Cationic Self-diffusion in Solid Choline Perchlorate Studied by ^{1}H NMR

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The ^{1}H spin-lattice and spin-spin relaxation times, and the second moment of the ^{1}H NMR linewidth of choline perchlorate, $[(CH_3)_3NCH_2CH_2OH]ClO_4$, were measured in its highest-temperature solid phase, i. e. above 275 K. X-ray powder patterns taken at ca. 380 K revealed that in this phase the crystal has a CsCl-type cubic structure (a = 6.326(4) Å and Z = 1). From ^{1}H NMR experiments it was found that the cations in this phase undergo isotropic rotation and translational self-diffusion. From the ^{1}H T_1 measurements, the activation energies of the cationic rotation and self-diffusion were evaluated to be 21.4 ± 0.4 and 62 ± 3 kJ mol^{-1}, respectively.

Key words: Ionic plastic phase; Self-diffusion; Crystal structure; Nuclear magnetic resonance.

Introduction

The molecular dynamics and phase transitions of choline salts have extensively been investigated [1 - 5] because of the marked susceptibility to radiation damage found in choline chloride [6, 7]. McDowell et al. [2] measured ^{1}H NMR spin-lattice relaxation times in the Zeeman and rotating frames (T_1 and $T_{1\rho}$) of choline perchlorate at 150 to 310 K and found a solid-solid phase transition at 272 K. Above 272 K the choline cation was found to perform self-diffusion as well as isotropic rotation. This behaviour of the cations is similar to that in the ionic plastic phase of methyl-substituted ammonium [8, 9], guanidinium [10, 11], and alkali metal salts [12 - 14]. In the present paper we have measured the ^{1}H NMR T_1 and spin-spin relaxation times (T_2) and performed X-ray powder diffraction and differential scanning calorimetry (DSC) of choline perchlorate above 250 K in order to learn about its ionic plasic phase.

Experimental

$[(CH_3)_3NC_2H_4OH]ClO_4$ was prepared by neutralizing choline with perchloric acid. The obtained crystals were recrystallized twice from methanol. Found: C, 29.53; H, 6.51; N, 6.96 %. Calcd: C, 29.49; H, 6.93; N, 6.88 %. Before the measurements, the sample was dried under vacuum (ca. 10^{-1} Pa) at room temperature for 5 h and then at 80 °C for 5 h. Phase transition temperatures and the corresponding enthalpy changes were determined by a Perkin-Elmer DSC7. X-ray powder patterns were taken at ca. 380 K using a Philips X'pert PW3040/00 diffractometer. The second moment (M_2) of the ^{1}H NMR linewidth was determined by use of a JEOL JNM-MW-40S spectrometer. The ^{1}H NMR spin-lattice time (T_1) was measured at 32 and 9.8 MHz using a pulsed spectrometer [15], while the spin-spin relaxation time (T_2) and the linewidth parameter (T_2^*) were measured at 32 MHz. The $180° - t - 90°$ pulse sequence and Hahn's spin-echo method [16] were employed for the determination of T_1 and T_2, respectively. T_2^* was obtained from the shape of the free induction decay after a 90° pulse by assuming exponential decay.

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Results and Discussion

The solid-solid phase transition was located at 275 K by DSC, in agreement with the 272 K reported by McDowell et al. [2]. The enthalpy and entropy changes at the transition were determined to be 12.4 ± 0.2 kJ mol^{-1} and 45.1 ± 0.8 J K^{-1} mol^{-1}, respectively. A thermal anomaly attributable to the melting was detected at ca. 560 K. Its peak had a somewhat extended tail on the low-temperature side owing to impurities originating from decomposition; a gradual

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Table 1. Observed and calculated 2θ values of X-ray powder patterns of the high-temperature phase of choline perchlorate at ca. 380 K, $\lambda(CuK_{\alpha 1}) = 1.5406$ Å, (cubic, $a = 6.326(4)$ Å, $Z = 1$, $V = 253.2(5)$ Å^3, and $D_x = 1.335(3)$ Mg m^{-3}).

$2\theta_{obsd}/°$ (± 0.02)	Intensity	$2\theta_{calcd}/°$	$h\,k\,l$
13.98	6	13.99	100
19.82	100	19.83	110
24.37	8	24.35	111
28.17	6	28.19	200
31.61	7	31.60	210
34.71	4	34.71	211

change in the sample colour to brown was observed above ca. 530 K. The enthalpy and entropy of fusion were roughly estimated to be 9.0 ± 0.9 kJ mol^{-1} and ca. 16 J K^{-1} mol^{-1}, respectively. The extremely large value of the entropy change at the solid-solid transition compared with that of fusion implies that both cations and anions have acquired the greatest part of their motional freedom in the high-temperature solid phase. This high mobility can also be derived from the entropy of fusion lower than 20 J K^{-1} mol^{-1}, which value has been accepted as a criterion of forming the plastic phase in molecular crystals [17].

The X-ray powder diffraction angles (2θ) obtained at ca. 380 K could be interpreted as due to a CsCl-type cubic lattice with $a = 6.326(4)$ Å, $Z = 1$, $V = 253.2(5)$ Å^3, and $D_x = 1.335(3)$ Mg m^{-3}. The adequacy of the present analysis is shown in Table 1. The CsCl-type cubic structure implies that the cations and anions behave like spherical ions in the high-temperature solid phase, being consistent with the result of DSC.

The temperature dependence of M_2 determined above 250 K is shown in Figure 1. M_2 suddenly decreases at the transition point from the low- to high-temperature phase, and the value became 0.6 ± 0.1 G^2 (1 G = 1 × 10^{-4} T) at ca. 300 K in the high-temperature phase. This indicates the onset of isotropic rotation of the cation in this phase, because the observed value is comparable to 0.52 G^2 calculated for isotropically rotating cations using the structural data determined in the present investigation. A further decrease in M_2 to less than 0.05 G^2 was observed upon heating in this phase, indicating that the isotropic rotation is followed by translational self-diffusion of the cations.

The temperature dependences of ^{1}H T_1, T_2, and T_2^* obtained above 250 K are shown in Figure 2. T_1 showed a maximum around 450 K at the resonance frequency of 9.8 MHz. From the M_2 results, the

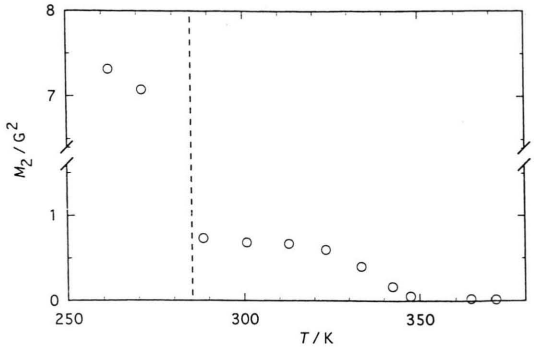

Fig. 1. The temperature dependence of the second moment (M_2) of the ^{1}H NMR linewidth observed in $[(CH_3)_3NC_2H_4OH]ClO_4$. The broken line shows the phase transition temperature determined by DSC.

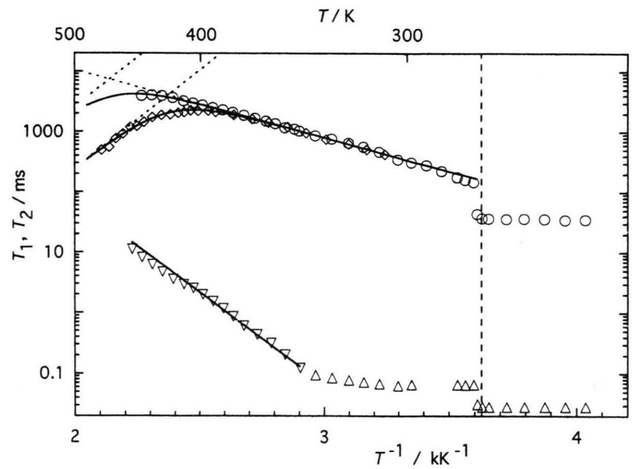

Fig. 2. Temperature dependences of ^{1}H NMR spin-lattice relaxation time (T_1), spin-spin relaxation time (T_2), and linewidth parameter (T_2^*) of $[(CH_3)_3NC_2H_4OH]ClO_4$. T_1 (○) observed at 32 MHz; T_1 (◇) at 9.8 MHz; T_2 (∇) and T_2^* (△) at 32 MHz. Solid and dotted lines are the best-fitted calculated values. The broken line shows the phase transition temperature determined by DSC.

relaxation processes on the low- and high-temperature sides of the T_1 maximum are attributable to the cation isotropic rotation and self-diffusion, respectively. The T_1 was analysed by assuming the presence of two superimposed relaxation processes, given by

$$T_1^{-1} = T_{1rot}^{-1} + T_{1dif}^{-1}. \tag{1}$$

Here, T_{1rot} is the contribution from the cationic rotation whose correlation time τ_{rot} is expected to be short enough to satisfy the condition of $\omega\tau_{rot} \ll 1$, where ω is the Larmor frequency. T_{1dif} arises from the cationic self-diffusion, which is assumed to be slow in this temperature range; i.e., the condition $\omega\tau_{\rm dif} \gg 1$ is fulfilled, where $\tau_{\rm dif}$ is the correlation time of cationic self-diffusion. Applying these two conditions for the two kinds of cationic motions to the BPP equation [18], we can rewrite (1) as

$$T_1^{-1} = 5\,C_{\rm rot}\,\tau_{\rm rot} + 2\,C_{\rm dif}\,\omega^{-2}\tau_{\rm dif}^{-1}, \qquad (2)$$

where $C_{\rm rot}$ and $C_{\rm dif}$ denote motional constants of the two cationic motions. We assume Arrhenius-type temperature dependences of $\tau_{\rm rot}$ and $\tau_{\rm dif}$:

$$\tau = \tau_0\,\exp(E_a/RT). \qquad (3)$$

Applying (2) and (3) to the T_1 data, we evaluated the activation energies for the cationic self-diffusion and isotropic rotation to be 62 ± 3 and 21.4 ± 0.4 kJ mol^{-1}, respectively.

The increase in T_2 from 0.12 to 11 ms above 345 K in the high-temperature phase is attributed to the cationic self-diffusion, because the onset of this motion was shown in the M_2 analysis given above. When T_2 can be expressed by the BPP-type equation under the condition of $\omega\tau_{\rm dif} \gg 1$, we have [18]

$$T_2 \propto \tau_{\rm dif}^{-1}. \qquad (4)$$

The activation energy of cationic self-diffusion was evaluated to be 58 ± 3 kJ mol^{-1} from the slope of the log T_2 vs. T^{-1} plots, by using (3) and (4).

The obtained activation energies are comparable with 25 and 62 kJ mol^{-1} for the cationic isotropic rotation and self-diffusion, respectively, determined for the second-highest temperature solid phase of $[(CH_3)_3NC_2H_4OH]BF_4$ [19], whose structure is CsCl-type cubic [20] and isomorphous with that of the high-temperature phase of the perchlorate. In the CsCl-type cubic phase of tetrafluoroborate, the anions were also found to perform isotropic rotation and self-diffusion by ^{19}F NMR [19]. The ClO_4^- ion having a size and shape similar to that of BF_4^- ion is, therefore, expected to perform the same motions in the CsCl-type cubic phase of perchlorate. From the dynamical behaviour of the cation and anion and the small magnitude of the entropy of fusion, we can conclude that the high-temperature phase of choline perchlorate is ionic plastic.

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