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PHASE TRANSITIONS AND BROADENING OF CHLORINE NQR SPECTRUM OF 1,1,1-TRICHLORO-2-METHYL-2-PROPANOL HEMIHYDRATE

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It was found that 1,1,1-trichloro-2-methyl-2-propanol hemihydrate exhibits two phase transitions at 192 K and 198 K. By quenching the compound from room temperature to 77 K, a metastable phase was obtained. The results of the dielectric and chlorine NQR measurements suggest a random orientation of molecules in the metastable phase.

In general, the chlorine NQR spectra of organic compounds can be observed easily. But, in the case of 1,1,1-trichloro-2-methyl-2-propanol hemihydrate, chloretone, its NQR signals were not so easily detected as other organic compounds. In order to find out its reason, the dielectric and thermal properties of this compound were examined.

Commercial chloretone was purified by recrystallization from ethyl ether. The dielectric constant ε' and loss ε'' were measured with a transformer bridge, Ando Denki TR-1C, over the frequency range 30 Hz ~ 1 MHz. The dielectric measurements were carried out on compressed disks of 20 mm in diameter and 0.5 ~ 1.2 mm in thickness. The bulk densities of these disks were about 1.4 g/cm^3. The density calculated from the crystal structural data[1] is 1.48 g/cm^3. A differential scanning calorimeter, Rigaku DSC 8001, was used for the thermal analysis. The chlorine NQR spectra were obtained by a super-regenerative spectrometer.

The curves in Fig.1 show the dielectric constant-temperature relations of chloretone measured at 3 kHz. The curve (a) in Fig.1 was obtained in the course of heating a quenched sample (cooled from room temperature to 77 K within a few min). As the temperature was raised, the dielectric constant increased gradually and then decreased sharply at about 170 K. After this sharp decrease, the sample was annealed at about 180 K for 30 min, and again cooled slowly to 77 K. This annealed sample exhibited no anomaly in the temperature range 77 ~ 192 K (curve (b) in Fig.1). The DSC curves of chloretone are shown in Fig.2. The quenched sample (curve (a) in Fig.2) showed a little anomaly in the 170 ~ 190 K region. After the same annealing

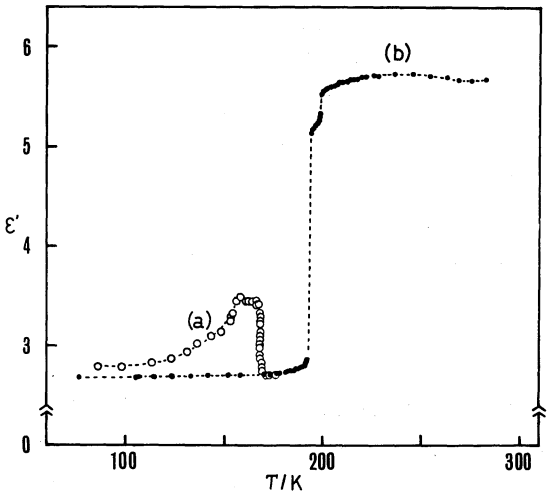

Fig.1. Dielectric constnat (ε')-temperature curves of chloretone measured at 3 kHz.

procedure mentioned above, this anomaly disappeared (curve (b) in Fig.2). The dielectric and thermal behavior indicates that the quenched sample corresponds to a metastable phase (phase-I') and that it is transformed into a stable phase (phase-I) at about 170 K. As can be seen from the curve (b) in Fig.1, the dielectric constant rises sharply at 192 K, indicating a phase transition (phase-I to phase-II). A less drastic, but clearly discontinuous rise at 198 K shows another transition (phase-II to phase-III). Two endothermic peaks of the DSC curves in Fig.2 correspond obviously to these transitions.

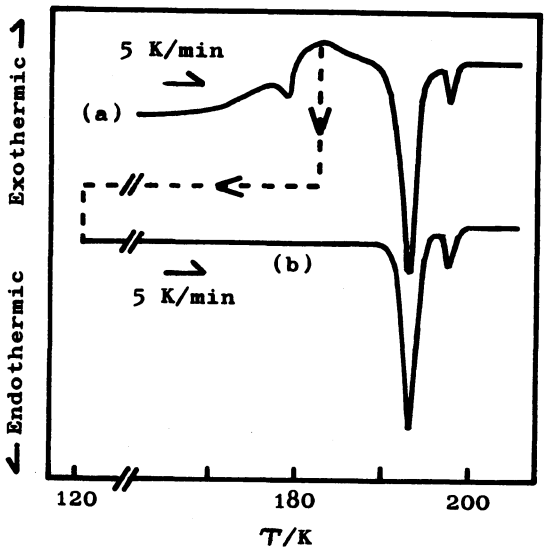

Fig.2. DSC curves of chloretone.

Phase-I' exhibited the anomalous dispersions in the frequency and temperature regions investigated. The intensity of the maximum absorption ε''_{max} was the order of 10^{-1}. Cole-Cole plots indicated a considerable distribution of relaxation times. For phase-II, an absorption ($\varepsilon''_{max} \sim 0.02$) was observed in audio frequency region and a second absorption seemed to appear at frequencies higher than 1 MHz. In the case of phase-III, the frequency dependence of ε'' suggested the presence of an absorption in the higher frequency range. James and McDonald reported that molecular orientational freedom exists in the crystal of pentamethylethanol hemihydrate,[2] which is isomorphous to the room temperature phase (phase-III) of chloretone.[1] The dielectric behavior of chloretone indicates the possibility of dipole orientation in the solid.

The chlorine NQR signals could not be detected for phase-I'. This is due presumably to a random orientation of molecule associated with the dipole orientation. For phase-I obtained by annealing a quenched sample with the same annealing procedure mentioned above, nine weak NQR signals were observed at 77 K. Their frequencies are 38.767, 38.735, 38.688, 38.583, 38.409, 38.325, 38.303, 38.255, and 38.135 MHz. It was found that the S/N ratios of these signals were much improved by further annealing. Therefore, immediately after the transformation from phase-I' to phase-I, the randomly oriented molecules probably remain to some extent. Further details of this study will be discussed elsewhere.

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