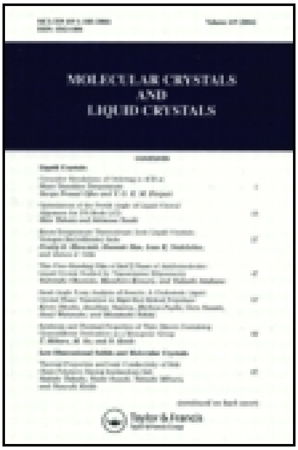

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An X-Ray Study of a Ternary Lyotropic Liquid Crystal

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An X-Ray Study of a Ternary Lyotropic Liquid Crystal

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X-ray diffraction was used to study the structure of a ternary lyotropic mixture of 63 wt% potassium palmitate, 7 wt% potassium laurate and 30 wt% water in the temperature range 65°C to 12°C. In addition to the usual lyotropic phases common to soap-water systems, we have also found a rectangular phase which exists in the temperature range between 41°C and 35°C, confirming the identification of this phase by DMR. There is also some evidence for a different rectangular phase at temperatures below 35°C, as suggested by DMR data.

Keywords: x-rays, diffraction, ternary, lyotropic, ribbon phase, rectangular phase

INTRODUCTION

In addition to the common lamellar and hexagonal phases usually found in amphiphile-water phase diagrams,[1,2] Luzatti and co-workers have reported several intermediate phases.[3] Among these phases is the rectangular phase R_α shown schematically in Figure 1. This structure consists of long rod-like amphiphilic aggregates packed into a two-dimensional rectangular arrangement. For the case of the potassium palmitate–water system this structure can be found for a mixture of 59% potassium palmitate with 41% water. At higher concentrations of amphiphile the structure is either lamellar L_α or the gel phase. In this paper, we report X-ray evidence for the existence of rectangular structures in a ternary amphiphile-water mixture, in support of previously reported DMR evidence for such structures.[4,11]

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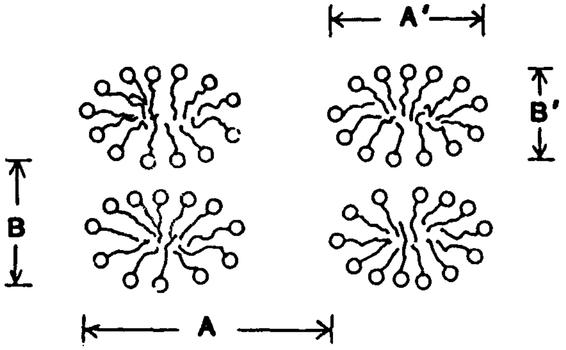

FIGURE 1 Structure of the rectangular phase R_α for the 59 wt% potassium palmitate binary mixture in water (See references 2 and 3).

EXPERIMENTAL

Samples were prepared by mixing previously synthesized and purified potassium palmitate and laurate with distilled water in sealed containers which were then heated at 70°C for about twelve hours. The sample material was subjected to several cycles of heating, stirring and centrifuging to ensure homogeneity, and was then stored in a 70°C oven till used.

For the X-ray measurements the samples were pressed into a specimen holder consisting of a 0.50 mm thick polished stainless steel ring with a 4.0 mm diameter hole drilled through its center. The stainless steel ring was covered top and bottom with 0.127 mm thick beryllium foils. One foil was permanently sealed to the ring with epoxy cement, and the other was sealed with a teflon gasket. Before each use the specimen holder was thoroughly cleaned. After preparation the specimen holder was clamped to a temperature stage in the instrument. Temperature was controlled by a recirculating fluid bath.

The instrument used for the X-ray measurements was an Elliot toroidal reflection vacuum camera[5] mounted on an AMR microfocus X-ray generator[6] having a projected focal spot size of 100 microns square and operated at 40 kV, 5 mA. Exposure times were of the order of 10 hours.

The diffraction patterns obtained were essentially powder patterns. The diffraction ring diameters were measured with a Norelco film reader, and relative intensities were determined with a Nonius microdensitometer interfaced to a microprocessor. Details of the experimental arrangement are given elsewhere.[7]

Measurements were made on three different samples of the material over a temperature range from about 12 to 71°C. The procedure for a given specimen was as follows: The specimen was initially raised to a temperature of 80°C and then cooled at a rate of 0.5°C/min. At various selected temperatures an equilibration time of 2 hours was used before an X-ray exposure was begun. After the lowest temperature exposure was completed, the specimen was raised again to 65°C, allowed to equilibrate overnight, and a second series of exposures begun.

In addition to the measurements on the ternary mixtures, measurements were also made on three different binary potassium palmitate–water mixtures (70%, 67.7% and 59% potassium palmitate by weight) and on anhydrous (crystalline) potassium palmitate.

RESULTS

General remarks

As is often the case with low water concentration samples in soap-water systems the diffraction patterns for the ternary mixture departed from the ideal powder pattern, showing effects of non-random orientation and, at temperatures below about 55°C, the presence of particulate amounts of crystalline material which gave spotty diffraction rings (see Figure 2). The relative intensity of the spotty rings increases with decreasing temperature from 55°C. Figure 3 shows a photometer scan of such a film at 62.9°C, and Figure 4 shows a scan at 40.4°C, with the various diffraction features labeled as L (lamellar), R (rectangular), G (gel), P (particulate crystalline material). The justifications of these designations are discussed below.

The diffraction patterns for the binary mixtures were more uniform, although for these mixtures also the presence of particulate material was noted at temperatures below about 58°C.

Ternary mixture

Figure 5 shows a graph of the various diffraction peaks for the ternary mixture as a function of temperature, omitting those peaks which were labeled P. For temperatures above 41°C, three low angle diffraction peaks and one wide angle peak are shown. The spacings of the peaks labeled L_2 and L_3 correspond to the second and third order reflections of L_1 (approximately 38 Å at 50°C). These spacings increase with decreasing temperature. The wide angle peak, labeled

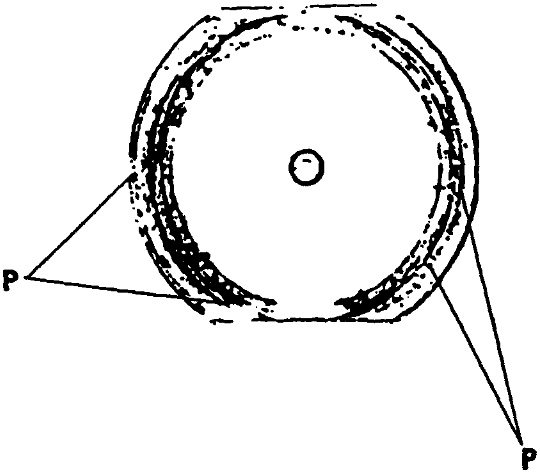

FIGURE 2 Exposed film for the ternary potassium palmitate–potassium laurate–water mixture at 50.7°C. The spotty features labeled P represent particulate reflections.

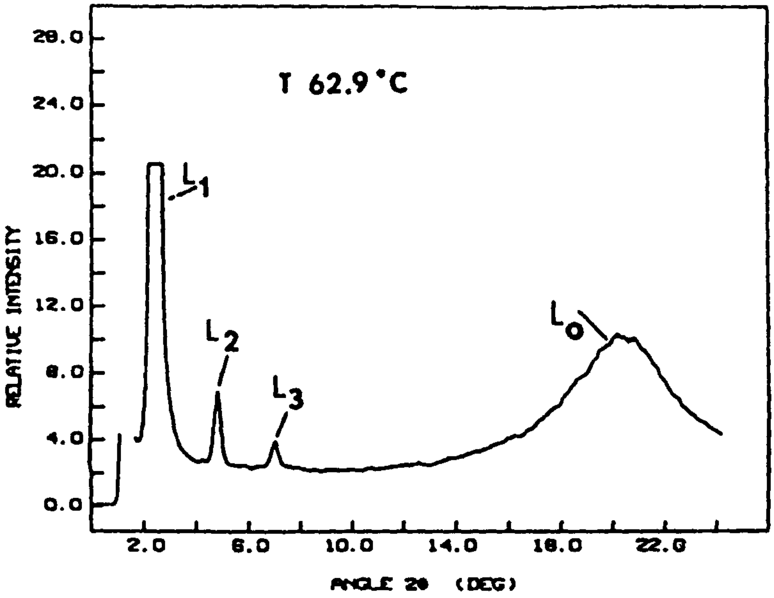

FIGURE 3 Photometer scan of a film for the ternary mixture exposed at 62.9°C. L, lamellar reflections.

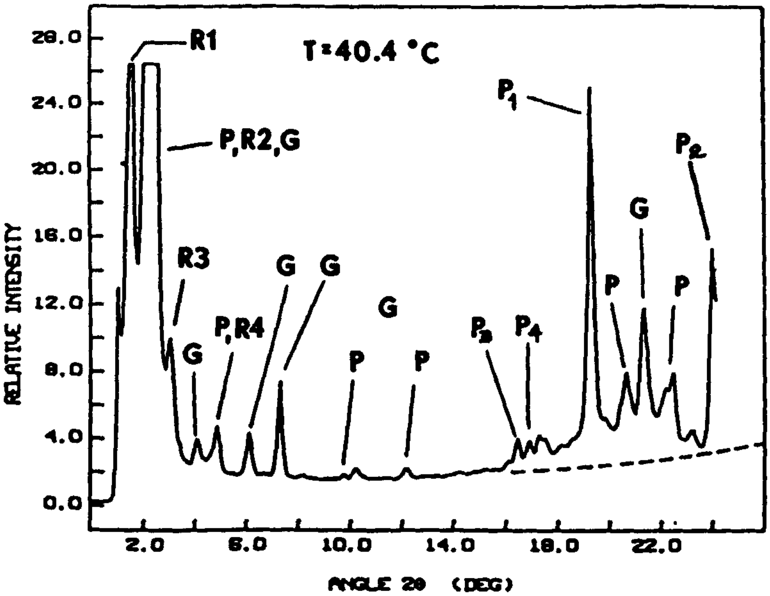

FIGURE 4 Photometer scan of a film for the ternary mixture exposed at 40.4°C. R, rectangular reflections; G, gel reflections; P, particulate reflections.

L_0, has a spacing of about 4.5 Å, which is relatively constant with temperature, and is rather broad and diffuse.

Below 41°C and down to the lowest temperature measured (12.5°C) the diffraction lines labeled G are observed. These spacings are relatively constant with temperature, and the lines labeled G_2 through G_7 correspond to the second through seventh order reflection of G_1 (approximately 45 Å). Note that G_6 was apparently too weak to be detected. The wide angle peak, labeled G_0, has a spacing of 4.27 Å, which is also relatively constant with temperature. In contrast to L_0, this peak is quite sharp.

In the range from 36 to 41°C, four other low angle lines, labeled R, are observed. The spacings of R_1 and R_3 decrease significantly with decreasing temperature, while the R_2 and R_4 spacings are constant with temperature. The spacing of R_3 corresponds to the second order of R_1, and that of R_4 to the second order of R_2. The spacing of R_1 at 40°C is about 60 Å, while that of R_2 is about 40 Å. In addition, there is present at wide angles a very broad weak hump underlying the other diffraction features (see Figure 4).

In the range from 25 to 30°C, there are two lines labeled S_1 and S_2. The spacing of S_1 at 30°C is about 42.5 Å, while that of S_2 is about 21 Å.

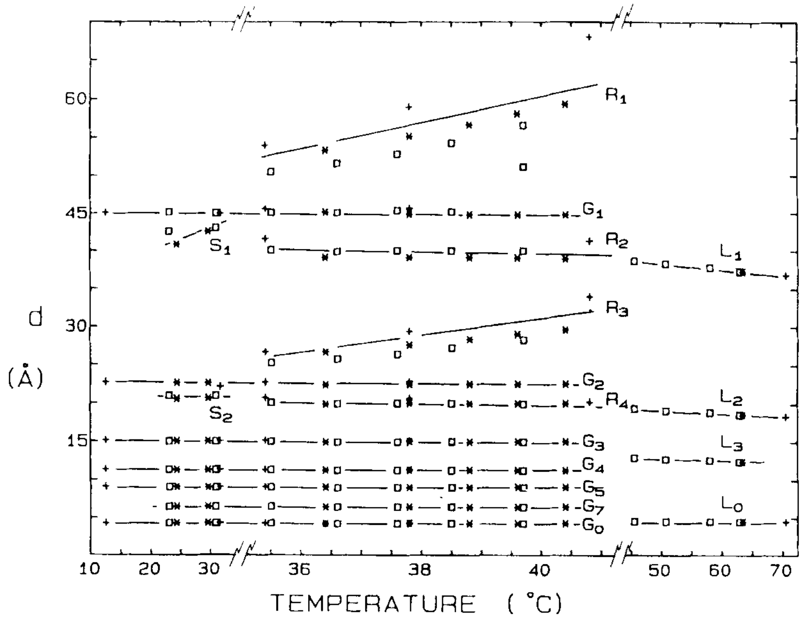

FIGURE 5 Plot of temperature dependence of the d-spacings of various reflections for the ternary mixture. L, lamellar reflections; G, gel reflections; R, rectangular reflections; S, possible rectangular reflections. The different shape symbols represent measurements taken from three different runs through the temperature range.

Binary mixtures

For the 70 wt% potassium palmitate binary mixture with water, measurements were made of the lamellar spacings in the L_α phase as a function of temperature. Figure 6 is a plot of the first order low angle line over the range from 50 to 85°C and shows that the spacing increases with decreasing temperature from 36 Å to 40 Å. The second and third order lines were also measured and followed a similar trend.

For the 67.7 wt% potassium palmitate binary mixture with water, measurements were made of the low angle spacings in the gel phase. These spacings are essentially independent of temperature. Table I compares the spacings of these lines with the corresponding lines from the ternary mixtures, labeled G in Figure 5.

For the 59 wt% potassium palmitate binary mixture, measurements were made over the range from 55 to 75°C, for which a rectangular phase had been previously reported, and the results are plotted in Figure 7. From 59 to 75°C, the line labeled R_3 is the second order

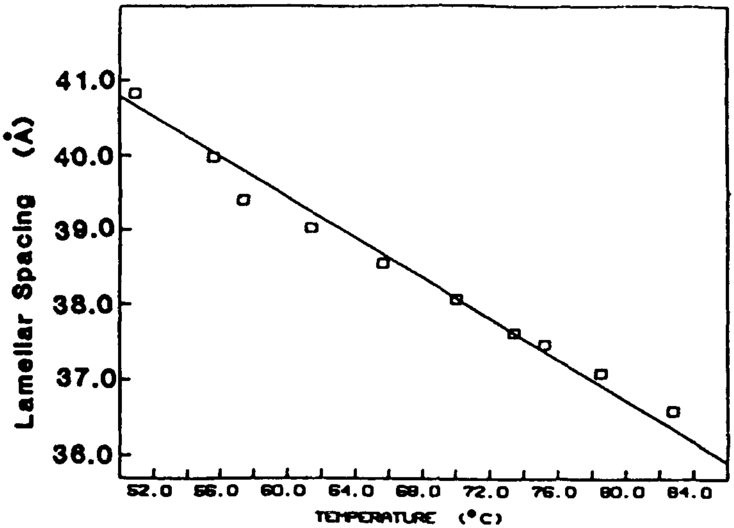

FIGURE 6 Plot of temperature dependence of the spacing for the first order lamellar line for the L_α phase of a 70 wt% potassium palmitate mixture in water.

reflection of R_1 and R_4 is the second order of R_2. The spacing of R_1 increases with decreasing temperature (from 54.5 Å at 75°C to 56.5 Å at 59°C), unlike the corresponding line in the ternary mixture. The spacing R_2 remains constant with temperature at 39.5 Å. Also present in this temperature range is a broad diffuse high angle line with its maximum at about 4.5 Å.

TABLE I

Comparison of gel lines of binary (67.7% potassium palmitate) mixture and of ternary (63% potassium palmitate, 7% potassium laurate) mixture

Spacing in Å	
Binary	Ternary
45.42 ± 0.30[a]	45.11 ± 0.30[a]
22.78 ± 0.15	22.56 ± 0.15
15.13 ± 0.04	15.07 ± 0.06
11.35 ± 0.03	11.29 ± 0.03
9.09 ± 0.01	9.03 ± 0.03
7.58 ± 0.01	7.57 ± 0.01
6.48 ± 0.01	6.45 ± 0.01
4.29 ± 0.01	4.27 ± 0.01

[a] The uncertainties indicated are either the uncertainty in the experimental measurements or the rms deviation of several values from the average, whichever is larger.

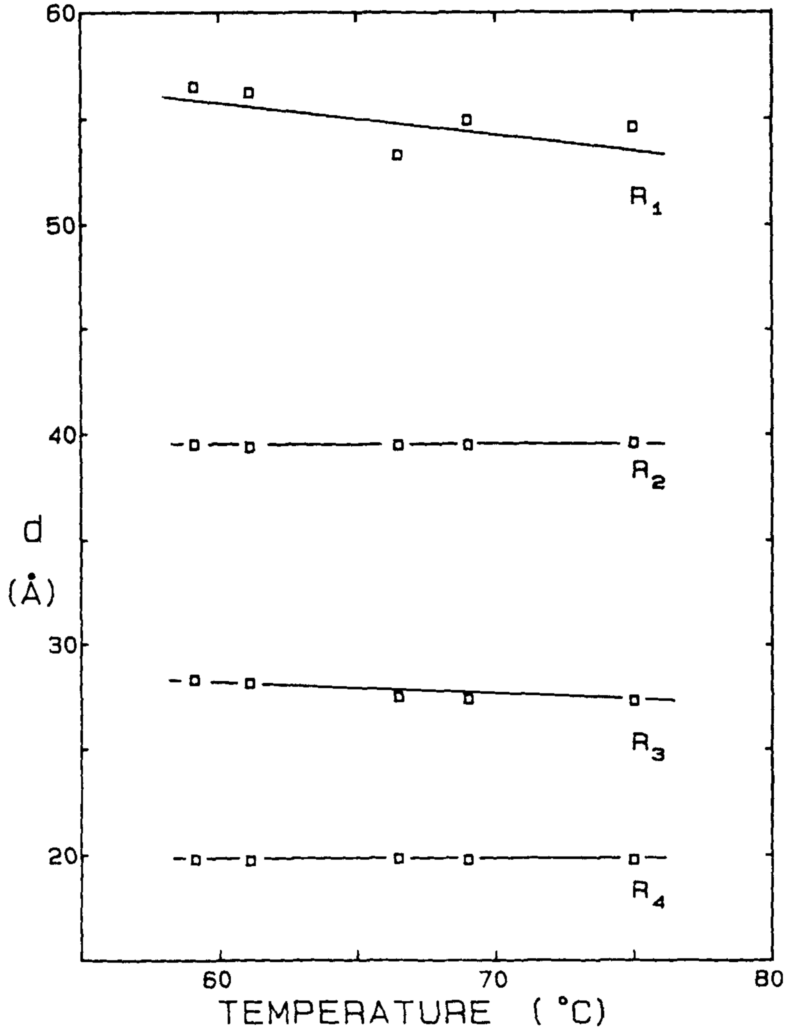

FIGURE 7 Plot of the temperature dependence of the spacing of the four rectangular phase lines for the 59 wt% potassium palmitate binary mixture in water.

DISCUSSION

The features labeled P on the photometer scans (Figures 3 and 4) are associated with the spotty diffraction rings of Figure 2. The averages over three different runs of the measured values of the d-spacings corresponding to these spotty rings are tabulated in Table II, along

TABLE II

Comparison of measured spacings of particulate lines with spacings calculated from triclinic unit cell for anhydrous potassium palmitate[8][a]

Measured spacings (averaged over 3 runs) Å	Calculated spacings	
	Spacing Å	h k l
37.90 ± 0.25	37.75	0 0 1
18.92 ± 0.13	18.88	0 0 2
12.61 ± 0.15	12.58	0 0 3
9.44 ± 0.02	9.44	0 0 4
7.57 ± 0.02	7.55	0 0 5
5.61 ± 0.02	5.59	0 1 0
5.46 ± 0.02	5.48	0 1 1
5.28 ± 0.02	5.29	0 1 2
5.04 ± 0.02	5.01	0 1 3
4.71 ± 0.02	4.70	0 1 4
4.41 ± 0.02	4.38	0 1 5
4.16 ± 0.02	4.14	1 0 0
4.04 ± 0.02	4.03	1 0 2
3.91 ± 0.02	3.91	1 0 3
3.77 ± 0.02	3.77	1 0 4

[a] The uncertainties indicated are either the uncertainty in the experimental measurements or the rms deviation of several values from the average, whichever is larger.

with values calculated from the triclinic unit cell determined by Lomer for crystalline anhydrous potassium palmitate.[8] We have also confirmed the calculated values of these spacings by direct measurements on anhydrous potassium palmitate. Based on the comparisons of Table II, we assign the features labeled P to crystalline potassium palmitate. The precipitation of crystalline fragments from amphiphile-water mixtures at relatively low water content and temperature is not uncommon.

The diffraction lines labeled G on the photometer scans (Figure 4) and in Figure 5 are attributed to the gel phase, which is relatively more highly ordered than the L_α phase. Thus we observe up to the seventh order of diffraction of the basic lamellar repeat distance. In addition, the wide angle diffraction line at 4.25 Å is much sharper than the corresponding broad line in the L_α phase, indicating a "freezing" of the hydrocarbon chains.

The question arises as to whether the crystallization of the fragments of potassium palmitate results in a change of the composition of the remaining solution because of the excess water expelled from the crystallized material. Such a change in composition should be evident from a change in the measured layer spacings, since it has been shown that the spacing of the layers in the gel phase depends upon the water content of the mixture.[9] Figure 5 shows that the spacing of the diffraction lines labeled G does not change with temperature even though the amount of crystalline material is increasing with decreasing temperature. We therefore conclude that the water expelled from the precipitating crystalline material cannot enter homogenously into the remaining solution, but rather forms pockets of free water. Further evidence for the existence of free pockets of water is provided by electron microscope studies.[10]

The diffraction lines labeled R_1 through R_4 in the ternary mixture are observed in the temperature range from 36 to 41°C. These lines show a different temperature dependence than the corresponding lines in binary potassium palmitate–water solutions, as is evident from a comparison of Figure 5 for the ternary compound with Figure 7 for the binary compound. It therefore seems reasonable to assign these features to a different structure, namely the ribbon-like aggregates identified in the DMR work.[4] For the ternary compound the R_2 dimension (40 Å) is associated with the "thickness" of the ribbon and is only slightly larger than the repeat distance associated with the thickness of the L_α lamellae (L_1 at 45°C is 39 Å). The R_1 dimension is then associated with the "width" of the ribbon.

Because the R_2 spacing is about the same as the L_1 spacing, it is reasonable to assume that the hydrocarbon chains in the ribbons are melted. Evidence for this should appear as a low broad hump with a maximum at about 4.5 Å in the width angle region of the diffraction pattern shown in Figure 4. Inspection of Figure 4 (data taken at 40.4°C) indicates that such a hump underlies the diffraction lines from 16 to 22° 2θ. Inspection of data taken at a temperature of 38.8°C indicates a similar but weaker hump. Determination of the height and precise shape of the hump requires decomposition of the observed diffraction pattern into its various components, based on a knowledge of the shapes of the various diffraction features. Such a decomposition depends very heavily on the shapes assumed for the lower portions of the various diffraction lines and the degree of overlap with each other. In the present case, we are only able to say qualitatively that the intensity of the hump decreases with temperature over the range in which it is observed.

The decrease in the d-spacing for R_1 (and its second order R_3) while R_2 (and its second order R_4) remains constant as temperature decreases (see Figure 5), suggests that the ribbon phase coexists with the gel phase and is competitive with it, so that the ribbons become narrower with decreasing temperature as they "lose" material to the gel phase. One would also expect to observe this process in the temperature dependence of the intensity of the R_1 and R_3 diffraction lines. Unfortunately, these lines are not sufficiently well resolved from the gel reflections (lines labeled G in Figures 4 and 5) and the particulate reflections (labeled P in Figure 4) to permit unambiguous determination of their intensities. However the qualitative decrease in intensity of the broad hump associated with diffraction from the melted chains (as discussed in the preceding paragraph) offers some support for this interpretation. At about 36°C the ribbons themselves undergo a transition to the gel phase.

Recent DMR studies of the water in this system have suggested a residual biaxiality below the 36° transition temperature from the ribbon phase to the gel phase.[11] This residual biaxiality has been interpreted in terms of a coexisting rectangular phase of cylindrical aggregates. The question arises as to whether the two diffraction lines S_1 and S_2 observed in the range from 24 to 31°C can be regarded as further evidence of such a phase. Such a conclusion would be reinforced if higher order lines, e.g, S_3 and S_4, had been observed. Unfortunately, S_1 and S_2 are of so low intensity that their higher orders are probably not observable. Nevertheless, if it is assumed that the lines S_1 and S_2 do represent the rectangular phase, then it is possible to calculate the radius r of the cylindrical aggregates by combining the X-ray data with the asymmetry parameter obtained from the DMR spectral profiles. As shown by Chidichimo et al.[11] in their equation (7),

$$(A - 2r)/(B - 2r) = (1 - \eta)/(1 + \eta),$$

where A is the spacing of S_2 and B is the spacing of S_1, and η is the asymmetry parameter of the DMR profile.

Using values of 0.5, 20.8 and 42.8 for η, A and B respectively at 30°C, the value of r is calculated to be 4.9 Å. The extended length of the potassium palmitate molecule has been reported as being 21 Å.[9] Thus the calculated value of r is too small.

The lines S_1 and S_2 also do not fit extensions of the plots for R_1 and R_2 to lower temperatures.

CONCLUSIONS

The X-ray data support the earlier DMR evidence for the existence of a ribbon-like phase in the ternary potassium palmitate–potassium laurate–water system.[4] This phase has rectangular symmetry, but a different temperature dependence than the rectangular phases previously reported for the binary potassium palmitate–water system.[3] There is also some support in the X-ray data for the existence of a rectangular phase at temperature below those for which the ribbon phase exists.[11] There is apparently some inconsistency between the interpretations of the X-ray and DMR data for this phase, however. Alternative, more consistent, interpretations are possible, using a less simplistic explanation of the DMR asymmetry parameter and a centered, rather than simple, rectangular lattice for indexing the two diffraction lines assigned to the low temperature rectangular phase. Before pursuing such speculations further measurements are desirable, preferably with a system exhibiting more diffraction lines for this phase.

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