Malaysian Red Palm Oil in a Surfactant Association Structure

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ABSTRACT: The interlayer spacings of a lamellar liquid-crystalline structure, before and after incorporation of red palm oil, were determined by means of small-angle X-ray diffraction. The results agreed with earlier investigations on refined, bleached, and deodorized palm olein for the anionic host. The cationic host, after addition of red palm oil, showed two features of interest. First, the results showed a drastic decrease of its extrapolated interlayer spacing, and, second, the slope exhibited a value twice that of the host value.
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KEY WORDS: Cetyltrimethylammonium bromide, lamellar liquid crystal, red palm oil, small-angle X-ray diffraction, sodium dodecylsulfate.

In a previous contribution (1), we reported the molecular arrangement of Malaysian vegetable oil, or refined, bleached, and deodorized (RBD) palm olein, in the lamellar liquid-crystalline structure of water combined with an ionic surfactant/co-surfactant. The experimental results obtained from the small-angle X-ray diffractograms indicated that the RBD palm olein molecules were partitioned between the nonpolar methyl group layers. On the other hand, the presence of RBD palm olein reduced the tendency of water molecules to penetrate the layered structure.

In this short communication, we present results of small-angle X-ray diffraction (2,3) on a similar vegetable oil, but without removing the pigment in the oil. This resulting vegetable oil, red palm oil (RPO), is a new generation of cooking oil in which the pigments (carotenes) are retained in the refined oil. We feel that this investigation should fulfill an important need, especially with recent growing interest in the interaction of dye/pigment in amphiphatic structures such as microemulsions (4,5) and lamellar liquid crystals (6).

EXPERIMENTAL PROCEDURES

Materials. Components, source, and purity for the lamellar liquid-crystalline structure have been given previously (1). RPO was prepared by dissolving crude palm oil (CPO) in hexane (1:4, vol/vol). The oil solution was then refrigerated at 0°C overnight. The crystals formed (stearin fraction) were separated from the liquid fraction by filtration. After removal of the solvent, red olein (RO) was obtained. Phosphoric acid (0.15 wt%) was added to RO, followed by activated clay, to remove impurities. After filtration, RPO was obtained. The experiment was handled in a nitrogen atmosphere. The fatty acid composition was analyzed by gas–liquid chromatography (Table 1). Color was measured in a Lovibond Tintometer (Tintometer, Ltd., London, United Kingdom) in a 5.25″ Lovibond cell to give a value of 54 R. The carotene content was 242.5 ppm.

TABLE 1
Fatty Acid Composition of Red Palm Oil

Fatty acids		%
Lauric	$C_{12:0}$	0.2
Myristic	$C_{14:0}$	0.9
Palmitic	$C_{16:0}$	41.0
Stearic	$C_{18:0}$	3.2
Oleic	$C_{18:1}$	45.1
Linoleic	$C_{18:2}$	8.9
Linolenic	$C_{18:3}$	0.3
Arachidic	$C_{20:0}$	0.4

Sample preparation. Liquid crystal samples for the X-ray studies were prepared as described previously (1). RPO was added to the samples, vortexed, and centrifuged, which were then checked by cross polarizers, optical microscopy, and small-angle X-ray diffraction to establish phase behavior.

Small-angle X-ray measurement. A Rigaku-Denki (Tokyo, Japan) small-angle scattering goniometer Model 1 with a Philips 1120/90 X-ray generator (Philips, Tokyo, Japan) with an Ni-filtered Cu source gradient at 40 kV and 40 mA was used. The diameter of the ring was determined by a double-beam recording microdensitometer Mk IIIC (Joyce, Loebl & Co. Ltd., London, England).

RESULTS AND DISCUSSION

Interlayer spacings were calculated from the small-angle X-ray diffractogram pattern. The measurements were made for the components across the liquid-crystal phase range. The composition by weight of the cationic surfactant (cetyltrimethylammonium bromide (CTAB)/hexan-1-ol- and anionic surfactant [sodium dodecyl sulfate (SDS)/hexan-1-ol] were 70:30

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and 50:50, respectively. The water content of the former compositions was in the range of 30–40 wt%, while it was 45–55 wt% for the latter. This corresponds to volume ratios of water of 0.4–1.22. RPO [10 wt%/(surfactant + cosurfactant)] was then added to the liquid-crystalline samples.

A plot of the interlayer spacing (d) for the compositions with CTAB/hexan-1-ol weight ratio of 70:30 without RPO is shown in Figure 1. The interlayer spacings observed in these compositions increased linearly from 37.6 to 45.4 Å with the water content. Incorporation of RPO in these systems, as shown in Figure 2, also shows similar dependence on the water content. There is a marked difference, however, in the slope after addition of RPO.

Figure 3 shows the behavior for SDS/hexan-1-ol before and after addition of RPO. The interlayer spacings of the lamellar liquid-crystalline structure, prior to the addition of RPO, increased from 37.6 to 45.4 Å with water content of 45–55 wt%. Upon addition of 10 wt% RPO, based on the amphiphile combination, the interlayer increased in the same fashion, but with a higher value, from 39.6 to 49.8 Å, with increased water content.

The interlayer spacing observed from the small-angle X-ray patterns provides additional information about the condition of the lamellar structure, but the interlayer spacing of the amphiphilic molecules and the aqueous layer must be considered separately (7). The extension of the amphiphilic part of the structure d_0 is obtained by extrapolation of the interlayers in Figures 1–3 to zero water content. These values are given together with the values of the slopes for the straight lines (Table 2). The values, 25.2 Å for the cationic host and 20.9 Å for the anionic host, suggest not fully extended chains of the lamellar structure. This is expected because of disorder with gauche conformation along the chains. The extrapolated value is the same for the lamellar liquid crystal of the anionic SDS system, while a decrease of about 10 Å is observed for the cationic system (Table 2). Conversely, the slopes showed an increase in both systems after addition of RPO, with the cationic system showing a higher value. The higher slope value suggests a lower penetrating effect in the cationic system. Obviously, the presence of RPO molecules, being hydrophobic in nature, restricts the penetration of water into the layered structure.

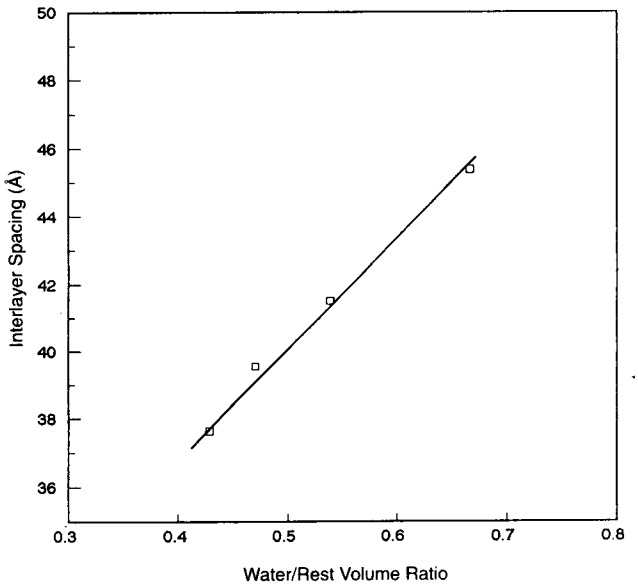

FIG. 1. Interlayer spacing as a function of the volume ratio of water to other components (rest) for the cationic, cetyltrimethylammonium bromide/hexan-1-ol, weight ratio of 70:30.

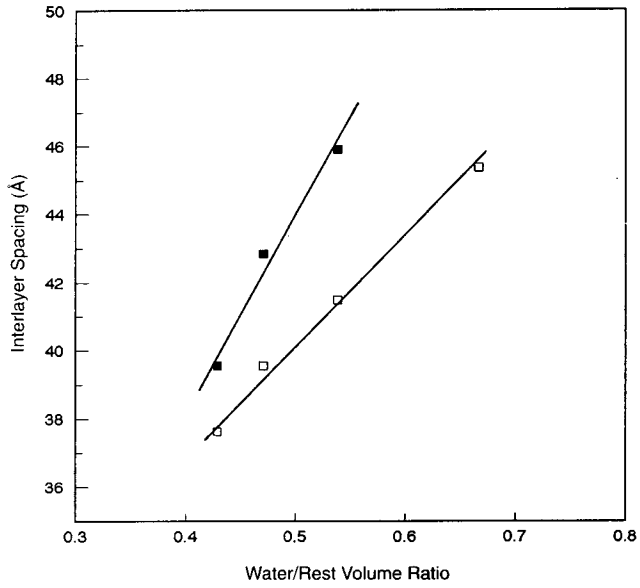

FIG. 2. Interlayer spacing as a function of the volume ratio of the water to other components (rest) for the cetyltrimethylammonium bromide/hexan-1-ol weight ratio of 70:30 (□) before and (■) after addition of red palm oil.

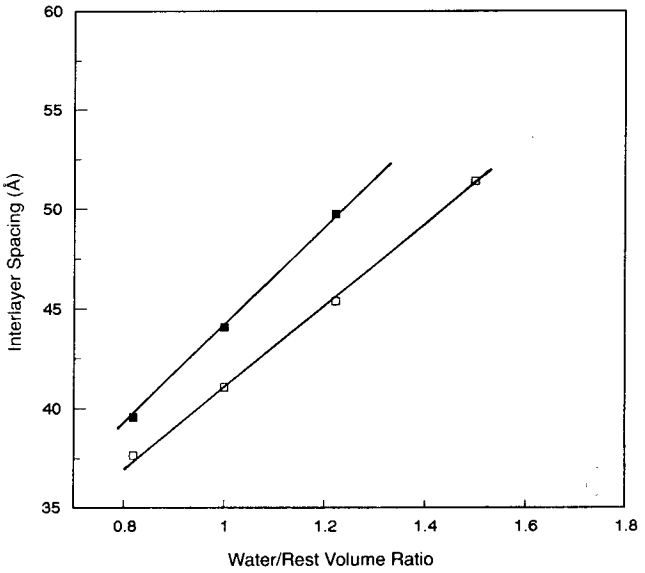

FIG. 3. Interlayer spacing as a function of the volume ratio of the water to other components (rest) for the anionic, sodium dodecyl sulfate/hexan-1-ol, weight ratio of 50:50 (□) before and (■) after addition of red palm oil.

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

Compound	d_0 (Å)	Slope
Cationic (CTAB)		
0% RPO	25.2	31.0
10% RPO	15.7	56.6
Anionic (SDS)		
0% RPO	20.9	20.2
10% RPO	20.9	25.3

[a]CTAB, cetyltrimethylammonium bromide; RPO, red palm oil; SDS, sodium dodecyl sulfate.

The value of 15.7 Å for the amphiphilic part d_0 of the cationic system after addition of RPO (Table 2) is both interesting and informative. From a previous study (1), addition of the same amount of RBD palm olein resulted in an increase in the d_0 value (30.0 Å) for the same cationic system. It seemed that the presence of the pigments (carotenes) caused a major perturbation in the molecular organization of the lamellar liquid-crystalline structure. The perturbation causes all the fractions in the methyl layer to penetrate the hydrocarbon chains of the amphiphiles, which resulted in the increase of gauche bends in the chains. It is also essential to realize that the increase of interlayer spacing in the SDS system after addition of RPO is simply due to the water not penetrating into the amphiphilic layer.

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