^1H NMR and Thermal Studies of CH_3NH_3Br in a Metastable Solid Phase Newly Found above 483 K

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By differential thermal analysis a new high-temperature solid phase of methylammonium bromide was found between 483 K and its "melting point" (510 K). ^1H NMR absorption measurements revealed the presence of rapid 3D translational self-diffusion and overall rotation of methylammonium cations in this phase. These cationic motions are quite analogous to those of methylammonium iodide in its ionic plastic phase. Surprisingly, this plastic-like phase is metastable, the stable phase in the same temperature range being liquid.

1. Introduction

We have reported that simple methylammonium (MA) salts, such as the nitrate [1], the iodide [2], and the perchlorate [3], exhibit an unusual solid phase just below the melting point, the MA^+ cations becoming free to rotate and to diffuse. This phase can be named "ionic plastic phase" because the thermal properties and molecular dynamics of the cations are quite analogous to those of the molecules in the well-established plastic crystals [4].

(MA)Br in the α'-form (room temperature) forms tetragonal crystals belonging to the space group P4/nmm with $Z = 2$ [5, 6] (hereafter we call it phase III). This phase is isomorphous with the room temperature phase of (MA)I, which is transformed into an ionic plastic phase at 414 K [2]. The bromide has a high-temperature phase (α) [7, 8], hereafter called phase II, whose crystals belong to the same space group as phase III but with a different ionic arrangement [7, 9]. The structure of phase II is isomorphous with the room temperature phase of (MA)Cl [7, 9] which melts, on heating, at 505 K without forming the plastic phase [10]. In this study, ^1H NMR measurements and differential thermal analysis (DTA) have been undertaken to clarify whether phase II of the bromide is, like the iodide, transformed into a high-temperature phase before melting.

2. Experimental

Methylammonium bromide was prepared by neutralizing an aqueous solution of methylamine with hydrobromic acid. Crystals obtained by evaporating the solvent were recrystallized from ethanol. The hygroscopic polycrystalline samples were carefully handled in a glove box and dried under vacuum. The powdered samples, put in glass ampouls for the ^1H NMR and DTA measurements, were finally dried by pumping for about 24 h at ca. 120 °C and then sealed off under dry argon gas.

^1H NMR absorption as well as ^1H spin-lattice and spin-spin relaxation times (T_1 and T_2, respectively) were measured with an apparatus already reported [11, 12]. Inversion recovery and Hahn's spin echo method were employed to determine T_1 and T_2, respectively. DTA was carried out with an apparatus already described [13].

3. Results and Discussion

Figure 1 shows the DTA curve recorded on increasing the temperature at a rate of ca. 1 K/min. The endothermic anomaly around 390 K, corresponding to the phase transition III → II, has already been reported [7], although on heating the starting temperature varied within ±5 K in our runs. When phase II was heated further, a new solid phase, denoted as phase I, appeared above 483 ± 1 K, at

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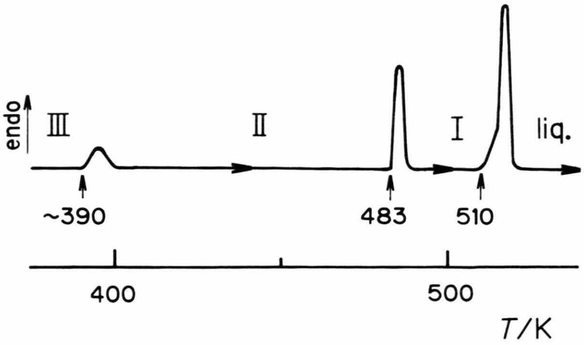

Fig. 1. The DTA curve of CH_3NH_3Br heated at a rate of ca. 1 K/min from room temperature up to ca. 540 K.

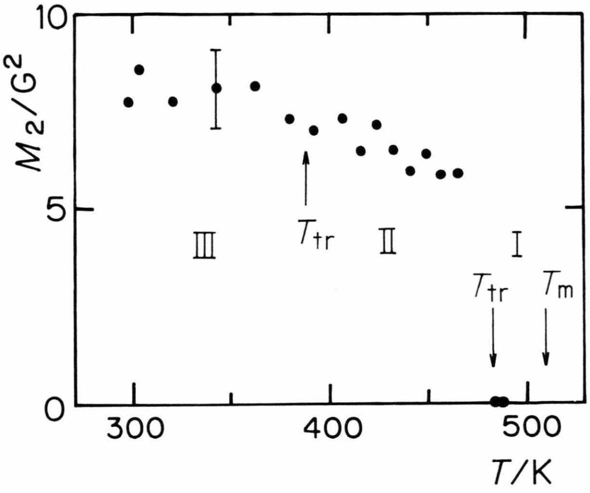

Fig. 2. Temperature dependence of the second moment M_2 of ^{1}H NMR absorption recorded between 300 and 485 K. Arrows indicate phase transition temperatures (T_{tr}) and the melting temperature (T_m).

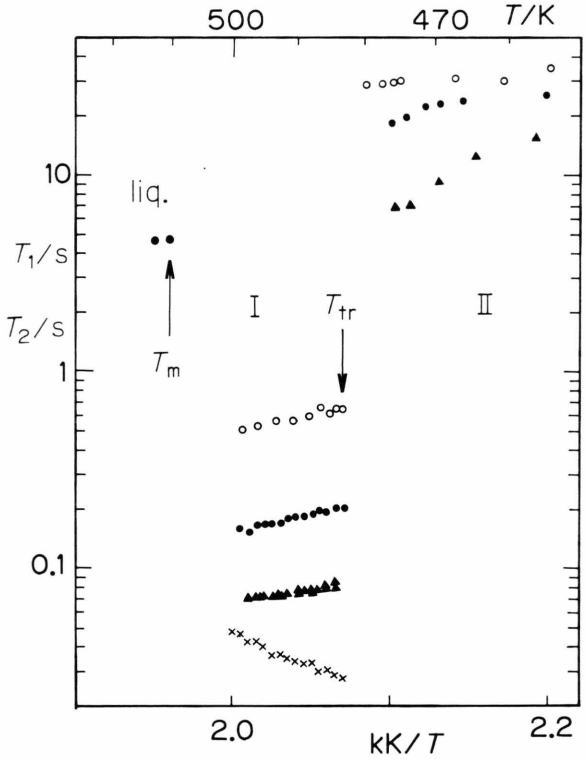

Fig. 3. Temperature dependences of ^{1}H NMR spin lattice relaxation times (T_1) observed at 45.5 (○), 20.0 (●), and 10.5 (▲) MHz and T_2 determined at 20.0 MHz (×). Arrows indicate the phase transition temperature (T_{tr}) and the melting temperature (T_m).

which temperature a large endothermic anomaly was observed. On heating further, phase I melted at 510 ± 1 K. As shown in Fig. 1, the endothermic melting anomaly exhibited a tail on the low temperature side; its starting temperature, however, could be definitely determined. Since phase I was expected to bear features similar to those of the high-temperature solid phase of (MA)I, we measured ^{1}H NMR absorptions at high temperatures to obtain information about the motional state of the cation.

The temperature dependence of the ^{1}H NMR second moment M_2 is shown in Figure 2. An almost constant M_2 of ca. 8 ± 1 G^2 was observed up to ca. 400 K. This M_2 value can be explained by the rotation of the cation about its C–N bond axis [7]. Above 400 K, M_2 gradually decreased and became ca. 6 G^2 around 460 K, indicating the onset of another cationic motion. No appreciable change of M_2 was observed at the phase transition temperature of ca. 390 K. In phase I, extremely narrow absorption lines with M_2 of less than 0.01 G^2 were observed. This clearly indicates that the MA^+ cations perform rapid 3D translational self-diffusion as well as isotropic overall rotation faster than 10^4 Hz. The presence of these motions strongly suggests that phase I of the bromide is an ionic plastic phase analogous to the ε phase of the iodide.

We measured ^{1}H T_1 with the Larmor frequencies (ω) of 10.5, 20.0, and 45.5 MHz in the phases II and I, and also in the liquid phase. To better characterize phase I, ^{1}H T_2 at 20 MHz was observed at various temperatures in this phase. The temperature dependences of these relaxation times are shown in Figure 3.

With increasing temperature, a remarkably frequency-dependent T_1 decrease was observed in the high-temperature region of phase II. This indicates that contributions from the BPP type relaxation mechanism [14], probably due to a new cationic motion, become appreciable at higher temperatures in phase II, in accordance with the M_2 decrease observed in the same temperature range. Nutation of the cations seems to be the most probable mechanism for this relaxation process.

The ^{1}H T_1 value observed in phase I decreased with increasing temperature and showed a definite frequency dependence. These results can be explained by applying the BPP theory in the slow-motion approximation [14]. Self-diffusion of the cations is the most probable mechanism for the ^{1}H spin-lattice relaxation in phase I. However, contributions from some other mechanisms than the self-diffusion should be considered to explain the observed frequency dependence of T_1 because the observed T_1 values do not exactly follow the relationship

$$T_1 \propto \omega^2 \tag{1}$$

which is predicted from the BPP theory [14].

An interesting and extremely unusual phenomenon was observed in phase I: The ^{1}H spin-lattice relaxation observed just above T_{tr} (483 K) gradually became nonexponential with elapsing time when the temperature was kept constant at 483 ± 1 K. Practically speaking, ^{1}H magnetization with a long T_1 (~ 3 s) began to be mixed with the component of the original short T_1 (~ 200 ms) in the measurements repeatedly performed for a long time at the Larmor frequency of 20 MHz. The fraction of the long T_1 component increased with the time at constant temperature, whereas that of the short T_1 decreased. 32 h after setting the temperature at 483 K, the relaxation could be roughly described by the long T_1 alone, and, at that time, the sample in the glass ampoule, just after having been taken out from the *rf* probe of the spectrometer, was mostly molten. These observations indicate that phase I is metastable and that the stable phase at the same temperature is liquid. Accordingly, the melting observed at 510 K as an endothermic anomaly in the DTA measurements is unassignable to a usual phase transition between stable equilibrium states. The foregoing "melting point" detected is considered as the temperature of a transition from an over-heated state to the liquid state.

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