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

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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.

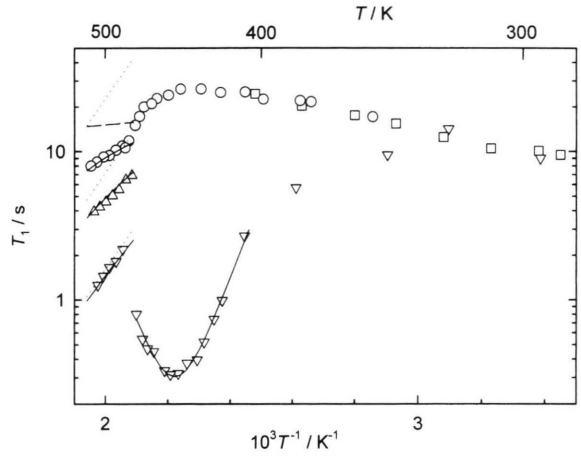


Fig. 1. Temperature dependence of $^1$H $T_1$ observed for $(CH_3NH_3)_2ZnCl_4$ at 8.5 (▽), 18 (△), 20 (□), and 32 (○) MHz. Solid lines are best-fitted values calculated by (1) and (2). Dotted and dashed lines are calculated $T_{1DD}$ and $T_{1SR}$ values, respectively.

$(CH_3NH_3)_2ZnCl_4$ 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, $\omega_H$, 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 $\tau$, $\omega_{Cl}$, 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 $\tau_d$ 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 $\tau_r$ 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 $\omega_H\tau_d \gg 1$ and $\omega_H\tau_r \ll 1$ 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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