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STUDIES OF STRUCTURE AND MOLECULAR DISTRIBUTION IN LYOTROPIC RIBBON AGGREGATES

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Abstract A lyotropic phase consisting of elongated ribbon aggregates on a rectangular lattice is formed with a ternary mixture of potassium palmitate (KP), potassium laurate (KL) and water. Deuterium NMR and x-ray studies of molecular factors which affect the formation of the aggregate system are reviewed. By selective deuteration of the lipids it is shown that the KL and KP molecules are not uniformly distributed throughout the ribbon aggregate. The less abundant KL molecules with the shorter hydrocarbon chain are more concentrated at the edges of the ribbons where there is high curvature whereas the more abundant KP molecules are more concentrated in the central lamellar region of the aggregate. The shape of the ribbon and molecular ordering within the ribbon are also reviewed.

INTRODUCTION

It is well known that varieties of different aggregate structures can be formed by mixtures of surfactants and water.[1-6] On the other hand, the molecular factors which govern aggregate formation are not completely understood. Our interest has been to isolate some of these molecular factors by choosing a simple system of compounds which provide a simple aggregate structure which can be easily probed and studied. We report here a review of our results on a ternary mixture of potassium palmitate (KP), potassium laurate (KL) and water. At a suitable concentration of these materials, this system can provide a sequence of simple aggregate structures as the temperature is varied over a temperature range from 25 to 100°C. These structures include: An elongated cylindrical aggregate on a

rectangular lattice, an elongated ribbon aggregate also on a rectangular lattice, and a lamellar bilayer structure. The transformation of the system from one phase to another involving these structures has been followed using ^{2}H-NMR[7-10] and x-rays.[11,12] The ^{2}H-NMR technique on selectively deuterated materials, we have found to be particularly useful in that it provides a signal which depends on: The aggregate shape and dimensions, the distribution of the lipid components within the aggregate and between different coexisting aggregate structures, and the molecular ordering within the aggregate.

In this paper we review our results on two particular ternary mixtures shown in Table I.

TABLE I Lipid-water mixtures and associated phases where the symbols RB_α, R_α, L_α, and L_β stand for phases consisting of elongated ribbon aggregates, elongated cylindrical aggregates, lamellar bilayers with melted chains and lamellar bilayers with frozen chains respectively.

	Mole %			
Composition	KP	KL	H_2O	Phases
I	12.33	1.67	86.00	$L_\beta+R_\alpha \xleftrightarrow{36^\circ} L_\beta+RB_\alpha \xleftrightarrow{41^\circ} L_\alpha$
II	7.95	1.11	90.97	$L_\beta+R_\alpha \xleftrightarrow{36^\circ} RB_\alpha \xleftrightarrow{51^\circ} RB_\alpha+L_\alpha$

Maintaining the molar compositions I and II in Table I above we have used various selectively deuterated materials to study different molecular features of the aggregate systems. An advantage of the KP, KL, water system is that the head groups of the two lipid components are the same. They differ in chain length only allowing us to isolate this molecular feature in aggregate formation.

THE RIBBON STRUCTURE

X-ray studies have been carried out on system I by Benigni et al.[11,12] At temperatures above 41°C in the

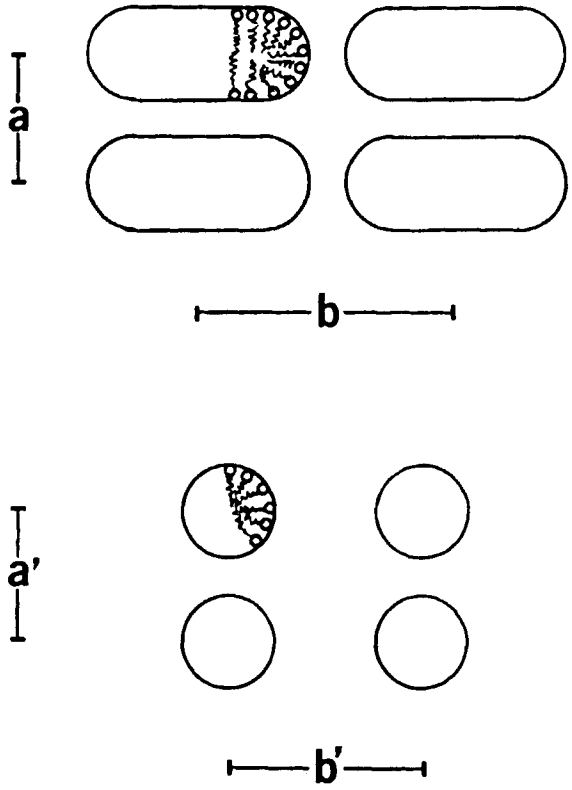

FIGURE 1. Illustration of the rectangular lattice for: A. elongated ribbon structures. B. Elongated cylindrical structures.

system the diffraction patterns resemble those of the lamellar L_α structure.[11] The low angle reflections occur as integer multiples of a bilayer spacing. A measured bilayer spacing of 36.4 Å was reported for the mixture of system I. ^{2}H-NMR observations show the hydrocarbon chains to be melted. Polarizing microscope studies at these temperatures also show the familiar oily streak texture associated with the neat phase.

Below 41°C the x-ray diffraction patterns become more complicated with several new finely textured diffraction

halos appearing in the small angle region. These lines can be grouped into two sets of spacings. The choice of indices defines a two-dimensional primitive rectangular unit cell where each spacing is given by $1/d^2 = (h/a)^2 + (k/b)^2$ where $\underline{a}$ and $\underline{b}$ represent the short and long unit cell parameters respectively.[11] Based on this indexing scheme the lattice structure is shown in Figure 1.

The value of $\underline{a}$ was measured to 45.5 Å and approximately constant with temperature whereas the value of $\underline{b}$ decreased with decreasing temperature reaching a value of 55.4 Å at 33°C. The x-ray diffraction patterns show that at temperatures below 41°C the ribbon phase coexists with a lamellar phase with a bilayer spacing of 38 Å.[11] ^{2}H-NMR detects this coexisting lamellar phase as well as shows that it is of an L_β type in which the end chains are rigid.[8,9]

Deuterium NMR studies of system I were performed on four different samples involving differently deuterated groups: KP-α-d_2, where the α-position of the KP chain was deuterated; KP-d_3, methyl group deuterated; KP-d_{31}, perdeuterated potassium palmitate; and ^2H_2O in which only the water was deuterated. Figure 2 shows representative spectral patterns for different deuterated substituents which are characteristic of each phase.[7-9]

The utility of the ^{2}H-NMR measurement in aggregate studies is that the time scale of the measurement is sufficiently long that a molecule has ample time to diffuse over all of its relevant orientations within the aggregate. With a diffusion constant, $D \sim 10^{-6}$ cm^2/sec and a measurement time $t \sim 10^{-4}$ sec a molecule diffuses a distance within the aggregate of $\sim \sqrt{Dt} = 10^{-5}$ cm = 1000 Å. As the ^{2}H-NMR signal is strongly dependent upon the molecular orientation in the aggregate, self-diffusion over the aggregate modulates the signal and yields an average signal that reflects the shape and dimension of the aggregate. The quantities measured from the deuterium signal are the quadrupole coupling constant[7] $\nu_Q = e^2q_zQ/h$ and the asymmetry parameter[7] $\eta = (q_x-q_y)/q_z$. The quantities q_i are the principal components of the electric field gradient tensor at the nuclear site created by the carbon-deuteron or oxygen-deuteron bonds within the molecule. These are the quantities which are time averaged by molecular motion.

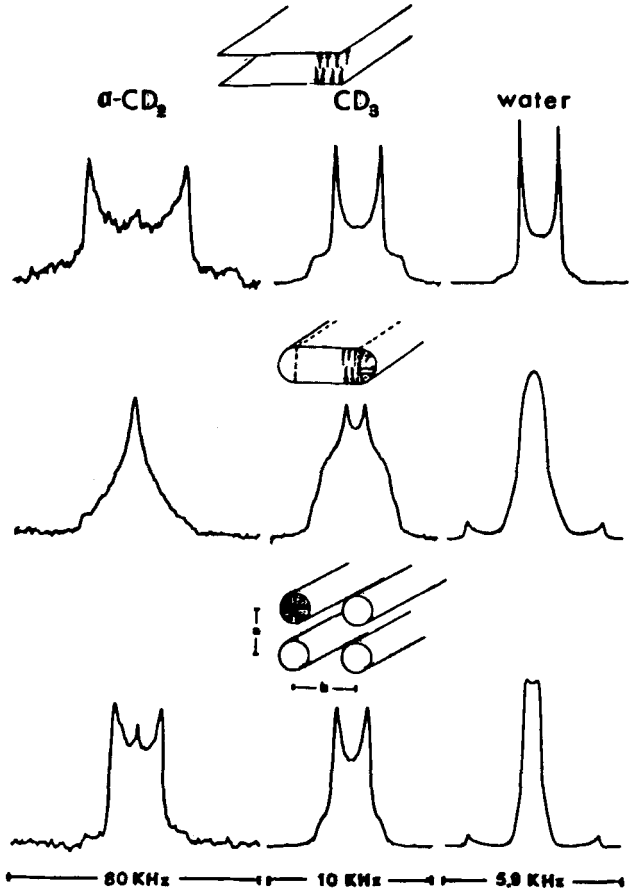

FIGURE 2. Aggregate structure and associated spectral patterns of a mixture consisting of 12.33 mole % KP, 1.67 mole % KL, and 86.00 mole % water. The ^{2}H-NMR spectral patterns on the left are from KP-α-d_2; in center from KP-d_3 and on the right from ^2H_2O. The small outer peaks on ^2H_2O spectra are from the L_β phase. The L_β spectra are not shown above on the KP-α-d_2 and KP-d_3 spectra.

The spectral patterns shown in the high temperature phase of Figure 2 are all quite characteristic of the L_α phase. The shape of the patterns are all nearly identical and demonstrate that the phase is uniaxial (η=0). Each of these spectral patterns can be readily simulated with one adjustable parameter, namely ν_Q^L (L, representing the L_α phase). The magnitude of this quantity is representative of the time average orientational order of the deuterated segment in the L_α phase. The α-position of the hydrocarbon chain is more ordered than the methyl segment as evidenced by the broader pattern. The ^2H_2O signal is quite narrow since the water diffuses throughout the region between the lipid bilayers during the course of the NMR experiment yielding a time average of the order everywhere between the bilayer.

The spectral patterns for the lipids observed in the low temperature phase (lower set in Fig. 2) are uniaxial like those in the high temperature phase, but approximately half the width in which $|\nu_Q^C| \simeq |\nu_Q^L|/2$ where the superscripts C and L stand for the cylindrical and lamellar aggregates respectively. This is a well known characteristic of the cylindrical structure.

It is noted that the ^2H_2O signal from the lower temperature region is, unlike the lipid signals, by no means characteristic of uniaxiality. This feature is easily understood in that the cylinders are packed on a rectangular lattice. Unlike the lipid molecules which are confined to diffuse within the cylindrical aggregates during the measurement time, the water molecules diffuse among the aggregates and the time average of the signal reflects the asymmetry of the rectangular lattice. An estimate of the ratio a/b can be determined from the measured value of η from the water signal which is consistent with the x-ray measurement.[9]

At temperatures intermediate between 41 and 36°C the ^2H-NMR spectral patterns reflect the ribbon shaped aggregates. A simulation of these spectral patterns requires a finite value for both ν_Q and η which we label as ν_Q^{RB} and η^{RB} for the ribbon structure. Values for these quantities are obtained from fits to the experimental spectral patterns. It is also possible to calculate values for ν_Q^{RB} and η^{RB} based on a simple model whereby the ribbon structure is visualized as consisting of a central

lamellar region (L in Figure 3) capped on each side by one-half of a cylinder (region C of Figure 3). If we let W be the probability of a lipid molecule residing in the lamellar, L, region and 1-W the probability of residing in the cylindrical end, C, region then it is a straight forward calculation that:[7]

$$\nu_Q^R = \begin{cases} \frac{-(3W+1)}{2}\,\nu_Q^C & \text{for } \frac{1}{3} \le W \le 1 \\ \nu_Q^C & \text{for } 0 \le W \le \frac{1}{3} \end{cases} \qquad (1)$$

$$\eta^R = \begin{cases} \frac{3-3W}{1+3W} & \text{for } \frac{1}{3} \le W \le 1 \\ 3W & \text{for } 0 \le W \le \frac{1}{3} \end{cases}$$

Figure 4 shows the values of W obtained by measured values of ν_Q^{RB}, η^{RB} and the use of Eqs. (1).

The temperature dependence reflects the change in the aggregate size with temperature. In system I the size of the lamellar region decreases with decreasing temperature until 36°C where the system undergoes a phase transition in which the aggregates become cylindrical in shape. It is interesting that the values of W are different for the α and the methyl positions of the chains. The simple model above does not predict this feature. It is believed that this is due to a slightly different time average conformation of the molecule in the cylindrical end such that the terminal methyl group experiences the lamellar order more often than the α-position similar to that sketched in Figure 3. The fact that the value of W for the α position and the water is nearly the same reflects the fact that the water, while diffusing over the surface of the aggregate, averages in the same way as the α-position which is also near the surface. If d is the size of the lamellar region and r the radius of the cylindrical end (see Figure 3) then one can model[7,9] the value of $W = 2d/(2d+2\pi r) = (1+\pi r/d)^{-1}$. From this model the values of d/r range from ~1.5-0.4 as the

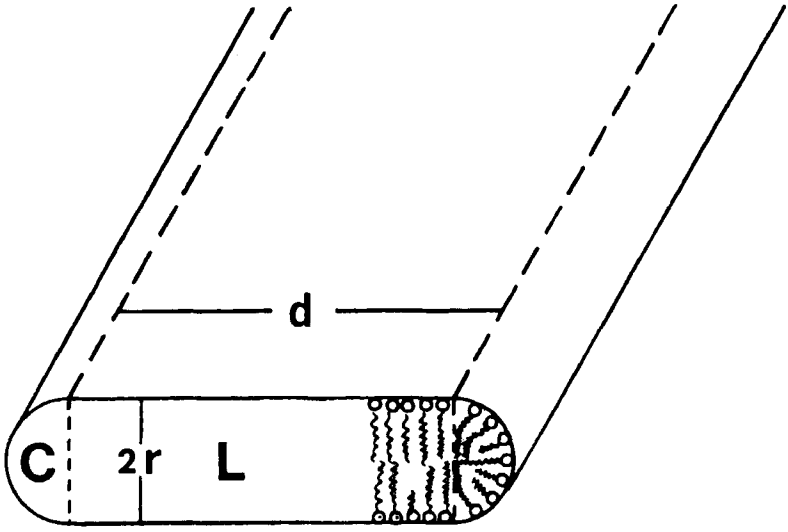

FIGURE 3. Illustration of the ribbon structure and the symbols used in the text. The model illustrates the preference of the short chain lipid in the regions of curvature and preference of the more abundant long chain lipid in the lamellar region.

temperature is decreased from 41 to 36°C which implies that the ribbons are more nearly cylindrical than lamellar in dimension. It will be shown next, however, that this calculation is not entirely correct. The calculation assumes that the molecule is unbiased in its preference for the lamellar or cylindrical regions. Next, we shall show evidence that KP prefers the lamellar region and KL prefers the cylindrical region.

MOLECULAR DISTRIBUTION

The relative distribution of KL and KP within the aggregate structure is easily determined with deuterium NMR by measuring the value of W for each component.[10] Such a study was carried out using system II of Table I.

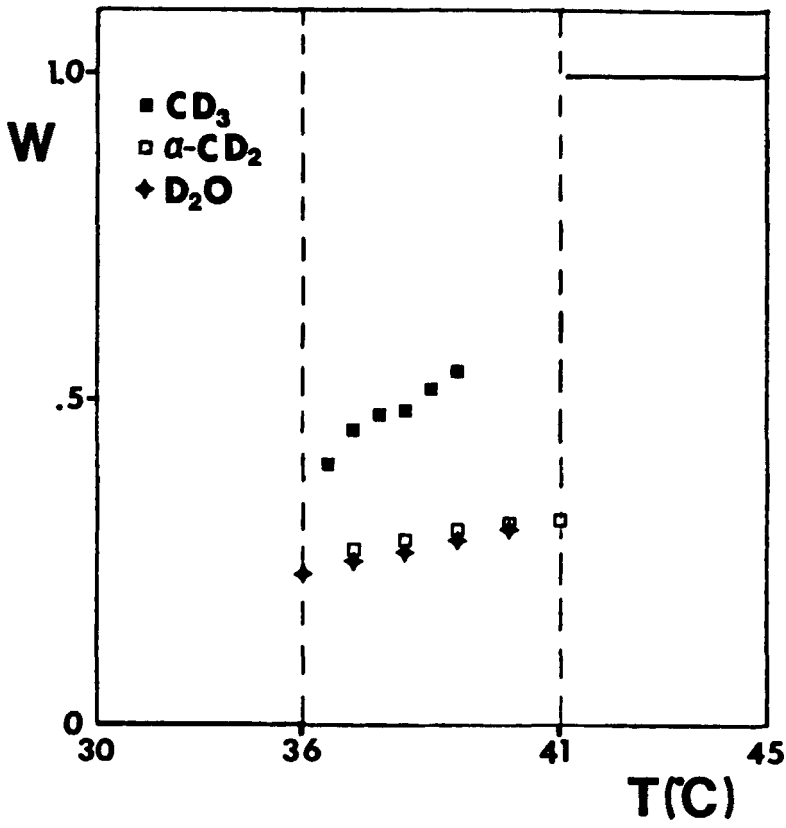

FIGURE 4. Measured temperature dependence of the probability, W, that the deuterated segment of the KP molecule resides in the lamellar region of the ribbon aggregate.

At this particular concentration of KP, KL and water, a pure ribbon phase over an interval of temperatures can be formed. Table II shows the measured values of W for four differently deuterated compounds at a temperature within the ribbon phase.[10] It is recognized in this table that the probability that a KL molecule lies in the lamellar region as measured from both deuterated sites is significantly less than that for a KP molecule. This feature is, in fact, what one might expect in that the less abundant shorter chain lipids would be expected to pack easier in the cylindrical edge region of the aggregate where there is high curvature.

TABLE II Measured values of the probability W that a molecule resides in the lamellar region of the aggregate for the ternary system of composition II (of Table I) at the temperature of 44°C. Values shown for four differently deuterated compounds.

Material (Deuterated Positions)	W ± .05
KP (α-position)	0.35
KL (α-position)	0.15
KP (methyl position)	0.60
KL (methyl position)	0.40

Another interesting observation on this system was that there was no L_β phase observed in the spectra of the KL. Even the L_α signal which dominates the KP spectra at high temperatures is considerably reduced in the KL spectra. This is added evidence that the KL lipids prefer the structures where there is curvature.

Finally, as observed in composition I, the methyl groups show a larger value of W than the α positions. This points out the inadequacy of the model which involves

two simplifying assumptions: 1) The ordering of the methyl segment of the chain is the same in the lamellar as in the cylindrical edge of the aggregate. 2) The edges of the ribbon can be modeled as the half of a perfect cylinder. A more accurate model of the ribbon structure would therefore be one in which the edges of the ribbon are not as simple as described above.

DISCUSSION

The presence of the small mole % of KL in the KP-water system therefore has the effect of fracturing the lamellar structure at lower temperatures into elongated ribbon aggregates. The KL lipids prefer to reside in the regions of high curvature (cylindrical edges) of the ribbon aggregates. As the temperature is changed and the ribbons become more cylindrical in shape the KP lipids leave the ribbon aggregates, migrate to the coexisting L_β phase.

These studies[7-10] have provided us with a clearer view of some of the molecular factors involved in aggregates formed from ternary mixtures. The ^{2}H-NMR technique appears well suited for these types of studies. It is fortunate that the size of the aggregates and the rate of molecular diffusion are well suited for the time scale of the ^{2}H-NMR measurement and their study. Measurements on other lipid systems are in progress.

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