

THEORY OF DIPOLAR RELAXATION IN LAMELLAR SYSTEM : APPLICATION TO LYOTROPIC MESOPHASES

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ABSTRACT

We propose an analytical theory of dipolar spin relaxation for lamellar geometry. The theoretical frequency variation of the longitudinal rate is drastically dependent of the anisotropy of the diffusion and on the thickness of the bilayer. An application to lamellar lyotropic liquid crystal gives information about the surfactant-organic counterion interaction.

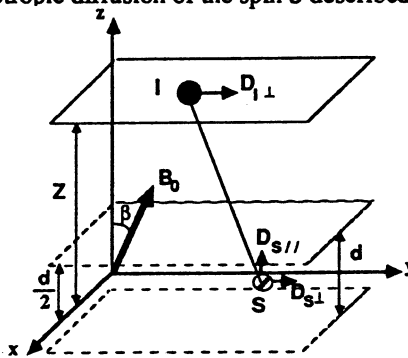
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INTRODUCTION

Nuclear spin relaxation has proven useful to obtain structural and dynamical informations on quasi-two dimensional (2D) systems. These informations come generally from the frequency and temperature dependences of the spin relaxation rates. This requires spin relaxation models particularly adapted to this low dimensional geometry. We propose a theory of dipolar spin relaxation for lamellar geometry more general than our previous analysis where we have considered that the two different spin species diffuse only in parallel planes (1). Here one spin species diffuses on an infinite plane while the other diffuses within a layer of finite thickness d (2). We give analytical expressions of the frequency dependence of the spectral densities and spin relaxation rates. These later are found drastically dependent of the anisotropic diffusion ratio and on the thickness of the layer. An application of this theory allows to define the spatial distribution of a ionic solute in the interstitial water of a bilayer from the frequency of the ^{31}P longitudinal relaxation rates of the polar head of the surfactant. This gives some information about the surfactant organic counterion and the hydration degree of the phosphate group.

THEORY

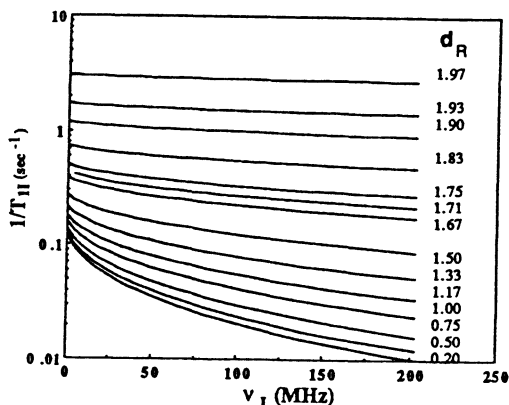
The present work provides a theoretical foundation for the analysis of spin-lattice relaxation in lyotropic mesophases. We consider the spin relaxation by intermolecular dipolar interactions between a nuclear spin species (I) diffusing in the infinite plane of a layer component and an other spin species (S) diffusing within an infinite layer of finite thickness d (Figure 1). We emphasize the case of an anisotropic diffusion of the spin S described by an unbounded diffusion perpendicular to the normal axis z and a bounded diffusion parallel to z axis ($-d/2 \leq z \leq d/2$). The standard theory of dipolar relaxation for a heteronuclear translational diffusion has been applied assuming that the motions of I and S are independent and described by an intermolecular diffusion equation. The solution of such equation can be expressed as a product of an unbounded and a bounded terms. The first one describes the relative unbounded diffusion with a diffusion coefficient $D_{\perp} = D_{I\perp} + D_{S\perp}$ written as a sum of the translational diffusion of the spins I and S in the direction perpendicular to the z axis. The second term describes the bounded diffusion, with a diffusion coefficient $D_{S//}$ in the direction parallel to the z axis. There is a boundary condition of zero flux in the z direction when the position of S takes the values $z = \pm d/2$ (Figure 1), i.e. in the limit of the layer of thickness d . In order



that the spin species I and S be in different layers, we impose a distance of minimum approach $d < 2Z$. We have introduced two dimensionless reduced parameters : $D_R = D_{\parallel}/D_{\perp}$ for the anisotropic diffusion ratio and $d_R = d/Z < 2$ for the geometry. All the calculations (spectral densities and longitudinal relaxation rates) can be done analytically (1).

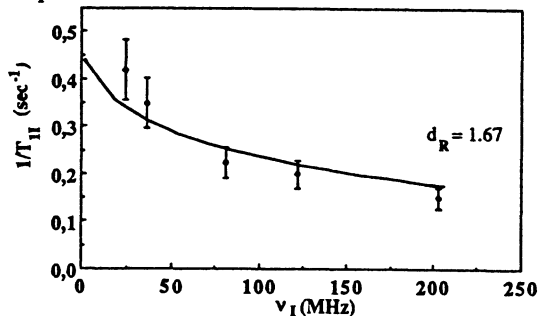
In Figure 2 we present the calculated variations of $1/T_{1I}$ with the frequency ν_I when varying the geometry through d_R . Here I stands for a phosphorus nuclei diffusing laterally and S represents a proton diffusing within an infinite layer of finite thickness d . These have been done with $Z = 6\text{\AA}$ and $\beta = \pi/2$.

The influence of the finite thickness d on $1/T_{1I}$ is particularly evident on the frequency dependences shown in Fig. 2. One notes a large frequency dependence (one order of magnitude between 0 and 200 MHz) for $d_R = 0.2$ (quasi 2D case) and almost no variation for $d_R = 1.97$ (quasi 3D case). The intermediate cases shown on this figure point out the usefulness of the theory for the comparison with experimental data. The calculations have been made with $D_R = 0.01$.



APPLICATION TO LYOTROPIC LAMELLAR PHASES

We have applied this theory to the pyridinium octylphosphate lyotropic mesophases. This phase is obtained by changing the water concentration reaching the surfactant/water molar fraction $x = 0.26$. The area per polar head is 33\AA^2 as shown by X ray scattering. The polar layers are constituted by water and phosphate groups, the average distance between the phosphorus layers, measured by X ray scattering, being ca. 12.5\AA . The ^{31}P longitudinal relaxation rates were determined for three values of the ratio $\text{C}_5\text{D}_5\text{N}/\text{C}_5\text{H}_5\text{N}$ between 0 and 1 with heavy water in order to obtain the intermolecular contribution ($^{31}\text{P} - ^1\text{H}$ of the pyridin) of the ^{31}P spin-lattice relaxation rate. The self diffusion coefficient of the octylphosphate anion OCTP was measured by the pulsed field gradient method on the OCTP/ $\text{C}_5\text{D}_5\text{N}/\text{D}_2\text{O}$ system yielding $D_{\perp}^I = 8.9 \cdot 10^{-7} \text{cm}^2/\text{s}$ and $D_{\parallel}^I = 10^{-8} \text{cm}^2/\text{s}$. Similar method on pyridinium yields $D_{\perp}^S = 1.2 \cdot 10^{-6} \text{cm}^2/\text{s}$ and $D_{\parallel}^S = 10^{-8} \text{cm}^2/\text{s}$. In Fig. 3 we have displayed the best fit of the ^{31}P longitudinal relaxation rates induced by the pyridine protons. This is achieved for $d_R = 1.67$ and $D_{\perp} = D_{\perp}^I + D_{\perp}^S = 1.2 \cdot 10^{-6} \text{cm}^2/\text{s}$ and $D_{\parallel} = 2 \cdot 10^{-8} \text{cm}^2/\text{s}$. One then finds an homogeneous distribution of such cation in an accessible layer thickness of $d = Z d_R = 10.44\text{\AA}$. This leads to a hydration degree of 1.75, i.e. less than two water molecules fixed on the polar head surfactant.



References

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2. J.-P. Korb, Th. Bredel, C. Chachaty and J.R.C. Van der Maarel, *J. Chem. Phys.* (to be published)