

Impact of Viscosity on Dielectric Relaxation Time of Some Organic Molecules

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The real (ϵ') and imaginary (ϵ'') parts of dielectric constants of the polar dielectric samples of 2-Bromo 4-fluoroanisole and 1-Bromo 2,4-Difluorobenzene in solution form with benzene as a solvent were determined at microwave frequency of 9.08 GHz at an ambient temperature of 25 °C. The estimated maximum loss tangent ($\tan \delta_{\max}$) is used to determine relaxation time (τ) of the two polar molecules. The viscosity (η) of pure benzene and mixed solvents of benzene and paraffin was determined using a conventional Ostwald's viscometer. The dependence of τ on η is discussed in the light of macroscopic and microscopic viscosity concepts. The observed τ value increased with η till $\eta = 1.2$ cp and remained almost constant for the higher values. The non-linear behavior of τ with η for ($\eta > 1.2$ cp) exhibits the dynamic nature of viscosity, which incorporates the concept of viscoelastic relaxation. The dynamic viscosity (η_D) and viscoelastic relaxation time (τ_{ve}) were determined.

KEYWORDS:

1. INTRODUCTION

Dielectric spectrometry is a powerful tool for investigation the transient species that happens as intermediates in chemical and physical Processes. In the recent years, the studies on dielectric relaxation behavior of polar molecules in non-polar solvents underneath variable conditions of compositions and frequency has elicited right smart interest, owing to their quality in investigation molecular and intra-molecular motions, solute-solute interactions, solute-solvent interactions and their molecular conformations. The study of the variation of dielectric time constant with viscosity has been an extended pursued concept.¹ The dielectric properties of a substance like dielectric constant (ϵ'), dielectric loss (ϵ''), relaxation time have provided an insight into the structure of the molecules of the system. In liquids, the molecule has rotational freedom and its dispersion happens at microwave frequency. Therefore studying the dielectric properties at microwave frequency can reveal the dielectric relaxation of polar molecules and its variation with respect to the interaction with the neighboring polar as well as non polar molecules. The investigation of dielectric relaxation phenomena has provided a vital approach to explore the structural behaviour

of complex organic polar molecules in different non-polar solvents. to investigate the structural behaviour of molecules, it's necessary to examine numerous dielectric parameters that are connected with inter and intramolecular association and internal rotation with temperature variation. Viscosity of the solvent significantly influences the dielectric relaxation time of the solute molecule. This study helps in drawing certain quantitative conclusions regarding molecular motion and inters molecular forces in liquids, liquid mixtures, dilute solutions and multi-component polar solutes in dilute solution.² The study of effect of viscosity on dielectric relaxation time of a polar molecule has been first performed by Debye.³ many researchers^{4,5} have proposed relations between viscosity and dielectric relaxation time of a polar dielectrics, which might be generally classified as theoretical and strictly empirical. Theoretical models will additional be classified as (a) Debye's model,⁶ that predicts linear dependence of relaxation time on viscosity, irrespective of size and form of the encircling molecules, (b) Hill's model,⁷ that is predicated on the local viscosity impact between species at the molecular level or mutual consistency, (c) Visco elastic model,⁸ that is predicated on the visco-elastic relaxation within the medium caused by shear elastic waves made by the rotating dipole and (d) Magee's model⁹-that considers the dielectric relaxation to be a co-operative development, such the dielectric relaxation involves regions of the liquid, and not simply the rotation of one molecule.

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The empirical relations an important the relationships projected by Fischer,¹⁰ Chitkuk and Higasi¹¹ and Krishnaji et al.,¹²

The study of the variation of dielectric relaxation time with viscosity helps in drawing bound quantitative conclusions regarding molecular motion and inters molecular forces in liquids, liquid mixtures, dilute solutions and multi component polar solutes in dilute solutions.^{13, 14} The dielectric relaxation behaviour of mixtures of various industrially and biologically helpful polar solvent molecules studied by many authors.^{14–23}

However, no excellent empirical or theoretical relations are found so far to point the dependence of dielectric time constant on viscosity. Therefore, there is need of new experimental investigations, which can offer an insight. Some to study makes an attempt are created by to review the behavior of relaxation time of polar organic molecules on solvent viscosity for understanding the relaxation mechanisms, viscosity on dielectric time constant of a polar molecule whereas it might it would a lot of more to use these studies in understanding the visco-elastic behaviour of the encircling medium. With this objective, this communication reports the studies on the impact of solvent consistency on the dielectric relaxation time of the polar dielectric solute; 2-Bromo-4-fluoroanisole [$\text{BrC}_6\text{H}_3(\text{F})\text{OCH}_3$] and 1-Bromo-2,4-difluorobenzene [$\text{BrC}_6\text{H}_3\text{F}_2$]. This investigation reports the studies on impact of solvent viscosity on the dielectric relaxation time of the polar solutes; a pair of-Bromo 4-fluoroanisole (molecule-1) and 1-Bromo 2,4-difluorobenzene(molecule-2).

2. MATERIALS AND METHODS

The polar dielectric samples 2-Bromo-4-fluoroanisole [$\text{BrC}_6\text{H}_3(\text{F})\text{OCH}_3$] and 1-Bromo-2,4-difluorobenzene [$\text{BrC}_6\text{H}_3\text{F}_2$] (SIGMA ALDRICH Co. USA) and benzene and paraffin (S.D. Fine Chem. Pvt. Ltd. India) were used as the starting materials. Solvents (I to VIII) were prepared by mixing paraffin with the known proportion of (100, 80, 60, 40, 20, 15, 10 and 5 percent by volume) of benzene respectively. Viscosity of the prepared solvents was measured by using a conventional Ostwald's viscometer. Dilute solutions of the two polar dielectric organic compounds were prepared in each of the solvents separately. The measurement of dielectric constant (ϵ') and dielectric loss (ϵ'') of the liquid samples were carried out at 9.08 GHz frequency on a microwave slotted section set up as shown in the block diagram (Fig. 1). It consists of

- Gunn Power Supply
- Gunn Oscillator
- Calibrated attenuator
- Standing wave indicator and detector
- dielectric cell with variable reflecting plunger.

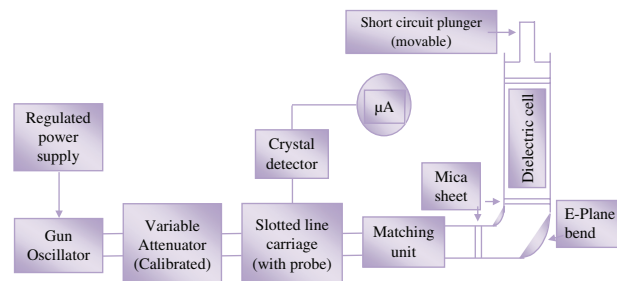


Fig. 1. The block diagram of microwave slotted section set up.

A digital micro ammeter (APLAB-5056) is used for the measurement of detector crystal current. The dielectric absorbing cell used in the measurements was fabricated in the laboratory from brass rectangular wave-guide of dimensions (1 inch \times 0.5 inch \times 0.05 inch). The inner portion of the cell was coated with a uniform layer of Ag in order to ensure conductivity of wall surfaces and to avoid contamination of the walls due to the organic samples.

The dielectric loss tangent for a dilute solution of the polar solute is calculated using the Debye formula²⁴

$$\tan \delta = \frac{(\epsilon' + 2)^2}{\epsilon'} \frac{4\pi CN\mu^2}{27KT} \frac{\omega\tau}{1 + \omega^2\tau^2} \quad (1)$$

Where, ϵ' —dielectric constant, N = Avagadro's number, μ —dipole moment, C —Concentration of the solution, τ —dielectric relaxation time, K —Boltzmann constant and T —absolute temperature.

Within a given range of viscosity values, if ϵ' changes slightly, then the quantity

$$\frac{(\epsilon' + 2)^2}{\epsilon'} \left[\frac{4\pi CN\mu^2}{27KT} \right] = P \quad (2)$$

may be treated as constant for a given solvent medium.

Therefore,

$$\tan \delta = P \frac{\omega\tau}{1 + \omega^2\tau^2} \quad (3)$$

$\tan \delta$ has a maximum value of $P/2$, when $\omega\tau = 1$.

As viscosity of the solvent is varied the loss tangent goes through a maximum only if the relaxation time of the solute molecule is lower than that corresponding to $\omega\tau = 1$. From the maximum of $\tan \delta$, the constant 'P' is determined and hence μ is calculated.

Solving the quadratic equation for τ

$$\frac{\tan \delta}{(\tan \delta)_{\max}} = \frac{2\omega\tau}{1 + \omega^2\tau^2} \quad (4)$$

Two roots are obtained; the lower root or higher root is taken depending on whether the viscosity is lower or higher than that corresponding to $\omega\tau = 1$. This gives ' τ ' at that corresponding viscosity. Thus ' τ_0 ' at zero percent of paraffin can be found, this value corresponds to ' τ ' in solution in the particular solvent used. From these measurements ' μ ' and ' τ ' of the molecules have been computed.

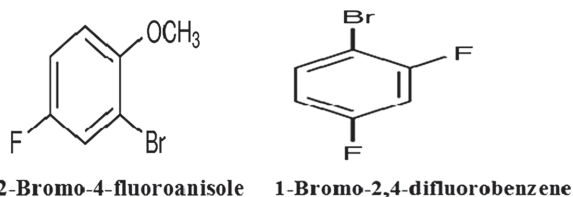


Fig. 2. Structural formula of 2-Bromo-4-fluoroanisole [$\text{BrC}_6\text{H}_3(\text{F})\text{OCH}_3$] and 1-Bromo-2,4-difluorobenzene [$\text{BrC}_6\text{H}_3\text{F}_2$].

The above measurements have been interpreted in terms of visco-elastic relaxation. The visco-elastic relaxation time (τ_{ve}) and rigidity modulus (G_∞) have been evaluated by plotting the graph of $\log(\eta)$ versus $\log(\tau)$ for different mixed solvents. The dynamical viscosity (η_d) corresponding to the non-linear part of the plot was obtained by extrapolating to the linear part.

The visco-elastic relaxation time (τ_{ve}) of the molecules in each viscous medium was calculated using the relation.

$$\tau_d = \frac{\eta_s}{[1 + (\omega\tau_{ve})^2]} \quad (5)$$

The limiting value of the rigidity modulus G_∞ in each mixed solvent was calculated using the formula,

$$\tau_{ve} = \frac{\eta_s}{G_\infty} \quad (6)$$

According to Magee,⁹ the relation between static relaxation time (τ) and static viscosity (η) is given by

$$\frac{1}{\tau} = \frac{\eta'}{\tau'\eta} + \frac{1}{\tau'} \quad (7)$$

Where, η' —limiting viscosity and τ' —limiting relaxation time.

The plot of $(1/\eta)$ versus $(1/\tau)$ provides the ratio (η'/τ') as slope and $(1/\tau')$ as intercept, from which η' and τ' can be obtained.

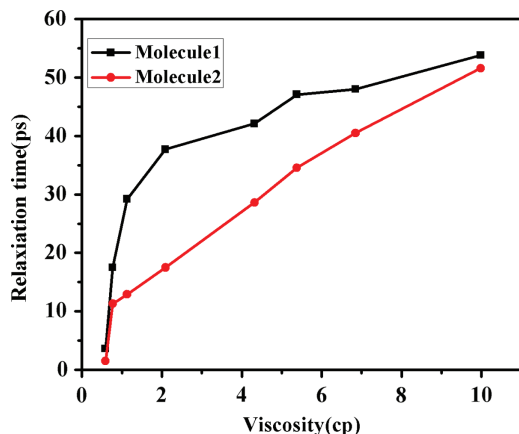


Fig. 3. variation of $\log \tau_s$ with $\log \eta_s$.

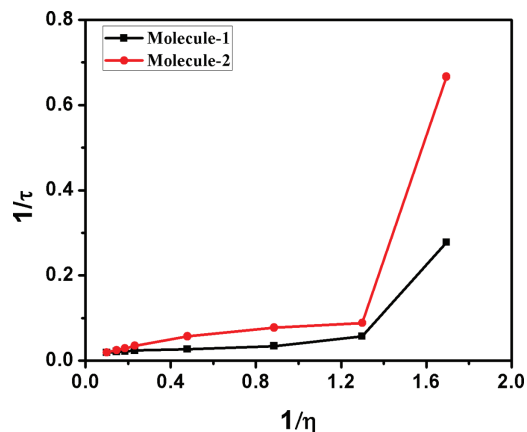


Fig. 4. Variation of Relaxation time ($1/\tau$) with viscosity ($1/\eta$).

3. RESULTS AND DISCUSSION

In the present work, the studies on two polar molecules; 2-Bromo-4-fluoroanisole [$\text{BrC}_6\text{H}_3(\text{F})\text{OCH}_3$] and 1-Bromo-2,4-difluorobenzene [$\text{BrC}_6\text{H}_3\text{F}_2$] were undertaken separately, using mixed solvents of (benzene + paraffin), in which the role of paraffin was to increase viscosity of the medium. The first molecule, $\text{BrC}_6\text{H}_3(\text{F})\text{OCH}_3$ has a dipole moment of 1.77D.

Figure 3 Represents the variation of $\log \tau_s$ with $\log \eta_s$. It can be seen that, for the polar molecule- $\text{BrC}_6\text{H}_3(\text{F})\text{OCH}_3$, $\log \tau_s$ increased linearly up to the viscosity value of 1.2 cp, beyond which it increased slowly and attained almost a constant value. The linear behavior of the curve has deviated considerably when the percentage of paraffin in benzene is increased, since viscosity is also dynamic in nature due to microwave frequency. This incorporates the concept of visco-elastic relaxation, which is generally true for dielectric systems obeying Debye theory of relaxation.

The second molecule, $\text{BrC}_6\text{H}_3\text{F}_2$ exhibited less non-linearity of the graph of $\log \tau_s$ against $\log \eta_s$. This is attributed to higher charge symmetry. Since, $\text{BrC}_6\text{H}_3\text{F}_2$ has comparatively smaller dipole moment of 1.08D and therefore, it has more charge symmetry resulting in to less non-linearity of the curve. The variation of τ

Table I. Viscosity dependence of dielectric parameter. Molecule: 2-Bromo, 4-fluoroanisole. $T = 300^\circ\text{A}$ $MW = 205.03$.

Solvent no.	η_s (CP)	ϵ'	$\epsilon'' \times 10^{-3}$	τ_s (PS)	η_d (CP)	τ_{ve} (PS)	G_∞
I	0.59	2.359	12.69	03.6	—	—	—
II	0.77	2.289	12.28	17.5	—	—	—
III	1.13	2.247	10.63	29.2	0.95	7.55	0.150
IV	2.09	2.193	10.24	37.7	1.05	17.51	0.119
V	4.32	2.152	08.20	42.1	1.07	30.51	0.142
VI	5.38	2.138	07.49	47.1	1.09	34.65	0.155
VII	6.85	2.132	07.37	48.0	1.15	39.06	0.175
VIII	9.98	2.100	06.63	53.8	1.20	47.36	0.211

Note: $a_D = 1.26^\circ\text{A}$; $\mu = 1.77\text{D}$; $a_n = 1.29^\circ\text{A}$; $a_{SR} = 1.96^\circ\text{A}$; $a_M = 3.14^\circ\text{A}$; $(G_\infty)_{\text{Mean}} = 0.159 \times 10^{10}$ dynes/cm²; $\tau' = 64.94$ PS; $\eta' = 2.86$ CP.

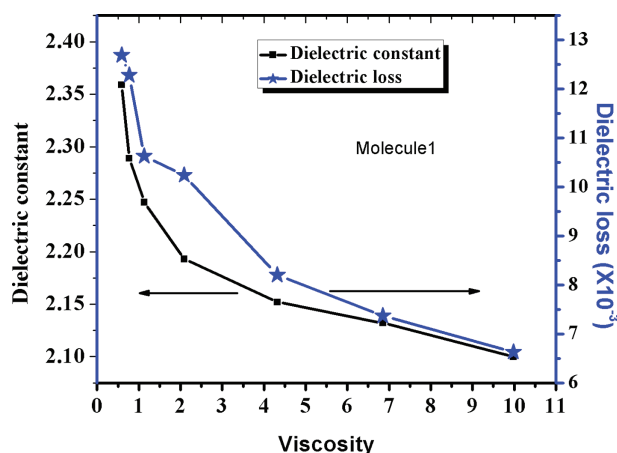
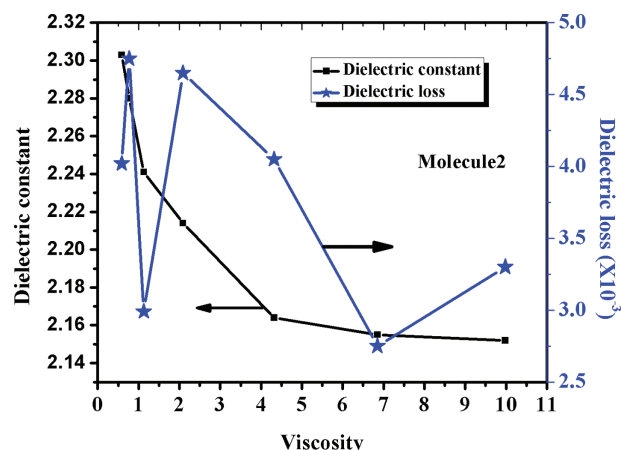
Table II. Viscosity dependence of dielectric parameter. Molecule: 2-Bromo, 2,4-Difluorobenzene. $T = 299^\circ\text{A}$ $MW = 193.00$.

Solvent no.	η_s (CP)	ϵ'	$\epsilon'' \times 10^{-3}$	τ_s (PS)	η_d (CP)	τ_{ve} (PS)	G_∞
I	0.59	2.303	4.02	01.5	–	–	–
II	0.77	2.280	4.75	11.3	–	–	–
III	1.13	2.241	2.99	12.9	–	–	–
IV	2.09	2.214	4.65	17.5	1.51	10.83	0.193
V	4.32	2.164	4.05	28.6	2.63	14.05	0.307
VI	5.38	–	–	–	–	–	–
VII	6.85	2.155	2.75	40.5	3.98	14.88	0.460
VIII	9.98	2.152	3.30	51.6	5.25	16.64	0.600

Notes: $a_V = 0.98^\circ\text{A}$; $a_D = 0.93^\circ\text{A}$; $a_{SR} = 1.42^\circ\text{A}$; $a_M = 2.99^\circ\text{A}$; $(G_\infty)_{\text{Mean}} = 0.390 \times 10^{10}$ dynes/cm²; $\mu = 1.08D$; $\tau' = 50.00$ PS; $\eta' = 5.80$ CP.

with respect to η is not rapid for the former molecule [BrC₆H₃(F)OCH₃], whereas, it is pronounced for the latter molecule [BrC₆H₃F₂]. Therefore rate of increase of τ with η is not same for different polar molecules. If the Debye relation between τ and η ($\tau = 4\pi\eta a^3/KT$) were strictly followed, one expects the variation of τ in the same order as η varies.

Following smyth²⁵ the effect of ' η ' on ' τ ' is such that if the shape of molecule undergoing dipole orientation departs little from that of the sphere, it can rotate without any considerable displacement of the surrounding molecules. Thus the relaxation time may become insensitive to the macroscopic viscosity of the medium, contrary to this, if the molecule is unsymmetric in shape, its rotation around at least one axis may involve the displacement of neighbouring molecules and the corresponding relaxation time will depend markedly upon the viscosity of the medium. In the present study the molecules chosen are not associate in nature and more or less spherical in shape, the measurements being taken at a fixed temperature and the same type of solute–solvent interactions are being involved, the departure from linear relation

**Fig. 5.** Variation of dielectric constant and loss as a function of viscosity (molecule1).**Fig. 6.** Variation of dielectric constant and loss as a function of viscosity (molecule2).

between $\log \tau$ versus $\log \eta$ may be attributed to the dynamical nature of the viscosity (η_D) but not to the measured macroscopic viscosity (η). These observations seem to be true when we consider the results obtained by replacing by ' η ' by ' η_D '.

The variation between $1/\tau$ versus $1/\eta$ is shown in Figure 4 exhibit almost linearity in nature, any other molecule studied in the literature. The various parameters namely, evaluated for each molecule are listed in the Tables I and II. These are namely, ϵ' , ϵ'' , τ and G_∞ respectively along with corresponding viscosity values (η_s) in the second column. At the foot, other parameters like μ (Eq. (1)), τ' and η' obtained from Figures 1(b) and 2(b) the intercepts and slopes of the plot $1/\tau_s$ versus $1/\eta_s$ for each molecule, the values of $G_\infty = (\eta_s/\tau_{ve})$ and molecular radii (a_D) estimated by using τ (Debye), τ_{ve} (viscoelastic) (a_v), molar volume a_M and stoke's relation a_{SR} are presented.

The variation of dielectric constant and loss of both molecules are represented in Figures 5 and 6 with viscosity. It is ascertained that, the dielectric constant decreases with increase in viscosity for both molecules. The rotation of the dipole molecules in a very viscous medium provides rise to frictional heat loss expressed as power factor, and conjointly to a contribution to the dielectric constant that vanishes when the dipoles are prevented from responding by too great viscosity. Dependent upon the dimensions of the orienting molecule and the viscosity of the medium, determines a time of relaxation for the polar molecules which has been evaluated by Debye using the law of Stokes for the rotation of a particle in a viscous medium.

4. CONCLUSIONS

The polar dielectric samples of 2-Bromo 4-fluoroanisole and 1-Bromo 2,4-Difluorobenzene in solution form with benzene as a solvent were determined at microwave frequency of 9.08 GHz. The viscosity (η) of pure benzene

and mixed solvents of benzene and paraffin was determined using a conventional Ostwald's viscometer. The dependence of τ on η is discussed in the light of macroscopic and microscopic viscosity concepts.

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