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Phase Transitions and Ionic Motions Including Self-Diffusion in Solid Trimethylammonium Tetrafluoroborate Studied by ^{1}H and ^{19}F NMR

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^{1}H and ^{19}F NMR of $(CH_3)_3NHBF_4$ were measured in the three solid phases. In Phase I existing above 453 K, the cations and anions were found to perform rapid self-diffusion as well as isotropic reorientation. In Phase II ($384 \le T/K \le 453$), the onset of self-diffusion of the anions and the isotropic reorientation of the cations was observed. In Phase III stable below 384 K, C_3 reorientations of the CH_3 groups and the whole cation, and the anionic isotropic reorientation were detected.

Recently, we have reported the presence of an ionic plastic phase for 1,1-dimethylhydrazinium tetrafluoroborate.1) In this phase both $(CH_3)_2NNH_3^+$ and BF_4^- ions were found to perform rapid self-diffusion as well as isotropic reorientation from the temperature dependence studies of ^{1}H and ^{19}F NMR. This is the first study, to our knowledge, on the self-diffusional motions of both ions in the ionic plastic phase. Most studies on the molecular dynamics in this phase reported so far have been concentrated on the cations2-13) because of the lack of experimental methods suitable for investigating the anion dynamics. Only isotropic reorientations of the anions in $(CH_3)_nNH_{4-n}ClO_4$ (n = 1 - 3), which have been known to form the ionic plastic phase,4,5,8,9) were investigated by Jurga *et al.* using ^{35}Cl NMR.14) ^{19}F NMR can be measured as easily as ^{1}H NMR and also the strong magnetic dipolar interaction between ^{1}H and ^{19}F provides the information about the anion dynamics through the ^{1}H NMR measurement.15-19) Tetrafluoroborates are, accordingly, expected to be good candidates for investigating dynamical properties of the cations and anions in ionic plastic phases.

From this viewpoint, trimethylammonium tetrafluoroborate, $(CH_3)_3NHBF_4$, is a noticeable system because of the easily movable cation in solid state owing to its higher symmetry and more spherical shape than dimethylhydrazinium ions. Zabinska *et al.*20) carried out differential scanning calorimetry (DSC) and found three solid phases in $(CH_3)_3NHBF_4$ above *ca.* 100 K. The transition and fusion temperatures have been reported at 378, 446, and 481 K, respectively. Thus, we may expect that highly disordered states of both cations and anions are realized in the highest-temperature solid phase of $(CH_3)_3NHBF_4$.

In the present investigation, we have made measurements of the temperature dependence of ^{1}H NMR spin-lattice relaxation time (T_1) and the second moment (M_2) of the ^{1}H and ^{19}F NMR absorptions for $(CH_3)_3NHBF_4$, in order to reveal the presence of highly movable cations and anions in the three solid phases.

$(CH_3)_3NHBF_4$ was prepared by neutralizing trimethylamine with tetrafluoroboric acid. The obtained crystals were recrystallized twice from methyl alcohol. Found: C, 24.48; H, 6.92; N, 9.52%. Calcd for $(CH_3)_3NHBF_4$: C, 24.52; H, 6.86; N, 9.54%. Phase transition temperatures and the corresponding enthalpy changes were redetermined by a home-made DTA apparatus[21)] and a Parkin-Elmer DSC7 calorimeter, respectively. M_2 of ^{1}H and ^{19}F NMR absorptions was determined by use of a JEOL JNM-MW-40S spectrometer. ^{1}H NMR T_1 was measured at 32 and 11.5 MHz using a pulsed spectrometer;[22)] the 180° - t - 90° pulse sequence was employed.

Two solid-solid phase transitions at 384 and 453 K and the melting at 489 K were located by DTA. These temperatures are somewhat higher than those observed by Zabinska *et al.*,[20)] while our melting point agrees well with 489.2 K reported by Gatner.[23)] The solid phases are designated in the order of decreasing temperature as Phases I, II, and III. The enthalpy changes at the phase transitions (III → II and II → I) and fusion determined by DSC were 1.1 ± 0.2, 3.36 ± 0.05, and 9.5 ± 0.2 kJ mol^{-1}, respectively; then the associated entropy changes were evaluated to be 2.9, 7.4, and 19 JK^{-1}mol^{-1}. The fairly low entropy of fusion (ΔS_f = 19 JK^{-1}mol^{-1}) comparable to that ($\Delta S_f \leq 20$ JK^{-1}mol^{-1}) in the plastic phase of molecular solids[24)] implies that Phase I is a highly orientationally-disordered state.

The temperature variations of ^{1}H and ^{19}F M_2 determined above 250 K are shown in Fig. 1. In Phase III, we observed almost constant ^{1}H and ^{19}F M_2 values of 2.3 ± 0.1 and 1.7 ± 0.1 G^2 (1G = 1 × 10^{-4} T), respectively. By comparing these data with the reported M_2 for trimethylammonium salts[9,25)] and ammonium tetrafluoroborate,[16)] the cationic and anionic motions in this phase were found to be the reorientations of the CH_3 groups and the whole cation about respective C-N and N-H axes, and the isotropic reorientation of the anion about its center of gravity, respectively. With increasing temperature in Phase II, ^{1}H and ^{19}F M_2 gradually decreased and became 0.5 and less than 0.1 G^2, respectively, at *ca.* 445 K. This indicates the onset of the isotropic reorientation of the cations and self-diffusion of the anions. ^{1}H M_2 of < 0.1 G^2 observed in Phase I indicates that both cations and anions perform rapid self-diffusion as well as isotropic reorientation.

Temperature dependence of ^{1}H T_1 above 290 K is shown in Fig. 2. The T_1 increase with temperature in Phase III is attributable from the results of ^{1}H M_2 to the reorientation of the whole cation about its C_3 axis. The activation energy (E_a) for this motion derived from the slope of ln T_1 *vs.* T^{-1} plots is 27 kJ mol^{-1}. No remarkable

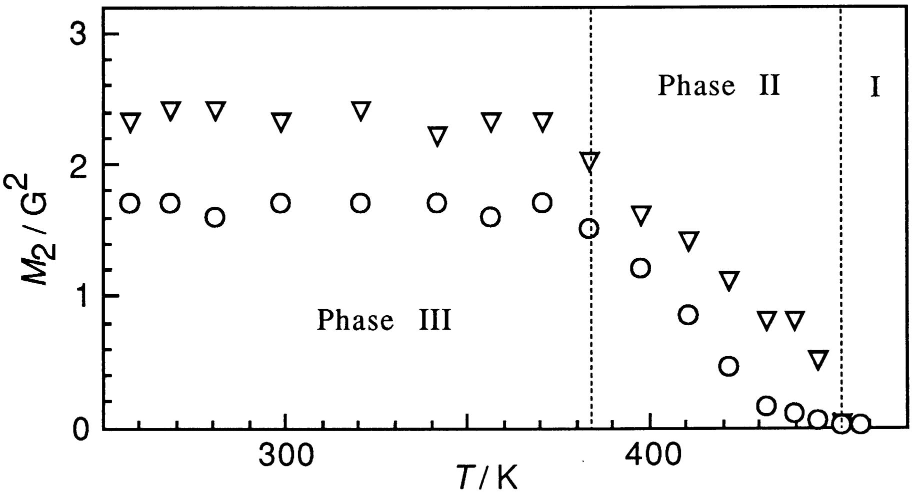

Fig. 1. Second moments (M_2) of ^{1}H (∇) and ^{19}F (O) NMR absorptions observed for $(CH_3)_3NHBF_4$.

discontinuity in T_1 was observed at the transition (III → II), implying that the cationic reorientation is little affected at this transition. In the high-temperature region of Phase II, both T_1 observed at 32 and 11.5 MHz showed the non-exponential recovery of ^1H magnetization; this recovery curve was separated into two relaxation times, T_{1s} and T_{1l} ($T_{1s} < T_{1l}$), according to the following equation:

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

Here, M_0 and $M_z(t)$ are the z-components of the ^1H magnetization at thermal equilibrium and at time t after 180° pulse, respectively, and A_s and A_l are the constants ($A_s + A_l = 1$). Since we obtained almost constant coefficients, $A_s \approx 4/14$ and $A_l \approx 10/14$, in the whole non-exponential temperature range, the non-exponential behavior of T_1 is attributable to the cross relaxation due to the magnetic dipole interaction between ^1H and ^{19}F nuclei[15,18,19] modulated by the anionic self-diffusion which takes place in this phase as expected from the ^{19}F M_2 decrease. $E_a = 71$ kJ mol^{-1} was evaluated from the linear portion of the ln T_{1s} *vs.* T^{-1} plots.

In Phase I, the recovery became exponential and the ^1H spin-spin relaxation time (T_2) observed at 32 MHz by Hahn's spin-echo method[26] was longer than 30 ms. This indicates that the cationic self-diffusion is a dominant relaxation process in this phase and the T_1 minimum observed at 11.5 MHz is assigned to this motion; we evaluated $E_a = 21$ kJ mol^{-1} from the gradient of the ln T_1 *vs.* T^{-1} plots observed at 32 MHz. The anionic self-diffusion is considered to be too fast to affect ^1H T_1 in this phase as predicted from the results of ^1H T_1 in Phase II, which is reasonable in view of the size difference of the two ions.

From the dynamical behavior of both ions and the low ΔS_f revealed in the present investigation, we expect that Phase I is an ionic plastic phase as found for $(CH_3)_2NNH_3BF_4$.[1] It is noteworthy, however, that

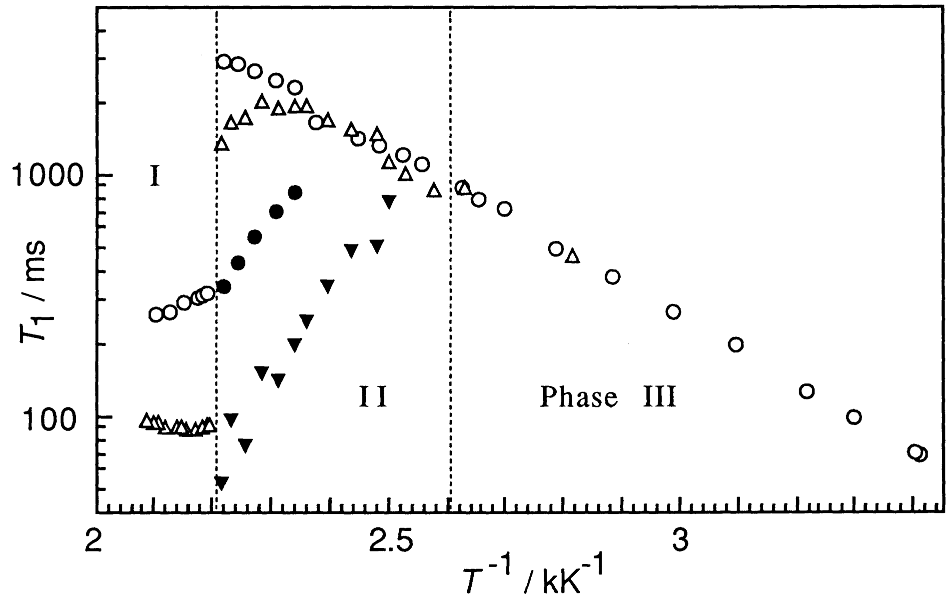

Fig. 2. ^1H spin-lattice relaxation times (T_1) observed at 32 MHz (○ : T_1 and T_{1l} and ● : T_{1s}) and 11.5 MHz (△ : T_1 and T_{1l} and ▼ : T_{1s}) for $(CH_3)_3NHBF_4$.

there exist remarkable discrepancies between $(CH_3)_3NHBF_4$ and $(CH_3)_2NNH_3BF_4$ in the entropy changes into the plastic phase (ΔS_{tr}) and ΔS_f, namely, ΔS_{tr} = 7.4 and ΔS_f = 19 $JK^{-1}mol^{-1}$ for the former, while ΔS_{tr} = 21 and ΔS_f = 11 $JK^{-1}mol^{-1}$ for the latter, although the size and shape of the cations in the two salts are almost the same. Thus the microscopic plastical nature of $(CH_3)_3NHBF_4$, such as the degree of orientational disorder, the diffusion mechanism of ions, seems to be quite different from that of $(CH_3)_2NNH_3BF_4$.

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