Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

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Version of record first published: 21 Mar 2007.

To cite this article: J. Charovlin & P. Rigny (1971): NMR Study of Molecular Motions in the Mesophases of Potassium Laurate-D_2O System, Molecular Crystals and Liquid Crystals, 15:3, 211-224

To link to this article: http://dx.doi.org/10.1080/15421407108083237

Molecular Crystals and Liquid Crystals. 1971. Vol. 15, pp. 211–224

NMR Study of Molecular Motions in the Mesophases of Potassium Laurate—D_2O System†

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Received October 23, 1970; *in revised form January* 25, 1971

Abstract—In the presence of water amphiphilic molecules display a large number of phases. As shown by X-ray studies the structures of these phases are characterized by a large scale periodic organization of aqueous and paraffinic media. Moreover, in the mesophases, these same X-ray diagrams show that this long range order coexists with a short range disorder in the paraffinic chains moiety.

Previous studies of the NMR line shape of paraffinic protons had suggested this disorder to be dynamical. We present and discuss here pulsed NMR measurements, performed on the paraffinic protons of potassium laurate—D_2O samples, in the lamellar mesophase, in order to gain a better knowledge of the details of the motions involved.

The complex shape of the free precession decay can approximately be analysed into " solid-like " (gaussian) and " liquid-like " (exponential) components. This suggests that the motion is not uniform along the paraffinic chain: protons close to the polar head are less mobile than those at the end of the chain. The first experience residual dipolar interactions (measured by the second moments of the gaussian signals) while these are averaged out for the second which exhibits a transverse relaxation time T_2 (measured by the time constant of the exponential signal). Despite the complexity of the free precession decay the measured value of relaxation time T_1 is the same for all the protons and is frequency independent.

Second moments and relaxation data indicate that the surfactant molecules undergo rapid deformations ($\tau_R \simeq 10^{-9}$ sec.) about the C—C bonds which (modulating intramolecular interactions) are responsible for T_1 and that a slow molecular diffusion ($\tau_S \simeq 10^{-6}$ sec.) over macroscopic distances is responsible for T_2, averaging out intermolecular interactions.

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† Presented at the Third International Liquid Crystal Conference in Berlin, August 24–28, 1970.

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1. Introduction

From soaps to more sophisticated biological phospholipids, amphiphilic molecules form, in the presence of water, liquid crystalline phases. The short and intermediate length fatty acids and their salts give the clearest examples of such lyotropic liquid crystals. These molecules contain a hydrocarbon chain and a terminal polar group. The property of amphiphily describes their behaviour in a solvent, commonly water. The polar head is hydrophilic and the hydrocarbon chain hydrophobic. In a solvent the polar heads associate and thus define a surface which separates the aqueous medium from the paraffinic one. The geometrical shape of this surface depends on the water content and the temperature. In fact these lyotropic systems are also thermotropic; it is the action of both solvent and temperature which gives rise to the original and complex polymorphism of these systems, ranging from the solid crystalline state to the isotropic liquid via the liquid crystalline mesophases.

The phase diagrams of soap-water and lipid-water systems have long been studied using crystallographic methods. Great progress towards the understanding of these mesophases is being made with X-ray scattering techniques. These liquid crystalline phases are characterized by:(1)

1. Large scale organization, the distribution of aqueous and hydrocarbon media is periodic in one, two, or three dimensions;
2. Small scale disorder within both media, particularly the paraffinic one.

The second point, affecting short range interactions, can be studied using NMR techniques which allow one to investigate local static and dynamic structures. This has been illustrated by previous studies on the behaviour of water in similar structures: some water molecules are strongly bounded to the barrier surface defined by the polar heads while others are free from the surface. A molecular exchange takes place between the two sets.(3,4) In the paraffinic moiety the disorder was shown to be dynamical and it was suggested that the motion of a CH_2 group in a chain should depend very much on its distance from the polar head.(2,3) Recent EPR experiments on spin labelled lipids lead to similar conclusions.(5)

In order to obtain more quantitative information concerning the motions of the paraffinic chains we have undertaken pulsed NMR experiments on CH_2 protons of the potassium laurate—D_2O system in its lamellar mesophase. After introducing the effects of molecular motions on NMR signals, we shall present preliminary relaxation data suggesting the existence of two types of motions: slow molecular diffusion and progressive deformations of the paraffinic chains.

2. Study of Molecular Motions by Pulsed NMR

In pulsed NMR(6a), one puts a spin system out of its state of thermal equilibrium in the external magnetic field H_0. A RF pulse tilts the nuclear magnetization out of the H_0 direction. After this excitation, the spin system recovers equilibrium in two simultaneous ways:

1. In a plane normal to H_0, the transverse component decays to zero in a time T_2, giving the so-called free precession signal;
2. Along H_0, the longitudinal component recovers its equilibrium value in a time T_1.

These two relaxation processes must be distinguished since in the first case the process does not require energy exchange (the transverse spin components simply get out of phase), while in the second case the spin system must exchange with the lattice an energy of the order of the coupling energy of the spins with the magnetic field H_0.

In non-metallic systems these two types of relaxation are generally induced by the spin–spin dipolar interactions and their modulation by lattice motions.

A. EFFECTS OF MOTIONS ON NMR SIGNALS

In a rigid solid each nuclear spin, fixed on a lattice site, experiences the local magnetic field due to the dipolar magnetic moments of neighbouring spins. The distribution of the local fields gives the NMR absorption line a gaussian shape characterized by a second moment m_2. In pulsed experiments the transverse components of the spins are forced out of phase with this static distribution in a time

$$T_2^{RL} \simeq m_2^{-1/2} \quad (RL \text{ for rigid lattice, } m_2 \text{ in sec}^{-2}).$$

The free precession signal decays according to

$$S_{(t)} = S_{(0)} \exp\left(-\frac{m_2}{2}t^2\right)$$

which is the Fourier transform of the gaussian line.(6a)

When a molecular motion, faster than $m_2^{1/2}$ sets in, the dipolar couplings between nuclear spins are averaged out and the absorption line width is due to second order effects of the modulated interaction. Experimentally, the absorption line gets narrower than the rigid lattice one and its shape tends to be Lorentzian. The free precession signal then decays as

$$S_{(t)} = S_{(0)} \exp\left(-\frac{t}{T_2}\right)$$

which is the Fourier transform of a lorentzian line of width T_2^{-1}.

It was shown,(7) in this motionally narrowed case, that the efficiencies of the relaxation mechanisms depend upon the Fourier spectrum of the frequencies of motion. Very useful approximations of the formula derived in Ref. 7 couple the relaxation rates to the motional correlation time

$$(T_1)^{-1} \simeq 2h^2\tau(1+\omega_0^2\tau^2)^{-1} \tag{1}$$

$$(T_2)^{-1} \simeq 2h^2\tau \tag{2}$$

where h^2 is the square of the modulated interaction and ω_0 is the nuclear Larmor frequency.

NMR is a powerful tool for the study of molecular motions. It can detect a molecular movement as soon as its frequency is of the order of the rigid lattice line width (a few 10^4 hertz). From the degree of line narrowing, one can identify the type of motion involved. From the effect on T_1, one can deduce its frequency, if in the range of a few 10^7 hertz. Even very slow motions, down to a few hertz, can be detected now since the development of measurements of T_1 in the rotating frame.(8)

B. Dynamically Heterogeneous Systems

As was shown in the preceding paragraph NMR properties of materials are strongly influenced by the motions of nuclei: this gives rise to complex signals whenever several motions coexist in a system or when the rates of the motions are distributed over a range of values. The system is then heterogeneous with respect to its dynamical structure.

Previous NMR studies(2,3) suggested that such a situation prevails in the case of the paraffinic chains of lipid-water systems in the liquid crystalline state. The degree of motion of a CH_2 group should depend very much on its distance from the polar head, the end of the chain being expected to move rather freely while the beginning should be more rigid. Under these conditions, the absorption line will contain both narrow and broad components. The latter are generally difficult to extract from the absorption spectrum and to analyse. In order to surmount this difficulty we have made free precession experiments where broad components of the absorption line are Fourier transformed into fast decaying components; their observation is limited only by the recovery time of the pulsed apparatus.

The signal of the protons of a definite CH_2 group will have the form(6b):

$$S_{(t)} = S_{(0)} \exp\left(-\frac{m_2}{2} t^2 - \frac{t}{T_2} \right)$$

where the second moment m_2 corresponds to residual dipolar interactions while the transverse relaxation time T_2 is due, on the contrary, to the modulated part of this interaction. T_2 and m_2 are, of course, complicated functions of the distance of the CH_2 group from the polar head and of the details of the motions.

3. Experimental

A. Samples

Our experiments were made with the potassium laurate—D_2O system(9) ($CH_3(CH_2)_{10}CO_2K$—D_2O hereafter called $C_{12}K$—D_2O). The anhydrous soap was prepared in the Laboratoire de Génétique Moléculaire (C.N.R.S.): the fatty acid is neutralized by potash in ethanolic solution and slowly crystallized, the product is washed in ethanol then dried. The heavy water is isotopically pure at 99.78%. The different concentrations were prepared by weighing of the required quantities of $C_{12}K$ and D_2O. Homogeneized by heating to 80 °C the solutions were also centrifuged back and forth through a constriction of the sample tube to increase homogeneity and to eliminate air bubbles. The concentrations, going from 14% to 30% D_2O (in weight) were chosen to give samples in the lamellar mesophase between 40 and 90 °C. In this phase the soap molecules are organized in parallel and equidistant bimolecular layers (smectic mesophase). The soap lamellae, full of disordered paraffinic chains, are limited by the polar heads which keep the aqueous medium apart from the hydrocarbon one.

B. APPARATUS

The second moments, m_2, and the transverse relaxation time, T_2, were obtained from direct analysis of the free precession decay observed after a " $\pi/2$ pulse " which tilts the magnetization from the direction of the external magnetic field H_0 to a plane normal to it. The longitudinal relaxation time, T_1, was obtained by the conventional " recovery " method(6a) using two " $\pi/2$ pulses " separated by variable time intervals. The pulsed spectrometer is of the single coil type, the dead time is 15 μs at 10 MHz and 8 μs at 30 MHz. Experiments were performed at different temperatures, from 40 to 90 °C, by means of a thermally controlled flow of gaseous nitrogen around the sample tube.

4. Results and Interpretation

A. FREE PRECESSION DECAYS

The critical analysis of the free precession decays is given in Ref. 10, in this paragraph we sum up the essential results. Figure 1 shows the semi-logarithmic plot of a typical free precession signal obtained from the CH_2 protons of a $C_{12}K—D_2O$ sample in the lamellar mesophase. The complex shape of the signal can be interpreted in terms of the previously mentioned heterogeneity of the motions of the paraffinic chains. It can be decomposed into three parts: two linear in t^2, one linear in t. Following the discussion of § 2–B we analyse it as the superposition of two " solid-like " ($T_2 \gg m_2^{-1/2}$) and one " liquid-like " components. This analysis does not necessarily imply discontinuities in the behaviour of the CH_2 groups along the chain but considering three regions must be a good approximation.

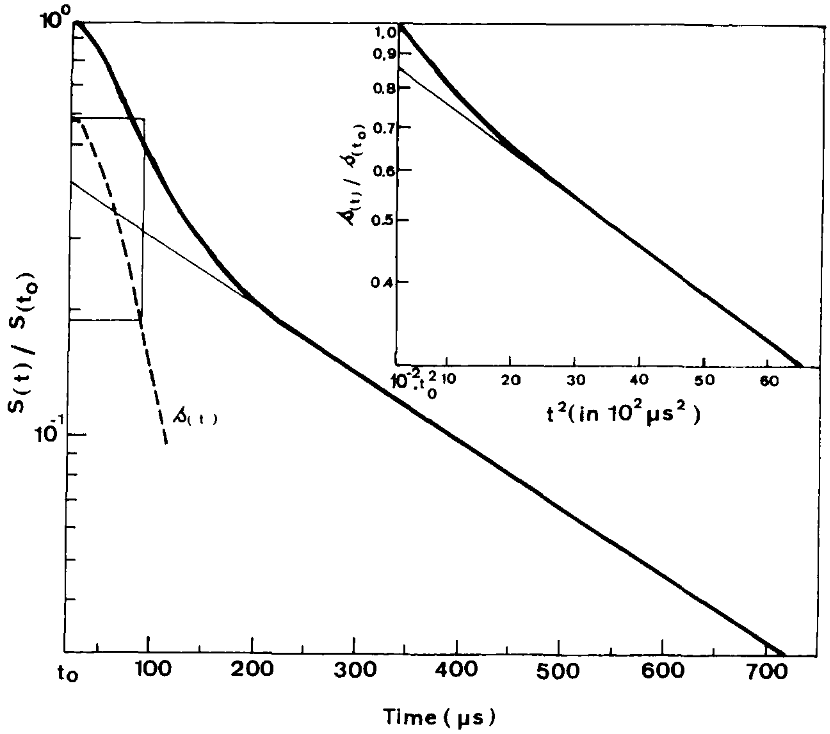

Figure 1. Logarithmic plot of the free precession decay, $S_{(t)}$, obtained at 30 MHz after a $\pi/2$ pulse, from a $C_{12}K$—28% D_2O sample in the lamellar phase at 90 °C. t_0 is the sum of the pulse width plus the recovery time of the apparatus. $s_{(t)}$ enlarged in the inset as a function of t^2, is the difference between the total decay and its exponential part.

It seems reasonable to assume that protons close to the polar head are less mobile than others and that they give the " solid-like " signal of largest second moment. Only a rough maximum value of 6 gauss^2 (determined at 90 °C for a 14% D_2O sample) can be given for this second moment for, in this fast decay region, part of the signal is lost in the apparatus recovery time. Then the second moment decreases, first to a water content and temperature independent value of 0.57 ± 0.09 gauss^2 in the second " solid-like " region, finally to zero in the " liquid-like " one. This last region very likely concerns protons of the chain end, its decay is characterized by a transverse relaxation time $T'_2 = 270 \pm 20$ μsec. Extracted from Fig. 1, the percentages of protons in each part of the

TABLE 1 Relative fractions (in %) of Protons of the Paraffinic Chains in “ Solid-like ” and “ Liquid-like ” Regions as a Function of the Water Content. The $C_{12}K—D_2O$ samples are all in the lamellar mesophase at 90 °C.

Water content: $\frac{D_2O \text{ weight}}{\text{total weight}}$		0.14	0.22	0.25	0.28	0.30
“ Solid-like ” spins	$m_2 = 6$ gauss^2	31	15	9	6	0
	$m_2 = 0.57$ gauss^2	44	50	50	51	54
“ Liquid-like ” spins	$m_2 = 0$ and $T_2 = 270$ μsec	25	35	41	43	46

chain are indicated in Tables 1 and 2 for several temperatures and D_2O concentrations. It can be seen that the “ liquid-like ” component is not due to the very mobile methyl protons, for they represent no more than 13% of the total protons number; nor is it due to residual H_2O in D_2O. An increase of mobility can be expected when temperature or water content increase, this is the general trend one observes in Tables 1 and 2 where the mobile part of the chain becomes more important with temperature and concentration.

TABLE 2 Relative Fraction (in %) of Protons of the Paraffinic Chains in “ Solid-like ” and “ Liquid-like ” Regions as a Function of Temperature for a $C_{12}K$—28% D_2O Sample in the Lamellar Mesophase.

Temperature (°C)		44	55	73	90
“ Solid-like ” spins	$m_2 = 6$ gauss^2	8	7	7	6
	$m_2 = 0.57$ gauss^2	66	64	58	51
“ Liquid-like ” spins	$m_2 = 0$ and $T_2 = 270$ μsec	26	29	35	43

The shape of the free precession signals have been interpreted here as coming from partially averaged dipolar interactions. The order of magnitude of the first second moment, $m_2 \simeq 6$ gauss^2, compares well with the values obtained for alkanes rotating around their longitudinal axis.(11) The absence of frequency second moment variations indicates that the anisotropic moment responsible for the partial averaging of the dipolar interactions is fast compared to the second moment reduction.(6b) Similar shapes can also result from molecular diffusion in an inhomogeneous magnetic field; however a test consisting of a study of the spin system responses to suitable excitations has been proposed(10) and enables one to choose between the two alternatives. No effect of field inhomogeneity is apparent with our samples.

Other authors, investigating similar systems, have reported frequency dependent line widths(12) or free induction decays(13) while we have not been able to see such a dependence from 7 to 30 MHz. We believe these discrepancies to be due to differences in samples preparations; the mean size of the monocrystalline domains being perhaps an important factor governing the reorientation ability, in the magnetic field, of each diamagnetically anisotropic domain.

B. RELAXATION TIMES

The transverse relaxation time T_2 of the " liquid-like " protons is 270 ± 20 μsec; it increases slightly with temperature with an activation energy of the order of 0.5 kcal/mole. The T_2 of " solid-like " protons ought to be obtained by other methods (e.g. $T_{1\rho}$ measurements). Only one longitudinal relaxation time T_1 is observed within our limit of error. Its value at 90 °C is 0.68 ± 0.04 sec. It increases with temperature having an activation energy of 5.5 kcal/mole as shown in Fig. 2. The measurements were made from 7 to 30 MHz but no frequency dependence was observed. This last result immediately shows that a motion rapid compared to the inverse Larmor frequency is responsible for T_1 (equation 1). Its characteristic correlation time is $\tau_R < 10^{-8}$ sec. But for such a fast motion, the associated T_2 would be equal to T_1,(7) T_2 being smaller than T_1 a slower motion is responsible for T_2. Under these conditions accurate values of the characteristic times of the motions and of the strength of the interactions they modulate cannot be given without further experiments.

C. PROPOSED MODEL

The rapid motion, responsible for the longitudinal relaxation, probably consists of internal isomeric rotations about the C—C bonds of the paraffinic chain. The measured T_1 activation energy is consistent with the heights of the barriers hindering internal

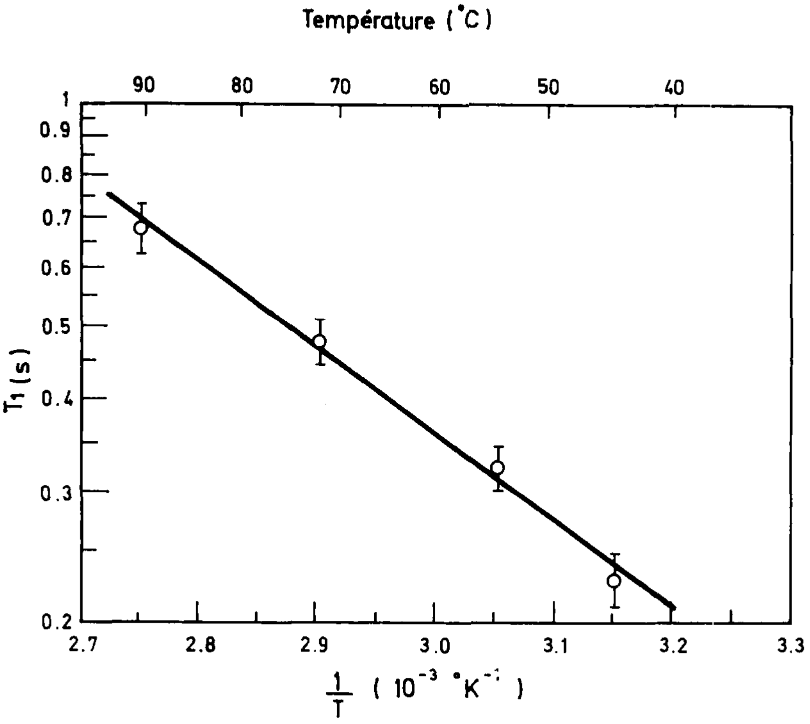

Figure 2. Longitudinal relaxation time T_1 plotted as a function of the inverse absolute temperature. The measurements were made with a $C_{12}K$—28% D_2O sample in the lamellar phase, at a frequency of 30 MHz. The activation energy is 5.5 kcal/mole.

rotations in alkanes[14] and assuming these rotations to be described by an harmonic potential the characteristic time τ_R of this rapid motion can be estimated with[15]

$$\tau_R{}^{-1} \simeq \frac{kT}{\hbar} \exp\left(-\frac{\Delta E}{kT}\right)$$

giving a rough value of $\tau_R \simeq 10^{-9}$ sec.

Such a motion is also met in long chain polymers where it seems to be a predominant T_1 relaxation mechanism.[16] However in our case the single T_1 behaviour would be inconsistent with the " three parts in the chain " model considered in paragraph 4-A unless we introduce spin diffusion.[17] This point will be discussed later. A general deformation results from all these segmental fast motions.

In the lamella, the laurate molecule is in such an anisotropic medium that this general motion can be schematized as having its amplitude and isotropy increasing from the polar head to the methyl end; this can explain the progressive averaging of the spin–spin dipolar interactions and so the decrease of the second moment from 6 gauss^2 close to the polar head to zero at the end of the chain. Such a statement has to be developed considering the rotameric jump probability according to the position of the C—C bond in the chain, as will be stressed in the next paragraph.

The slower motion, responsible for the transverse relaxation, could be a two dimensional diffusion of the laurate molecule in the plane of the lamellae modulating the intermolecular dipolar interaction. Taking an average intermolecular interaction of 2 gauss^2 one can deduce, from the experimental T'_2 and equation 2, a characteristic time τ_S for this slow diffusion of roughly 10^{-6} sec. The existence of such a diffusion has not been directly proved in the lamellar phase but a similar motion can be seen, in an obvious way, in the cubic isotropic mesophase of the same system $C_{12}K—D_2O$.(10) It is very likely that diffusion also occurs in lamellar mesophase but its effects on the NMR properties differ from those in the cubic mesophase owing to the anisotropy of the structure.

D. Discussion

In setting forth the model of the motions existing in the system under study a few points were stated although we need more experimental results to support them. We are going to reconsider them from a more critical point of view.

First, spin diffusion was invoked to explain the uniqueness of T_1 even though three types of spins can be considered in the chain. Spin diffusion acts as follows: if part of an heterogeneous spin system is strongly coupled to the lattice, while the rest is weakly coupled, the first part may act as an energy sink for the whole system, spin–spin interactions in the rest of the system can conduct energy to the fast relaxing part at a rate $\tau_D{}^{-1}$ of the order of the dipolar spin–spin coupling (expressed in sec^{-1}). Such a mechanism makes the spin lattice relaxation time T_1 uniform over the whole system and the relaxation rate can be limited either by the diffusion rate or by the relaxation rate of the energy sink. At the temperatures of our experiments (from 40 to 90 °C) the reorientation of the methyl groups is very rapid(17) and the rate flow, $T_1^{-1} \simeq 10^{-1}$ sec^{-1}, of their Zeeman energy to the lattice is too small compared to the measured relaxation rate $T_1^{-1} \simeq 1$ sec^{-1}, so that they cannot act as an energy sink. The diffusion rate in the " solid-like " part of the chain being very fast $\tau_D^{-1} \simeq 10^4$ sec^{-1} the longitudinal relaxation rate is certainly limited by the capacity of an energy sink which is to be found in the fast rotameric jumps taking place in the whole " liquid-like " part of the chain. In this condition the measured relaxation rate must be equal to the relaxation rate of one proton in the " liquid-like " part weighted by the ratio of the number of " liquid-like " protons to the total number of protons. This effects the correlation time τ_R by a factor of about 2 (see Table 1).

In presenting the model it was also stated that from the fast isomeric rotations a general swinging of the methyl end of a chain results, the polar head being fixed on the water-soap interface. An important problem is the relation between the local correlation time and the one for this general swinging motion. The general idea about a theoretical model is that an isomeric rotation, giving the methyl end too wide a displacement, would have to be less probable than those distorting the chain progressively. This supposes that the motions in a chain have to be treated from a collective point of view; the probability of occurrence of one rotameric jump depending upon the conformation of the chain. In this model the general deformation of the chain would be characterized by a longer correlation time than the one of the fast local isomeric rotations. Such a slower motion, modulating intermolecular interactions, could be taken as responsible for the transverse relaxation instead of the molecular diffusion. However, the activation energy of T_2 is very much smaller than that of the isomeric rotations giving rise to the swinging motion. This seems to indicate that this last motion is not effective for the transverse relaxation which seems to be due to the molecular diffusion.

5. Conclusion

The molecular motions existing in the lamellar mesophase of the potassium laurate-D_2O system have been investigated by means of pulsed NMR; our interest was focussed on the dynamical disorder of the paraffinic chains. Relaxation data obtained on this system show evidence of two types of motions which can be schematized in the following way:

—isomeric fast rotations about the C—C bonds deform the paraffinic chain; their effects increasing from the polar head to the methyl end. They progressively average to zero the intramolecular spin–spin interactions. Their characteristic time is of the order of 10^{-9} sec;

—a slower motion, which is a two-dimensional diffusion of the laurate molecule in the plane of its lamellae, has a correlation time of the order of 10^{-6} sec.

The order of magnitude of these times are somewhat out of the ranges of motion rates accurately attainable by the simple NMR methods we have used. Moreover, the discussion has shown that this model was a very crude one and that several points need further developments:

—the isomeric rotations relax the Zeeman energy, but the uniformization of T_1 by spin diffusion and the localization on the chain of the energy sink have to be emphasized;

—a statistical description of the general folding of the chain, resulting from these isomeric rotations will be very useful in casting light on the progressive averaging of the dipolar intermolecular interactions as well as on the modulation of intermolecular ones by this motion;

—molecular diffusion modulates also the latter and its role in the transverse relaxation has to be more precisely defined.

Answers to these questions need, in particular, an extension of NMR experiments towards the investigation of slower molecular motions.

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