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Dielectric Dispersion and Relaxation Mechanism in Some Trifluoro Compounds at Microwave Frequencies

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The permittivity and dielectric loss of 2,2,2-trifluoroethanol and trifluoroacetic acid have been measured in benzene solutions at three microwave frequencies, 24.01, 9.83, and 6.01 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 the complex plane plots (a' *vs.* a''). The complex plane plots for 2,2,2-trifluoroethanol and trifluoroacetic acid are of the Cole-Cole type. The relaxation time (τ_0) and distribution parameter (α) have been calculated. The values of dipole moments (μ) of these compounds have also been calculated and reported. The relaxation mechanism in these two compounds has been explained.

Fluoro compounds have been of great interest because of their high value of permittivity in liquid state.[1] Ethanol and acetic acid are associated liquids and have a tendency to dimerize even at a very low dilution in benzene solution by intermolecular hydrogen bonding. The present investigations on 2,2,2-trifluoroethanol and trifluoroacetic acid have been made to study the effect of the replacement of CH_3 group by CF_3 group in ethanol and acetic acid on intermolecular hydrogen bonding. The dielectric dispersion and relaxation mechanism studies in these compounds have been carried out in dilute solutions of benzene[2] for the first time, to study their dielectric behaviour in explaining their molecular structure. The studies have been carried out in dilute solutions because this enables us to reduce to a considerable extent the dipole-dipole interaction and solute-solute co-operative phenomenon and also to avoid the ambiguity[3–5] concerning the internal field.

Method of Measurement and Analysis of Data. The static permittivity was measured at a frequency 1 MHz by means of a Toshniwal dipolemeter type CL01 (INDIA) based on the principle of heterodyne beat method. The cell used for the purpose was calibrated with standard liquids. Refractive indices of all the solutions were measured for sodium D-line by the help of an Abbe's refractometer and the square of the refractive index gave the values of optical permittivity ($\varepsilon_\infty = n_D{}^2$).

The permittivity (ε') and dielectric loss (ε'') at microwave frequencies 24.01, 9.83, and 6.01 GHz were determined by the measurement of wavelength in the dielectric and standing wave ratio using a short circuited movable plunger by the method suggested by Heston *et al.*[6] adapted for short circuited termination. All measurements were carried out at 35 °C. The values of ε_0, ε_∞, ε', and ε'' thus obtained are recorded in Table 1.

The compounds used were obtained from Messrs Fluka, A. G. (Switzerland). They were of puriss grade having 99% purity. Their constants were checked with the literature values before use. Benzene, Analar grade (B.D.H., India) was used for making solutions and was distilled twice before use.

It has been observed that the permittivity and dielectric loss in solutions are linear functions of concentration.[7] Thus one can represent the permittivity and dielectric loss by the following equations:

Table 1. Values of ε_0, ε', ε'', and ε_∞ at different frequencies for 2,2,2-trifluroethanol and trifluoroacetic acid in benzene solution at constant temperature of 35 °C

Frequency / Concentration (wt. fraction)	1 MHz ε_0	Optical ε_∞	9.83 GHz ε'	9.83 GHz ε''	Frequency / Concentration (wt. fraction)	24.01 GHz ε'	24.01 GHz ε''	6.01 GHz ε'	6.01 GHz ε''
2,2,2-Trifluoroethanol									
0.0000	2.260	2.229	2.259	—	0.0000	2.256	—	2.260	—
0.0111	2.328	2.226	2.309	0.021	0.0112	2.304	0.027	2.332	0.031
0.0218	2.396	2.220	2.378	0.036	0.0218	2.339	0.055	2.391	0.037
0.0323	2.460	2.217	2.439	0.056	0.0318	2.405	0.076	2.458	0.046
0.0416	2.518	2.211	2.491	0.072	0.0439	2.433	0.101	2.522	0.056
0.0519	2.584	2.208	2.543	0.089	0.0515	2.472	0.121	2.569	0.062
Trifluoroacetic acid									
0.0000	2.255	2.229	2.259	—	0.0000	2.260	—	2.262	—
0.0123	2.318	2.223	2.308	0.046	0.0121	2.279	0.038	2.330	0.032
0.0251	2.370	2.217	2.338	0.068	0.0292	2.299	0.065	2.382	0.055
0.0378	2.428	2.211	2.381	0.083	0.0400	2.313	0.083	2.420	0.071
0.0486	2.470	2.208	2.395	0.100	0.0523	2.328	0.100	2.460	0.088
0.0646	2.534	2.202	2.446	0.120	0.0665	2.348	0.123	2.500	0.107

$$\left.\begin{aligned} \varepsilon_0 &= \varepsilon_{10} + a_0 W_2 \\ \varepsilon' &= \varepsilon_1 + a' W_2 \\ \varepsilon'' &= a'' W_2 \\ \varepsilon_\infty &= \varepsilon_{1\infty} + a_\infty W_2 \end{aligned}\right\} \quad (1)$$

where ε_0 and ε_∞ are the static and the optical permittivity respectively. The subscript 1 refers to the pure solvent, W_2 is the concentration of the polar solute in weight fraction and a's are the slopes of the st. lines obtained by plotting the dielectric quantity against concentration. The slopes thus obtained are recorded in Table 2.

Table 2. Values of the slopes of plots of ε' and ε'' *versus* concentration for 2,2,2-trifluoroethanol and trifluoroacetic acid

Frequency	a'	a''
2,2,2-Trifluoroethanol		
1 MHz	a_0=6.20	...
6.01 GHz	5.90	0.85
9.83 GHz	5.40	1.65
24.01 GHz	4.28	2.30
Optical	a_∞=−0.40	—
Trifluoroacetic acid		
1 MHz	a_0=4.20	...
6.01 GHz	3.22	1.40
9.83 GHz	2.72	1.48
24.01 GHz	1.50	1.60
Optical	a_∞=−0.38	—

The values of τ_0 and α for 2,2,2-trifluoroethanol and trifluoroacetic acid have been calculated from the Cole-Cole[8] arc plots using the slopes (a', a''). These plots are shown in the Figs. 1 and 2.

Higasi[9] has also proposed that the values of relaxation time and the distribution parameter may be determined from the measurement of a' and a'' at a single frequency in the dispersion region. The equations for τ_0 and α are as follows:

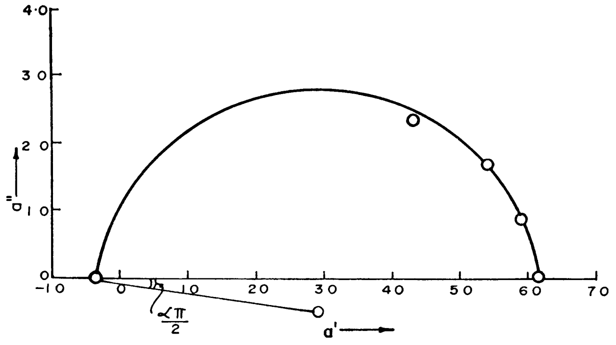


Fig. 1. The a', a'' plot of trifluoroethanol.

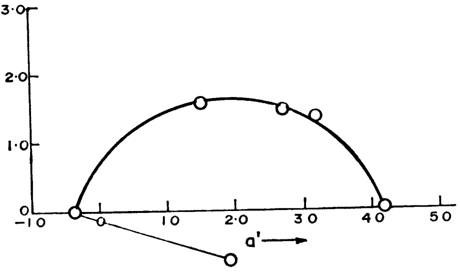


Fig. 2. The a', a'' plot of trifluoroacetic acid.

$$\tau_0 = \frac{1}{\omega}\left(\frac{A^2+B^2}{C^2}\right)^{1/2(1-\alpha)} \quad (2)$$

$$1-\alpha = \left(\frac{2}{\pi}\right)\tan^{-1}\left(\frac{A}{B}\right) \quad (3)$$

$$\left.\begin{aligned} A &= a''(a_0 - a_\infty) \\ B &= (a_0 - a')(a' - a_\infty) - a''^2 \\ C &= (a' - a_\infty)^2 + a''^2 \end{aligned}\right\} \quad (4)$$

For trifluoroethanol and trifluoroacetic acid, we have calculated τ_0 and α from Eqs. (2) and (3) using the data at 9.83 GHz. The values of τ_0 and α determined by these two methods have been compared in Table 3.

Table 3. Values of τ_0, α and μ for trifluoroethanol and trifluoroacetic acid

Compound	τ_0 (ps)		α		μ (D)
	Cole-Cole	Higasi	Cole-Cole	Higasi	
Trifluoroethanol	3.63	3.39	0.10	0.11	2.52[a]
Trifluoroacetic acid	8.91	8.58	0.21	0.22	2.26[b]

a) Present work, literature value not available. b) Literature value 2.28 D[20] (gas).

The dipole moments of these solute molecules have been calculated by the Eq. (5) proposed by Higasi[10]

$$\mu = A(a_0 - a_D)^{1/2} \quad (5)$$

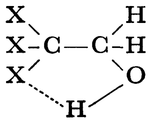
where A is a constant and is given by

$$A = \left[\frac{27kT}{4\pi N}\,\frac{M_2}{(\varepsilon_1+2)^2 d_1}\right]^{1/2} \quad (6)$$

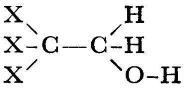
Here d_1 is the density of the solvent and M_2 is the molecular weight of the solute. The values of dipole moments (μ) are also recorded in Table 3.

Results and Discussion

The complex plane plot a' *vs.* a'' in case of 2,2,2-trifluoroethanol is a Cole-Cole plot. The low value of relaxation time τ_0=3.63 ps corresponds to the relaxation time of the hydroxyl group. Further the small value of distribution parameter (α=0.10) points to the fact that the predominant mode of relaxation is the rotation of the hydroxyl group and not the rotation of the molecule as a whole. The tan δ-concentration curve is a straight line and does not show anomalous absorption so that there is no possibility of association as in the case of ethanol and other alcohols in benzene solution[11] which have a tendency for dimerization even at very low concentration. Krishnamurthy and Sundarajan[12] have examined the possibility of two extreme conformations, the *cis* and *trans* forms which refer to hydroxyl hydrogen being near or away from halogens. They have computed the equilibrium constant and corresponding free energies for isomerization of *cis*$\rightleftharpoons$*trans*, from the knowledge of the experimental and theoretical moments for the two conformers. Their results indicate that for trichloro and tribromo ethanols the equilibrium lies to the left (Structure I). This



I *cis*



II *trans*

implies a stabilization of the *cis*-structure by intramolecular hydrogen bonding X—H–O. In tribromoethanol, the hydrogen-bonded form predominates to greater extent than in trichloroethanol. From spectroscopic studies Krueger and Mettee[13] have found that the intramolecular hydrogen bonding in trihaloethanols increases in the order $F_3C<Cl_3C<Br_3C$, a trend which is reverse of the normal accepted order of propensity of hydrogen bonding by halogens. The measurements of relaxation time and distribution parameter confirm the *trans*-structure (Structure II) of 2,2,2-trifluoroethanol. The dipole moment increases from tribromoethanol to trifluoroethanol *i.e.*

$Br_3C \cdot CH_2OH$	1.73 D[12]
$Cl_3C \cdot CH_2OH$	2.04 D[12]
$F_3C \cdot CH_2OH$	2.52 D*

(* present work.)

The dielectric studies of trifluoroacetic acid show that the molecule of trifluoroacetic acid remains in monomeric form in benzene solution as distinct from acetic acid and trichloroacetic acid[14] ($\mu=1.1$ D) which exist in the dimeric form even in dilute solutions. Tan δ-concentration curve is a straight line and shows no anomalous absorption. The complex plane plot a' *vs.* a'' is a Cole-Cole arc which shows that there is a symmetrical distribution of relaxation times. The relaxation time measurements ($\tau_0=8.91$ ps) show that the molecule relaxes predominantly by overall rotation, the other possibilities being rotation of carboxyl group about C–C axis and that of the hydroxyl group undergoing a torsional or restricted rotation, since the hydroxyl hydrogen does not lie in the plane of the rest of the carboxyl group. The large value of the distribution parameter ($\alpha=0.21$) points towards these possibilities.

The electron diffraction[15] and spectroscopic measurements[16,17] indicate the presence of a single bond between the hydroxyl oxygen and carboxyl carbon, with the hydroxyl group turned so that its hydrogen is well out of the OCO plane. By combining vectorially the group moment 1.73 D for the carboxyl group acting at the calculated angle 74° with the C–C bond, with the moment 2.35 D of 1,1,1-trifluoroethane[18,19] the value of 2.50 D is obtained which is in reasonable agreement with the observed value of 2.28 D[20] (gas). Thus the presence of the three atoms of fluorine which greatly increase the acidity of the molecule, does not greatly alter the moment of the carboxyl group. The hydroxyl hydrogen does not lie in the plane of the rest of the carboxyl group and is undergoing a torsional or restricted rotation with the hydrogen on an average well outside this plane.[20] The possibility of the existence of the molecule in isomeric planar form is not completely excluded.

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