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# Low-frequency collective chain dynamics in a model biomembrane

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Proton NMR was employed as a probe for the collective hydrocarbon chain dynamics in decylammonium chloride ($C_{10}H_{21}NH_3Cl$), a model biomembrane undergoing an irreversible structural phase transition sequence. Our rotating frame spin-lattice relaxation measurements revealed a low-frequency critical collective chain dynamics in the kHz regime, which is associated with the interdigitated to noninterdigitated chain configurational phase transition.

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## I. INTRODUCTION

Phase transitions in biomembranes, known to be triggered by the organic chains, have been attracting much attention [1]. In accordance, many workers have been interested in model biomembranes such as lipid bilayers showing similar structural characteristics, and much sharper transitional behaviors [2]. Kind *et al.* were able to describe the typical phase transition sequence in a model membrane $(C_{10}H_{21}NH_3)_2CdCl_4$ (C10Cd for short) by introducing a Landau theory similar to that in the liquid crystals, using a nematic order paramenter and a smectic order parameter, the tilt angle [3,4]. In fact, these compounds can be considered as systems in which a smectic bilayer is embedded in a crystalline matrix.

Kind *et al.* measured the order parameters in C10Cd using $^{13}C$ NMR (nuclear magnetic resonance) and $^{14}N$ NQR (nuclear quadrupole resonance) [3,4]. The nematic order in the hydrocarbon chain was measured from the chemical shift tensor by $^{13}C$ NMR, and the orientational order of the $NH_3$ polar head from the electric field gradient tensor by $^{14}N$ NQR. While the nematic order in the liquid crystals can be directly calculated from the dipolar splitting of the $^1H$ NMR line shape [5], the nematic order has been measured mainly from the chemical shift tensor by $^{13}C$ NMR in the intercalated layer structure compounds, since a strong intermolecular dipolar coupling would tend to obscure the dipolar splitting in the $^1H$ NMR line shape [3,4,6].

Decylammonium chloride (C10Cl), which undergoes an irreversible $i \rightarrow \delta$ phase transition from an interdigitated to a noninterdigitated chain configuration, shows the following transition sequences:

$$\begin{array}{ccccc} & 320\text{ K} & & 328\text{ K} & \\ i & \rightarrow & \delta & \rightarrow & \alpha \\ \epsilon & \leftarrow & \delta & \leftarrow & \alpha \\ & 307\text{ K} & & 325\text{ K} & \end{array}$$

The $\delta \rightarrow \alpha$ transition is accompanied by a smectic C to smectic A phase transition of the bilayer. Few structural studies have been done, due to difficulties in the crystal growth. On the other hand, the alkylammonium chain configurations in each phase are fairly well known. In the *i* phase where the hydrocarbon chains adopt an all-trans conformation, the chains are interdigitated, forming a three-dimensional structure, and are tilted with respect to the layer-normal axis. In the $\delta$ phase where the hydrocarbon chains are not interdigitated with each layer forming a two-dimensional sheet, some conformational defects, involving the end-gauche and the kink-type conformation, are formed with the chain axes being kept parallel to each other. The tilting of the hydrocarbon chain disappears in the $\alpha$ phase due to more active conformational defects. In the $\epsilon$ phase, the interdigitated chain configuration is not recovered, but the hydrocarbon chain adopts an all-trans conformation [7,8].

We have reported a $^1H$ NMR spin-lattice relaxation study of the critical phenomena in C10Cl, in which a critical slowing down and a dimensional crossover of the orientational order parameter of the $NH_3$ polar group were described with the kinetic Ising model [9]. On the other hand, it is expected that the rigid hydrocarbon chain dynamics occurs at a much lower frequency than that of laboratory frame NMR. Thus, it is the purpose of the present work to investigate the low-frequency hydrocarbon chain dynamics employing the $^1H$ NMR rotating frame spin-lattice relaxation time measurements in this intercalated layer-structure compound.

## II. EXPERIMENT

The *n*-decylammonium chloride (C10Cl) was prepared at room temperature by bubbling gaseous HCl through the corresponding amine in benzene. After neutralization the solution was gradually cooled down to 6 °C and filtered. White needle-like crystals were obtained and recrystallized twice in ethanol solution. The phase transition sequence of the resultant C10Cl was verified by DSC (differential scanning calorimetry) [10]. The purity of the sample was checked by the elemental analysis (EA), x-ray fluorescence (XRF), and IR measurements, which indicated that the chemical formula of the sample agrees within 1% (i.e., purity of higher than 99%) with the ideal chemical formula of C10Cl.

A home-built pulsed NMR spectrometer was used for the

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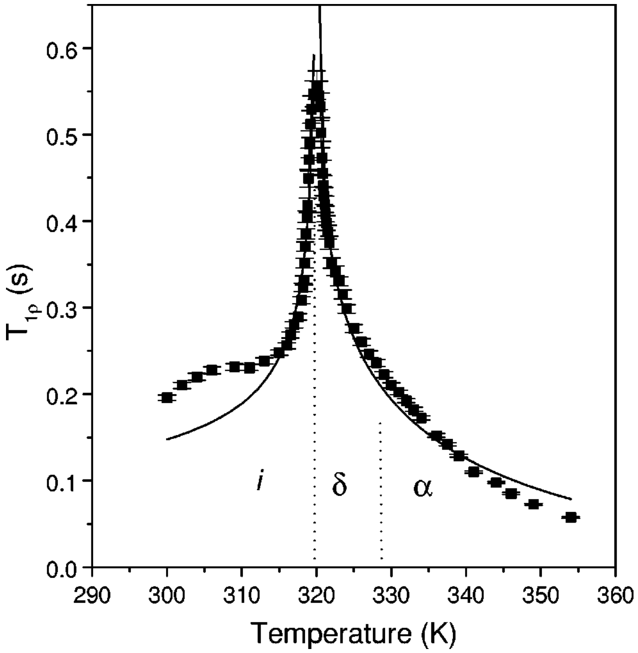

FIG. 1. Temperature dependence of the rotating frame spin-lattice relaxation time measured at 55 kHz. The solid lines are fitted to Eqs. (2) and (3).

45 MHz $^1$H NMR line shape measurements, and a BRUKER MSL 200 spectrometer was employed for the rotating frame spin-lattice relaxation time measurements at the frequency of the rotating frame of 55 kHz. The line shapes were obtained by Fourier-transforming the FID (free induction decay) signals, and were fitted into separate line components. The line shape and relaxation measurements in this work were made separately at each temperature on heating.

### III. RESULTS AND DISCUSSION

Figure 1 shows the rotating frame spin-lattice relaxation time ($T_{1\rho}$). It is noticed that the $T_{1\rho}$ shows a pronounced divergence only at the $i \rightarrow \delta$ transition but not at the $\delta \rightarrow \alpha$ transition. Following our previous study of the laboratory frame spin-lattice relaxation time ($T_1$) [9], the kinetic Ising model was introduced for the critical slowing down reflected in $T_{1\rho}$. Then in the slow motion limit $\omega_1^2 \tau_q^2 \gg 1, T_{1\rho}$ can be described by

$$T_{1\rho} = A\left[\frac{T_c - T}{T_c}\right]^{\gamma-\Delta}\left(1 - \left[\frac{T_c - T}{T_c}\right]^{2\beta}\right)^{-1} \tag{1}$$

below the $i \rightarrow \delta$ phase transition temperature, and by

$$T_{1\rho} = A' e^{E_a/RT}\left[\frac{T - T_c}{T_c}\right]^{\gamma-\Delta} \tag{2}$$

above the transition temperature, where $\Delta$, $\gamma$, and $\beta$ are the critical exponents of the correlation time, static susceptibility, and the order parameter, and where the proportionality constant $A$ is a quantity related to the correlation function and includes the frequency of the rotating frame. The phase transition temperature of $T_c = 320$ K was used for the fitting. As shown in Fig. 1, the $T_{1\rho}$ data was well fitted to Eq. (2) below the transition temperature with $A = 0.057 \pm 0.008$ s$^{-1}$, using the reported *three-dimensional* kinetic Ising model values $\gamma = 1.25$ and $\beta = 0.33$, and $\Delta = 1.6$, which value was obtained from our previous study of the laboratory-frame spin-lattice relaxation time [9]. The three dimensionality below the transition temperature can readily be assumed from the interdigitated chain configuration.

Above the transition temperature, the $T_{1\rho}$ was well fitted to Eq. (3) using the reported *two-dimensional* Ising values $\gamma = 1.75$ and $\Delta = 2.0$, with an activation energy $E_a = 24$ kJ/mol and $A' = (7 \pm 1) \times 10^{-6}$ s$^{-1}$. The two-dimensionality is also readily expected from the noninterdigitated chain configuration. Thus, the rotating frame spin-lattice relaxation exhibits the same dimensional crossover as was revealed by our laboratory frame spin-lattice relaxation [9]. However, it is worthwhile to note that the activation energy of 24 kJ/mol obtained in the low-frequency regime in the current study turns out to be greater than that of 18 kJ/mol obtained from the measurements at 45 MHz [9]. It thus appears that the $T_{1\rho}$ represents a low-frequency motion of the hydrocarbon chain different from that in the higher-frequency regime.

It may be interesting to note that the temperature dependence of both the line shape (i.e., the dipolar splitting representing the nematic order) and relaxation in C10Cl is apparently driven by fluctuations in spite of the irreversible nature of the interdigitated/noninterdigitated transition as well as its huge hysteresis. This would indicate that in a small temperature range in the critical regime, critical fluctuations take place through the transition accompanied by the irreversibility and the hysteresis, until it is well over. In fact, our work represents one of the few investigations of the kind, if any, as far as the authors are aware, and further theoretical exploration certainly appears in order. In fact, our previous work of the laboratory frame relaxation also was explained only by introducing fluctuations as in the current case of the rotating-frame relaxation [9].

If $T_1$ and $T_{1\rho}$ are dominated by the same critical fluctuation, in the kinetic Ising model the two relaxation times are expected to be related as [11]

$$T_{1\rho} \sim \left(\frac{\omega_1}{\omega_0}\right)^2 T_1, \tag{3}$$

according to which the rotating frame spin-lattice relaxation time should be $10^6$ times smaller than the spin-lattice relaxation time. However, $T_{1\rho}$ turns out to have the same order of magnitude as $T_1$ in our system, indicating that the origin of the critical fluctuations reflected by $T_{1\rho}$ is distinct from that reflected by $T_1$. A likely candidate for the low-frequency fluctuation is a central peak type of spectral density originating from the solitonlike slow collective chain motion, whose width is comparable to the frequency of the rotating frame $\omega_1$.

While the high-frequency fluctuations can be ascribed to the local motions of the hydrocarbon chain such as the kink motions and the NH$_3$ polar head motions, the low-frequency fluctuations may arise from the ultraslow whole chain motion of the lipid bilayers associated with the interdigitated to noninterdigitated chain configurational transition. This interpretation can be supported by the fact that in the rotating frame spin-lattice relaxation measurements a critical divergence is observed only at the $i \rightarrow \delta$ transition where the hydrocarbon chain undergoes an interdigitated to noninterdigitated chain configurational transition of the lipid bilayers. Unlike the case of the laboratory frame spin-lattice relaxation [9], no anomaly was observed at the $\delta \rightarrow \alpha$ transition which is believed to resemble the smectic $C$ to smectic $A$ transition in liquid crystals.

In summary, we have studied the collective chain dynamics in $C_{10}H_{21}NH_3Cl$ by means of proton nuclear magnetic resonance measurements. The rotating frame spin-lattice relaxation time representing the ultraslow hydrocarbon chain motions showed a critical divergence only at the $i \rightarrow \delta$ transition, which may be attributed to the interdigitated to noninterdigitated chain configurational phase transition of the lipid bilayers. The origin of the critical fluctuations manifested in the rotating frame relaxation data was found to be different from that manifested in the corresponding laboratory frame data. In other words, the activation energies obtained from the two relaxation data were different, and the ratio of the two relaxation times [Eq. (3)] deviated from that expected for the case of the same critical fluctuations.

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