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Dielectric Relaxation Studies of Trihalogenated Esters in Different Solvents at Microwave Frequency

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The dielectric permittivity ε' and dielectric loss ε'' have been measured at 9.83 GHz for the solutions of four trihalogenated esters in six non-polar solvents having wide range of viscosities at 35 °C. The static permittivity ε_0 at 1 MHz and high frequency limiting permittivity $\varepsilon_\infty = n_D^2$ have also been measured at 35 °C. The normalized plots of log τ *vs.* log η for these esters are linear for non-interacting solvents only. The anomalous behaviour of these solutes in other solvents has been explained in terms of solute-solvent interactions. The distribution parameter α, the free energies of activation ΔF_τ, ΔF_η and the dipole moment μ of these esters have also been reported.

The relaxation time of a polar molecule in a non-polar solvent can be determined from the measurement of dielectric permittivity and dielectric loss. The relaxation time at a constant temperature depends upon mass and structure of the solute molecule, the intermolecular forces, viscosity of the medium and the interaction between the molecules of the solute and the solvent. As to how this relaxation time depends upon the viscosity of the medium has been a matter of considerable interest. Debye[1] considered the molecule as a sphere embedded in a continuous viscous fluid. The familiar Debye-Stoke's equation may be expressed as

$$\tau = \frac{4\pi\eta a^3}{KT}$$

in which η is the viscosity of the liquid and 'a' is the radius of the polar spherical molecule. The value of the molecular radius evaluated from the measured values of relaxation time and viscosity was considerably lower than those calculated from other sources (*viz.* van der Waals radius, molecular weight and density) for most of the cases. To overcome this discrepancy a number of modifications[2,3] in Debye equation and empirical[4,5] relations have been suggested. On the basis of present theories[6–8] it is expected that the relation between log τ and log η should be linear. This has been verified by many workers[9–11] using single solvent whose viscosity was changed by varying the temperature. The dependence of relaxation time of a polar solute in different solvents having different viscosities was studied by some workers[12,13] in a small range of viscosities. They found that the relation between log τ and log η no longer remains linear.

In present investigations dielectric relaxation time studies of four trihalogenated esters have been carried out in different solvents having wide range of viscosities with a view to study the dependence of relaxation time on the viscosity of the solvents. The esters have been selected as they are unassociated liquids and relax predominantly by overall rotation. The discrepancies have been explained in terms of solute–solvent interaction. The investigations also include determination of distribution parameter α, the free energies of activation ΔF_τ, ΔF_η and the dipole moment μ of these esters in different solvents.

Method of Measurement and Analysis of Data. The dielectric permittivity ε' and dielectric loss ε'' of solutions at microwave frequency 9.83 GHz were determined by the measurement of wavelength in dielectric and standing wave ratio using a short circuited movable plunger by the method suggested by Heston *et al*[14] adapted for short circuited termination. The following expressions were used for calculation of ε' and ε''

$$\varepsilon' = \left(\frac{\lambda_0}{\lambda_c}\right)^2 + \left(\frac{\lambda_0}{\lambda_d}\right)^2$$

$$\varepsilon'' = \frac{2}{\pi}\left(\frac{\lambda_g}{\lambda_d}\right)\left(\frac{\lambda_0}{\lambda_d}\right)^2 \frac{d\rho}{dn}$$

where ρ stands for inverse standing wave ratio.

The heterodyne beat method was used for determining the static permittivity ε_0 and ε_∞ was taken as square of the refractive index which was measured by an Abbe's refractometer. The density of the solution was found out by a pycnometer. The viscosity of the solvent was determined by an Ostwald viscometer. All the measurements were made at 35 °C and the temperature was controlled within ±0.5 °C by a thermostat.

The solutes methyl trifluoroacetate (Purum), ethyl trifluoroacetate (Puriss) and ethyl trichloroacetate (Purum) were obtained from Mr. Fluka A.G., Switzerland. These substances were used without any further purification. Methyl trichloroacetate 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 the literature values.

Benzene AnalaR grade (B.D.H., India), carbon tetrachloride guaranteed reagent (E. Merck), *n*-heptane pure grade and cyclohexane AnalaR grade (Riedel, Hungary) were used after double distillation. *p*-Dioxane AnalaR grade (B.D.H., India) and decalin pure grade (Riedel, Germany) were used as such.

The dielectric relaxation time τ and the distribution parameter α were calculated by using Higasi's single frequency measurement method.[15] The expressions for τ and α are as under

$$\tau = \frac{1}{\omega}\left(\frac{A^2+B^2}{C^2}\right)^{1/2(1-\alpha)}$$

$$1 - \alpha = \frac{2}{\pi}\tan^{-1}\frac{A}{B}$$

where

$$A = a''(a_0 - a_\infty)$$

$$B = (a_0 - a')(a' - a_\infty) - a''^2$$
$$C = (a' - a_\infty)^2 + a''^2$$

a_0, a', a'' and a_∞ are the slopes defined by the relations

$$\varepsilon_0 = \varepsilon_{10} + a_0 W_2$$
$$\varepsilon' = \varepsilon_1' + a' W_2$$
$$\varepsilon'' = a'' W_2$$
$$\varepsilon_\infty = \varepsilon_{1\infty} + a_\infty W_2$$

The polarization at infinite dilution $(P_2)_\infty$ was calculated with the help of Halverstadt and Kumler equation[16] as given below

$$(P_2)_\infty = \frac{3M_2 a_0 V_1}{(\varepsilon_1 + 2)^2} + M_2(\beta + V_1)\frac{\varepsilon_1 - 1}{\varepsilon_1 + 2}$$

where M_2 is the molecular weight of the solute and β is defined by $V_0 = V_1 + \beta\ W_2$. Where W_2 represents the weight fraction of the solute, ε_1 and V_1 are the static permittivity and specific volume of solvent and ε_0 and V_0 are the static permittivity and specific volume of the solution. With this value of $(P_2)_\infty$ and accepted bond refractivities the dipole moment was evaluated.

The free energies of activation for dielectric relaxation ΔF_τ and for viscous flow ΔF_η have been calculated using Eyring's equation.[17]

Results and Discussion

The values of d, ε_0, ε', ε'' and ε_∞ for five solutions of different concentrations of methyl trifluoroacetate, methyl trichloroacetate, ethyl trifluoroacetate and ethyl trichloroacetate in different solvents and n-propyl trichloroacetate in cyclohexane have been measured. The values of slopes a_0, a', a'' and a_∞ and β are recorded in Table 1. The values of τ, α and μ are given in Table 2(a) and 2(b).

It is evident from Table 2(a) that the relaxation time in each solvent increases with the increase in molecular size. This shows that relaxation time of the solute molecule is sensitive to molecular size. The large value of relaxation time for each of these molecules indicates that they relax predominantly by overall rotation.

Figure 1 gives the normalized plots of log τ *versus* log η for the above mentioned esters. The plots are linear for the solvents n-heptane, cyclohexane and decalin. In these solvents the relaxation time increases as the viscosity of the sovlent increases and the increase is in agrement with the relation $\tau = A\eta^x$ proposed

Table 1. Values of the slopes a_0, a', a'', a_∞ and β

Solvent	a_0	a'	a''	a_∞	β
Methyl trifluoroacetate					
n-Heptane	3.10	2.66	0.80	−0.10	−0.60
Benzene	5.16	3.53	1.68	−0.34	−0.33
Cyclohexane	3.60	2.53	1.17	−0.20	−0.89
Carbon tetrachloride	9.20	6.66	3.00	−0.60	+0.22
p-Dioxane	6.83	4.75	2.80	−0.25	−0.19
Decalin	4.13	2.36	1.30	−0.14	−0.28
Ethyl trifluoroacetate					
n-Heptane	3.80	3.30	1.20	−0.15	−0.55
Benzene	6.02	3.46	2.46	−0.46	−0.28
Cyclohexane	4.30	2.50	1.75	−0.26	−0.39
Carbon tetrachloride	10.13	4.88	4.50	−0.78	+0.24
p-Dioxane	8.00	4.16	3.00	−0.12	−0.17
Decalin	5.10	2.31	1.85	−0.17	−0.28
Methyl trichloroacetate					
n-Heptane	2.24	2.00	0.64	+0.06	−0.80
Benzene	3.60	2.75	1.38	−0.06	−0.45
Cyclohexane	2.55	2.12	0.80	0.00	+0.61
Carbon tetrachloride	5.44	4.22	1.88	0.00	+0.45
p-Dioxane	4.50	3.00	1.50	+0.07	−0.28
Decalin	3.00	1.85	0.88	−0.05	−0.50
Ethyl trichloroacetate					
n-Heptane	2.50	2.00	0.87	+0.08	−0.78
Benzene	3.88	2.11	1.70	−0.10	−0.42
Cyclohexane	2.93	1.89	1.02	0.00	−0.53
Carbon tetrachloride	6.53	3.53	2.20	0.00	+0.11
p-Dioxane	4.58	1.94	1.50	+0.06	−0.14
Decalin	3.45	1.33	1.13	−0.05	−0.38
n-Propyl trichloroacetate					
Cyclohexane	3.00	1.80	0.90	0.03	−0.44

Table 2(a). The values of relaxation time and distribution parameter for trihalogenated esters in non-polar solvents

Sclvent	Methyl trifluoroacetate		Methyl trichloroacetate		Ethyl trifluoroacetate		Ethyl trichloroacetate		n-Propyl trichloroacetate	
	τ(ps)	α	τ(ps)	α	τ(ps)	a	τ(ps)	α	τ(ps)	α
n-Heptane $\eta = 0.374$ cp	4.3	0.14	4.7	0.04	6.5	0.04	6.8	0.07	—	—
Benzene $\eta = 0.520$ cp	7.5	0.23	7.8	0.07	11.8	0.16	14.2	0.10	—	—
Cyclohexane $\eta = 0.750$ cp	5.8	0.21	6.0	0.09	11.3	0.11	12.7	0.18	19.3	0.28
Carbon tetrachloride $\eta = 0.797$ cp	6.9	0.20	7.3	0.11	14.2	0.10	16.6	0.22	—	—
p-Dioxane $\eta = 0.987$ cp	9.3	0.09	9.4	0.20	15.2	0.19	21.9	0.24	—	—
Decalin $\eta = 1.831$ cp	10.8	0.31	10.3	0.32	18.1	0.22	25.9	0.29	—	—

Table 2(b). The values of dipole moment (in Debye) for trihalogenated esters in non-polar solvents

Solvent	Methyl trifluoroacetate	Ethyl trifluoroacetate	Methyl trichloroacetate	Ethyl trichloroacetate	*n*-Propyl trichloroacetate
n-Heptane	2.48	2.88	2.33	2.60	—
Benzene	2.66	2.95	2.49	2.70	—
Cyclohexane	2.43	2.82	2.29	2.61	2.76
Carbon tetrachloride	2.64	2.90	2.28	2.63	—
p-Dioxane	2.79	3.19	2.58	2.78	—
Decalin	2.40	2.87	2.27	2.62	—

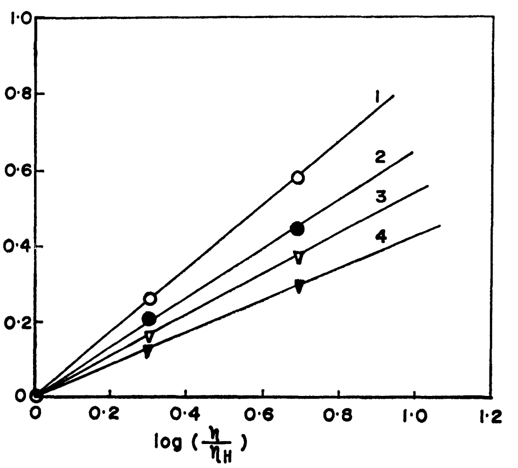
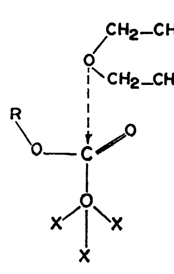


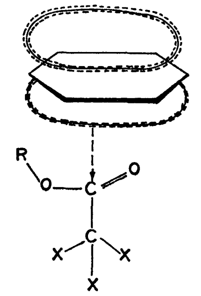
Fig. 1. The normalized plots of $\log \tau$ *vs.* $\log \eta$ for trihalogenated esters.
1: Ethyl trichloroacetate, 2: Ethyl trifluoroacetate, 3: Methyl trifluoroacetate, 4: Methyl trichloroacetate.

by Higasi.[6] Here x is a parameter less than unity. For spherical molecules x is very small and for non-spherical molecules x is nearly unity. The values of x obtained for these molecules lie between 0.50 and 0.85 hence these molecules are not spherical. Thus it may be concluded that the Higasi equation explains the dielectric behaviour of polar solutes in non-polar solvents of different viscosities provided the solvent molecules are inert to solute molecules.

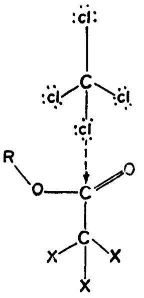
The relaxation time for all these esters in benzene, *p*-dioxane and carbon tetrachloride shows an anomalous behaviour. The viscosity of benzene is less than that of cyclohexane whereas the relaxation time in benzene is more than that in cyclohexane. Similarly, although carbon tetrachloride and cyclohexane have nearly equal viscosity but the relaxation time in carbon tetrachloride is more than that in cyclohexane. The relaxation time in *p*-dioxane is quite large. Since the molecules have been studied in quasi-isolated state and as such the dipole-dipole interactions are negligible, this anomalous behaviour can be explained in terms of solute–solvent interactions. It is a well known fact that the ester molecule is a resonance hybrid in which carbonyl carbon assumes positive character. This positive character is further accentuated by the three electron attracting halogen atoms attached to the α carbon. This positive carbonyl carbon is liable to interact strongly with the oxygen lone-pair electrons in *p*-dioxane and π electrons of benzene ring forming complexes with these solvents resulting in large values of relaxation time. Though carbon tetrachloride is a symmetrical and non-polar molecule yet each chlorine atom in carbon tetrachloride has three lone pairs of electrons and it can function as electron donor. Hence there is a possibility of interaction between the positive carbonyl carbon of the ester with the solvent carbon tetrachloride. Apart from the solute–solvent interactions the sticky nature of carbon tetrachloride may also play a considerable role in increasing the relaxation time of the ester molecule.



(i)



(ii)



(iii)

The value of dipole moment of each solute in different non-interacting solvents Table 2(b) is almost the same. The small difference may possibly be due to the solvent effect. The dipole moment of ethyl trifluoroacetate and ethyl trichloroacetate is higher than that for methyl trifluoroacetate and methyl trichloroacetate in each solvent. This is a general trend expected for members of a homologous series,[18] the effect being more pronounced for the second member of the series. This increase in moment may be attributed to the induction effects but no quantitative explanation has been advanced so far.[19] The dipole moment values for all these esters in cyclohexane, benzene and *p*-dioxane enable us to study the solute–solvent interactions in greater details. The difference $(\mu_D - \mu_C)$ and $(\mu_B - \mu_C)$, where μ_D, μ_B and μ_C refer to dipole moment of these esters in *p*-dioxane, benzene and cyclohexane respectively, are listed in Table 3.

Table 3. $(\mu_D - \mu_C)$ and $(\mu_B - \mu_C)$

Solute	$\mu_D - \mu_C$ (Debye)	$\mu_B - \mu_C$ (Debye)
Methyl trifluoroacetate	0.36	0.23
Ethyl trifluoroacetate	0.33	0.13
Methyl trichloroacetate	0.30	0.21
Ethyl trichloroacetate	0.17	0.09

TABLE 4. THE VALUES OF FREE ENERGIES OF ACTIVATION ΔF_τ AND ΔF_η FOR TRIHALOGENATED ESTERS

Solvents	ΔF_τ kcal/mol				ΔF_η kcal/mol
	Methyl trifluoroacetate	Ethyl trifluoroacetate	Methyl trichloroacetate	Ethyl trichloroacetate	
n-Heptane	2.03	2.27	2.13	2.30	3.01
Benzene	2.36	2.63	2.38	2.75	3.19
Cyclohexane	2.21	2.61	2.22	2.68	3.25
Carbon tetrachloride	2.31	2.75	2.34	2.84	3.22
p-Dioxane	2.49	2.79	2.49	2.96	3.27
Decalin	2.58	2.89	2.55	3.11	4.01

The difference is appreciable for all these molecules which indicates strong solute–solvent interactions. The $(\mu_D-\mu_C)$ values are higher than $(\mu_B-\mu_C)$ values which shows that the interactions of these esters with *p*-dioxane are stronger than those with benzene. It is interesting to note that difference values for fluoro compounds is more than that for corresponding chloro compounds. This is probably due to more electron attracting character of fluorine atom than chlorine atom which makes the carbonyl carbon more positive in fluoro compunds in comparison to that in chloro compounds.

The finite value of distribution parameter α calculated for these esters suggests that in these esters there are two possible relaxation mechanisms of Debye type *i.e.* overall rotation and intramolecular rotations. It is not possible to resolve the two relaxation times from single frequency measurements. If measurements are made at a number of microwave frequencies and a graph is plotted between a' and $a''\omega$ two distinct straight lines are obtained from which τ_1 and τ_2 can be evaluated. The systematic increase of α with increase of viscosity may be interpreted in terms of the disparity in two relaxation mechanisms involved in the relaxation processes. Almost regular rise of α implies that molecular relaxation time increases with viscosity where as the intramolecular does not seem to increase very much with the viscosity of the medium. It is evident from Table 2(a) that the distribution parameter increases with increase in chain-length *i.e.* from methyl to *n*-propyl trichloro esters. This increase in distribution parameter with chain length can be attributed to the number of shapes which the molecule can acquire by twisting around C–C bonds.[19] However, in case of trifluoroacetates it is observed that the distribution parameter decreases with chain-length. It is probable that addition of each CH_2 group in trifluoro esters tends to make the molecule more and more symmetric about O=C–O and thereby decreasing distribution parameter as has been suggested by Rajyam and Murty.[20] This fact needs further verification. It is expected that *n*-propyl trifluoroacetate might have a much smaller value of α, but could not be verified in this laboratory due to non-availability of this compound.

The free energies of activation ΔF_τ and ΔF_η for dielectric relaxation and for viscous flow respectively are listed in Table 4. It is evident from the table that the free energy of activation for dielectric relaxation increases with increase in molecular size. The free energy of activation for viscous flow is greater than that for the dielectric relaxation process. This is in agreement with the fact that the process of viscous flow involves greater interference by neighbours than in the case of relaxation process, because the former takes place by both rotation as well as translation where as the latter involves rotation only.[21,22]

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