MOLECULAR MOTIONS AND PHASE TRANSITIONS

NMR RELAXATION TIMES STUDIES OF SEVERAL LECITHINS

R. BAR-ADON AND H. GILBOA, *Department of Chemistry, Technion, Israel Institute of Technology, Haifa, Israel*

ABSTRACT The spin-lattice relaxation time, T_1, and the dipolar energy relaxation time, T_D, were measured as a function of temperature. The materials studied were samples of anhydrous L-dipalmitoyl lecithin, DL-dipalmitoyl lecithin, L-dimyristoyl lecithin, DL-dimyristoyl lecithin and their monohydrates, and of anhydrous egg yolk lecithin. It is shown that T_D is a much more sensitive parameter than T_1 for the determination of the Chapman phase transition. Comparison between T_1 and T_D provides information about new types of slow molecular motions below and above the phase transition temperature. It is suggested that the relaxation mechanisms for T_1 and T_D in the gel phase are governed by segmental motion in the phospholipid molecule. A new metastable phase was detected in dimyristoyl lecithin monohydrates. This phase could only be detected from the dipolar energy relaxation times.

INTRODUCTION

The structure of biological membranes has been thoroughly investigated of late. According to the model proposed by Singer and Nicolson (1), the major components determining the membrane structure and its function are lipids and proteins. The major function of the lipids in the biological membrane is to form a network in which the proteins are embedded. Therefore, it is very important to determine the structural and dynamic properties of the phospholipids. The amphiphilic molecules which form the bilayer structure have been investigated using various physical methods, such as differential scanning calorimetry (DSC) (2), x-rays (3), density measurements (4), Raman and infrared (IR) spectroscopy (5), neutron diffraction (6), electron spin resonance (EPR) (7–9), and nuclear magnetic resonance (NMR) (10–12). Consequently, many of the structural properties of the bilayer are well understood (13).

Magnetic resonance methods (11, 12, 14–16) have been found to be useful in determining various dynamic properties of the phospholipids above and below the Chapman phase transition (17). In the present work the spin-lattice relaxation time T_1 and dipolar relaxation time T_D were measured as a function of the temperature in anhydrous samples of dipalmitoyl lecithin (DPL), dimyristoyl lecithin (DML), egg yolk lecithin (EYL), and the DPL and DML monohydrates. The relaxation times were measured to obtain information about the phase transitions and the dynamical properties of these compounds. To study the slow and fast molecular motions in the phospholipids, the different temperature dependence of T_1 and T_D was taken into account. It is shown that the dipolar-energy relaxation time T_D is a very sensitive parameter for the study of the gel-to-liquid crystalline phase transition. In the DML monohydrate, T_D values were used to determine a new metastable phase undetected by T_1 measurements. The dynamical behavior of the chains was studied by comparing the measured

values of the relaxation times in the gel phase with calculated values from a model. We suggest that the molecular motions cannot be represented by the assumption that the molecule rotates as a rigid body. Only through the introduction of segmental motions can the relaxation behavior be interpreted satisfactorily.

THEORETICAL BACKGROUND

Relaxation Times and Molecular Motions

The NMR technique is an established tool for the investigation of molecular motions and molecular dynamics in solids and liquids (18). The dynamics of the spins affect the line-shape of the resonance signal. We shall discuss only the effect of molecular motions on the spin-lattice relaxation rate in the solid phase. In a sample containing nuclei with spins $I = 1/2$, the main relaxation mechanism goes through the dipole-dipole interaction between the spins. We consider only this mechanism.

In solids or ordered phases a system of spins in a high magnetic field can be considered to be composed of two heat reservoirs. The first and dominant one comes from the Zeeman interaction of the spins with the large external magnetic field; the second, much smaller one is from the dipolar interaction between the spins. The experimental procedure for studying spin-lattice relaxation is to raise the temperature and detect the time needed to approach thermal equilibrium with the lattice. The Zeeman spin-lattice relaxation time is T_1 and the dipolar energy spin-lattice relaxation time is T_D.

In a typical NMR experiment, the Zeeman energy is several orders of magnitude larger than the dipolar energy; as a result, ultraslow motions that affect T_D do not affect T_1, whereas faster motions will affect both T_1 and T_D. A small rigid molecule in the solid phase undergoes a molecular motion. For ultraslow molecular motion with a correlation time τ_c the relaxation rate for the dipolar energy of the system is given by (19, 20):

$$\frac{1}{T_D} = \frac{1 - P}{\tau_c} \qquad 0 < P < 1, \tag{1}$$

where P is a geometrical factor that depends on the solid structure and motional mechanism.

The above relaxation mechanism is called the "strong" collision mechanism. When the molecular motion is faster, it contributes to the Zeeman relaxation rate through the "weak" collisional mechanism. The equation is:

$$\frac{1}{T_1} = K\left(\frac{\tau_c}{1 + \omega_0^2\tau_c^2} + \frac{4\tau_c}{1 + 4\omega_0^2\tau_c^2}\right), \tag{2}$$

where K is a constant depending on the molecular structure. The fast molecular motion contributes to the dipolar energy relaxation rate and can be described to a very good approximation by (20):

$$\frac{1}{T_D} = K'\left(\tau_c + \frac{5\tau_c}{1 + \omega_0^2\tau_c^2}\right), \tag{3}$$

though other approximations can be used (21, 22).

The discrimination between the two mechanisms could be achieved through the tempera-

ture dependence of the relaxation time T_D. The temperature dependence of the correlation time τ_c can be assumed to be:

$$\tau_c = \tau_\infty \exp\left(\frac{\Delta E}{RT}\right) \tag{4}$$

where τ_∞ is the correlation time at very high temperatures. It is obvious from Eq. 4 that at lower temperatures τ_c becomes longer. The T_D dependence on τ_c values is different in the two relaxation mechanisms above. In the strong collision mechanism T_D is proportional to τ_c, while for weak collision mechanism T_D is proportional to τ_c^{-1}. Hence, cooling the sample will result in longer T_D values for the strong collision mechanism and shorter T_D values for the weak collision mechanism.

The temperature dependence of T_1 and T_D, according to Eqs. 1–3, is summarized in Table I.

So far the spin-lattice relaxation dependence on one type of molecular motion, for example, the isotropic rotation of the molecule in the lattice, has been discussed. If another type of motion exists, for example, translational diffusion in the lattice, it will have a different correlation time and will influence both relaxation rates, T_1^{-1} and T_D^{-1}. The measured relaxation rate will include both mechanisms, unless one is much more effective than the other, in which case the experimental results will reflect almost solely the more effective relaxation mechanism.

Let us assume that there are two types of molecular motions, a fast one with correlation time τ_{cF} and low activation energy, and a slow motion with correlation time τ_{cS} and a higher activation energy. As indicated above, the relaxation time will depend on the relaxation mechanism for each of the motions. Let us assume further that at low temperatures the ultraslow molecular motion is too slow to affect the relaxation rate of the dipolar energy and that the relaxation mechanism of the fast molecular motion is in the weak collision range. When the sample is heated, τ_{cS} and τ_{cF} become shorter. At first the temperature dependence is due solely to changes in τ_{cF}, i.e., T_D becomes longer at high temperatures. At a certain temperature the ultraslow molecular motion begins to contribute to the dipolar relaxation rate through the strong collision mechanism. The relaxation through this mechanism might be more effective than through the other mechanism. The temperature dependence of T_D will become different, i.e., it will be shorter at higher temperatures. In the case described above, it is shown that T_D measurement is a good method for determining new types of ultraslow molecular motions. These ultraslow motions affect neither T_1 nor the linewidth of the NMR

TABLE I
THE DEPENDENCE OF THE SPIN-LATTICE RELAXATION TIMES T_1 AND T_D ON THE TEMPERATURE

	Weak collision mechanism		Strong collision mechanism
	Fast molecular motion	Slow molecular motion	Ultraslow molecular motion
Effect on T_1	$T_1 \propto T$	$T_1 \propto T^{-1}$	—
Effect on T_D	$T_D \propto T$	$T_D \propto T$	$T_D \propto T^{-1}$

signal. As the temperature rises, τ_{cS} becomes shorter. At short τ_{cS} values a change of the relaxation mechanism will occur from the strong collision into the weak collision mechanism, resulting in a change in the temperature dependence of T_D, which may affect the spin-lattice relaxation time T_1. Such a change in the temperature dependence of T_D was observed (19, 21, 24).

So far the relaxation behavior of a small rigid molecule and its dependence on molecular motions has been described. For a large nonrigid molecule there may be several types of segmental motions. The motion of nucleus i may be different from any other nucleus; consequently, each nucleus may have a specific relaxation time T_{1i} and T_{Di}. In a solid or ordered phase where the dipole-dipole interaction between the spins is large, one observes an average relaxation rate of all the interacting spins in the system, resulting from the spin diffusion mechanism (25). Hence, even if several nuclei differ in their dynamical properties from others, only a single relaxation time would be detected:

$$\frac{1}{T_{1t}} = \sum_i n_i \frac{1}{T_{1i}} / \sum_i n_i. \tag{5}$$

T_{1t} is the overall spin-lattice relaxation time, T_{1i} is the hypothetical relaxation time of nuclei i caused by the structural and dynamical properties of the molecule in the absence of the spin diffusion mechanism, and n_i is the number of type i nuclei. An identical equation for T_D can be assumed where

$$\frac{1}{T_{Dt}} = \sum_i n_i \frac{1}{T_{Di}} / \sum_i n_i. \tag{6}$$

The temperature dependence of T_1 and T_D for a large molecule with segmental motions is much more complicated than for small rigid molecules. This is because the relaxation time depends on several τ_i values, each of which may have a different temperature dependence.

The Effect of Asymmetric Environment on the Relaxation Time

A methylene group in a parafinic chain undergoes internal rotations, which affect the relaxation time of the two protons. This problem was treated by Anderson (26) and later by Tsutsumi (27). The energy profile of the two methylene protons as a function of the rotation angle, according to the model used by Anderson, is described in Fig. 1. The relaxation times T_1 and T_D for the weak collision mechanism are given by:

$$\frac{1}{T_1} = \left(\frac{\gamma^2 M_2}{2}\right)\left\{\frac{3Q_A Q_B}{\lambda_1}\left[\frac{1}{1+(\omega/\lambda_1)^2} + \frac{4}{1+(2\omega/\lambda_1)^2}\right] + \frac{Q_B}{\lambda_2}\left[\frac{1}{1+(\omega/\lambda_2)^2} + \frac{4}{1+(2\omega/\lambda_2)^2}\right]\right\} \tag{7}$$

and:

$$\frac{1}{T_D} = \frac{2}{3}\gamma^2 M_2\left[\frac{3Q_A Q_B}{\lambda_1}\left(1 + \frac{5}{1+\left(\frac{\omega}{\lambda_1}\right)^2}\right) + \frac{Q_B}{\lambda_2}\left(\left(1 + \frac{5}{1+\left(\frac{\omega}{\lambda_2}\right)^2}\right)\right)\right] \tag{8}$$

where ω is the Larmor frequency, γ is the gyromagnetic ratio, M_2 is the second moment, λ_1 =

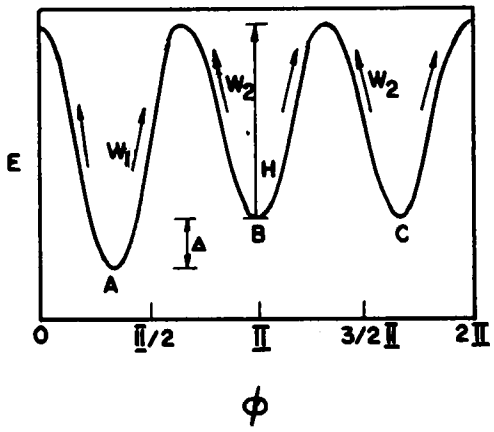


FIGURE 1 Potential energy curve for a rotating methylene group. W_1 and W_2 are the jump transition probabilities between the potential wells.

$W_2 + 2W_1$, $\lambda_2 = 3W_2$, $Q_A = W_2/(W_2 + 2W_1)$, and $Q_B = W_1/(W_2 + 2W_1)$. If we assume that λ_1^{-1} λ_2^{-1} are correlation times, then T_1 would depend on two different correlation times, which are a function of the transition probabilities W_1 and W_2.

To obtain a more general picture of relaxation rate as a function of both parameters W_1 and W_2, a three-dimensional plot is given in Fig. 2. In this figure the relaxation rate (T_1^{-1}) contours

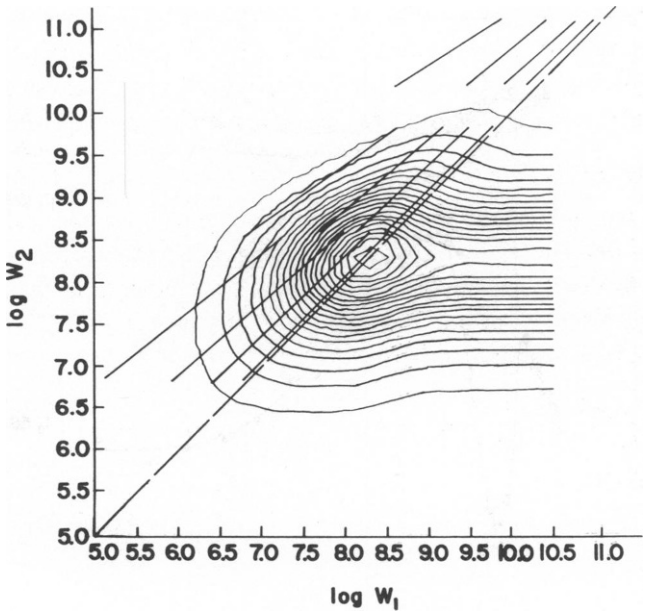


FIGURE 2 Spin-lattice relaxation rates T_1^{-1} as a function of the transition probabilities W_1 and W_2. For the outer contour T_1^{-1} = 1 s^{-1}, and for the inner contour T_1^{-1} = 20 s^{-1}. T_1 values as a function of temperature from 250 to 350 °K are given by the straight lines for various values of H and Δ. For the upper set of lines H = 3,000 cal/mol; in the middle set, H = 5,000 cal/mol; and for the lower set, H = 7,000 cal/mol. Δ values from right to left are Δ = 100, 500, 1,000, 2,000 cal/mol.

are given. For the outer contour $T_1^{-1} = 1\ s^{-1}$ and for the inner contour $T_1^{-1}{}_1^{-1} = 20\ s^{-1}$. For a parafinic hydrocarbon chain only the part above the dashed line is relevant, though the other part may be relevant to other systems.

The temperature dependence of W_1 and W_2 can be written as:

$$W_1 = W_1^0 \exp\left[-(H + \Delta)/RT\right]$$
$$W_2 = W_2^0 \exp\left(-H/RT\right). \tag{9}$$

According to eqs. 9 log W_2 and log W_1 are linear functions of the reciprocal temperature T^{-1}. On plotting log W_2 as a function of T^{-1}, straight lines on Fig. 2 are drawn depending on the values of H and Δ. It was discussed elsewhere (28) that as the motion becomes less isotropic, T_1^{-1} becomes smaller or T_1 becomes longer. Nevertheless, in the extreme narrowing region a very small region, where T_1^{-1} is smaller when the motion is more anisotropic, can be found. It could best be noted by keeping log W_2 constant at a value between 8.5 and 9 and reducing the value of W_1. Fig. 2 may be used as a guide for finding the relaxation rate temperature dependence in parafinic chains where some methylene groups have low H and Δ values, others have higher H and Δ values, and the overall relaxation rate T_{1r}^{-1} is given by Eqs. 6.

EXPERIMENTAL

Materials

L-$\beta\gamma$ dipalmitoyl α lecithin (L-DPL), DL-$\beta\gamma$ dipalmitoyl α lecithin (DL-DPL), L-$\beta\gamma$ dimyristoyl α lecithin (L-DML), and DL-$\beta\gamma$ dimyristoyl α lecithin (DL-DML) were obtained from Fluka AG (Buchs,

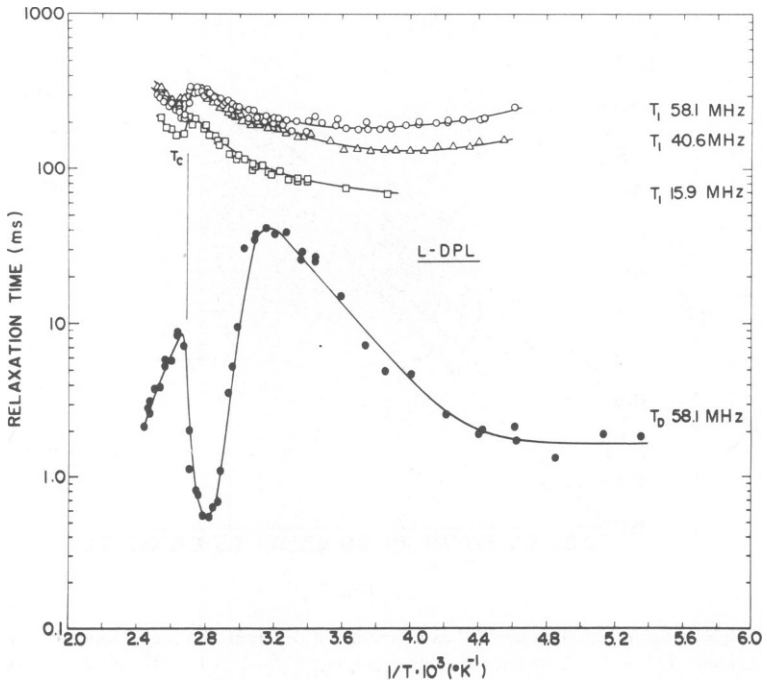


FIGURE 3 The relaxation times T_1 and T_D of anhydrous L-DPL as a function of reciprocal temperature. T_c is the Chapman phase transition temperature.

Switzerland). EYL was obtained from BDH Chemicals Ltd. (Poole, England). The purity of the phospholipids was determined by thin layer chromatography before and after the measurements to give one point; only DL-DPL needed further purification, and this was done according to the method of Lindblom et al. (29).

Preparation of the Samples

The pure phospholipid was degassed on a vacuum line for several days. The sample was sealed and then equilibrated at 90–100°C for 2 d. EYL prepared by the same method was kept in the refrigerator. The monohydrates of DL-DPL and L-DPL were prepared by equilibration of the anhydrous lecithin and D_2O vapors (30). The monohydrates of L-DML and DL-DML were prepared on a vacuum line by adding a measured volume of D_2O vapors. To avoid surface phenomena like creeping of the substance on the wall of the NMR tube, the NMR tube was treated with Siliclad, which changes the surface properties of the glass. Helium gas in a pressure of ~300 mm Hg was added to gain a better homogeneity in the heating of the sample.

NMR Measurements

The measurements were carried out on a Bruker pulsed spectrometer (Bruker AG, Karlsruhe, Germany; model B-KR 322S). The temperature was stabilized with B-ST 100/700 unit. After each series of measurements the unit was calibrated on a reference sample using copper-Constantan thermocouple. The accuracy is assumed to be ±1°C. T_1 was determined using the pulse sequence $180°$-τ-$90°$. The signal was detected with a pulsed-gated integrator. T_D was determined by the Jeener and Broekaert method (31) $90°_x$-t-$45°_y$-τ-$45°_x$, where $t \simeq 20$ μs. The signal after the third pulse was detected on a transient recorder (Bruker B-C 104).

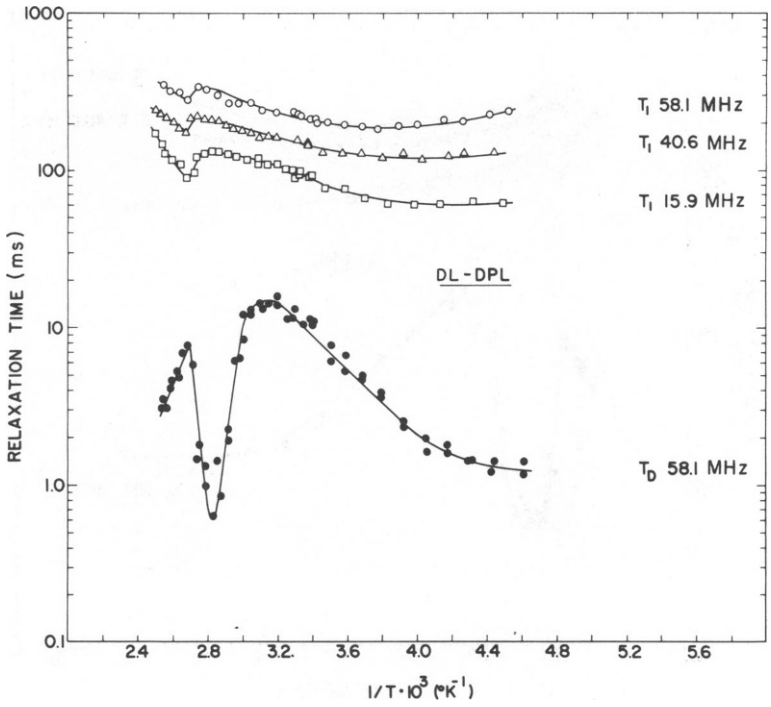


FIGURE 4 The relaxation times T_1 and T_D of anhydrous DL-DPL as a function of reciprocal temperature.

RESULTS AND DISCUSSION

Anhydrous Phospholipids

The relaxation times T_1 for L-DPL, L-DML, DL-DPL, DL-DML, and EYL as a function of reciprocal absolute temperature at three frequencies 15.9, 40.6, and 58.1 MH_z are given in Figs. 3–7. The values of T_D measured at 58.1 MH_z as a function of the reciprocal absolute temperature are given as well.

Comparison of Figs. 3–7 shows that the general behavior of the relaxation times T_1 and T_D in the five samples is quite similar. The temperature dependence of the spin-lattice relaxation time T_1 is very small in all samples, but there is a substantial frequency dependence. Note that at the transition to the liquid crystalline phase there is a small decrease in T_1 values, as has been observed (14) earlier, and that above the phase transition temperature T_1 values increase again.

T_D values in the lecithin samples have remarkable temperature dependence. As mentioned before, the general temperature dependence is quite similar for all the anhydrous samples. We shall separate the T_D temperature dependence into three regions: (*a*) the low temperature region, (*b*) the region just below the phase transition, and (*c*) above the phase transition temperature. In region *a* T_D values decrease as T^{-1} (K^{-1}) increases. At low temperatures T_D is ~2 ms and increases to a maximum of ~10–50 ms, depending on the lecithin sample. We have

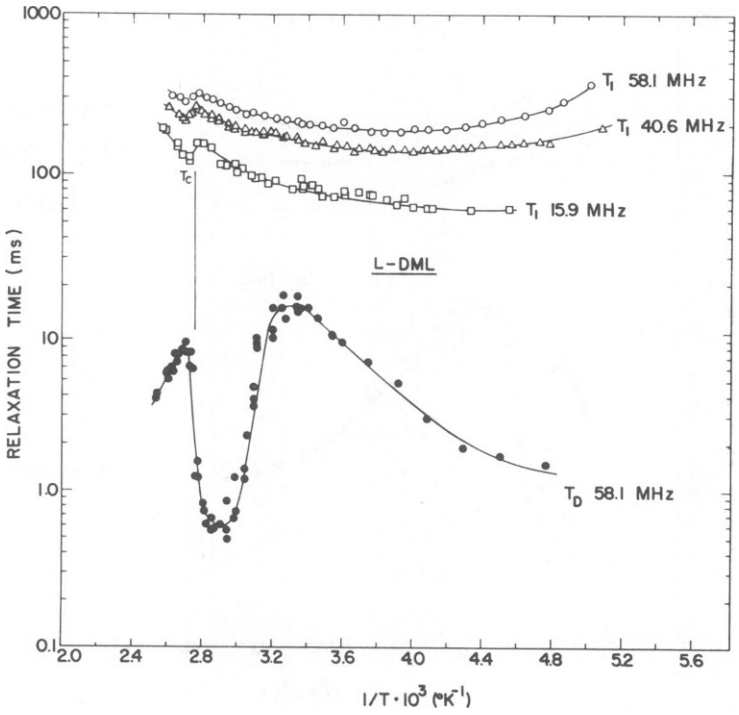


FIGURE 5 The relaxation times T_1 and T_D of anhydrous L-DML as a function of reciprocal temperature. T_c is the Chapman phase transition temperature.

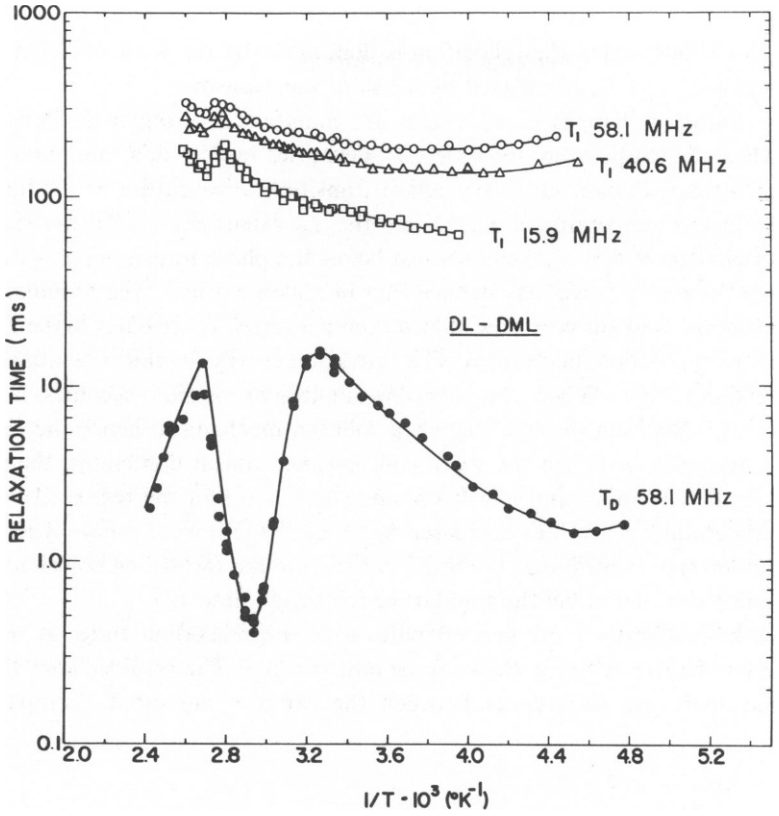


FIGURE 6 The relaxation times T_1 and T_D of anhydrous DL-DML as a function of reciprocal temperature.

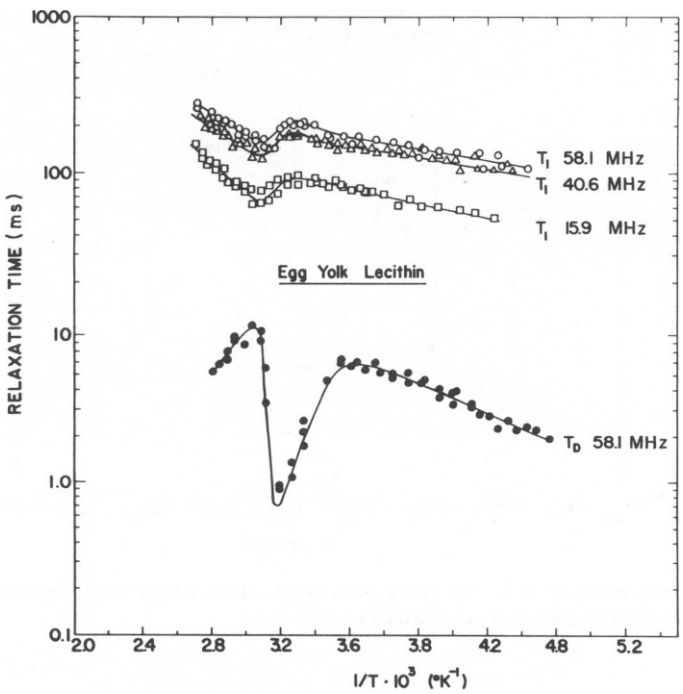


FIGURE 7 The relaxation times T_1 and T_D of anhydrous EYL as a function of reciprocal temperature.

concluded that in this region the relaxation is dominated by the weak collision mechanism, i.e., in this region T_1 and T_D are relaxed by the same mechanism.

The most dramatic changes in T_D values are manifested in region *b*. Below the phase transition, when the temperature increases, T_D decreases rapidly to a minimum value of <1 ms and then increases again up to the phase transition temperature or a little above this temperature. In the temperature range where the T_D values decrease dramatically, the T_1 values do not change. When T_D increases just below the phase transition, T_1 values decrease slightly. From these results we may deduce that in region *b* a new type of molecular motion occurs. This motion, which is very slow at lower temperatures, contributes to the T_D relaxation through the strong collision mechanism. The activation energy for this relaxation mechanism seems to be quite high. When the ultraslow molecular motion becomes faster, it will contribute to T_D relaxation through the weak collision mechanism, hence the change in the temperature dependence. When the weak collision mechanism dominates, the new type of motion will contribute to T_1 and it will become shorter. (*c*) In the region above the phase transition temperature, T_D values decreased again as if there were a new type of ultraslow molecular motion that contributed to the T_D values through the strong collision mechanism. This slow motion does not affect the spin-lattice relaxation time T_1.

So far we have described the general pattern of the relaxation times as a function of temperature for the five samples, shown to be quite similar. The results shown in the figures establish that there are differences between the samples measured. Comparing L-DPL

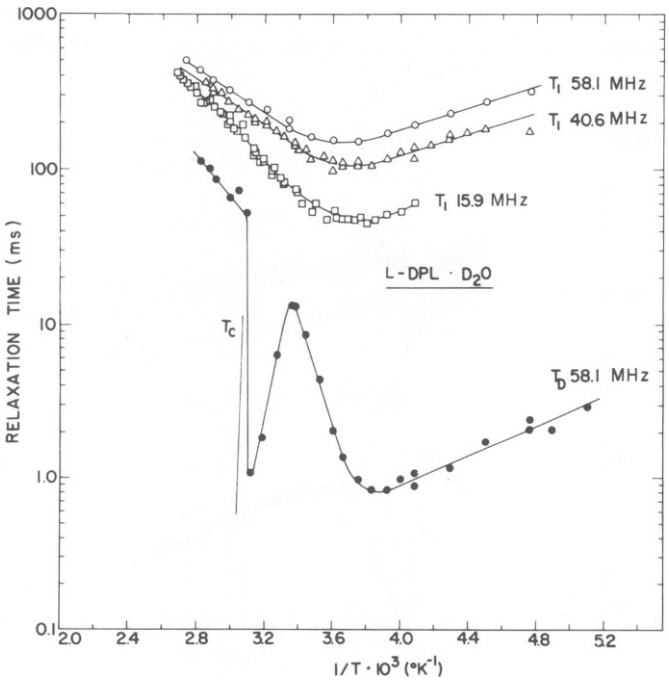


FIGURE 8 The relaxation times T_1 and T_D of L-DPL monohydrate as a function of reciprocal temperature. T_c is the Chapman phase transition temperature.

(optically active) and DL-DPL (racemic), one sees that the main difference is in the T_1 frequency dependence. In DL-DPL there is a substantial frequency dependence, whereas in L-DPL it is much smaller. While the temperature dependence of T_D in the two samples is generally the same, T_D values below the phase transition in L-DPL are longer than in DL-DPL. These experimental results can be explained if we assume that the crystal structure of the optically pure compound and its racemic isomer are not identical, which results in different dynamical properties.

The Lecithin Monohydrates

Four monohydrates were studied: L-DPL · D_2O, DL-DPL · D_2O, L-DML · D_2O, and DL-DML · D_2O. The relaxation times T_1 and T_D of the samples are given in Figs. 8–11. The figures show that there is a large difference in the relaxation time temperature dependence of the DPL monohydrates and the DML monohydrates. The major differences are in the T_D temperature dependence and in the T_1 behavior near the phase transition. For DPL the temperature dependence of T_D is similar for both monohydrates. At the lowest temperatures the T_D relaxation behavior is determined by the strong collision mechanism. As the temperature increases it seems that the same molecular motions contribute through the weak collision mechanism. A new type of molecular motion is present below the phase transition

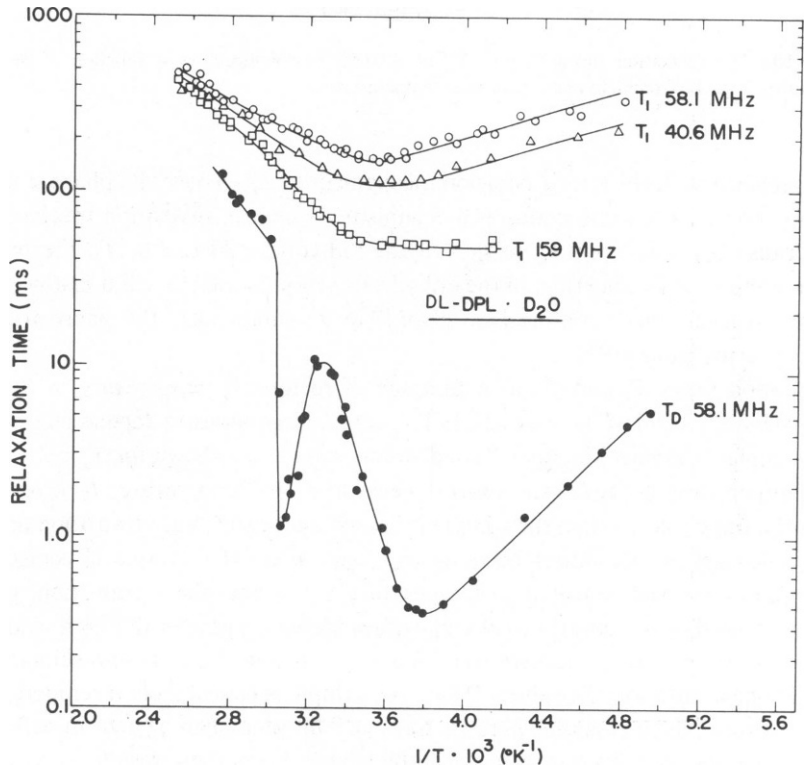


FIGURE 9 The relaxation times T_1 and T_D of DL-DPL monohydrate as a function of reciprocal temperature.

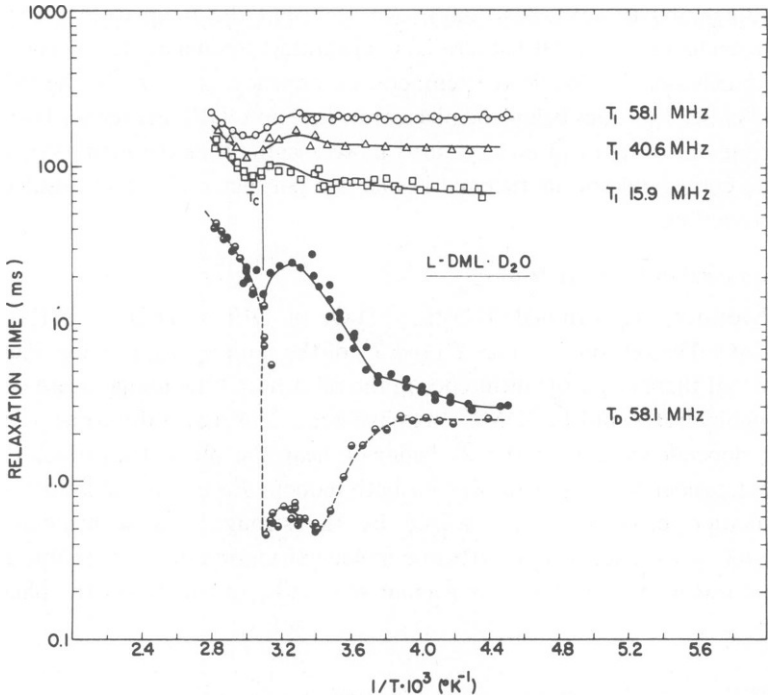


FIGURE 10 The relaxation times T_1 and T_D of L-DML monohydrate as a function of reciprocal temperature. T_c is the Chapman phase transition temperature.

and contributes through the strong collision mechanism to T_D. Above the phase transition the relaxation is through the weak collision mechanism. Thus, the relaxation mechanism above the phase transition is different from that in the anhydrous DPL. For T_1, the temperature dependence is more noticeable than in the anhydrous samples and there is a distinct frequency dependence; however, there is almost no change in T_1 values near the phase transition, in contrast to the anhydrous DPL.

The relaxation times T_1 and T_D as a function of reciprocal temperature in the monohydrates of DML are given in Figs. 10 and 11. The general temperature dependence of T_1 values in the two samples is almost identical. Two different curves are shown for T_D below the phase transition temperature, because after several weeks at room temperature, T_D gives the values denoted by the full circles. When the sample is heated above the phase transition temperature and then cooled again, T_D values become low; even when the sample is cooled to liquid nitrogen temperature and reheated to temperature below the phase transition, the low T_D values are measured. After several weeks T_D values increase again to the high values. Values between the two graphs were not measured. We may conclude from these results that there is a metastable phase with low T_D values. When the sample is cooled from a temperature above the phase transition, the metastable phase is formed. This phase can be determined only by T_D values; the T_1 values are the same as in the stable phase. From these results we may conclude that in the metastable phase there exist ultraslow molecular motions that do not affect the spin-lattice relaxation time T_1, where the T_D values are affected. In the stable phase of

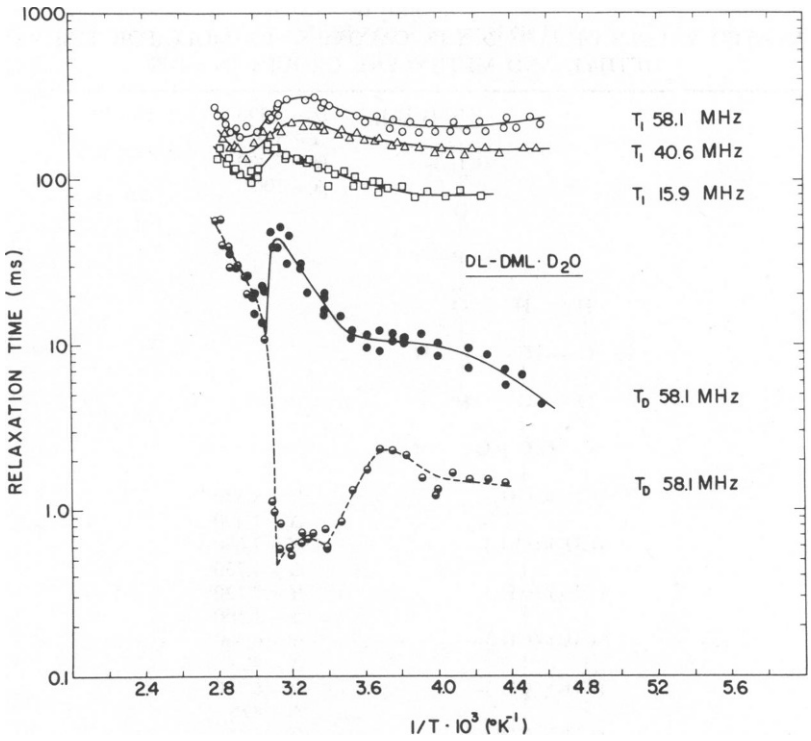


FIGURE 11 The relaxation times T_1 and T_D of DL-DML monohydrate as a function of reciprocal temperature.

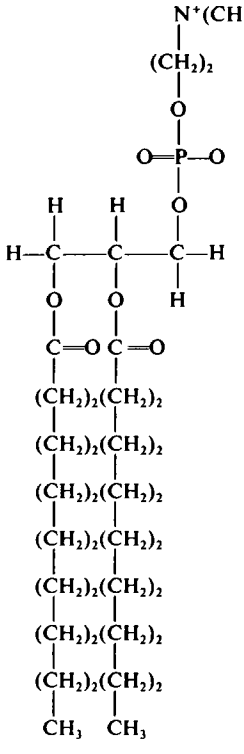
dimyristoyl monohydrates, T_D values obtained were reproducible upon heating or cooling the sample, as long as the temperature was not higher than the phase transition, in which case the metastable phase was formed again.

Molecular Motions in the Gel Phase

The measured T_1 values show little temperature dependence below the phase transition, although a frequency dependence was detected. To understand these results and correlate them with molecular motions, we used several models to calculate the relaxation times. In one of these models it has been suggested (32) that the phospholipid molecule behaves like a rigid rod with unisotropic molecular motions. Calculations using this model did not reproduce the experimental behavior. In another model (33) it was assumed that segmental motions in the solid phase may contribute to the peculiar relaxation behavior, such as the temperature dependence of T_1 in amino acids. We have divided the phospholipid molecule into three large segments and assumed that all the protons in each segment have the same correlation time. Calculations of T_1 as a function of the temperature in which this model was used failed to reproduce the observed experimental behavior for L-DPL. However, significant temperature dependence was obtained using this model. The model proposed by Anderson (26) for the relaxation of the methyl and methylene protons was then used. Specific values of H and Δ

TABLE II

CALCULATED VALUES OF H AND Δ IN CALORIES PER MOLE FOR THE VARIOUS METHYL AND METHYLENE GROUPS IN L-DPL



$N^+(CH_3)_3$	H = 5,390
	Δ = 378
$(CH_2)_2$	H = 5,300
	Δ = 500
$(CH_2)_2(CH_2)_2$	H = 8,570
	Δ = 1,490
$(CH_2)_2(CH_2)_2$	H = 7,090
	Δ = 1,230
$(CH_2)_2(CH_2)_2$	H = 7,120
	Δ = 1,100
$(CH_2)_2(CH_2)_2$	H = 6,980
	Δ = 983
$(CH_2)_2(CH_2)_2$	H = 6,170
	Δ = 875
$(CH_2)_2(CH_2)_2$	H = 6,100
	Δ = 785
$(CH_2)_2(CH_2)_2$	H = 6,020
	Δ = 696
CH_3 CH_3	H = 5,230
	Δ = 238

were given to the terminal and the choline methyl groups. The methylene protons along the chain were divided into groups of two, with values of H and Δ assigned for each group. The T_1 values of the protons in the glycerol backbone were assumed to be very long, so that their contribution to the overall relaxation rate T_{1f}^{-1} was negligible. When using Eqs. 5–8 for calculating T_{1f} and T_{Df} as a function of temperature, the best fit to the experimental results gave the values of H and Δ cited in Table II. The calculated results are given in Fig. 12. Calculations of the relaxation behavior were carried out only for L-DPL. As can be seen, too many free parameters were used in the calculation, so that the values of H and Δ obtained may not have real physical meaning; only the manifestation of the relaxation mechanism was obtained through the calculations. This is why we did not attempt to calculate the relaxation times for other samples.

The authors are grateful to Mr. M. Razi for his help in using his computer plotting program, "The GRAMO System for Interactive Graphical Optimization" used in Fig. 2, and to Prof. A. Leowenstein for carefully reading the manuscript and for useful suggestions.

Received for publication 5 March 1980 and in revised form 30 October 1980.

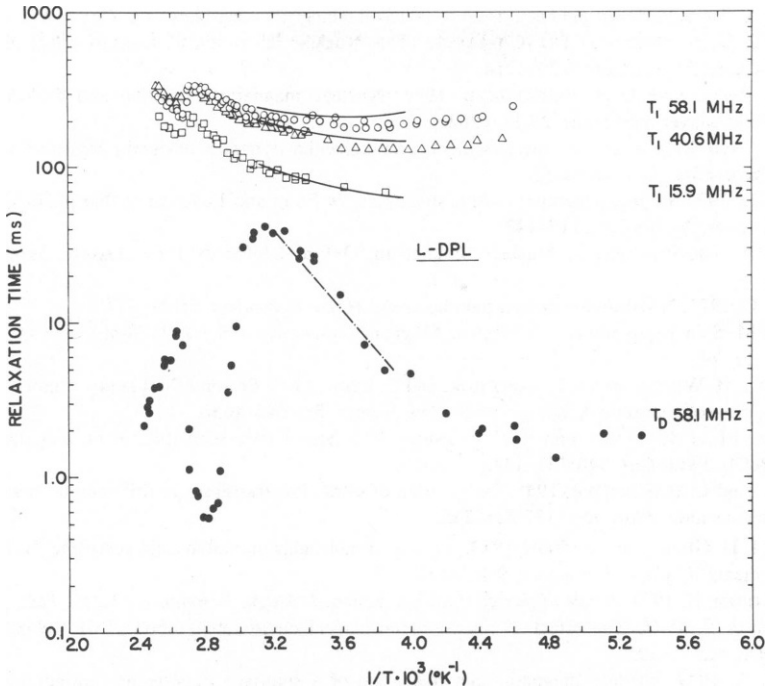


FIGURE 12 Calculated relaxation time values of L-DPL (see text for details). (—) T_1 values, (—·—) T_D values. The experimental values are given as well.

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