Intramolecular Rotation in Some Trihalogenated Esters at Microwave Frequencies

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The permittivity and dielectric loss of methyl, ethyl and n-propyl trichloroacetate in decalin solution have been measured at four microwave frequencies viz., 30.20, 24.50, 18.26 and 9.83 GHz and also at 1 MHz and optical frequency at 35 °C. The permittivity and dielectric loss at different frequencies have been plotted against concentration (wt. fraction). The slopes of these straight lines have been used for complex plane plots (a'' vs a'). The dispersion curves which could not be resolved in benzene could be resolved in decalin due to the increase in viscosity of the solvent. Data have been analysed in terms of two relaxation processes i.e., overall rotation and group rotation.

The dielectric behaviour of a rigid molecule with polar groups is characterized by a single relaxation mechanism, but as soon as flexibility is introduced into the molecular structure, the relaxation becomes more complicated. Fischer [1] and his collaborators made early experiments to assess the influence of freely rotating polar groups on the effective relaxation time of larger molecules. Smyth [2–7] and his collaborators have carried out extensive studies of intramolecular motion of polar groups. In a number of cases it is possible to resolve the absorption curve into two Debye-type components corresponding to overall rotation and intramolecular rotation if the two relaxation times are sufficiently different. Davies and Meakins [8] have been able to resolve the absorption curves of phenols in which bulky constituents serve to increase τ_1 and so separate it from τ_2. Higasi [9] has suggested that the resolution of an absorption curve into two simple Debye type curves is possible if $\tau_1/\tau_2 \gtrsim 5$. The authors have carried out studies on methyl, ethyl and n-propyl trichloroacetate in benzene solution [10] and observed that whereas in the case of methyl and ethyl trichloroacetate it was not possible to resolve the dispersion curve, the bulky propyl group enabled the resolution into two distinct Debye type curves.

Yet another possibility of resolving the absorption curve is offered by the fact that τ_1 is dependent on the viscosity whereas τ_2 is practically not. With this end in view we have studied the above mentioned esters in decalin solution ($\eta = 1.831$ C.P.), the viscosity of decalin being about three times that of benzene.

Method of Measurement and Analysis of Data

The static permittivity (ε_0) was determined at 1 MHz with a dipole meter working on the principle of the heterodyne beat method. The refractive index was measured with an Abbe refractometer. A standing wave method has been used in the microwave range (9.83, 18.26, 24.50 and 30.20 GHz). The experimental arrangement was similar to that described in Reference [11]. ε' and ε'' were determined by Heston's [12] method adapted for short circuited termination. All measurements were carried out at 35 °C and the temperature was controlled within ± 0.5 °C by a thermostat.

Ethyl trichloroacetate (purum) was obtained from Messrs Fluka A.G., Switzerland. Methyl and n-propyl trichloroacetate were synthesized by the usual method of esterification using trichloroacetic acid and excess of methyl and n-propyl alcohol, respectively. The boiling points, densities and refractive indices of the synthesized compounds were found to be in good agreement with literature values. Decalin pure grade supplied by Riedel Germany was used as such.

The values of ε' and ε'' at each frequency (including ε_0 and $n_D{}^2$) have been plotted against the molar concentration of the solute. The corresponding mean squares fitted linear slopes a_0, a', a'' and a_D are recorded in Table 1.

a'' has been plotted against a' in Figs. 1 to obtain dispersion loci. The dispersion loci show a hump and have been separated into two non-interacting Debye type dispersions. The two relaxation times (τ_1 and τ_2) corresponding to these two dispersion regions can be represented by the equation

$$\frac{a^* - a_\infty}{a_0 - a_\infty} = \frac{C_1}{1 + j\,\omega\,\tau_1} + \frac{C_2}{1 + j\,\omega\,\tau_2}, \qquad (1)$$

where $C_1 + C_2 = 1$.

The values of τ_1 and τ_2 have been estimated by the extrapolation method given by Mountain and Walker [13]. For this purpose a_{02} and $a_{\infty 1}$ have been obtained by extrapolation (Fig. 1). Since the two regions (1 and 2) are completely resolved,

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Table 1. Values of the Slopes of ε' and ε'' vs. Concentration for Trichloro Esters in Decalin.

Frequency	a'	a''
Methyl trichloroacetate		
1 MHz	3.00	—
9.83 GHz	1.85	0.88
18.26 GHz	1.15	0.55
24.50 GHz	1.00	0.55
30.20 GHz	0.60	0.55
Optical	−0.05	—
Ethyl trichloroacetate		
1 MHz	3.45	—
9.83 GHz	1.50	1.00
18.26 GHz	1.00	0.60
24.50 GHz	0.65	0.35
30.20 GHz	0.50	0.50
Optical	−0.05	—
n-Propyl trichloroacetate		
1 MHz	3.60	—
9.83 GHz	1.35	0.75
18.26 GHz	0.60	0.55
24.50 GHz	0.50	0.50
30.20 GHz	0.45	0.50
Optical	−0.05	—

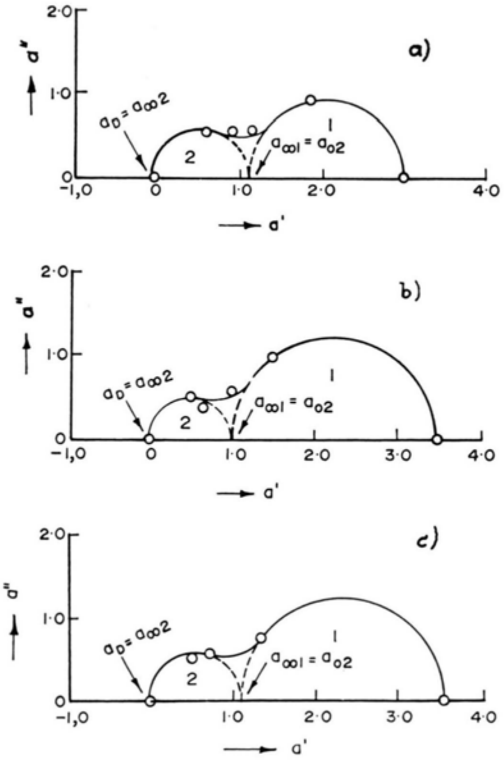

Fig. 1. a' vs. a'' plot for
a) Methyl trichloroacetate,
b) Ethyl trichloroacetate,
c) N-propyl trichloroacetate in decalin at 35 °C.

$a_{\infty 1} = a_{02}$. Thus for region 1, a_{01} and $a_{\infty 1}$ are known and hence the relaxation time is easily obtained from Higasi's equation [14]

$$\tau = \frac{1}{\omega} \sqrt{\frac{a_0 - a'}{a' - a_\infty}} . \tag{2}$$

The relaxation time τ_2 has been calculated in a similar way by taking a_{02} and $a_{\infty 2}$ from the plot. The ratio of the weight factors C_1 and C_2 has been estimated from the relation

$$\frac{C_1}{C_2} = \frac{a''_{\max}\,(\text{region } 1)}{a''_{\max}\,(\text{region } 2)} . \tag{3}$$

From (3) and using $C_1 + C_2 = 1$, approximate values of C_1 and C_2 are obtained. The calculated values of τ_1, τ_2 and C_2 are recorded in Table 2.

Table 2. Values of τ_1, τ_2 and C_2 for Trichloroesters at 35 °C.

Ester	τ_1 p. sec.	τ_2 p. sec.	C_2
Methyl trichloroacetate	20.8	4.8	0.4
Ethyl trichloroacetate	32.0	5.0	0.3
n-Propyl trichloroacetate	48.6	6.4	0.3

Discussion

Whereas the values of τ_1, corresponding to overall rotation of the studied compounds are much greater in decalin than in benzene because of the greater viscosity of decalin as compared to that of benzene, the value of τ_2 (6.4 p. sec), corresponding to group ratiation, in case of n-propyl trichloroacetate in decalin is practically the same as that in benzene (6.8 p. sec). Thus the relaxation time corresponding to group rotation is independent of the viscosity. The values of τ_2 in methyl and ethyl trichloroacetate are lower than that in n-propyl trichloroacetate. The possible groups which may contribute to the intramolecular rotation are rotation of O—R around —COR linkage and rotation of —COOR (which is equivalent to rotation of $-CCl_3$ around C—C bond) around C—C bond. According to Sutton [15] free rotation of —OR around —COR linkage is constrained owing to the resonance which imparts double bond character to the C—O bond. Thus the calculated value of τ_2 may be attributed to the rotation of $-CCl_3$ or —COOR group around C—C bond. It is obvious from Table 2 that the relaxation time τ_1 increases with the chainlength which is the usual behaviour of polar solutes in non-polar solvents. The small change in τ_2 with chainlength may be attributed to the increase in the size of the molecule and the steric hindrance within the molecule changing slightly for different molecules.

The value of C_1 is greater than C_2 and hence it may be concluded that in these esters the main contribution to the dielectric relaxation is due to overall rotation of the molecule and the contribution of the dipolar group is small.

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