned between the polar head groups (zone A in Fig. 6), exhibits a lower penetrating effect in the cationic system. The higher slope value (Table 2) for the cationic liquid crystal speaks to this behavior. The RBD palm olein, however, does not have a pronounced effect on the water added in this system because the same slope is obtained before and after addition of this compound.

Therefore, the dislocation observed in the optical pattern (Figs. 1 and 2) may be explained by the location of the added RBD palm olein. It is obvious that the increase of interlayer spacing would be proportional to the added volume, provided the compound were localized between the methyl groups (zone C in Fig. 6) in the layered structure, and that no change in interlayer spacing would be observed if the added compound entirely penetrated the palisade layer (zone B in Fig. 6) of the structure. This can be illustrated by the equation:

$$d_0^{\text{calc}} = d_a^o\,(1 + \phi_r/\phi_a) \qquad [1]$$

TABLE 2
Values for the Extrapolated Interlayer Spacings and Slopes of the Straight Lines[a]

Compound	$d_{o'}$ (Å)	Slope
Cationic (CTAB)		
0% RBD palm olein	25.2	28.6
5% RBD palm olein	26.8	28.6
10% RBD palm olein	30.0	28.1
Anionic (sodium octanoate)		
0% RBD palm olein	21.8	14.1
5% RBD palm olein	21.8	14.8

[a]CTAB, cetyltrimethylammonium bromide; RBD, refined, bleached and deodorized.

in which d^{oa} is the extrapolated interlayer spacing in the amphiphile/cosurfactant lamellar structure, ϕ_r is the added RBD palm olein and ϕ_a is the volume of the amphiphile/cosurfactant combination.

From Equation 1 it is clear that the interlayer will increase with added RBD palm olein. Formal calculation with this

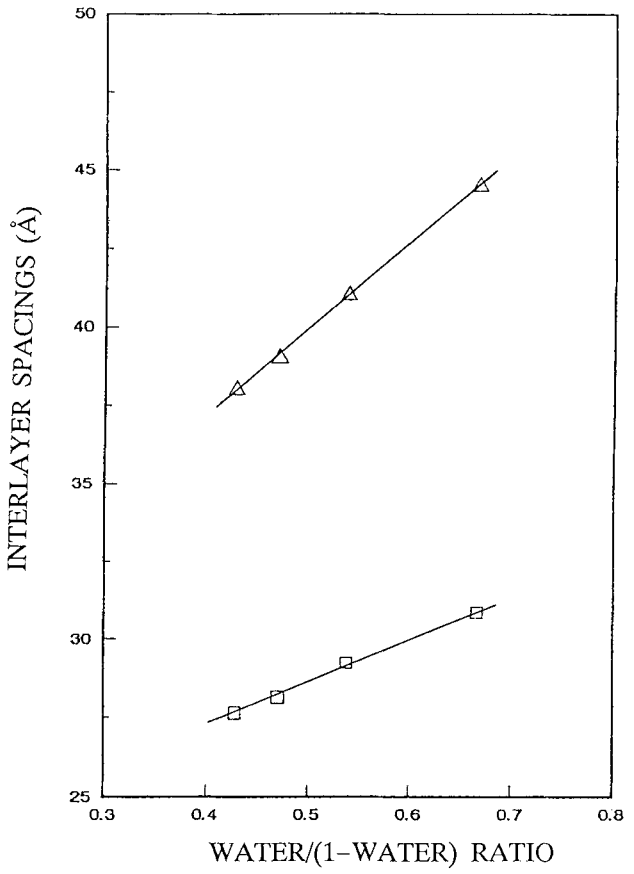


FIG. 7. Variation of interlayer spacing with water fraction for both systems without refined, bleached and deodorized palm olein: △, cationic; □, anionic system.

equation is, however, omitted because the authors feel that it is adequate to postulate the location of RBD palm olein by interpreting the slopes obtained for the various straight lines (Table 2). The fact that the extrapolated interlayer spacing is increased and the slope is maintained is suggestive enough to postulate that the RBD palm olein penetrates zone B (Fig. 6) and that, at higher levels, it is located mainly in zone C (Fig. 6) of the layered structure. This location, which resulted in higher extrapolated interlayer spacings, is the contributing factor to the dislocation in the observed optical pattern. The smaller value for the extrapolated interlayer spacing may be due to the tilt or disorder of the extended hydrocarbon chains. A formal calculation, assuming a fully extended C_{16} hydrocarbon chain, gives a value of 37.8 Å, which represents a difference of about 12 Å. This reduction may correspond to approximately six gauche bends in each chain.

The behavior of RBD palm olein in the anionic liquid crystal, however, is interesting. Upon the addition of RBD palm olein, the interlayer spacing (Fig. 5) increases in the range investigated but with a slight increase in the slope. An intercept between the two lines occurs at zero water content. This may be attributed to the fact that, at low water content, the added RBD brings all the fractions of sodium octanoate and octanoic acid, located in zone C of Figure 6, to penetrate into zone B of Figure 6, causing a temporary disorder in the organization. Calculation for the expected interlayer spacing at zero water content indicates that the hydrocarbon chain is fully extended. The disordering in the organization causes the optical pattern to change, as was observed under the polarizing microscope.

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