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$_3$)$_3$NCH$_2$CH$_2$OH]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 $^1$HT$_1$ 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 plastic phase.

Experimental

[(CH$_3$)$_3$NCH$_2$CH$_2$OH]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.

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...
Table 1. Observed and calculated 2θ values of X-ray powder patterns of the high-temperature phase of choline perchlorate at ca. 380 K, λ(CuKα), = 1.5406 Å, (cubic, a = 6.326(4) Å, Z = 1, V = 253.2(5) Å³, and \(D_x = 1.335(3)\) Mg m⁻³).

<table>
<thead>
<tr>
<th>2θ°_obsd ± 0.02°</th>
<th>Intensity</th>
<th>2θ°_calc</th>
<th>h k l</th>
</tr>
</thead>
<tbody>
<tr>
<td>13.98</td>
<td>6</td>
<td>13.99</td>
<td>100</td>
</tr>
<tr>
<td>19.82</td>
<td>100</td>
<td>19.83</td>
<td>110</td>
</tr>
<tr>
<td>24.37</td>
<td>8</td>
<td>24.35</td>
<td>111</td>
</tr>
<tr>
<td>28.17</td>
<td>6</td>
<td>28.19</td>
<td>200</td>
</tr>
<tr>
<td>31.61</td>
<td>7</td>
<td>31.60</td>
<td>210</td>
</tr>
<tr>
<td>34.71</td>
<td>4</td>
<td>34.71</td>
<td>211</td>
</tr>
</tbody>
</table>

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, \(Z = 1\), \(V = 253.2(5)\) Å³, 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 \(M_2^2\) determined above 250 K is shown in Figure 1. \(M_2^2\) suddenly decreases at the transition point from the low- to high-temperature phase, and the value became 0.6 ± 0.1 G² (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 G² calculated for isotropically rotating cations using the structural data determined in the present investigation. A further decrease in \(M_2^2\) to less than 0.05 G² 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 \(^1\text{H} T_1\), \(T_2\), 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 \(M_2^2\) results, the 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

\[ T_1^{-1} = T_{1\text{rot}}^{-1} + T_{1\text{dif}}^{-1}. \]  

Here, \(T_{1\text{rot}}\) is the contribution from the cationic rotation whose correlation time \(\tau_{\text{rot}}\) is expected to be short enough to satisfy the condition of \(\omega \tau_{\text{rot}} \ll 1\), where \(\omega\) is the Larmor frequency. \(T_{1\text{dif}}\) arises from the cationic
self-diffusion, which is assumed to be slow in this temperature range; i.e., the condition \( \omega \tau_{\text{dif}} \gg 1 \) is fulfilled, where \( \tau_{\text{dif}} \) 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

\[
T_1^{-1} = 5 C_{\text{rot}} \tau_{\text{rot}} + 2 C_{\text{dif}} \omega^{-2} \tau_{\text{dif}}^{-1},
\]

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

\[
\tau = \tau_0 \exp(E_0/RT).
\]

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 \( \omega \tau_{\text{dif}} \gg 1 \), we have [18]

\[
T_2 \propto \tau_{\text{dif}}^{-1}.
\]

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 \([\text{CH}_3)_3\text{NCl}_2\text{H}_4\text{OH}]\text{BF}_4\) [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 \(^{19}\text{F} \) 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.