Self-Diffusion in the Ionic Plastic Phase of $(CH_3)_3NHClO_4$ Studied by ^1H NMR and Electrical Conductivity

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Z. Naturforsch. **51a,** 83–86 (1996); received December 4, 1995

Spin-lattice relaxation times (T_1) and spin-spin relaxation times (T_2) of ^1H NMR and the electrical conductivity (σ) of trimethylammonium perchlorate were measured in the ionic plastic phase obtainable above 480 K. In this phase, both the cation and anion were revealed to perform self-diffusion. The activation energy (E_a) of the cationic diffusion was evaluated to be 55 ± 4 and 50 ± 4 kJ mol^{-1} from ^1H T_1 and ^1H T_2 respectively, while E_a of the anionic diffusion was 64 ± 3 kJ mol^{-1} from the electrical conductivity.

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 $(CH_3)_3NH^+$ and ClO_4^- ions was investigated by Jurga et al. using differential scanning calorimetry and ^1H, ^2H, and ^{35}Cl 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 $P2_1$, $a = 5.749(1)$, $b = 8.670(2)$, $c = 7.5585(9)$ Å, $\beta = 102.66(1)°$, $Z = 2$), respectively, [4]. 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 (T_1), spin-spin relaxation times (T_2), 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

$(CH_3)_3NHClO_4$ 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 $180° - \tau - 90°$ 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 Electrodag 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 T_1 and T_2 determined for $(CH_3)_3NHClO_4$ above room temperature

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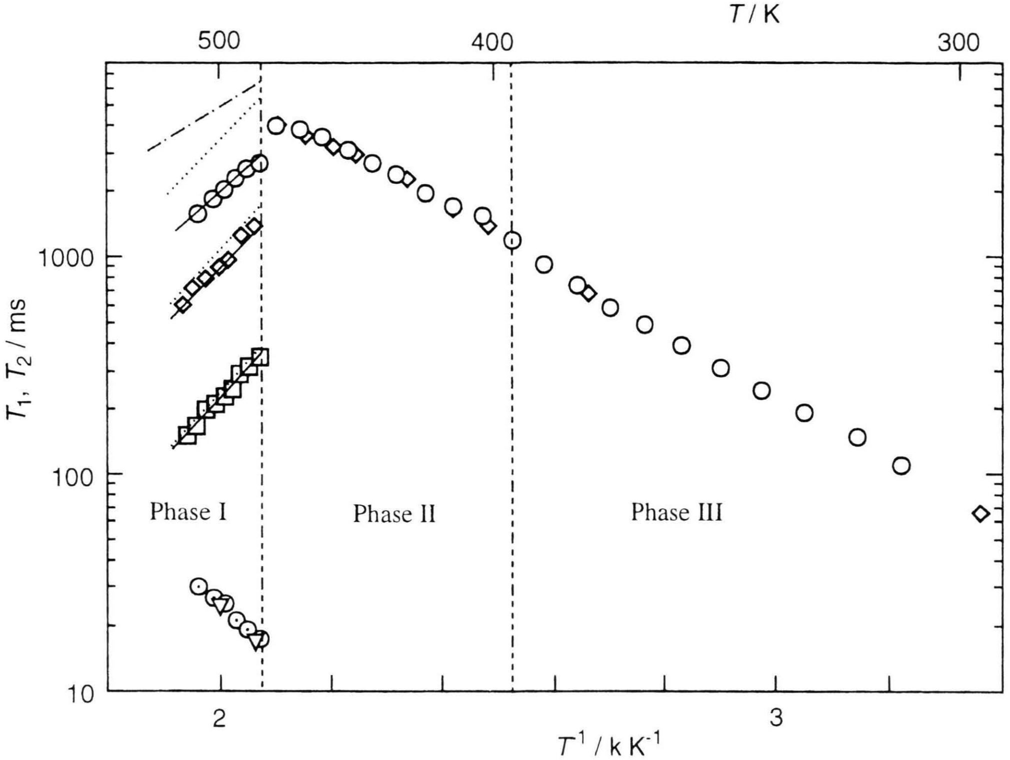

Fig. 1. Temperature dependences of ^{1}H T_1 observed for $(CH_3)_3NHClO_4$ at 8.5 (□), 18 (◇), and 32 (○) MHz, and ^{1}H T_2 at 18 (▽) and 32 (⊙) MHz. The best fitted values, calculated by using (1)–(3), are shown by solid lines consisting of the frequency independent T_{1SR} (dash-dotted line) and the frequency dependent T_{1DD} (dotted line). Broken lines indicate the transition temperatures determined in [4].

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 CH_3NH_3X (X = NO_3 [15], I [16], ClO_4 [17], 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_{1DD} and T_{1SR}:

$$T_1^{-1} = T_{1DD}^{-1} + T_{1SR}^{-1}, \tag{1}$$

where

$$T_{1DD}^{-1} = C_{DD}\,\omega^{-2}\,\tau_d^{-1}, \qquad T_{1SR}^{-1} = C_{SR}\,\tau_r^{-1}. \tag{2}$$

T_{1DD} denotes the relaxation time due to the magnetic dipole interaction among ^{1}H nuclei, modulated the cationic self-diffusion. C_{DD}, ω, and τ_d are the motional constant, the angular Larmor frequency, and the correlation time of cationic self-diffusion, respectively. On the other hand, T_{1SR} originates from the spin-rotation interaction due to the rapid isotropic rotation of the cation [19–21]. C_{SR} and τ_r are the motional constant and the correlation time of cationic isotropic rotation, respectively. In (1) and (2) we assumed that τ_r is much shorter than τ_d and that the conditions $\omega\tau_r \ll 1$ and $\omega\tau_d \gg 1$ are fulfilled. The correlation time can be approximated by an Arrhenius-type temperature dependence:

$$\tau_i = \tau_{i0} \exp(E_{ai}/R\,T), \qquad (i = d, r). \tag{3}$$

Using (1)–(3), we can calculate T_{1DD} and T_{1SR} separately, as shown in Figure 1. The activation energies evaluated for the cation self-diffusion and the isotropic rotation were 55 ± 4 and 25 ± 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 ± 4 kJmol^{-1}.

The electrical conductivity (σ), measured above 360 K, is shown in Figure 2. On heating, the conductivity gave a discontinuous jump from 8.5×10^{-4} to 2.3×10^{-2} Sm^{-1} at $T_{tr}(\mathrm{II} \rightarrow \mathrm{I}) = 480$ 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

$$D_\sigma = \lambda \sigma k T/(Ze)^2 N, \tag{4}$$

and

$$D_\sigma = D_{\sigma 0} \exp(-E_a/R T), \tag{5}$$

respectively, where λ, 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 ± 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_σ 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 τ_d using the relation

$$D_{nmr} = d^2/6\,\tau_d, \tag{6}$$

where d is the shortest jump distance which is assumed to be 5.845 Å. τ_d 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

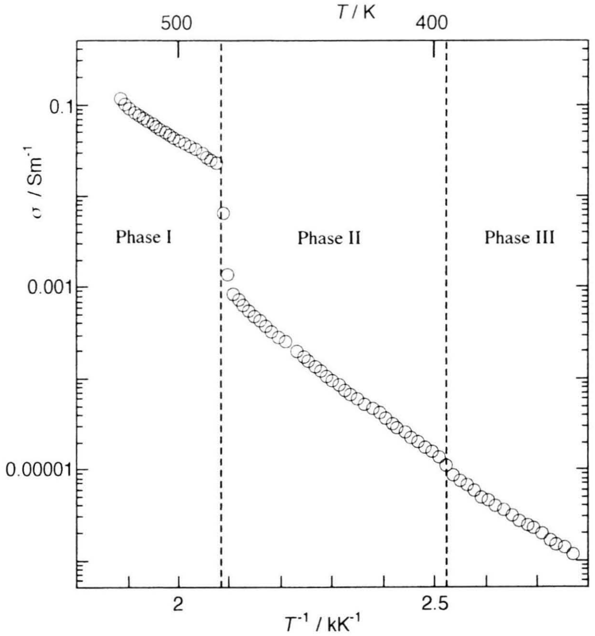

Fig. 2. Temperature dependence of the electrical conductivity σ observed for $(CH_3)_3NHClO_4$. Broken lines indicate the transition temperatures determined in [4].

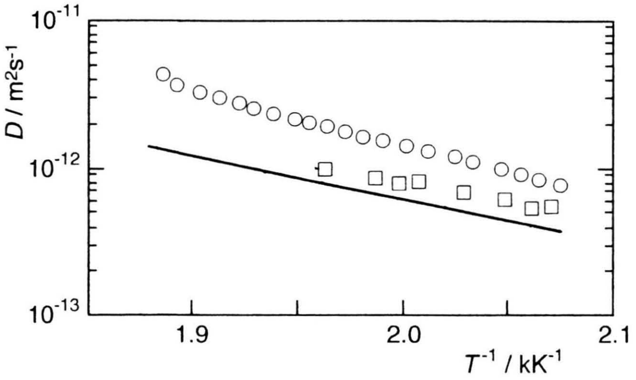

Fig. 3. Diffusion constant (D) determined from electrical conductivity σ (○), T_{1DD} (−), and T_2 (□).

$\omega \tau_d \gg 1$, the expression for T_{1DD} and T_2 are

$$T_{1DD}^{-1} = 51.80\, A\, \omega^{-2} \tau_d^{-1}, \tag{7}$$

$$T_2^{-1} = 26.91\, A\, \tau_d, \tag{8}$$

where

$$A = (3/20)\, \gamma^4 \hbar^2 a^{-6} c \tag{9}$$

and γ, 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_{nmr} values calculated using (6)–(9) with $c=10$ are shown in Figure 3. D_{nmr} was found to be comparable to D_σ, 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.

This work was supported by Grant-in-Aid for Scientific Research (No. 06640658) from the Ministry of Educations, Science and Culture, Japan.

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