1H NMR and Thermal Studies of CH₃NH₃Br 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 z'-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 (x) [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.

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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 ampoules 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 (T₁ and T₂, respectively) were measured with an apparatus already reported [11, 12]. Inversion recovery and Hahn's spin echo method were employed to determine T₁ and T₂, 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
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 $\varepsilon$ phase of the iodide.

We measured $^1$H $T_1$ with the Larmor frequencies ($\omega$) 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 $^1H$ $T_1$ 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 $^1H$ 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

$$T_1 \propto \omega^2$$

which is predicted from the BPP theory [14].

An interesting and extremely unusual phenomenon was observed in phase I: The $^1H$ spin-lattice relaxation observed just above $T_n$ (483 K) gradually became nonexponential with elapsing time when the temperature was kept constant at 483 ± 1 K. Practically speaking, $^1H$ 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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