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^1H and ^{19}F NMR Studies on Phase Transitions and Ionic Motions in Choline Tetrafluoroborate

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Three solid phases of $(CH_3)_3NCH_2CH_2OHBF_4$ were found between 160 K and the melting point (485 K) by DTA, DSC, and ^1H and ^{19}F NMR measurements; the phases designated as I, II, and III are stable above 402 K, between 402 and 268 K, and below 268 K, respectively. In Phase II, the cations and anions were found to perform rapid self-diffusion as well as isotropic reorientation. At the transition point (Phase II → I), "quenching" of the cationic self-diffusion was observed.

Choline salts have extensively been investigated by various physical means with attention to the nature of molecular dynamics and phase transitions$^{1)}$ because of marked susceptibility to radiation damage found in choline chloride.$^{2,3)}$ In these studies, it was revealed that choline salts have various solid phases with different degrees of motional freedom of the cations. In particular, choline iodide and perchlorate were shown to form unusual solid phases where the bulky choline ions perform self-diffusion as well as isotropic reorientation much faster than 10^5 Hz.$^{4-6)}$ This behavior of the cations is similar to that in "ionic plastic phase" found in methyl-substituted ammonium salts.$^{7)}$ Choline salts are, therefore, expected to be a noticeable system in view of our interest in molecular dynamics in solid, especially, in the ionic plastic phase.

In the present study, ^1H and ^{19}F NMR, differential thermal analysis (DTA), and differential scanning calorimeter (DSC) on choline tetrafluoroborate have been measured to investigate possible phase transitions and characterize the molecular motion of both cations and anions.

$(CH_3)_3NCH_2CH_2OHBF_4$ was prepared by neutralizing choline with tetrafluoroboric acid. The product was recrystallized twice from methanol. Found: C, 31.35; H, 7.44; N, 7.33%. Calcd for $(CH_3)_3NCH_2CH_2OHBF_4$: C, 31.44; H, 7.39; N, 7.34%. Phase-transition temperatures and the corresponding enthalpy changes were determined by a home-made DTA apparatus$^{8)}$ and a Perkin-Elmer DSC 7, respectively. The second moment (M_2) of ^1H and ^{19}F NMR absorptions was determined by use of a JEOL JNM-MW-40S spectrometer. ^1H NMR spin-lattice and spin-spin relaxation times (T_1 and T_2) and linewidth parameter (T_2*) were measured at 32 MHz using a pulsed spectrometer.$^{9)}$ The 180° - t - 90° pulse sequence and the Hahn's spin-

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echo method[10] were employed for the determination of T_1 and T_2, respectively. $T_2{}^*$ was obtained from the shape of free induction after a 90° pulse by assuming an exponential decay. Before the measurements, the sample put in a glass ampoule was dried *in vacuo* (*ca.* 10^{-1} Pa) at room temperature for 5 h and then at 80 °C for 5 h.

Two solid-solid phase transitions and the melting were located at 268, 402, and 485 K, respectively, by DTA. The solid phases are designated in the order of decreasing temperature as Phase I, II, and III. The enthalpy changes at the phase transitions (III → II and II → I) and fusion determined by DSC were 9.3 ± 0.1 and 1.4 ± 0.1, and 3.1 ± 0.2 kJ mol^{-1}, respectively. The associated entropy changes ($\Delta_{trs}S$) at these transitions were evaluated to be 35 and 3.5 J K^{-1} mol^{-1} in the same order, and the entropy of fusion ($\Delta_{fus}S$) became 6.4 J K^{-1} mol^{-1}. The extremely large value of $\Delta_{trs}S(\mathrm{III} \rightarrow \mathrm{II})$ compared with $\Delta_{fus}S$ implies that both cations and anions have acquired the greatest part of their motional freedom in Phase II and I. Moreover, it is noticeable that the obtained $\Delta_{fus}S$ value is much lower than 20 J K^{-1} mol^{-1}, which has been accepted as the criterion of forming the plastic phase in molecular crystals.[11]

The temperature variations of ^1H and ^{19}F M_2 determined above 160 K are shown in Fig. 1. Around 170 K, we obtained almost constant ^1H and ^{19}F M_2 values of 14.5 ± 0.5 and 2.9 ± 0.1 G^2 (1 G = 1×10^{-4} T), respectively. These values are explainable in terms of the reorientation of the CH_3 groups and the isotropic reorientation of the anions, by referring to the reported M_2 values for choline salts[4] and ammonium tetrafluoroborate.[12] The gradual decrease in both M_2 with increasing temperature in Phase III is attributable to the onset of the $(CH_3)_3N$- group reorientation about the long chain C-N axis. ^1H and ^{19}F M_2 suddenly decreased at $T_{trs}(\mathrm{III} \rightarrow \mathrm{II})$ and both values became 1.00 ± 0.05 G^2 at ca. 270 K, implying the presence of the isotropic reorientation of the cation in Phase II. The further decrease in both M_2 to less than 0.05 G^2 upon heating in this phase indicates the onset of self-diffusion of both ions.

Temperature dependences of ^1H T_1, $T_2{}^*$, and T_2 above 170 K are shown in Fig. 2. The T_1 increase with temperature observed in the low-temperature region of Phase II is attributable to the isotropic reorientation of the whole cation from the results of ^1H M_2, while the T_2 increase from 0.6 to 20 ms indicates the rapid cationic self-

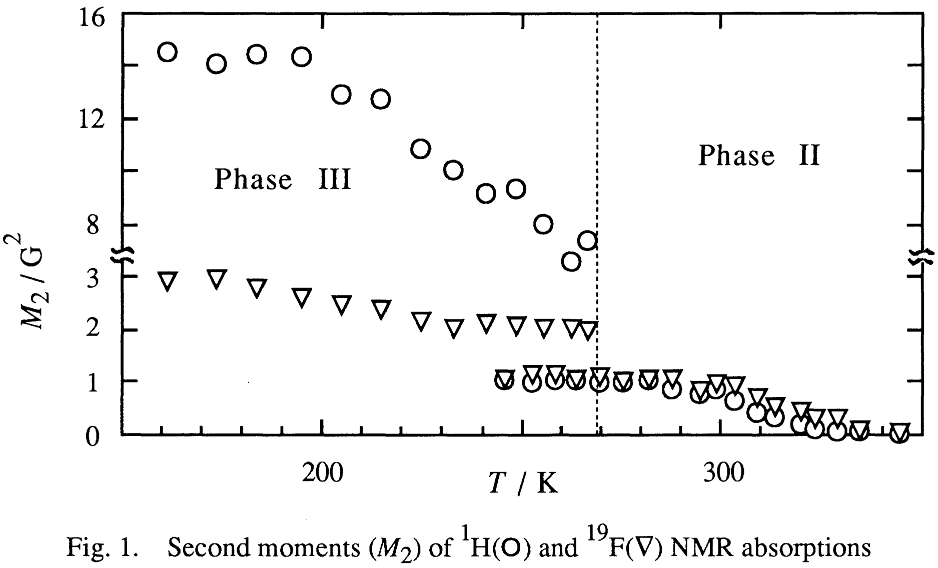

Fig. 1. Second moments (M_2) of ^1H(O) and ^{19}F(∇) NMR absorptions observed for $(CH_3)_3NCH_2CH_2OHBF_4$.

diffusion just like in liquid. The activation energies (E_a) for these motions derived from the slopes of ln T_1 and ln T_2 *vs.* T^{-1} plots are 25 and 62 kJ mol^{-1}, respectively. In the high-temperature region of Phase II, T_1 showed a non-exponential recovery of ^{1}H magnetization. Similar behavior of T_1 was also observed in Phase I. Two relaxation times, T_{1s} and T_{1l} ($T_{1s} < T_{1l}$) could be evaluated by assuming the recovery curve expressed as:

$$(M_0 - M_z(t)) / 2M_0 = A_s \exp(-t / T_{1s}) + A_l \exp(-t / T_{1l}).$$

Here, M_0 and $M_z(t)$ are z-components of the ^{1}H magnetization at thermal equilibrium and at time t after a 180° pulse, respectively, and A_s and A_l are constants ($A_s + A_l = 1$). In the whole non-exponential temperature range in Phase I and II, we obtained almost constant coefficients, $A_s \approx 4/18$ and $A_l \approx 14/18$, where 14 and 4 are the number of ^{1}H and ^{19}F nuclei in the formula of the present salt, respectively. The non-exponential behavior of T_1 is, accordingly, attributable to the cross relaxation due to the magnetic dipole interaction between ^{1}H and ^{19}F nuclei[13-15] modulated by the anionic self-diffusion taking place in this phase. The diffusional rate is considered to be faster than that of the cation in view of the size difference of the two ions. E_a = 25 kJ mol^{-1} was evaluated for the anionic self-diffusion in Phase II from the linear portion of the ln T_{1s} *vs.* T^{-1} plots. At T_{trs}(II → I), discontinuous changes in T_{1s}, T_{1l}, and T_2 were observed. In particular, T_2 decreased abruptly by two orders of magnitude and a T_2* value of 0.1 ms was obtained at 425 K in Phase I. This implies "quenching" of the cationic

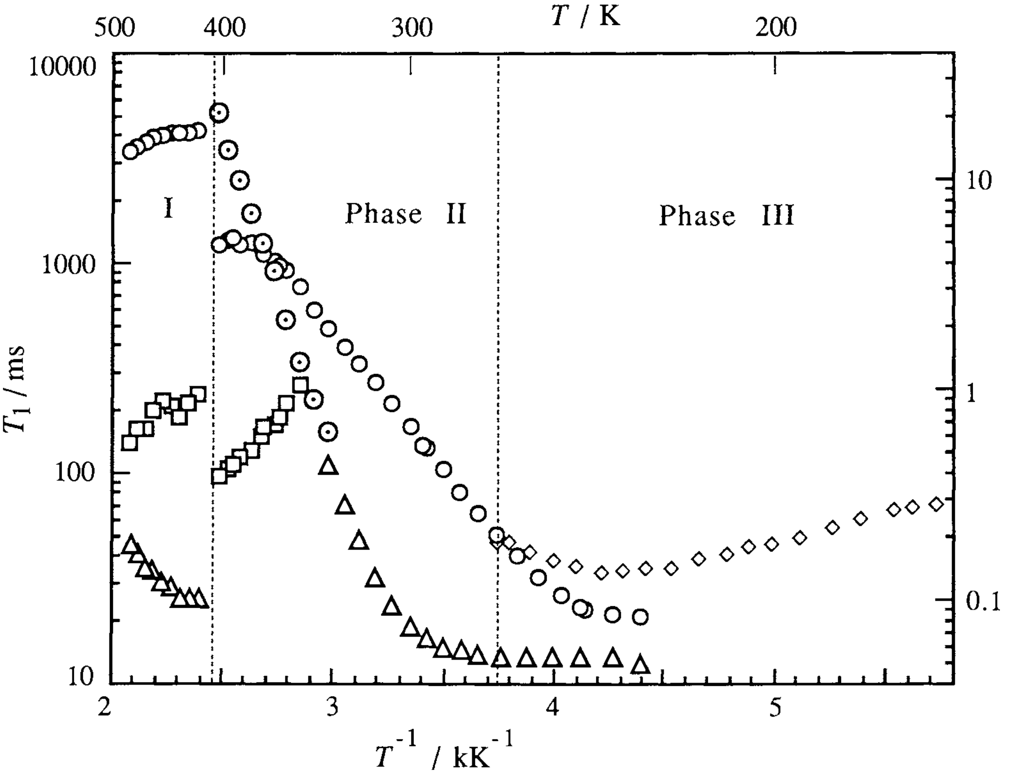

Fig. 2. Temperature dependences of ^{1}H T_1
(◇:T_1 in Phase III; O:T_1 and T_{1l} in Phase I and II; □: T_{1s} in Phase I and II),
T_2*(Δ), and T_2(⊙) observed in $(CH_3)_3NCH_2CH_2OHBF_4$ at 32 MHz.

self-diffusion at the transition point. On further increasing temperature in Phase I, however, T_2^* gradually increased again, suggesting the recovery of the cationic diffusion. A similar quenching of the cationic diffusion was reported in choline iodide.$^{5)}$ From the dynamical behavior of the cations and anions and the small magnitude of $\Delta_{\mathrm{fus}}S$ revealed in the present investigation, we conclude that choline tetrafluoroborate forms an ionic plastic crystal in both Phase II and I.

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