

DIELECTRIC RELAXATION IN LIQUID PHASE OF *t*-BUTYL CHLORIDE

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The complex dielectric permittivity of liquid *t*-butyl chloride in the microwave range ($\lambda_0 = 11.31, 4.47, 3.07$ and 1.11 cm) and the static dielectric constant at a frequency of 300 kHz have been measured. The results are presented in the form of Cole-Cole plots, which are seen to be semicircles. This means that the Debye model of dielectric relaxation is valid in the case of *t*-butyl chloride having nearly spherical molecules. These measurements confirm earlier findings indicating that the dielectric dispersion of *t*-butyl chloride falls within the microwave range. The dielectric relaxation times of $(\text{CH}_3)_3\text{CCl}$ have been calculated at different temperatures and the activation enthalpies of molecular rotation have been estimated on the basis of different models.

1. Introduction

Dielectric permittivity measurements constitute one of the methods of studying the dipole molecular dynamics in different states of matter. Such measurements have been developed especially well for the liquid state, as there are many simple classical models which may be used in the interpretation of the dynamics of molecules in a liquid [1, 2].

The interpretation of results in the case of most liquids is based on the classical theory, because the quantum mechanical approach to this problem is very difficult. Nevertheless, some authors have made attempts to develop a semi-classical theory by the introduction of a correlation function [14, 15]. The Debye theory is an extreme approximation of this kind of semi-classical theory, and it is valid for highly symmetrical molecules in the liquid phase.

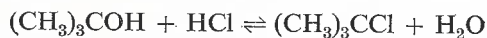
The derivatives of neopentane, having spheroidal molecules, are interesting organic compounds which exhibit molecular rotational freedom not only in the liquid phase, but sometimes also in the solid phase. Many such spheroidal molecules were shown by dielectric constant measurements to rotate in the solid phase for some distance below the melting point, and some of them can even rotate more easily in the solid than in the liquid state (Davies in [2]). *t*-butyl chloride is a good example of such substances. Both its liquid

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and solid phases were examined in some laboratories [3, 4]. Our dielectric measurements of *t*-butyl chloride are an extension of frequencies and temperatures. This enabled us to estimate the activation energy of molecular rotation immediately above the freezing point.

2. Preparation and purification of the material

Preparation of *t*-butyl chloride was carried out according to the formula



95 ml of *t*-butyl alcohol and 247 ml of concentrated hydrochloric acid of a density 1.19 g/ml were poured into a 500 ml distributor. This mixture was agitated for about 20 minutes. After standing in peace for some time, the solution becomes separated into two layers, of which the lower was drained off and rejected. The obtained product was washed with a 5% solution of sodium carbonate and subsequently with water to yield the neutral reaction ($\text{pH} = 7$). The acquired *t*-butyl chloride was dried with anhydric calcium chloride for several hours and percolated through a filter. It was then distilled and the fraction of a boiling point of 50.5°C was collected. The purity of the substance was also controlled by measuring its refractive index ($n_D^{20} = 1.3853$).

3. Experimental

Our laboratory is furnished with equipment for dielectric permittivity measurements in the kilohertz and microwave regions. At present, we are able to perform measurements in the range from 50 Hz to 300 kHz and at microwave frequencies corresponding to wavelengths in the 10, 4.5, 3 and 1.5 cm bands. At the low frequencies a Hungarian-made bridge, "ORION" type TT-0204/2, is used. The microwave apparatus for the 10 and 4.5 cm

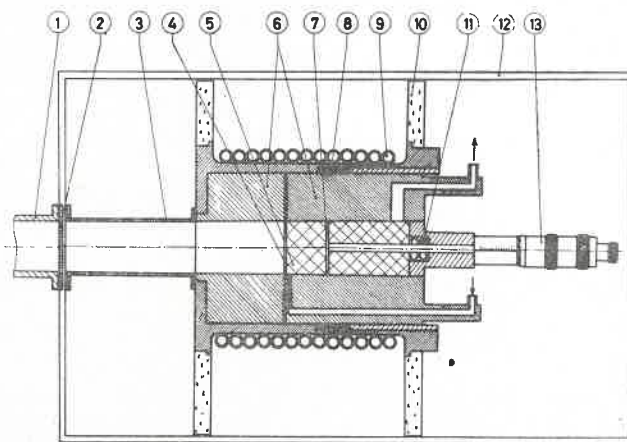


Fig. 1. Diagram of cryostat. 1 – Standard wave-guide, 2 – teflon window (0.3 mm thick), 3 – monel wave-guide, 4 – mica window, 5 – sample, 6 – brass vessel, 7 – plunger, 8 – temperature stabilization resistor, 9 – metal tubing for pumping nitrogen vapours, 10 – stands, 11 – teflon seal, 12 – vacuum housing, 13 – micrometer screw

bands was produced at the Industrial Institute of Telecommunications in Warsaw, whereas that for the 3 and 1.5 cm bands by "UNIPAN". The critical wavelengths of the various rectangular wave-guides are as follows: 144.28 mm for the 10 cm band, 69.70 mm for 4.5 cm band, 45.72 mm for the 3 cm band, and 22.336 mm for the 1.5 cm band.

A cryostat was built for each measuring set-up. These cryostats make it possible to cool samples in vacuum to temperatures near that of liquid nitrogen. The general scheme of the cryostat for the microwave region is shown in Fig. 1. An identical system of temperature stabilization was employed in all cryostats. The measuring vessel is wound around with metal tubing, through which nitrogen vapours are pumped. The tubing has copper wire wound about it; this coil constitutes one arm of the bridge which sends signals to the relay switching the pump driving the nitrogen on and off. A reference resistor is the second arm. Owing to the high heat capacity and good thermal insulation of the measuring vessel, temperature is stabilized to within $\pm 0.1^\circ\text{C}$. The temperature of the sample is measured by means of a copper-constantan thermocouple.

The measuring vessels of all set-ups are in the form of brass cylinders with a rectangular cavity of the same dimensions as the wave-guide. They consist of two segments, coated on the inside with silver, spaced by a thin mica window (mica thickness approx. 0.04 mm). Inside the vessel there is a mobile plunger coupled with a micrometer screw. The design of the plunger ensures that the surface current on the wave-guide is short-circuited.

The examined sample is placed between the plunger and the mica window. Sample thickness is established with an accuracy of ± 0.01 mm. When the sample is a liquid, the vessel is filled by means of two channels. The inlet of diameter 1 mm is positioned very closely to the mica window in the lower part of the wave-guide at the middle of the

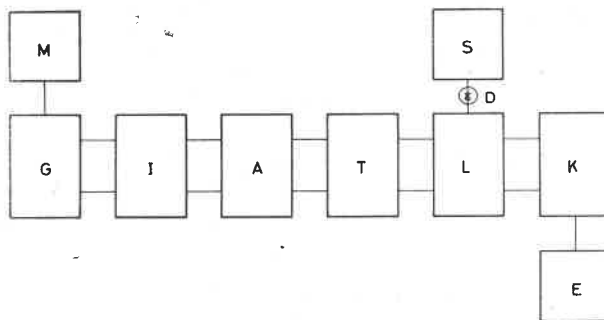


Fig. 2. Diagram of measuring set-up. M – 1000 Hz modulator, G – generator (reflex klystron), I – ferrite isolator, A – attenuator, T – tuner, L – slotted line, D – crystal diode, S – selective microvoltmeter, K – cryostat, E – equipment for temperature stabilization

wider wall, whereas the outlet is 10 mm in diameter and placed at the back of the vessel at the upper wall. This design lets the liquid in the active volume to be supplemented during cooling when the cryostat is oriented horizontally.

Figure 2 presents the general scheme of the measuring set-up. The section of the wave-guide between the slotted line and the vessel is made of monel sheet of low thermal conductivity in order to cut off the flow of heat to the sample *via* the wave-guide and to ensure a constant temperature along the slotted line.

Measurement of ϵ' for reference liquids, such as dioxane and carbon tetrachloride, were performed with each of the microwave measuring set-ups. The results obtained are in agreement with literature data. It was also ascertained that the parameters of the standing wave in the empty vessel remain independent of temperature within a broad range of temperatures.

The measuring vessels in the kilohertz range are in the form of co-axial cylinders of a self-capacity of 76 pF. The distance between the cylinders is 2 mm. The vessel is placed in a brass block, around which a spiral of metal tubing for the flow of nitrogen vapours is wound. The whole arrangement is placed in a Dewar vessel, covered at the top by a layer of felt. The temperature stabilization system is identical with that described above.

Dielectric permittivity measurements in the microwave range were accomplished according to the Roberts-Hippel method [5]. The thickness of the sample was fixed for the various temperature ranges so that the condition $d \approx 0.23\lambda_g$ or $d \approx 0.28\lambda_g$ would be satisfied, λ_g being the wavelength in the sample. Every measurement was repeated at least three times, while the results presented here are mean values. The results of measurements were processed by an "ODRA 1204" computer. The accuracies of the ϵ' and ϵ'' measurements were ± 2 and ± 5 per cent, respectively. The error of the measurements of ϵ'_0 was approximately 3 per cent.

4. Results

The dielectric permittivity measurements ($\epsilon^* = \epsilon' - i\epsilon''$) were made for *t*-butyl chloride in the range from room temperature to the freezing point (-25°C) at a frequency of 300 kHz and in the microwave range at wavelengths of 11.31, 4.47, 3.07 and 1.11 cm. The refractive index for light, n_D , was also measured in the range from $+40$ to 0°C and then extrapolated to -25°C , ϵ'_∞ was assumed to be equal to the square of the index of refraction.

By way of illustration, Fig. 3 shows the dependence of ϵ' and ϵ'' upon $\ln(\omega\tau)$ for two temperatures. It is seen here that the region of dielectric dispersion of liquid *t*-butyl chloride falls within the range of frequencies at which measurements were performed.

The results of measurements were presented in the form of Cole-Cole diagrams [7] (Fig. 4) with the relaxation time distribution constant $\alpha = 0$ in the entire temperature range. Hence we have that the Debye formula [6]

$$\epsilon^* = \epsilon' - i\epsilon'' = \epsilon_\infty + \frac{\epsilon'_0 - \epsilon'_\infty}{1 + i\omega\tau} \quad (1)$$

is valid here, where ϵ'_0 is the static permittivity, $\epsilon'_\infty = n_D^2$, ω is the angular frequency of the applied field, and τ is the dielectric relaxation time.

At each frequency the dielectric relaxation time was determined from the relation

$$\tau = \frac{V}{U} \frac{\lambda_0}{6\pi} \times 10^{-12} \text{ sec}$$

λ_0 is the free space wavelength corresponding to angular frequency ω . The mean values of τ are presented in Table I.

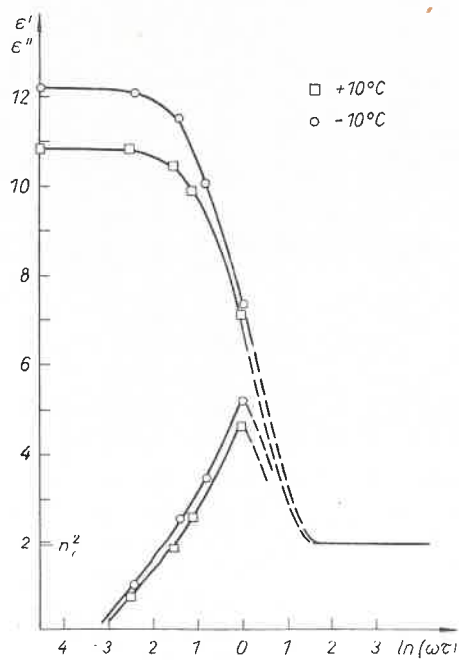


Fig. 3. Dispersion and absorption curves for two temperatures

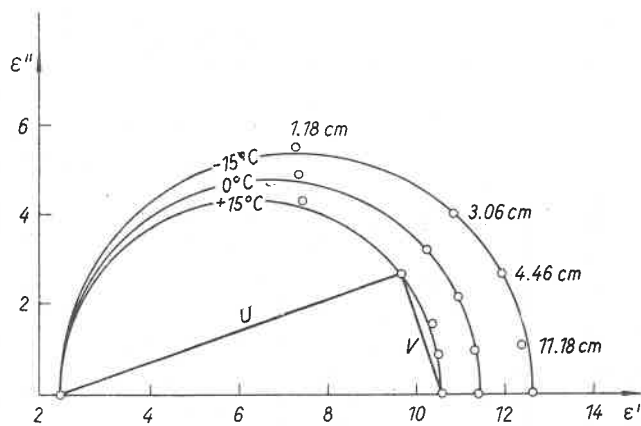


Fig. 4. Cole-Cole plots for three temperatures

TABLE I

$T [^{\circ}\text{C}]$	+20	+15	+10	+5	0	-5	-10	-15	-20
$\tau \times 10^{13} \text{ sec}$	4.93	5.05	5.17	5.35	5.51	5.75	6.02	6.30	6.65

5. Discussion

Dielectric relaxation is the exponential decay of the orientational polarization when an externally applied field is removed, and the relaxation time is taken as the time required for the polarization to drop to $1/e$ of its original value. Relaxation time, in general, is a function of temperature of the system, the structure of molecules and the molecular bonding. The dependence of relaxation time on temperature and height of the energy barrier restricting rotation of dipoles is usually written in the form of Arrhenius' activation equation

$$\tau = A \exp\left(\frac{\Delta H}{RT}\right) \quad (2)$$

where R is the gas constant, T is temperature in degrees Kelvin, and ΔH is the enthalpy of activation.

The coefficient A in Eq. (2) (interpreted as the reciprocal frequency of librational vibrations of a molecule in a potential well) is also a function of temperature. In Eyring's rate equation adapted to dipole rotation, $A = h/kT$ (h and k being the Planck and Boltzmann constants, respectively). Hence,

$$\tau = \frac{h}{kT} \exp\left(-\frac{\Delta S}{R}\right) \exp\left(\frac{\Delta H}{RT}\right) \quad (3)$$

where ΔS is the activation entropy, *i.e.* the difference in the entropy of a molecule in the ground state (in the potential well) and in the excited state (just above the potential barrier).

On the other hand, in Bauer's equation [9,2] derived especially for dipole rotation, $A = (2\pi I/kT)^{1/2}$ (I being the moment of inertia of the molecule), or

$$\tau = \left(\frac{2\pi I}{kT}\right)^{1/2} \exp\left(-\frac{\Delta S}{R}\right) \exp\left(\frac{\Delta H}{RT}\right). \quad (4)$$

Depending on the power n of temperature in the preexponential factor, different values of activation enthalpy ΔH are obtained,

$$\frac{\Delta \ln(T^n \tau)}{\Delta \left(\frac{1}{T}\right)} = \frac{\Delta H}{R}. \quad (5)$$

These values are related with one another [2] as

$$\Delta H_A = \Delta H_B + \frac{1}{2}RT = \Delta H_E + RT. \quad (6)$$

(The subscripts A , B and E refer to Eqs (2), (3) and (4), respectively.) This is illustrated in Fig. 5.

The model with the best physical grounds is that of Bauer, describing the rotation of dipoles rigidly linked with the molecule of a definite moment of inertia. Davies [2, 10]

made a very detailed analysis of all of these equations, finding that dielectric relaxation in liquids is described best by Bauer's equation because ΔS calculated from it has a positive value, whereas ΔS calculated from Eyring's equation is negative. The latter would mean that when a molecule jumps over the energy barrier there is a local increase in ordering.

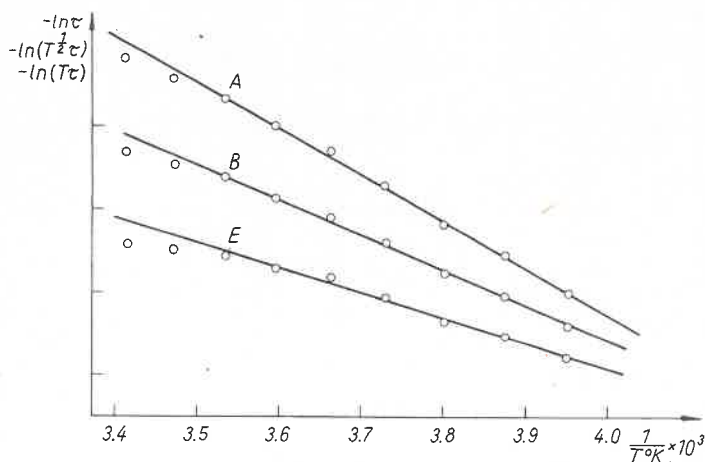


Fig. 5. $\ln(T^n\tau)$ vs $1/T^\circ\text{K}$ plots for three activation models (A - Arrhenius, B - Bauer, E - Eyring))

From our measurements we obtained the values for *t*-butyl chloride gathered in Table II.

TABLE II

	Arrhenius	Bauer	Eyring
ΔH [kcal/mol]	1.0 ± 0.12	0.91 ± 0.1 0.96^*	0.68 ± 0.1 0.67^*
ΔS [cal/mol·deg]		$+2.28 \pm 0.4$ $+1.4^*$	-4.28 ± 0.5 -4.4^*

* Smyth *et al.* [3].

These results agree very well with those obtained by Smyth [3] for the temperature range from $+40$ to $+4^\circ\text{C}$. The low value of activation enthalpy shows up the large freedom of rotation of the *t*-butyl chloride molecules in the liquid phase. The value $\Delta H(\eta) = 2.68$ kcal/mol calculated from results of viscosity measurements [12] implies that for such a symmetric molecule the processes of molecular rotation and viscous flow are quite independent of each other. This is contrary to the case for "normal" liquids, for which $\tau \sim \eta$ and $\Delta H(\eta) \approx H(\tau)$ [2]. This type of molecule maintains its freedom of rotation even in a certain range of temperatures of the solid phase, forming a so-called "plastic crystal phase". This plastic crystal phase of *t*-butyl chloride will be examined in a future paper [16].

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