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Paramagnetic nuclear relaxation study of the structure and dynamics of lyotropic lamellar phases

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Lamellar phases of double tailed sodium alkyl-phosphates/water systems have been investigated by ^{31}P and ^{13}C relaxations enhanced by paramagnetic divalent ions exchanging rapidly among the polar heads of the surfactant molecules. In order to extract both structural and dynamic information from these experiments, the paramagnetic probes have been chosen such that their electron spin–lattice relaxation times are significantly larger (Mn^{2+}, VO^{2+}) or smaller (Ni^{2+}) than the time scales of molecular motions generally found in the 0·1–2·0 ns range. The paramagnetic relaxation of surfactant nuclei results from intra- and intermolecular contributions, the latter corresponding to dipolar interactions in a two dimensional lattice. The sum of these contributions has been computed as an average over all accessible conformers resulting from the trans–gauche isomerizations of alkyl chains and fitted to the experimental relaxation rates at several magnetic field strengths. This procedure allows the determination of the populations of the main conformers, of the reorientational correlation times and of the lateral diffusion coefficient of the surfactant, which are sometimes difficult to obtain by other N.M.R. methods.

1. Introduction

The nuclear spin relaxation induced by a paramagnetic ion is a powerful method of studying organized systems like direct or reversed micelles and liquid-crystalline phases [1–3]. We report here an investigation of the structure and dynamics of dialkylphosphate/water lamellar phases where the ^{31}P and ^{13}C longitudinal relaxations are enhanced by divalent ions exchanging rapidly among the polar heads of the surfactant molecules (exchange rate 10^5–$10^7\,s^{-1}$).

2. Calculation of relaxation rates

The paramagnetic ions are chosen such that their electron spin–lattice relaxation times T_{1e} are significantly longer (Mn^{2+}, VO^{2+}) or shorter (Ni^{2+}) than the correlation times of the molecular motions (time scale 5×10^{-11}–5×10^{-9} s). The paramagnetic relaxation is the sum of intra- and intermolecular terms corresponding to dipolar interactions with the divalent ion directly bound to the polar head or attached to a neighbouring molecule.

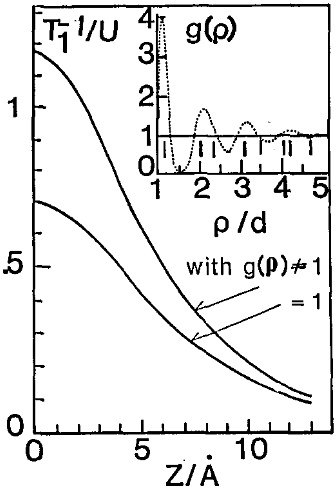

Figure 1. Computed dependence of the reduced relaxation rate of a nucleus upon its distance to the plane where the electron spins diffuse. The insert shows the radial distribution function of the polar heads.

2.1. *The intramolecular term*

The intramolecular term is expressed as

$$\left(\frac{1}{T_1}\right)_{\text{intra}} = 2\gamma_I^2\gamma_S^2\hbar^2 S(S+1)\sum_{k=-2}^{+2} J_1^{(k)}(\omega_I)\langle C_{2k}/r_{IS}^3\rangle^2, \tag{1}$$

where

$$\begin{aligned} C_{2,0} &= \tfrac{1}{2}(3\cos^2\theta - 1),\\ C_{2,\pm 1} &= \left(\frac{3}{2}\right)^{1/2}\sin\theta\cos\theta, \\ C_{2,\pm 2} &= \left(\frac{3}{8}\right)^{1/2}\sin^2\theta. \end{aligned} \tag{2}$$

Here θ is the variable angle of a r_{IS} vector with the Δ_M molecular axis see (figure 2). $\langle C_{2k}/r_{IS}^3\rangle$ represents an average over all the accessible conformers resulting from the trans-gauche isomerizations of the chains and is calculated using the methods of [4]. The spectral densities are of the form

$$J_1^{(k)}(\omega_I) = (A_1^{(k)}\cos^4\beta + \beta_1^{(k)}\cos^2\beta + C_1^{(k)})\frac{\tau_c}{1+\omega_I^2\tau_c^2}. \tag{3}$$

A, B and C are constants dependent of the second and fourth rank order parameters and β is the angle between the director and the magnetic field. All the experiments have been performed on oriented samples with $\beta = 90°$. The correlation time τ_C is either T_{1e} (Ni^{2+}) or corresponds to the reorientation of the Δ_M axis (Mn^{2+} or VO^{2+}).

2.2. *The intermolecular term*

The theory of intermolecular relaxation arising from the dipolar interaction between two spins I and S diffusing laterally in parallel planes separated by a distance z has been recently reported [5]. The intermolecular potential responsible for the non-uniform radial distribution $g(\varrho)$ at short distances ϱ between the head groups of each layer has been taken into account by means of a Smoluchowsky equation for the conditional probability encountered in the spin relaxation theory. The solution of this equation by the finite difference technique [6, 7] has permitted the calculation of the

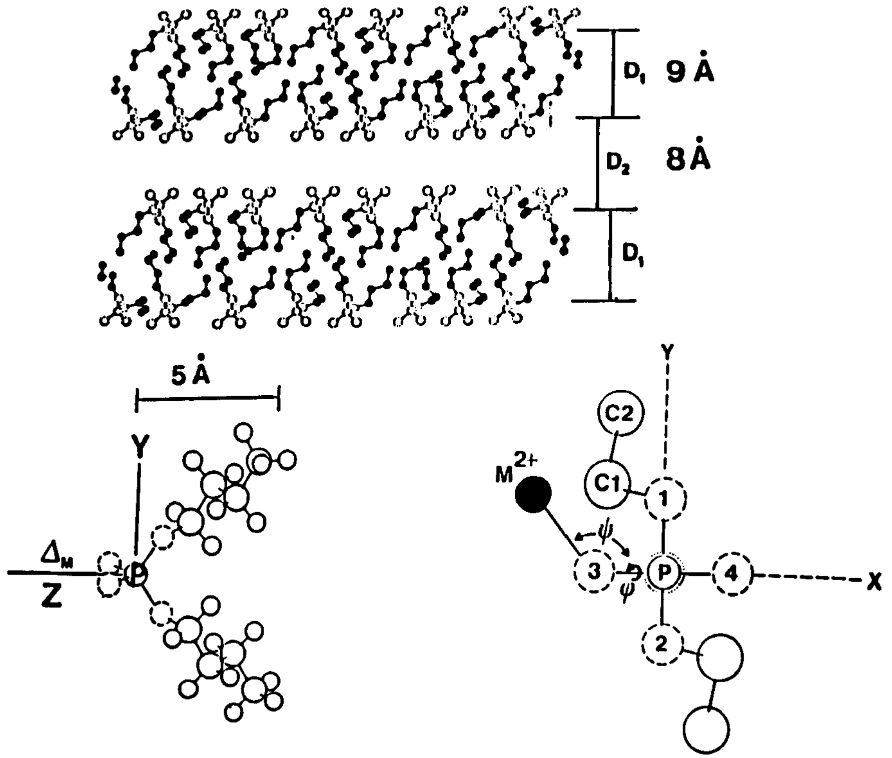

Figure 2. Representation of a dibutylphosphate anion double layer in a lyotropic lamellar phase and the geometry of binding of a divalent ion to the polar head. Here $\psi = 125°$ and M^{2+}-O $= 2{\cdot}2$ Å.

intermolecular relaxation rate given in operator form as

$$\left[\frac{1}{T_1}\right]_{\text{inter}} = \frac{8\pi}{3}\gamma_I^2\gamma_S^2\hbar^2 S(S+1)n_S \operatorname{Re}\left\{\sum_{m=-2}^{+2}|d_{m1}^{(2)}|^2\alpha_m^2\int_d^\infty \frac{d\varrho}{\varrho^2}E^{(m)}(\varrho, z)\right.$$
$$\left.\times\left[-D_L\left(\Gamma_\varrho - \frac{m^2}{\varrho^2}\right) - i\omega_I\right]^{-1} E^{(m)}(\varrho, z)\frac{g(\varrho)}{\varrho^3}\right\}. \qquad (4)$$

Here $E(\varrho, z)$ represents the dimensionless dipolar interaction between the spins I and S and n_S is the number of paramagnetic species per unit area. $D_L = D_I + D_S \simeq 2D_I$ is the relative lateral diffusion coefficient of these spins and Γ_ϱ is a dynamical operator coming from the radial part of the Smoluchowsky equation. The dependence of the intermolecular relaxation rate on Z is shown in figure 1.

3. Applications

The least squares fit of the sum of the inter- and intramolecular relaxation rates to the experimental values (see figure 3) was performed by adjusting the following parameters:

the angle ϕ defining the position of the paramagnetic probe relative to the polar head; the populations P_l of the most probable t, g^+ or g^- rotamers about the O–C and C–C bonds;

the correlation times τ_C and τ_L ($= d^2/D_L$, d being the distance of minimal approach between two surfactant molecules); these times are obtained from the magnetic field dependence of the relaxation rates.

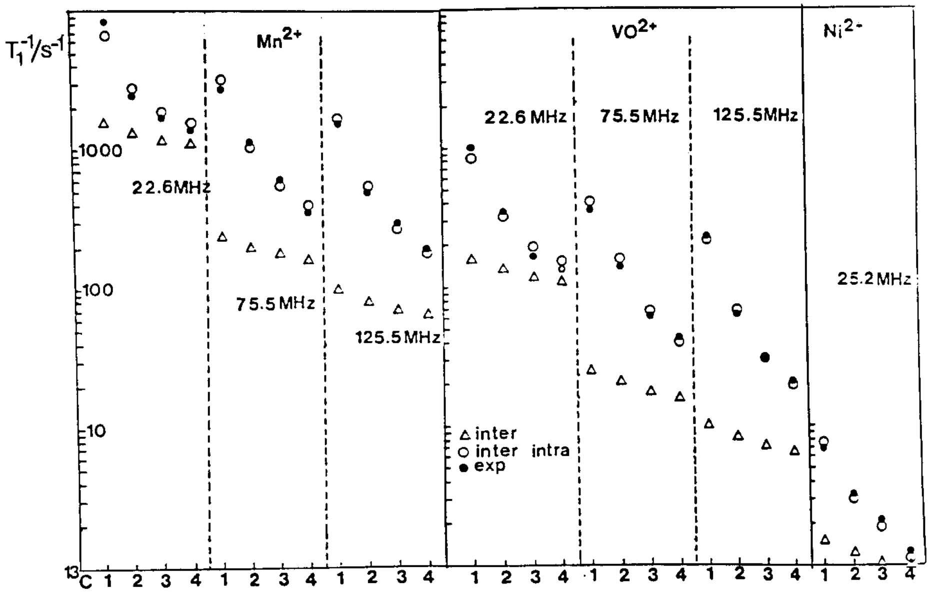

Figure 3. Experimental and computed ^{13}C relaxation rates at several frequencies in the dibutylphosphate (DBP) /water lamellar phase. The calculations have been performed with $\tau_C = 2 \times 10^{-9}$ s and $\tau_L = 2{\cdot}5 \times 10^{-8}$ s (Mn^{2+}, VO^{2+}) and $\tau_C = \tau_L \simeq T_{1e} = 10^{-11}$ s (Ni^{2+}). It may be pointed out that for carbons 3 and 4, the intermolecular contribution exceeds the intramolecular one at 22·6 MHz.

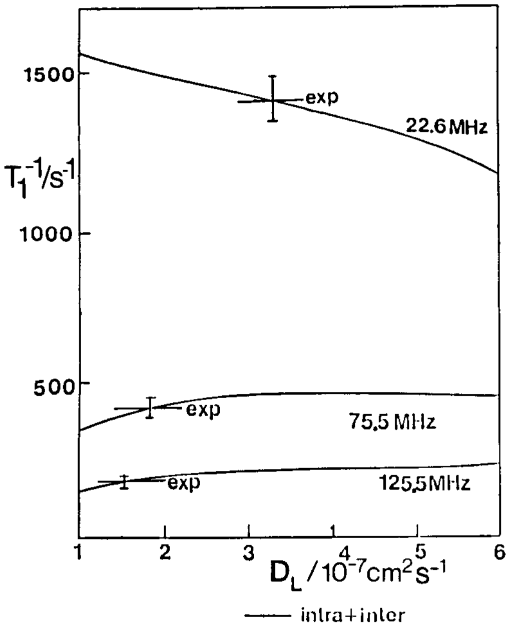

Figure 4. Estimate of the relative lateral diffusion coefficient of spins I and S ($\simeq 2D_l$) from the Mn^{2+} induced relaxation of carbon 4 in the DBP/H_2O lamellar phase. The vertical bars represent the experimental uncertainties.

The sodium dibutylphosphate (DBP) /water lamellar phase is a very convenient system with which to verify the validity of our approach to paramagnetic relaxation since well-resolved carbon-13 spectra are observed under all of our experimental conditions. The relaxation rates induced by the three divalent ions have been fitted with the same conformational parameters (see figure 3). For VO^{2+} and Mn^{2+} the effective correlation time $\tau_C = 2 \times 10^{-9}$ s corresponds to the reorientation of the Δ_M molecular axis about the director. It is indeed very close to the values obtained from ^{31}P relaxation in the absence of paramagnetic probes [8, 9]. In the case of Ni^{2+}, on the other hand, τ_C is equivalent to the electron spin relaxation time $T_1 = 10^{-11}$ s.

Comparison with experiment of the carbon-4 relaxation calculated as a function of D_L at several frequencies yields $D_L \simeq 2D_l = (2{\cdot}5 \pm 1) \times 10^{-7} cm^2/s$ (see figure 4), in agreement with the value derived from the ^1H induced relaxation of the DBP phosphorus in other lyotropic lamellar phases [9].

The analysis of the ^{13}C paramagnetic relaxation data shows, in agreement with deuteron N.M.R. studies [8, 9], that the most probable conformer of DBP is $tg^{\pm}\, tg^{\mp}\, g^{\mp}\, tg^{\pm}\, t$ (see table 1). The two corresponding molecular structures are consistent with a confinement in a cylinder of 5 Å length and 60 $Å^2$ elliptical section [8]. There are several other minor conformers which may contribute to the paramagnetic relaxation. These multiple conformations are conveniently displayed on a histogram giving the probabilities of finding each of the backbone atoms at a given distance from the interface (see figure 5).

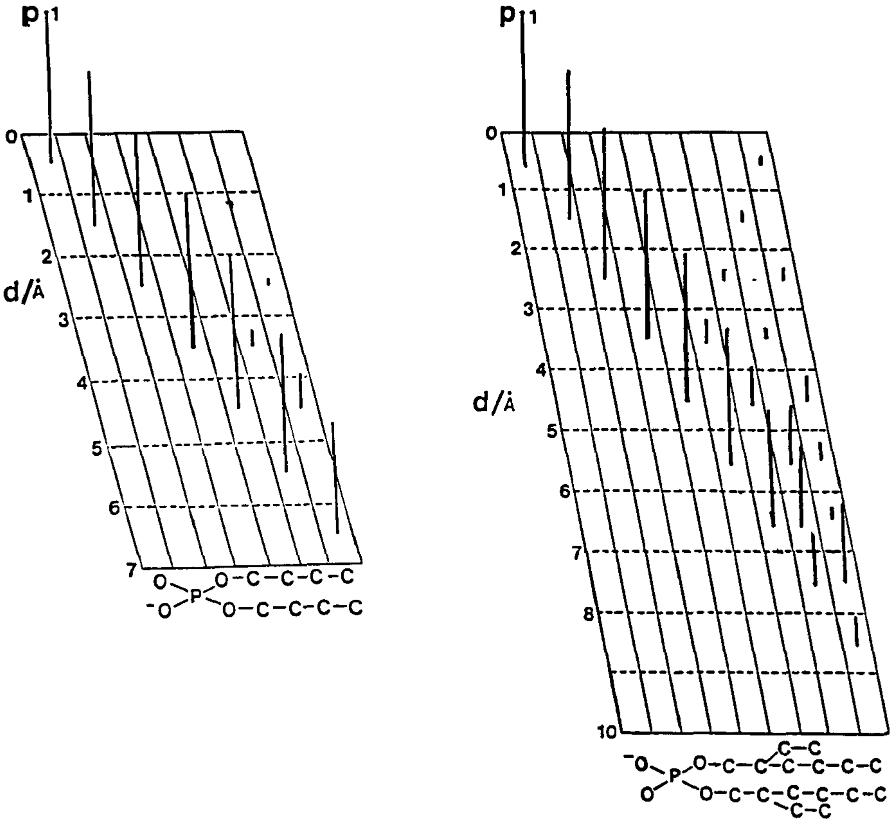

Figure 5. Histograms of the probability distribution of distances of nuclei to the DBP (left) and di-2-ethylhexylphosphate (DEHP, right) bilayer interface with water. For clarity, the probability distribution of DEHP ethyl carbons has been omitted.

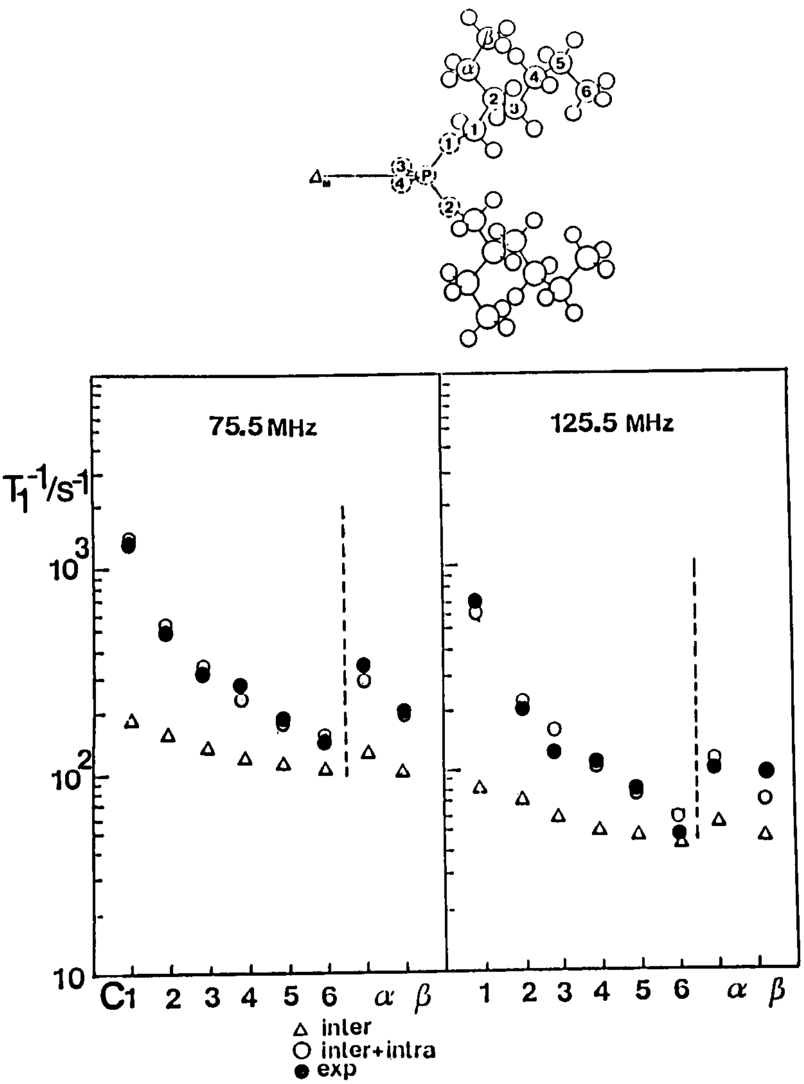

Figure 6. Experimental and computed ^{13}C relaxation rates induced by Mn^{2+} in the DEHP/H_2O lamellar phase. The calculations have been done with $\tau_C = 2{\cdot}5 \times 10^{-9}$ s and $\tau_L = 2{\cdot}5 \times 10^{-8}$ s.

Similar studies have been performed on the sodium di-2-ethylhexylphosphate (DEHP)/H_2O lamellar phase [10] using only Mn^{2+} as the nuclear relaxation reagent (see figure 6). DEHP gives a complicated ^2H N.M.R. spectrum that we did not suceed in analysing unambiguously in terms of molecular conformers. The lateral diffusion coefficient has been found to be of the order of $1{\cdot}5 \times 10^{-7}$ cm^2/s, in good agreement with the transitional diffusion coefficient determined in a cubic phase by the pulsed gradient spin-echo method, at Lund University [11]. In spite of the presence of the ethyl side group, the conformation of the DEHP molecule is the same as DBP up to carbon-4. The histogram shown in figure 5 given an estimate of the flexibility of the surfactant, showing in particular that the terminal carbons of the hexyl chains have a non-negligible probability of being present in the vicinity of the interface with water.

Rotamer populations obtained from the best fit of ^{13}C longitudinal relaxation rates.

Dibutylphosphate							
	O_2—P—O_1	—C_1	—C_2	—C_3	—C_4		
Rotamer†	g^+	t	g^-	t			
P_I‡	1	1	0·87	0·71			
Di-2-ethylhexylphosphate							
	O_2—P—O_1	—C_1	—C_2	—C_3	—C_4	—C_5	—C_6
Rotamer	g^+	t	g^-	t	t	t	
P_I	1	1	0·8	0·75	0·75	0·9	
	O_2—P—O_1	—C_1	—C_2	—C	—C		
	g^+	t	g^-	t			
	1	1	0·2	0·8			

† The sign of the gauche rotamer is arbitrary and may be reversed.

‡ To limit the number of adjustable parameters, the populations of the two other rotamers about each bond is assumed to be $\frac{1}{2}(1 - P_l)$ (see [4]).

By means of expressions similar to those in equations (1) and (3), it becomes possible to calculate the proton induced dipolar relaxation of ^{31}P. Taking into account the ^{31}P chemical shift anisotropy, we have been able to make a detailed investigation of the DEHP dynamical behaviour in the lamellar phase; this will be reported in a forthcoming paper [12].

4. Comparison with other experiments

The reliability of this method may be estimated by introducing the rotamer populations obtained from the ^{13}C paramagnetic relaxation, in the calculation of the deuteron quadrupolar splittings by means of the expression

$$\Delta\nu_q = \tfrac{3}{8}(3\cos^2\beta - 1)\chi_q\{\langle 3\,l_{zZ}^2 - 1\rangle S_{ZZ} + (S_{XX} - S_{YY})\langle l_{zX}^2 - l_{zY}^2\rangle\} \qquad (5)$$

where $\chi_q(\equiv 170\,\mathrm{kHz})$ is the quadrupolar coupling constant and $l_{z,X,Y,Z}$ is the direction cosines of C–H bonds in the frame of the molecular ordering tensor.

Dibutylphosphate:

Splittings kHz	1	2	3	4
Experimental	12·14	20·65	17·62	7·33
Calculated	11·47	25·72	23·20	6·75

Di-2-ethylhexylphosphate (hexyl chain):

	1	2	3	4	5	6
Experimental	6·72	16·23	11·88	9·61	7·63	2·17
Calculated	6·33	18·26	13·21	9·73	7·03	2·28

For both systems under study, we have taken $S_{ZZ} = 0{\cdot}85$ and $S_{XX} - S_{YY} = -0{\cdot}1$.

5. Conclusion

The method reported here may be applied to any oriented lyotropic lamellar phase provided that the paramagnetic probe is capable of binding to the polar heads and of exchanging rapidly among them. It provides two pieces of important information not readily available from other techniques: first an estimate of the surfactant lateral diffusion coefficient and secondly the mean depth of the chain carbons in the bilayer, the latter giving a picture of the residual flexibility of molecules confined in an ordered fluid. More detailed information of the theoretical approach and on the computation procedures will be reported in a forthcoming p^per [13].

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