^{1}H NMR Study of Ionic Motions in High Temperature Solid Phases of $(CH_3NH_3)_2ZnCl_4$

Hiroyuki Ishida
Department of Chemistry, Faculty of Science, Okayama University, Okayama 700-8530, Japan
Reprint requests to Prof. Dr. H. I.; E-mail: ishidah@cc.okayama-u.ac.jp

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The reorientation of the tetrahedral complex anion $ZnCl_4^{2-}$ and the self-diffusion of the cation in $(CH_3NH_3)_2ZnCl_4$ were studied by ^{1}H NMR spin-lattice relaxation time (^{1}H T_1) experiments. In the second highest-temperature phase, the temperature dependence of ^{1}H T_1 observed at 8.5 MHz could be explained by a magnetic dipolar-electric quadrupolar cross relaxation between ^{1}H and chlorine nuclei, and the activation energy of the anion motion was determined to be 105 kJ mol^{-1}. In the highest-temperature phase, the activation energy of the self-diffusion of the cation was determined to be 58 kJ mol^{-1} from the temperature and frequency dependence of ^{1}H T_1.

Key words: Nuclear Magnetic Resonance; Molecular Motion; Cross Relaxation; $(CH_3NH_3)_2ZnCl_4$.

Bis(methylammonium) tetrachlorozincate(II), $(CH_3NH_3)_2ZnCl_4$, forms at room temperature monoclinic crystals ($P2_1/a$), containing discernible tetrahedral $ZnCl_4^{2-}$ ions [1]. Pérez-Mato et al. reported the existence of two solid-solid phase transitions at 426 and 483 K from calorimetric, dielectric, thermal expansion, and optical measurements [2]. The transition at 426 K was also reported from Raman [3] and IR [4] spectra, but not found by DSC [5, 6], DTA, and ^{1}H NMR [5] measurements. The transition at 483 K is accompanied by large enthalpy and entropy changes [1, 5, 6]. Previous ^{1}H NMR studies revealed that the cation in the highest-temperature phase (Phase I) performs isotropic rotation and self-diffusion. The cation in the low temperature phases (Phase II and III) undergoes reorientation about its C-N bond axis [5]. However, the reorientational motion of the anion has not been clarified. In the present study, we measured the ^{1}H T_1 at 8.5 MHz, which is approximately equal to an average value of ^{35}Cl NQR resonance frequencies observed for eight salts containing tetrahedral $ZnCl_4^{2-}$ ions [7], and showed that the motion of anions could be detected from the ^{1}H T_1 through a cross relaxation mechanism between magnetic dipole (^{1}H) and electric quadrupole (^{35}Cl) energy levels. In addition, we measured ^{1}H T_1 at two different resonance frequencies in Phase I to obtain more detailed information on the cationic dynamics.

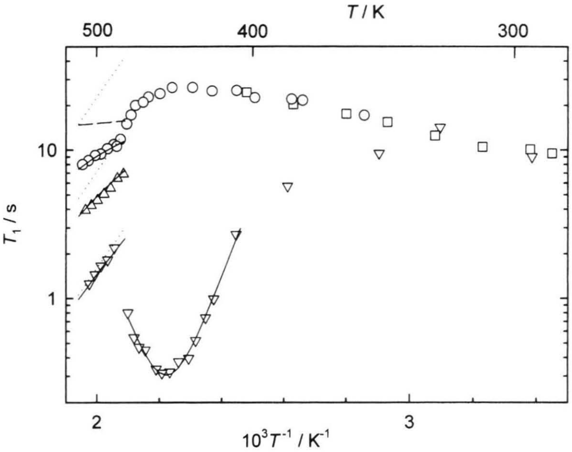

Fig. 1. Temperature dependence of ^{1}H T_1 observed for $(CH_3NH_3)_2ZnCl_4$ at 8.5 (▽), 18 (Δ), 20 (□), and 32 (○) MHz. Solid lines are best-fitted values calculated by (1) and (2). Dotted and dashed lines are calculated T_{1DD} and T_{1SR} values, respectively.

$(CH_3NH_3)_2ZnCl_4$ was prepared and purified by the method reported in [5]. ^{1}H NMR spin-lattice relaxation times were measured at 18 and 8.5 MHz using the pulse spectrometer reported in [5].

The temperature dependence of T_1 is shown in Fig. 1 together with the T_1 data previously observed at 32 and 20 MHz [5]. Above 380 K in Phase II, T_1 observed at 8.5 MHz decreased with increasing temperature and yielded a minimum of 0.31 s at ca. 450 K. This behavior is unexplainable by the magnetic dipole-dipole interactions between protons because the usual BPP theory using T_1 data at 20 and 32 MHz predicts that the onset of decrease in T_1 at 8.5 MHz is above 420 K, which is much higher than 380 K. Moreover, 8.5 MHz is approximately equal to an average value of ^{35}Cl NQR resonance frequencies in tetrahedral $ZnCl_4{}^{2-}$ ions, resulting in a strong cross relaxation between proton and chlorine nuclei. Therefore we believe that the relaxation mechanism at 8.5 MHz is mainly a modulation of ^{1}H...^{35}Cl magnetic dipolar interactions due to anionic reorientations. In fact, Yamamoto et al. studied anionic motions in $[(CH_3)_2NH_2]_2ZnCl_4$ by means of ^{35}Cl NQR and found that above room temperature the ^{35}Cl NQR spin-lattice relaxation time (T_{1Q}) decreases rapidly with increasing temperature to less than 10 ms owing to the reorientation of the anion about its pseudo-C_3 axis [8]. Such a motion is expected to occur in $(CH_3NH_3)_2ZnCl_4$ in the temperature region in question. When the resonance angular frequency of protons, ω_H, is comparable to the quadrupole resonance frequency of chlorine nuclei, ^{1}H T_1 is approximately given by [9]

$$T_1^{-1} = C\tau/\left(1 + (\omega_H - \langle\omega_{Cl}\rangle)^2\tau^2\right), \qquad (1)$$

where τ, ω_{Cl}, and $\langle\,\rangle$ are the correlation time of anionic motion, the resonance angular frequency of chlorine nuclei, and the powder and isotope averages, respectively. Assuming an Arrhenius relationship for the activation energy E_a for the anionic motion: $\tau = \tau_0 \exp(E_a/RT)$, we fitted (1) to the T_1 data, taking E_a, C, and $(\omega_H - \langle\omega_{Cl}\rangle)\tau_0$ as parameters. We obtained E_a of 104 ± 3 kJ mol^{-1}, which is comparable to that of 140 kJ mol^{-1} obtained in $[(CH_3)_2NH_2]_2ZnCl_4$ [7].

In Phase I, T_1 decreased with increasing temperature. This decrease is attributable to the self-diffusion of the cation from the previous NMR study [5]. However, the gradient of the log T_1 vs. T^{-1} plots observed became gentler with increasing the Larmor frequency, implying the presence of more than one relaxation mechanisms. A similar behavior of T_1 was also reported for the CsCl-type ionic plastic phase of CH_3NH_3X ($X = NO_3$ [10], I [11], ClO_4 [12], Br [13]). According to the analysis of the T_1 data of these salts, the present T_1 values could also be expressed by the superposition of two components, T_{1DD} and T_{1SR},

$$T_1^{-1} = T_{1DD}^{-1} + T_{1SR}^{-1}, \qquad (2)$$

where

$$T_{1DD}^{-1} = C_{DD}\omega_H^{-2}\tau_d^{-1},\ T_{1SR}^{-1} = C_{SR}\tau_r^{-1}. \qquad (3)$$

T_{1DD} denotes the relaxation time due to the magnetic dipole interaction among ^{1}H nuclei modulated by the cationic self-diffusion. C_{DD} and τ_d are the motional constant and the correlation time of cationic self-diffusion, respectively. T_{1SR} originates from the spin-rotation interaction due to the rapid uniaxial and/or isotropic rotation of the cation [14]. C_{SR} and τ_r are the motional constant and the correlation time of cationic rotation, respectively. In (2) and (3), we assume that τ_r is much shorter than τ_d and the conditions $\omega_H\tau_d$gg1 and $\omega_H\tau_r$ll1 are fulfilled. An Arrhenius-type temperature dependence can be approximated for the correlation time. Using (2) and (3), T_{1DD} and T_{1SR} was calculated separately, as shown in Figure 1. The activation energy evaluated for the cation self-diffusion was 58 ± 5 kJ mol^{-1}, which is much larger than 26 kJ mol^{-1} previously estimated from T_1 data measured only at 32 MHz [5]. On the other hand, E_a derived from T_{1SR} is 4 ± 2 kJ mol^{-1}. Thus, the spin-rotation interaction is due to the rapid uniaxial rotation of the cation, because this value is comparable to E_a of 3.8 kJ mol^{-1} for the reorientation of $CH_3NH_3{}^+$ about the C-N axis in $(CH_3NH_3)_2ZnCl_4$ [5].

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