Self-Diffusion in the Ionic Plastic Phase of (CH₃)₃NHCIO₄ Studied by ¹H NMR and Electrical Conductivity

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Spin-lattice relaxation times (T₁) and spin-spin relaxation times (T₂) of ¹H NMR and the electrical conductivity (σ) of trimethylammonium perchlorate were measured in the ionic plastic phase of (CH₃)₃NHCIO₄ at room temperature. The activation energy (Eₐ) of the cationic diffusion was evaluated to be 55 ± 4 kJ mol⁻¹ from ¹H T₁ and 1H T₂, respectively, while Eₐ of the anionic diffusion was 64 ± 3 kJ mol⁻¹ from the electrical conductivities.

Key words: Ionic plastic phase, Self-diffusion, Nuclear magnetic resonance, Electrical conductivity.

Introduction

According to studies of high-temperature powder X-ray diffraction and differential thermal analysis (DTA) above room temperature [1], trimethylammonium perchlorate forms three solid phases (named Phase I, II, and III in the order of decreasing temperature). The interrelation between the phase transitions and excited motional modes of (CH₃)₃NH⁺ and ClO₄⁻ ions was investigated by Jurga et al. using differential scanning calorimetry and ¹H, ²H, and ³⁵Cl NMR techniques [2, 3]. They found that in Phase I the cations perform isotropic reorientation and self-diffusion. Recently we redetermined the structure of the three solid phases by using powder and single crystal X-ray diffraction and revealed that Phase I, attainable above 480 K, crystallizes in a CsCl-type cubic structure with a = 5.845(1) Å. Phases II and III, stable between 398 and 480 K and below 398 K, respectively, were found to form a tetragonal structure (a = 9.912(4), c = 7.01(2) Å, and Z = 4) and an orthorhombic structure (space group P2₁, a = 5.749(1), b = 8.670(2), c = 7.5585(9) Å, β = 102.66(1)°, Z = 2), respectively. From the motion of the ions, revealed by Jurga et al., and the crystal structure we can conclude that Phase I is an ionic plastic phase. Such a phase has been recently shown to exist in various methyl-substituted ammonium [5, 6], guanidinium [7, 8], and alkali metal salts [9–11].

In the present investigation we have studied ¹H NMR spin-lattice relaxation times (T₁), spin-spin relaxation times (T₂), and the electrical conductivity (σ) above room temperature in detail in order to investigate the diffusional motion of the ions in the ionic plastic phase (Phase I).

Experimental

(CH₃)₃NHCIO₄ was prepared by neutralizing trimethylamine with perchloric acid. The obtained crystals were recrystallized twice from methanol. ¹H NMR spin-lattice relaxation times were measured at 8.5, 18, 32 MHz with a 180°–90° pulse sequence by a pulsed spectrometer already reported [12]. ¹H NMR spin-spin relaxation times were determined by a Hahn’s spin echo method [13] at resonance frequencies of 18 and 32 MHz. The electrical conductivity was measured by the complex impedance method with an Ando AG-4311 LCR meter in the frequency range 0.1–100 kHz [14]. Sample pellets of 1 cm diameter and ca. 1 mm thickness were prepared by pressing pulverized crystals. The two-terminal method using graphite electrodes (Acheson Electrotag 199) was employed. Before the measurements, the samples were dried under dynamic vacuum (ca. 10⁻¹ Pa) at room temperature for 4 h and at ca. 80 °C for 4 h.

Results and Discussion

The temperature dependence of T₁ and T₂ determined for (CH₃)₃NHCIO₄ above room temperature was investigated by ¹H NMR and the electrical conductivities are presented in the paper.
are shown in Figure 1. In Phase II and III, \( T_1 \) increased with temperature and was independent of the employed Larmor frequencies. At \( T_{tr}(III \rightarrow II) = 398 \) K, no detectable discontinuity in the \( T_1 \) curve was observed. In Phase I above \( T_{tr}(II \rightarrow I) = 480 \) K, \( T_2 \) increased with temperature from 17 to 30 ms. Such long \( T_2 \) values as well as the \( T_2 \) increase with temperature clearly indicate the occurrence of cationic self-diffusion, as pointed out by Jurga et al. [2, 3]. \( T_1 \) in this phase became frequency-dependent, and each \( T_1 \) measured at three different frequencies decreased on heating. The temperature gradient of the log \( T_1 \) vs. \( T^{-1} \) plots became gentler with increasing the Larmor frequency. A similar behavior of \( T_1 \) was reported for the CsCl-type ionic plastic phase of \( \text{CH}_3\text{NH}_3\text{X} (X = \text{NO}_3 \ [15], \text{I} \ [16], \text{ClO}_4 \ [17], \text{Br} \ [18]). 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 the two components, \( T_{1\text{DD}} \) and \( T_{1\text{SR}} \):

\[
T_1^{-1} = T_{1\text{DD}}^{-1} + T_{1\text{SR}}^{-1},
\]

where

\[
T_{1\text{DD}}^{-1} = C_{\text{DD}} \omega^{-2} \tau_d^{-1}, \quad T_{1\text{SR}}^{-1} = C_{\text{SR}} \tau_r^{-1}.
\]

Using (1)–(3), we can calculate \( T_{1\text{DD}} \) and \( T_{1\text{SR}} \) separately, as shown in Figure 1. The activation energies...
evaluated for the cation self-diffusion and the isotropic rotation were $55 \pm 4$ and $25 \pm 4$ kJ mol$^{-1}$, respectively. Plots of log $T_{1DD}$ and log $T_2$ vs. $T^{-1}$ show almost the same gradient, but with different signs. Since the BPP theory predicts $T_2 \propto \tau_d^{-1}$ in the motional narrowing range due to the cationing self-diffusion [22], the above fact indicates that $T_{1DD}$ and $T_2$ originate from the same relaxation process, i.e. cationic self-diffusion. The activation energy evaluated from the slope of log $T_2$ vs. $T^{-1}$ plots was $50 \pm 4$ kJ mol$^{-1}$.

The electrical conductivity ($\sigma$), measured above 360 K, is shown in Figure 2. On heating, the conductivity gave a discontinuous jump from $8.5 \times 10^{-4}$ to $2.3 \times 10^{-2}$ Sm$^{-1}$ at $T_m$(II-I) = 480 K and increased in Phase I to about $10^{-1}$ Sm$^{-1}$ around 530 K. The high electrical conductivity, amounting to $10^{-2}$--$10^{-1}$ Sm$^{-1}$, observed in Phase I indicates that rapid ionic diffusion occurs in this phase.

From the observed electrical conductivity we evaluated the activation energy ($E_a$) of the ionic diffusion process, using the Nernst-Einstein and Arrhenius relations expressed as

$$D_a = \lambda \sigma k T/(Ze)^2 N,$$  \hspace{1cm} (4)

and

$$D_a = D_{a0} \exp(-E_a/RT),$$ \hspace{1cm} (5)

respectively, where $\lambda$, $Ze$, and $N$ are the spatial correlation factor [23, 24], the electric charge of the diffusing ion, and the number of mobile ions per unit volume, respectively. The $E_a$ value of conductivity becomes $64 \pm 3$ kJ mol$^{-1}$, being larger than the values derived from the NMR data. Hence, the main contribution to the observed electrical conductivity is considered to be the anionic diffusion.

Figure 3 shows the temperature dependence of $D_a$ according to (4) with $\lambda = 0.65331$ and $N = 5.008 \times 10^{27}$ m$^{-3}$, assuming that the anions jump between the sites of a CsCl-type cubic lattice with $a = 5.845$ Å. We can also derive the microscopic diffusion constant $D_{nmr}$ for the cationic diffusion from the correlation time $\tau_a$ using the relation

$$D_{nmr} = d^2/6 \tau_a,$$ \hspace{1cm} (6)

where $d$ is the shortest jump distance which is assumed to be 5.845 Å. $\tau_a$ can be estimated from the $T_{1DD}$ and $T_2$ using the relation given by Sholl for the model in which random jumps of the cations occur between the simple cubic lattice sites [25, 26]. In the condition of $\omega \tau_d \gg 1$, the expression for $T_{1DD}$ and $T_2$ are

$$T_{1DD} = 51.80 A \omega^{-2} \tau_d^{-1},$$ \hspace{1cm} (7)

$$T_2^{-1} = 26.91 A \tau_d,$$ \hspace{1cm} (8)

where

$$A = (3/20) \gamma^4 h^2 a^{-6} c$$ \hspace{1cm} (9)
and $\gamma$, $a$, and $c$ denote the gyromagnetic ratio of a proton, the lattice constant of the crystal, and the number of resonant protons on each lattice site. The $D_{\text{nmr}}$ values calculated using (6)–(9) with $c = 10$ are shown in Figure 3. $D_{\text{nmr}}$ was found to be comparable to $D_{\text{v}}$, which suggests that the cations diffuse in Phase I almost as rapidly as the anions, and that the hindrance to the translational diffusion of the cation, which is bulkier than the anion, is comparable to that of the anion, while is heavier than the cation.

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