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Water Diffusion and Phase Transition Investigation in Lyotropic Mesophases. A NMR Study

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Measurements of water diffusion in non-aligned lyotropic mesophases have been made using the pulsed field gradient NMR technique (PFG-NMR). The investigated systems were mixtures of potassium palmitate and water (KP/H_2O). Deuterium nuclear magnetic resonance spectral profiles (D-NMR) were also analyzed on perdeuterated potassium palmitate.

Experimental data were taken in the $H\alpha$ mesophase, the $L\beta$ mesophase and in the intermediate region of the phase diagram between the $L\alpha$ and $H\alpha$ mesophases.

The results are discussed in terms of the mixture composition and of the amphiphilic aggregate structures.

The behavior of the water diffusion at the phase transition occurring between the $L\beta$ and $H\alpha$ mesophases suggests a new insight on the evolution of this transition across the two phase regions.

Furthermore the lyotropic mesophase occurring in the intermediate region has been identified.

1. INTRODUCTION

An analysis of water diffusion in the non-aligned lamellar $L\alpha$ lyotropic mesophase of potassium palmitate and water, in terms of the water percentage and of a 'structural factor' of the mesophase has been given elsewhere.[1]

It was found that in such mesophases, the water diffusion coefficient D_{NMR}, as measured by the PFG-NMR technique,[2,3] can be expressed according to the simple Eq. (1):

$$D_{\mathrm{NMR}} = f[(1 - P)D_W + PD_b] \quad (1)$$

Here D_W and D_b are the diffusion coefficients of free water and of water bound to the aggregate surface, respectively; P is the fraction (i.e. the probability) of bound water and f the structural factor. Physically f accounts for the constraints to water diffusion due to the lyotropic aggregates and therefore its value ranges between zero (no diffusion) to 1 (free water diffusion). Simple considerations supported by experimental results give f a value of 2/3 in the non-aligned $L\alpha$ mesophase of KP/H_2O mixtures[1] and suggests a higher value in more open lyotropic mesophases, such as the $H\alpha$ mesophase studied in the present work.

As is shown in Ref. 1, the structural factor can be obtained by applying Eq. (1) to a couple of lyotropic mixtures i and j of the same mesophase, having a different composition.

The following relation holds:

$$f = \frac{D^i_{\mathrm{NMR}} - K_{ij} D^j_{\mathrm{NMR}}}{(1 - K_{ij}) D_W} \tag{2}$$

where K_{ij} is the ratio P_i/P_j between the fraction of bound water in the samples i and j, respectively. Under the reasonable hypothesis that for a given mesophase the chemical bound water per unitary weight of amphiphile does not depend on the composition, and provided that the aggregate shape remains constant, it is possible to show, by straightforward stoichiometric calculation, that K_{ij} can be obtained from the water weight fractions W_i and W_j:

$$K_{ij} = \frac{W_j (1 - W_i)}{W_i (1 - W_j)} \quad . \tag{3}$$

The aim of the present work is to test the above phenomenological model in the case of the $H\alpha$ mesophase of KP/H_2O lyotropic mixtures, and to obtain an experimental value for the structural factor f. The purpose has been achieved by studying the water diffusion coefficient by the PFG-NMR method.

Simple physical considerations suggest that water diffusion is sensitive to phase transitions, occurring in lyotropic systems, and this has also been shown experimentally.[5,6] According to our model, any variation in the structure should possibly be reflected in a change of the structural factor f. Our investigation has been extended to the intermediate region between $L\alpha$ and $H\alpha$ mesophases, where according to Luzzatti et al.,[4] several different mesophases, such as the cubic, the rectangular, the hexagonal complex etc., can occur, depending on the temperature, the sample inhomogeneity and the presence of impurities. We have tested the possibility of using water diffusion in order to discriminate among the possible mesophases sandwiched between the *Lα* and *Hα* mesophases. As we will show, a single mesophase has been found in this region of the phase diagram; we will use for brevity the symbol *IM* (intermediate mesophase) for defining such a mesophase. During the progress of this work an interesting behavior of diffusion was observed when crossing transitions from the *Lβ* to the *Hα* and from the *Lβ* to the *IM* mesophases. In these transition regions, which are wide in temperature depending on the lyotropic composition, D_{NMR} shows a rather well defined, reproducible minimum. The detailed investigation of the water diffusion and D-NMR spectra gives new information on the building-up of lyotropic structure and on the mechanism of phase transitions.

2. EXPERIMENTAL

The lyotropic mixtures reported in Table I have been investigated by means of the PFG-NMR technique.

The sample composition has been selected on the basis of the KP/H_2O phase diagram.[7] The molar composition of samples A and B has been such that three regions of the phase diagram (*Hα*, *IM*, and *Lβ*) could be analyzed by varying the temperature, while those of samples C,D,E have been chosen in order to observe directly the *Lβ* to *Hα* transition. Samples containing perdeuterated KP (A,C) or deuterated water (B,D) have also been investigated by D-NMR, in order to check the occurrence of the supposed mesophases and the sample homogeneity. This procedure has been found very useful for monitoring the transition temperatures. Samples have been prepared following a standard procedure.[1] Diffusion measurements were obtained through a spin-echo experiment in the presence of a pulsed magnetic field gradient (PFG-NMR) following the known method.[2] The H-NMR echo signal was observed by using a POLARON pulsed NMR spectrometer working at 35 MHz, equipped with a DATALAB transient recorder, a ROCKWELL AIM 65 microcomputer for data acquisition and signal averaging, and a home made magnetic pulsed field gradient apparatus.

Details of the apparatus procedure and of the experimental conditions are described elsewhere.[1] According to the usual symbols we have in our experiments: the time interval between field gradient pulses, in the range: $4 \cdot 10^{-3}$ sec $\leq \Delta \leq 1.6 \cdot 10^{-2}$ sec; the time

TABLE I

KP/H_2O Lyotropic mixtures investigated by PFG-NMR and D-NMR technique. The * symbol indicates the presence of perdeuterated KP

Sample	Composition (wt%) KP	 H_2O	 D_2O	Mesophases
A *	57.5	42.5	0.0	*Lβ IM Hα*
B	51.7	42.9	5.3	*Lβ IM Hα*
C *	42.4	57.6	0.0	*Lβ Hα*
D	39.8	53.7	6.5	*Lβ Hα*
E	27.0	73.0	0.0	*Lβ Hα*

between the two rf pulses, $\tau = 1 \cdot 10^{-2}$ sec; the field gradient intensity $g = 90$ gauss/cm, and the field gradient pulse width, $\delta = 7 \cdot 10^{-4}$ sec. For the condition $\delta << \Delta$, D_{NMR} has been obtained by plotting the logarithm of the spin-echo attenuation against Δ. No evidence of restricted diffusion has been found. Temperature of the sample was controlled and measured within 0.1°C or better. The accuracy of D_{NMR} is typically of the order of 5 to 10%.

D-NMR spectral profiles have been obtained using a BRUCKER WM 300 spectrometer operating at 46 MHz. In order to avoid loss of signal due to receiver dead time, the quadrupolar echo method was used.[8]

3. RESULTS AND DISCUSSION

Figure 1 shows the water diffusion coefficient D_{NMR} as a function of the inverse temperature.

Data for sample C are not reported, since they are identical with those referring to sample D. In fact, the two samples are substantially identical, except for deuteration.

As stated before, depending on the sample composition, we may go from *Lβ* to *Hα* mesophase directly (C, D and E samples) or by passing through the *IM* mesophase (A and B samples). Figure 1 clearly shows two distinct regions that will be discussed separately:

1. Region I, characterized by a rectilinear trend of D_{NMR}, where we observe diffusion in the *Hα* or *IM* and *Hα* mesophases.
2. Region II, characterized by a D_{NMR} minimum, where we observe diffusion around the *Lβ-IM* or the *Lβ-Hα* transitions.

Spot measurements of D_{NMR} were extended to the *Lβ* mesophase in order to check its behavior on this side of the transition.

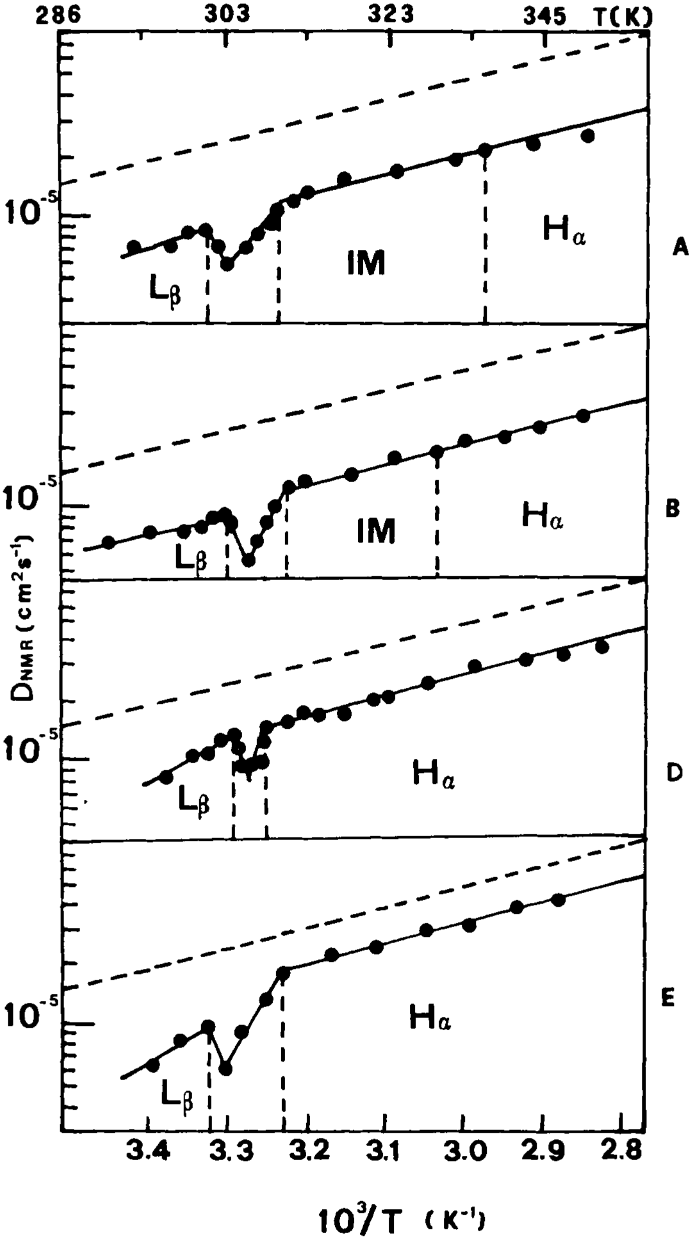

FIGURE 1 Temperature dependence of the water diffusion coefficient from the Lyotropic mixtures: A,B,D,E (see Table I), and from pure water (dash line). Dash vertical lines mark transitions.

a. Region I: Diffusion in *Hα* and *IM* mesophases

To clarify the discussion we show in Figure 2 diffusion data in the *IM* and *Hα* mesophases. For all samples D_{NMR} shows a rectilinear behavior as a function of inverse temperature, parallel with the pure water data. The slope corresponds to an activation energy of about (0.18 ± 0.02) eV, which is within the experimental error, the pure water diffusion activation energy, in the same temperature range.[9]

Water molecules seem to diffuse in these lyotropic mesophases as in a free water environment, except for a reduced mobility. Furthermore water diffusion decreases with decreasing water content.

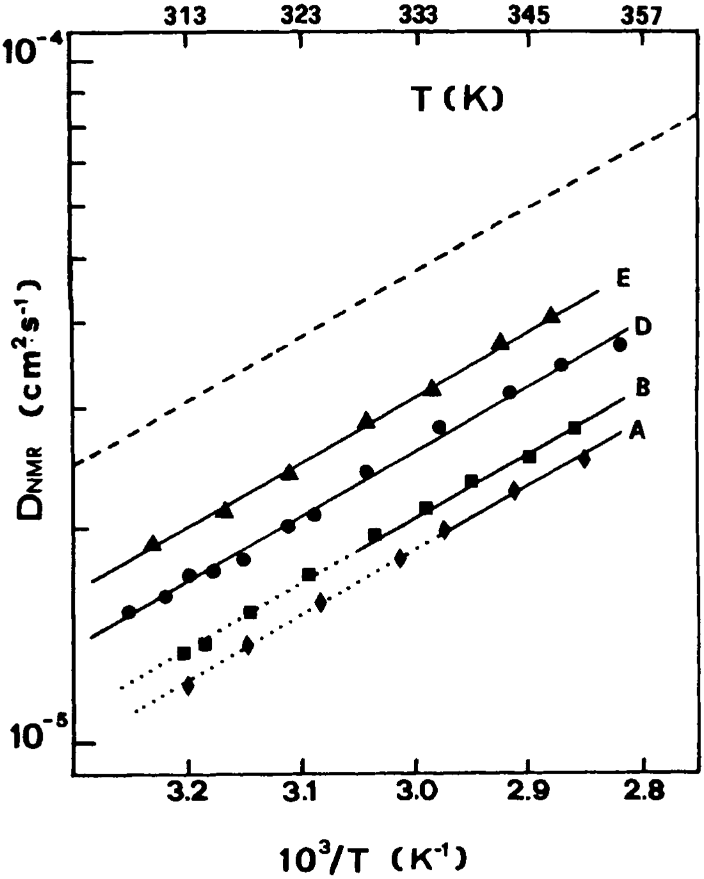

FIGURE 2 Temperature dependence of water diffusion coefficient from the Lyotropic mixtures A,B,D,E and from pure water (dash line):

a) hexagonal *Hα* mesophase (continuous line)
b) intermediate mesophase (dot line).

This effect is predicted by Eq. (1), provided that the bound water contribution to diffusion is negligible; in this case we have:

$$D_{\mathrm{NMR}} = f(1 - P)D_W \qquad (4)$$

so that D_{NMR} depends on the temperatures as does D_W.

It must also be noted that no significant variation of diffusion can be detected at the *IM*-*H*α transition, where value and slope are continuous. Therefore, according to our model, the same structural factor must be assigned to both *IM* and *H*α mesophases.

Before discussing the problem of the identification of the *IM* mesophase we should consider the data concerning the structural factor of the *H*α mesophase.

By means of Eq. (2), the structural factor has been calculated by pairing the four sets of data reported in Figure 2. The results are shown in Table II.

The values of *f*, which range around 3/4, are greater than that obtained in the case of *L*α mesophase which was found centered around 2/3, in the same range of temperature.[1] This appears physically reasonable considering the greater impediment to water diffusion between lamellar planes with respect to cylindrical-like aggregates.

However, we also note a slight, but significant difference among the values, which appears to increase with water content in the *H*α mesophase.

A possible explanation can be given on the basis of X-ray results[10] showing that, in such systems, the distance between the cylinder axes, *d*, increases with the water percentage, widening the channels to water diffusion. Considering a cluster of cylindrical aggregates having a common orientation and inserted in a hexagonal lattice, we define a reference frame *x*,*y*,*z* whose *xy* plane is parallel to one of the possible

TABLE II

Values of structural factor for *H*α mesophase obtained pairing data of Figure 2 (see text)

Samples pairs	Structural factor (PFG-NMR data)
A—B	0.74 ± 0.02
A—D	0.75 ± 0.02
A—E	0.77 ± 0.02
B—D	0.75 ± 0.02
B—E	0.78 ± 0.02
D—E	0.79 ± 0.02

lattice planes containing the amphiphilic aggregates. Let us also define D_x, D_y and D_z as the diffusion coefficients which would be measured along x, y and z, respectively. The water diffusion along the x and y axis is only affected by the chemical binding of the molecule on the aggregate surface ($f_x = f_y = 1$) and according to Eq. (1) we can write:

$$D_x = D_y = D_{\parallel} = [(1 - P)D_W + PD_b] \qquad (5)$$

Along the z axis a lower diffusion coefficient must be expected since the molecules can only travel across the inter-aggregate channel. A simple model can be based on the assumption that along z the diffusion coefficient is proportional to the fraction of empty space existing among the cylindrical aggregates. This quantity is simply given by the ratio $(d - d_c)/d$, d being the distance between the axis of the neighbouring cylinders and d_c the cylinders diameter.

Then:

$$D_z = D_{\perp} = \frac{d - d_c}{d}[(1 - P)D_W + PD_b] \qquad (6)$$

If the measurement axis is oriented in a direction defined by polar angles θ and φ, the measured diffusion coefficient is:

$$D = D_{\perp}\cos^2\theta + D_{\parallel}\sin^2\theta \qquad (7)$$

In our case the sample must be considered as a cluster of aggregates whose orientation is spherically distributed in the space.

Then the observed quantity must be averaged over all the possible orientations. In a PFG-NMR experiment we observe the attenuation of the echo signal due to the diffusion of nuclei occurring between the two magnetic field gradient pulses. The relation linking the diffusion coefficient and the echo attenuation is:[2,3]

$$R = \exp[-\rho D]; \quad \rho = \gamma^2\delta^2 g^2\left(\Delta - \frac{\delta}{3}\right) \qquad (8)$$

where γ is the gyromagnetic ratio of the observed nucleus and δ, g, Δ the quantities already defined in the experimental section. By using Eqs. (7,8) the 'powder' echo attenuation can be obtained according to:

$$\langle R\rangle_\theta = \frac{1}{2}\int_0^{\pi/2} \exp[-\rho(D_{\parallel}\sin^2\theta + D_{\perp}\cos^2\theta)]\,\sin\theta d\theta \qquad (9)$$

Since $\rho D_{\parallel}$ and $\rho D_{\perp}$ in our experimental conditions are estimated to be in the range between 0.1 and 0.3 (depending on the value of Δ), the integral in Eq. (9) can be evaluated by expanding the exponential function up to the linear term. The following approximate equation (approximation at the worst remains in the range of the measurement error) is obtained:

$$\langle R\rangle_{\theta} = \exp\left[-\rho\left(\frac{2}{3}D_{\parallel} + \frac{1}{3}D_{\perp}\right)\right] \tag{10}$$

This relation together with Eqs. (5,6) tell us that the quantity obtained when plotting $\langle R\rangle_{\theta}$ against Δ can be written as:

$$D_{\mathrm{NMR}} = \frac{1}{3}\left[2 + \frac{d - d_{\iota}}{d}\right]\left\{(1 - P)D_{W} + PD_{b}\right\} \tag{11}$$

comparing Eq. (11) with Eq. (1). We obtain the structural factor for the $H\alpha$ mesophase:

$$f_{H\alpha} = \frac{1}{3}\left[2 + \frac{d - d_{\iota}}{d}\right] \tag{12}$$

Observe that, if $d = d_{\iota}$, i.e. physically the lamellar limit, we obtain $f = 2/3$, the correct value for $L\alpha$ mesophase.[1]

Using Eq. (12) and X-ray data given in Ref. [10] we may estimate the following values for: 0.7 (sample A); 0.8 (sample B); 0.8 (sample D); 0.9 (sample E). These show, in a rather satisfactory agreement with values of Table II, that the value of f increases with increasing of the water content. Finally, neglecting the contribution to diffusion due to bound water, we have the following phenomenological equation:

$$D_{\mathrm{NMR}}^{H\alpha} = \frac{1}{3}\left[2 + \frac{d - d_{\iota}}{d}\right]PD_{W} \tag{13}$$

Using X-ray data,[10] the pure water diffusion data D_{W},[9] and the present diffusion results D_{NMR}, Eq. (13) allows us to estimate the fraction P of bound water. The results are reported in Figure 3.

b. Region II: Diffusion around the *Lβ-Hα* and *Lβ-IM* transitions

As shown in Figure 1, water diffusion coefficient D_{NMR} exhibits a well defined minimum at the $L\beta$-$H\alpha$ and $L\beta$-IM transitions.

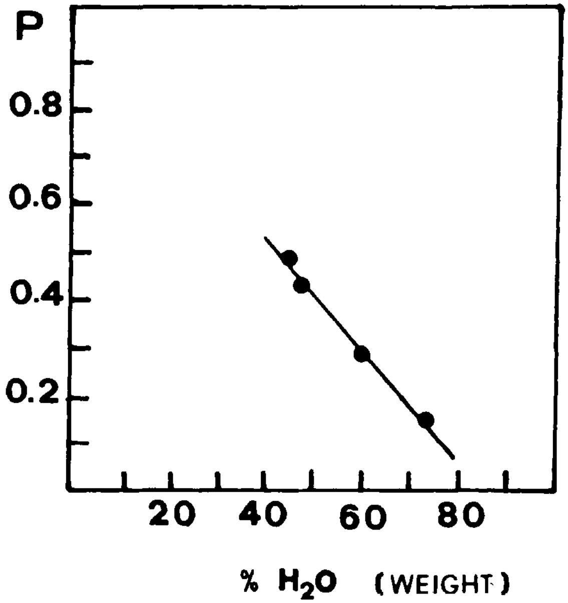

FIGURE 3 Bound water fraction P against water weight percentage in $H\alpha$ mesophase.

Considering at first the $L\beta$-$H\alpha$ transition, this minimum could appear surprising. At this transition in fact, the system consists of a mixture of $L\beta$ and $H\alpha$ mesophases, and the gradual appearance of cylindrical like aggregates between lamellar shaped aggregates should produce an increase of the diffusion coefficient.

In order to further investigate the $L\beta$-$H\alpha$ phase transition, D-NMR spectral profiles from perdeuterated KP have been recorded from sample C.

They are shown in Figure 4, spectrum (a) at the temperature of 300 K can be recognized as powder patterns due to the $-CD_3$ deuterons of KP molecules in the $L\beta$ mesophase. The broader singularities due to $-CD_2$-methylenic deuterons are out of scale. Spectra (b) and (c) show the coexistence of the $L\beta$ mesophase with amphiphilic cylindrical aggregates giving the central uniaxial powder pattern, where the sharp singularities of the methylic deuterons and several methylenic deuterons can be recognized. The order of the quadrupolar splitting for the CD_3 group is about 2KHz as it was previously observed in the $H\alpha$ mesophase of the potassium laurate and water system.[11] D-NMR spectra show that no unexpected phenomena occur at the phase transition, due, for example, to impurities or other uncontrolled factors. Therefore, the decreasing water diffusion coef-

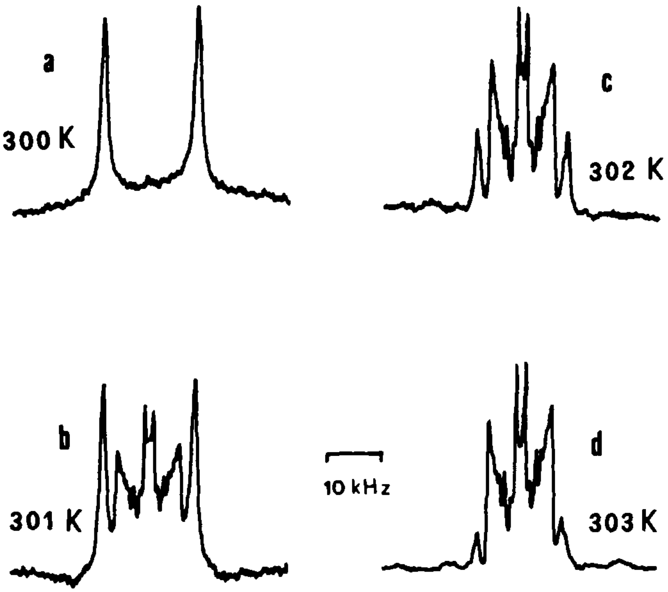

FIGURE 4 D-NMR spectra from perdeuterated KP (sample C of Table I) at different temperatures through *L*β-*H*α transition.

ficient must be explained in terms of some effect of the boundary on the water mobility as indicated by the appearance of cylindrical shaped aggregates. We can propose a simple model to explain at least qualitatively the observed minimum in the diffusion data.

As shown in Figure 5, the appearance of cylindrical aggregates, having a greater mean area per polar head, between the lamellar planes could generate localized restrictions in the interplanar gaps, acting as obstacles to the water diffusion. In other words, the growing of new aggregates in a spatial environment determined by the predominant *L*β mesophase should initially correspond to a reduction of the water mobility. With the further proceeding of the transformation of the lamellar aggregates into cylindrical aggregates, such an effect should be compensated by a gradual increasing of the *H*α mesophase, thereby opening new channels to diffusion. Obviously, the formation of the cylindrical aggregates should also increase the amount of bound water, thereby decreasing the diffusion, at least at the beginning of the transition when the lamellar mesophase is predominant on the hexagonal mesophase.

Identification of the *IM* mesophase should now be considered.

The diffusion data from samples A and B indicate that the *IM* mesophase must consist of aggregates having a cylindrical or nearly

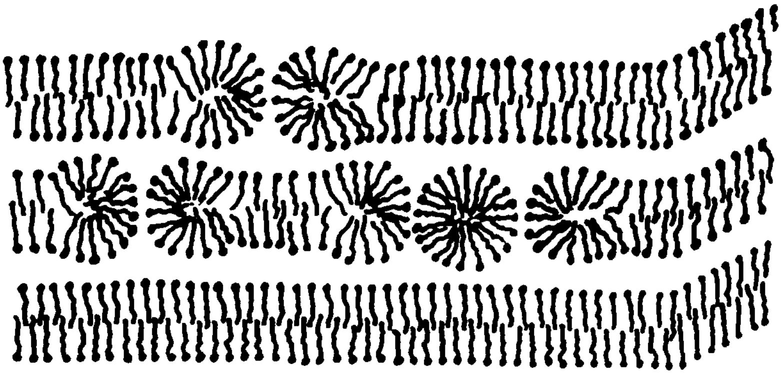

FIGURE 5 Illustration of a model for the spatial distribution of Lyotropic aggregates at $L\beta$-$H\alpha$ transition.

cylindrical shape, since the structural factor does not change at the *IM* to $H\alpha$ transition.

The occurrence of the cubic mesophase can be excluded since the system shows a very strong birefringence when observed through crossed polarizers. According to Luzzatti[4] the only reasonable possibility concerns the presence of a rectangular mesophase. This possibility is confirmed by the D-NMR spectral profiles of KP obtained from sample A, shown in Figure 6.

In the temperature range between 307 K and 335 K the spectral patterns show the presence of a strong biaxiality, which can be explained by the presence of ribbon-like aggregates inserted in a rectangular lattice.[12] A quantitative analysis of the spectral patterns shown in Figure 6 which could provide information on the shape of the aggregates[13] was beyond our present interest.

However, we should make some further comment. It has recently been shown[13] that ribbon aggregates can be obtained in ternary lyotropic system where two lipids of different length (potassium palmitate and potassium laurate) are mixed. The formation of such aggregates, where two regions of different curvature coexist, is due to the non uniform distribution of the lipid molecules within the aggregates.[14] This suggests that in the present case the occurrence of ribbon aggregates in the intermediate region of the KP/water system could be due to the presence of small amounts of impurities (KL or other lipids) in the sample. The ribbon could then be generated by a segregation of such impurities in well defined regions of the aggregates. This hypothesis could also explain the evolution of the $L\beta$ to *IM* transition. It is interesting to note that both diffusion D-NMR data indicate an equivalence of the $L\beta$ to $H\alpha$ and $L\beta$ to *IM*

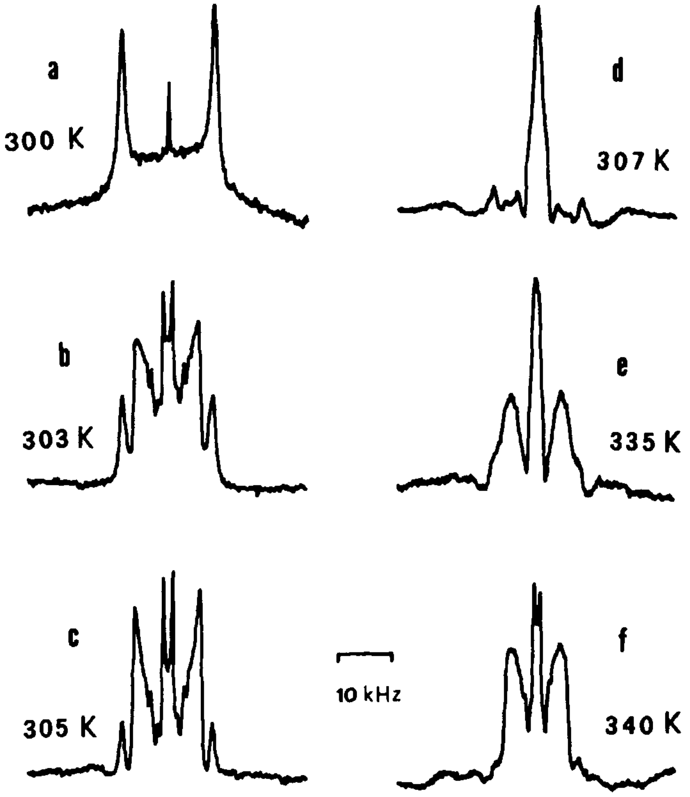

FIGURE 6 D-NMR spectra from perdeuterated KP (sample A of Table I) at different temperatures through *L*β-*IM* and *IM*-*H*α transitions.

transitions. In fact, spectra at 303 K and 305 K show the coexistence of the *L*β mesophase with elongated cylindrical aggregates similar to spectra from sample C (Figures 4c, 4d). Only when the *L*β mesophase has almost disappeared the aggregates change their shape from cylinders to ribbons. Such behavior would be expected if at the beginning of the transition the impurities remained trapped in the *L*β mesophase. Only when the *L*β mesophase disappears would the impurities enter into the already formed cylindrical aggregates forcing them to assume a ribbon shape.

Finally we can conclude that the phenomenological Eq. (1) can be applied even in the case of the *H*α mesophase.

The diffusion of water, obtained by using the PFG-NMR technique, gives valuable complementary information concerning the structure of a lyotropic system and the evolution of the system at phase transitions.

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References

1. G. Chidichimo, D. De Fazio, G. A. Ranieri and M. Terenzi, *Chem. Phys. Lett.*, **117**, 514 (1985).
2. E. D. Stejskal and J. E. Tanner, *J. Chem. Phys.*, **42**, 288 (1965).
3. E. D. Stejskal, *J. Chem. Phys.*, **43**, 3597 (1965).
4. U. Luzzatti, H. Mustacchi, A. Skoulios and F. Husson, *Acta. Cryst.*, **13**, 660 (1960).
5. R. Blinc, K. Easwaran, J. Pirs, M. Vilfan and I. Zumpancic, *Phys. Rev. Lett.*, **25**, 1327 (1970).
6. G. Chidichimo, J. W. Doane, A. Golemme, G. A. Ranieri and M. Terenzi, *Mol. Cryst. Liq. Cryst.* in press.
7. P. Ekwall, in '*Advances in Liquid Crystal*,' ed. G. H. Brown, Vol. 1, Academic Press, New York (1975).
8. J. H. Davis, K. R. Jeffrey, M. Bloom, M. I. Valic and T. P. Higgs, *Chem. Phys. Lett.*, **42**, 390 (1976).
9. J. H. Simpson and H. Y. Carr, *Phys. Rev.*, **111**, 1201 (1958).
10. V. Luzzati, in '*Biological Membranes*,' ed. D. Chapman, Vol. 1, Academic Press, New York (1968).
11. B. Mely, J. Charvolin and P. Keller, *Chem. and Phys. of Lipid*, **15**, 161 (1975).
12. G. Chidichimo, N. A. P. Vaz, Z. Yaniv and J. W. Doane, *Phys. Rev. Lett.*, **49**, 1950 (1982).
13. G. Chidichimo, A. Golemme and J. W. Doane, *J. Chem. Phys.*, **82**, 4369 (1985).
14. G. Chidichimo, A. Golemme, J. W. Doane and P. Westerman, *J. Chem. Phys.*, **82**, 536 (1985).