**1H NMR Study of Ionic Motions in High Temperature Solid Phases of (CH$_3$NH$_3$)$_2$ZnCl$_4$**

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The reorientation of the tetrahedral complex anion ZnCl$_4^{2-}$ and the self-diffusion of the cation in (CH$_3$NH$_3$)$_2$ZnCl$_4$ were studied by $^1$H NMR spin-lattice relaxation time ($^1$HT$_1$) experiments. In the second highest-temperature phase, the temperature dependence of $^1$HT$_1$ 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 $^1$HT$_1$.

**Key words:** Nuclear Magnetic Resonance; Molecular Motion; Cross Relaxation; (CH$_3$NH$_3$)$_2$ZnCl$_4$.

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Bis(methylammonium) tetrachlorozincate(II), (CH$_3$NH$_3$)$_2$ZnCl$_4$, 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 $^1$HT$_1$ 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 $^1$HT$_1$ through a cross relaxation mechanism between magnetic dipole ($^1$H) and electric quadrupole ($^{35}$Cl) energy levels. In addition, we measured $^1$HT$_1$ at two different resonance frequencies in Phase I to obtain more detailed information on the cationic dynamics.

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**Fig. 1.** Temperature dependence of $^1$HT$_1$ observed for (CH$_3$NH$_3$)$_2$ZnCl$_4$ at 8.5 ($\nabla$), 18 ($\Delta$), 20 ($\Box$), and 32 ($\circ$) 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$_3$NH$_3$)$_2$ZnCl$_4$ 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 $^{35}\text{Cl}$ 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 $^1\text{H}$...$^{35}\text{Cl}$ magnetic dipolar interactions due to anionic reorientations. In fact, Yamamoto et al. studied anionic motions in [(CH$_3$)$_2$NH$_2$]$_2$ZnCl$_4$ by means of $^{35}\text{Cl}$ NQR and found that above room temperature the $^{35}\text{Cl}$ 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$_3$NH$_3$)$_2$ZnCl$_4$ in the temperature region in question. When the resonance angular frequency of protons, $\omega_H$, is comparable to the quadrupole resonance frequency of chlorine nuclei, $^1\text{H} T_1$ is approximately given by [9]

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

where $\tau$, $\omega_{\text{Cl}}$, 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 $\langle \omega_H - \langle \omega_{\text{Cl}} \rangle \rangle\tau_0$ 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$_3$)$_2$NH$_2$]$_2$ZnCl$_4$ [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$_3$NH$_3$X (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, $T_{\text{IDD}}$ and $T_{\text{ISR}}$.

$$T_1^{-1} = T_{\text{IDD}}^{-1} + T_{\text{ISR}}^{-1}, \quad (2)$$

where

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

$T_{\text{IDD}}$ denotes the relaxation time due to the magnetic dipole interaction among $^1\text{H}$ nuclei modulated by the cationic self-diffusion. $C_{\text{DD}}$ and $\tau_d$ are the motional constant and the correlation time of cationic self-diffusion, respectively. $T_{\text{ISR}}$ originates from the spinrotation interaction due to the rapid uniaxial and/or isotropic rotation of the cation [14]. $C_{\text{SR}}$ and $\tau_r$ are the motional constant and the correlation time of cationic rotation, respectively. In (2) and (3), we assume that $\tau_r$ is much shorter than $\tau_d$ and the conditions $\omega_H \tau_{\text{agg}1}$ and $\omega_H \tau_{\text{ll}1}$ are fulfilled. An Arrhenius-type temperature dependence can be approximated for the correlation time. Using (2) and (3), $T_{\text{IDD}}$ and $T_{\text{ISR}}$ 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 $T_{\text{ISR}}$ is 4 ± 2 kJ mol$^{-1}$. Thus, the spinrotation 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$_3$NH$_3^+$ about the C-N axis in (CH$_3$NH$_3$)$_2$ZnCl$_4$ [5].

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