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DIELECTRIC RELAXATION STUDY OF t-CYANOBUTANE

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The complex dielectric permittivity of liquid t-cyanobutane (TBCN) at 500 kHz (static measurements), 1.98, 9.48, 21.88 and 36.64 GHz were performed at a temperature range of 293–323 K. The estimated effective dipole moment (3.64 D) and relaxation parameters of TBCN in the liquid state showed a contribution of cross-correlation.

1. *Introduction*

t-cyanobutane (TBCN) belongs to such organic compounds having the general formula $(CH_3)_3CX$ which exhibit two phase transitions in the solid phases [1–4]. These transitions separate the three solid phases. Calorimetric studies performed by Westrum and Ribner [4] demonstrated that TBCN melts at 292.1 K with entropy change $\Delta S = 7.60$ e.u. (cal/mole deg) whereas the phase I/phase II transition proceeds at 232.7 K ($\Delta S = 1.86$ e.u.) and the phase II/phase III transition at 213 K ($\Delta S = 0.26$ e.u.) The crystal structure is known for phase I only which crystallizes in tetragonal system ($a = b = 6.87$ Å and $c = 6.73$ Å) [5].

Dielectric studies performed by Clemett and Davies [6] demonstrated that, contrary to other similar compounds such as t-butyl chloride (TBC,X = Cl) [1], t-butyl bromide (TBB,X = Br) [7] and t-nitrobutane (TBN,$X = NO_2$) [8], the dipole rotation of the TBCN

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molecules becomes frozen immediately below the freezing point. These authors measured the temperature dependence of the static dielectric permittivity ε_0, over the temperature range of liquid and solid phase I but did not reach the phase transition temperature. This resulted most probably from a lack of knowledge of the phase conditions in solid TBCN. In addition, they measured the complex dielectric permittivity, $\varepsilon^* = \varepsilon' - i\varepsilon''$, for the solid phase in the 250–950 MHz frequency range, i.e., at much lower frequencies than critical frequency for dielectric relaxation process under consideration. Therefore, we decided to repeat these studies over the microwave frequency range from 2 to 37 GHz.

Studies of the quasielastic neutron scattering [9] demonstrated that in phase I of TBCN there is uniaxial rotation of molecules around the C—CN axis. Since a similar molecular process existing in phase II of TBN [10] is accompanied by wide-angle librations of molecular dipole moment, found in dielectric measurements [11], particular attention was paid to the measurements in solid phase of TBCN. The dielectric properties of phase I in TBCN together with the analysis of fIR spectra, will be presented in a separate paper [12]. The present paper deals mainly with the dielectric properties of the liquid phase of TBCN.

2. *Experimental*

The sample used here was identical to that investigated previously [10]. Measurements of the static dielectric constant ε_0 were performed using the heterodyne beat method at 500 kHz [11]. The dielectric permittivity, ε', and dielectric losses, ε'', for liquid TBCN were measured at the following frequencies: 1.98 GHz (capacitative method [13]) and 9.48, 21.92 and 36.64 GHz (reflection method [14]). At each frequency several measuring series were made, varying the temperature from the melting point up to about 335 K. On heating the sample reproducible results were obtained within the measuring errors of ±2% for ε_0, ±5% for ε' and ε'' whereas on cooling the results differed considerably from previous ones. This probably resulted from partial decomposition of sample at elevated temperatures. Further analyses were performed with those results of measuring series (during heating) which differed as little as possible from the average of all series.

3. *Results of studies*

The value of ε_0, ε' and ε'' obtained at particular frequencies are shown in figure 1.

It can be seen from the plot of ε_0 versus temperature that at the freezing point there is a large stepwise drop on the dielectric permittivity indicating that the molecular dipole rotation is frozen in the solid phase. However, in the phase I range ε_0 is considerably higher than the squared refractive index and only after the phase I/phase II transition does it drop down to a value close to n_D^2. This effect is analogous to that found previously in phase II of TBN [11]. This effect will be explained in separate paper [12].

Numerical values obtained for the liquid phase were analyzed based on the Cole–Cole equation [20]:

$$\varepsilon^* = \varepsilon' - i\varepsilon'' = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1 + (i\omega\tau)^{1-\alpha}},$$

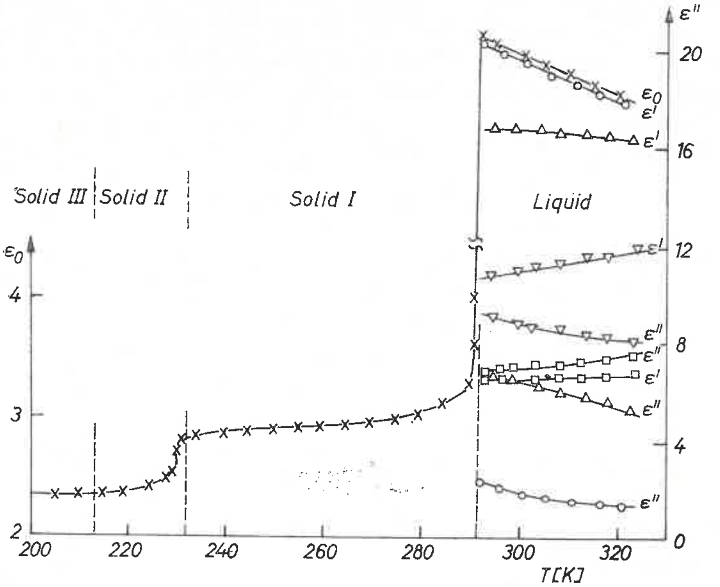

Fig. 1. Dependence of the complex dielectric constant ε^* on temperature for TBCN in the liquid phase. × — 500 kHz (static permittivity), ○ — 1.98 GHz, △ — 9.48 GHz, ▽ — 21.88 GHz, □ — 36.64 GHz

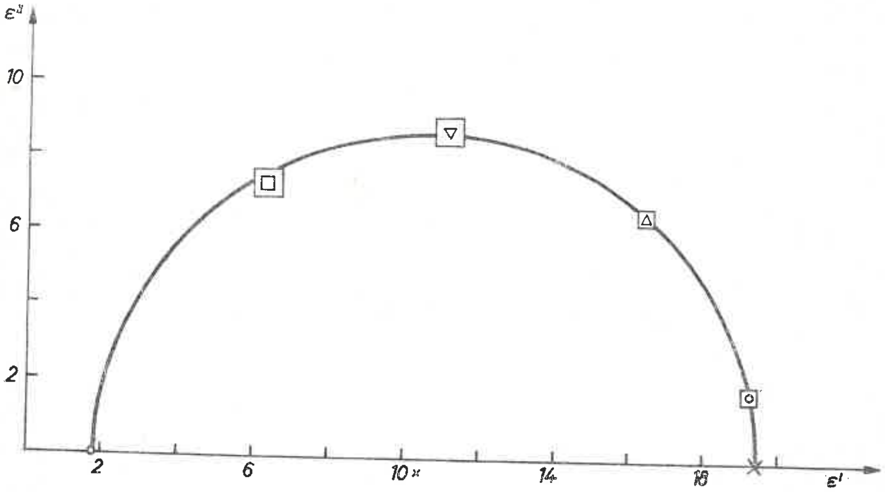

Fig. 2. Cole–Cole diagram for TBCN in the liquid phase (303 K) with marked error ranges (large rectangles) and semicircle centre. × — 500 kHz, ○ — 1.98 GHz, △ — 9.48 GHz, ▽ — 21.88 GHz, □ — 36.64 GHz

which is represented in the complex plane (ε', ε'') by circular arc with its centre below the ε' axis. Figure 2 shows the Cole–Cole diagram for one temperature of the liquid phase of TBCN. The circular arc was matched to the experimental points by the method of least squares with the squared refractive index taken as ε_∞. The empirical parameter of α is lower than 0.02 over the entire temperature range. The dielectric relaxation times, τ,

TABLE I

The dielectric relaxation times for liquid TBCN

T (K)	295	298	303	308	313	318
$\tau \times 10^{12}$ (sec)	8.32	7.88	7.43	7.09	6.85	6.53

determined from the diagrams are summarized in Table I. The error of determination is approximately 5%.

Activation enthalpy and entropy were calculated as described previously [1, 7, 8] i.e., by applying three different activation models differing in their pre-exponential factors [21]:

$$\tau = \tau_0 \exp(\Delta H/RT),$$

where τ_0 = constant (Arrhenius model), $\tau_0 = (2\pi J/kT)^{1/2} \exp(-\Delta S_B/R)$ for Bauer model or $\tau_0 = (h/kT) \exp(-\Delta S_E/R)$ — Eyring model, J is the moment of inertia of the molecule with respect to the axis which is perpendicular to the dipole moment direction. R, h and k have their usual meaning.

TABLE II

Activation enthalpy ΔH and entropy ΔS for four t-butyl derivatives in the liquid phase

Compound	Model	Arrhenius	Bauer	Eyring
$(CH_3)_3CCN$	ΔH (kcal/mole)	1.88	1.58	1.27
	ΔS (cal/mole · K)	—	+2.76	−3.50
$(CH_3)_3CCl$	ΔH	1.18	0.91	0.68
	ΔS	—	+1.17	−4.40
$(CH_3)_3CBr$	ΔH	1.38	1.10	0.83
	ΔS	—	+2.09	−4.00
$(CH_3)_3CNO_2$	ΔH	1.68	1.34	1.05
	ΔS	—	+1.54	−4.15

The results of ΔH and ΔS calculations for TBCN are summarized in Table II together with the values obtained earlier for other similar compounds [1, 7, 8]. The determination error of ΔH is ±0.1 kcal/mole.

4. *Discussion of results*

The dipole moment of TBCN molecule in the gaseous state as determined by Nugent [15] is $\mu_g = 3.95 \pm 0.05$ D. Taking into account the experimental values of ε_0 and using the Onsager equation, one obtains for liquid TBCN $\mu = 3.64 \pm 0.02$ D, i.e., much less than for a free molecule. The same value was obtained by Rogers [16] based on dielectric measurements in diluted benzene solutions. The Fröhlich–Kirkwood correlation factor, g, [17] is 0.85. This indicates that there are dipole correlations in liquid TBCN which lead to partial compensation of the dipole moments of adjacent molecules. Perhaps in the liquid phase of TBCN and in solutions some "microstructures" related with mutual interactions of the cyanide groups $-\mathrm{C{\equiv}N}$ are formed, similar to those observed by Bossis for $\mathrm{CH_3{-}C{\equiv}C{-}C{\equiv}N}$ [18].

The activation barriers which inhibit the dipole rotation of the TBCN molecules in the liquid phase are the highest among the four compounds of $(\mathrm{CH_3})_3\mathrm{C}X$ type mentioned above (Table II). This might result from the existence of such "microstructures".

An alternative explanation for this high activation barrier in liquid TBCN may be that the molecules of that compound have the least globular shape. The asymmetry factor determined as the ratio of the distance between the central carbon atom and van der Waals envelope for substituent X and for methyl group [21] is 1.00 for TBC, 1.09 for TBB, 1.07 for TBN and 1.18 for TBCN. Since the TBCN molecules are elongated towards the dipole moment, their rotation around the axis which is perpendicular to $\vec{\mu}$ is more inhibited than around the dipole axis. In phase I of TBCN the rotation of molecules around the C—CN axis is almost free [9].

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