Dielectric Relaxation Studies of 2-Ethoxybenzonitrile, 4-Ethoxybenzonitrile, 1-Bromo 2,4-Difluorobenzene, 2,6-Difluorobenzaldehyde and 2-Bromo 4-Fluoroanisole in Benzene

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ABSTRACT

Dielectric relaxation time of different molar concentrations of 2-Ethoxybenzonitrile, 4-Ethoxybenzonitrile, 1-Bromo 2,4-Difluorobenzene, 2,6-Difluorobenzaldehyde and 2-Bromo 4-Fluoroanisole in benzene solution has been measured by microwave plunger technique at a fixed frequency of 9.08 GHz (X band) and an ambient temperature. Different dielectric parameters have been determined by microwave conductivity method, Higasi method, Gopalkrishna method and Higasi et al. methods. On the basis of the observations, it was witnessed that the dielectric relaxation process could be treated as the rate process like the viscous flow process. Dielectric constant (ε'), dielectric loss (ε''), relaxation times (τ) and the dipole moments (μ), free energy of activation (ΔF_E) of all samples were reported for the first time.

KEYWORDS: Dielectric Constant, Dielectric Loss, Microwave Plunger Technique, Dipole Moment, Relaxation Time.

1. INTRODUCTION

The three electromagnetic properties appearing in Maxwell's equations are dielectric permitivity, permeability and effective electrical conductivity, in terms of which a dielectric material may be explained. For dielectric materials either lossy or loss less, the most identifying parameter is the dielectric constant or permittivity. Dielectric properties are intrinsic characteristics of the materials, explaining the behavior and degree of the wave-matter interaction when exposed to microwave field. These properties are very important in microwave heating and microwave sensing process design applications.[1] The interesting molecular parameters of any polar dielectric substance are the electric dipole moment (μ) and the dielectric relaxation time (τ); the former parameter gives the idea of electronic structure and molecular interactions and the later one is used to investigate molecular, inter- and intra-molecular motions and their relations to molecular structure, size, shape, the intra molecular forces causing internal friction and even liquid structure.[2,3] Dielectric constant is one of the important constitutive properties of the liquid which determines molecular properties. The knowledge of intensive properties like density (ρ), refractive index (n) and constitutive property like dielectric constant are essential to understand the molecular interactions and inherent properties of liquids and may directly be employed in various industrial requirements viz. pharmaceuticals, agriculture, polymer industry, electronic industry, ceramic industry, etc.[4]

Several measurement techniques have been reported for the measurement of dielectric constant (ε') and dielectric loss (ε'') of materials.[5] The cavity perturbation method for the measurement of dielectric constant is different from other methods and very sensitive. To obtain the acceptable results by this method, the sample must be very small compared to cavity itself and the cavity without and with sample must be very much alike.[6] Complex permittivity spectra of the mixtures of 1-propanol with aniline, 2-chloroaniline and 3-chloroaniline at different temperatures were measured in the frequency range between 10 MHz to 20 GHz using time domain reflectometry (TDR) technique by

Rana et al.[7] The measurement by TDR technique is very rapid with higher accuracy within a few percent of error, but the sample size required is very small and the substance under measurement must be homogeneous. Wee et al.[8] have presented the principles to determine the dielectric properties using microwave free-space transmission technique, which is also grouped under non-destructive and contact-less measuring methods. Among the various techniques, the microwave plunger technique of determination of dielectric constant and dielectric loss is a simple and inexpensive technique applicable for a variety of liquid samples.[9]

This paper reports, the measurement of dielectric constant (ε') and dielectric loss (ε'') of the polar solutes 2-Ethoxybenzonitrile, 4-Ethoxybenzonitrile, 1-Bromo 2,4-Difluorobenzene, 2,6-Difluorobenzaldehyde and 2-Bromo 4-Fluoroanisole a non-polar solvent (benzene) at a microwave frequency (9.08 GHz) by Microwave Plunger technique, computation of dipole moment (μ) and dielectric relaxation time (τ) by the four different methods and comparison of the results to interpret molecular structure for the first time. The dynamic dielectric behavior

of all five molecules was analyzed by studying the relaxation mechanisms. No attempt, so far, have been made to comparative study the dielectric behavior of these solutes molecular interaction at microwave regions by different methods. The different methods employed for the determination of relaxation time were as follows

(i) Microwave conductivity method
(ii) Gopalakrishna method
(iii) Higasi method and
(iv) Higasi et al. method.

2. MATERIALS AND METHODS

The 2-Ethoxybenzonitrile ($CH_3OC_6H_4CN$), 4-Ethoxybenzonitrile ($C_2H_5OC_6H_4CN$), 1-Bromo 2,4-Difluorobenzene ($BrC_6H_3F_2$), 2,6-Difluorobenzaldehyde ($F_2C_6H_3CHO$) and 2-Bromo 4-Fluoroanisole ($BrC_6H_3(F)OCH_3$) and benzene (C_6H_6) of spectroscopic grade (Sigma Aldrich Chemicals Pvt. Ltd.) were used as the starting materials. The dilute solutions all five polar solutes in benzene as a non-polar solvent were prepared with different concentrations to maintain the weight fraction (W_2). The solutions were kept for 24 hrs in a volumetric flask with stopper to ensure thermal equilibrium. The X-band microwave bench set up (SICO
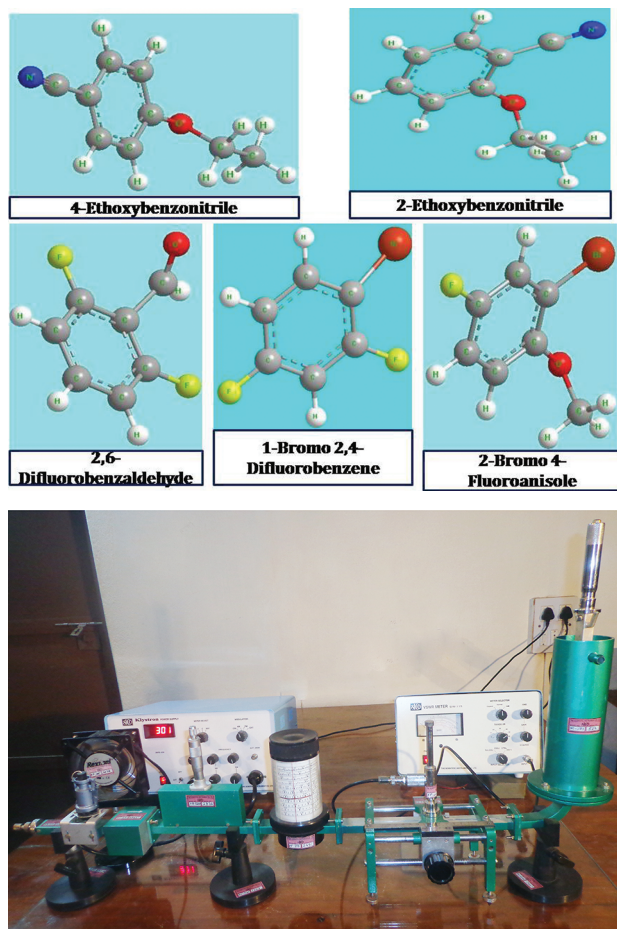
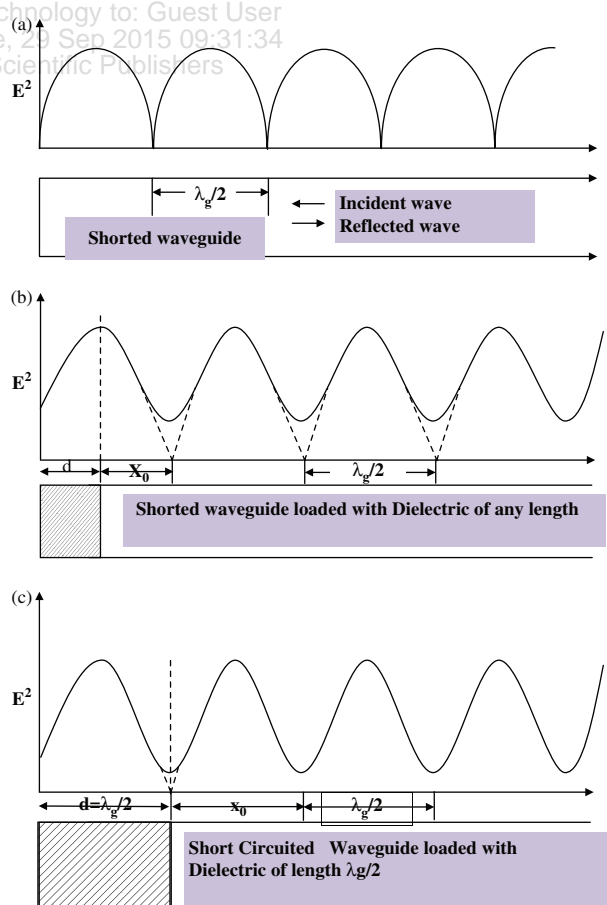**Fig. 1.** Structural formula of solutes and Photograph of experimental set up.

Fig. 2. Nodes and antinodes of the standing wave pattern.

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Ltd. India) was used to measure the guide wavelength, wavelength in dielectric and a standing wave ratio in the frequency range 8.5 to 12 GHz. The structural formula of all solutes and photograph of the experimental setup is as shown in Figure 1.

2.1. The Electromagnetic Theory

When an electromagnetic wave traveling through medium-1(air) strikes normally to the medium-2(dielectric), a part of it gets reflected and the rest gets transmitted. A standing wave pattern is thus produced in medium-1.

The complex relative permittivity of the dielectric material is expressed as

$$\varepsilon^* = \varepsilon' - j\varepsilon^{11} \tag{1}$$

The input impedance $z(o)$ at the boundary is given by

$$
\begin{aligned}
Z(O) &= Z'\left\{\frac{(E_{\min}/E_{\max}) - j\tan(2\pi x_0/\lambda g)}{1 - j(E_{\min}/E_{\max})\tan(2\pi x_0/\lambda g)}\right\} \\
&= Z'\left\{\frac{\rho_n - j\tan(2\pi x_0/\lambda g)}{1 - j\rho_n\tan(2\pi x_0/\lambda g)}\right\}
\end{aligned}
\tag{2}
$$

Where, $\rho_n = E_{\min}/E_{\max}$ is inverse voltage standing wave ratio (IVSWR), $E_{\min}$ and $E_{\max}$ are the electric field strength at a node and an antinode of the standing wave pattern respectively, z_1-impedance of the medium-1, λg-wavelength of the wave in the waveguide without sample and x_0 is the distance of the first node from surface of the dielectric in medium-1 (air) as shown in Figure 2.

If medium-2 (dielectric under test) is terminated in a short circuit, the input impedance at the interface,

$$Z(O) = Z_2 \tanh \gamma_2 d \tag{3}$$

Where Z_2, γ_2 and d being the characteristic impedance, propagation constant and length of the medium-2 respectively.

If we take liquid sample of length equal to the integral multiple of $\lambda_d/2$ placed in contact with the short circuit, then the value of x_0 the distance of the first minimum from the interface, is Zero. Hence $z_1 = 1$. So the Eq. (2) takes the form

$$Z(0) = \rho_n = \frac{E_{\min}}{E_{\max}} \tag{4}$$

From Eqs. (3) × (4), we get

$$\rho_n = Z_2 \tanh \gamma_2 d \tag{5}$$

Since $\gamma_2 = \alpha_d + J\beta_d$; $d = n\lambda d/2$, n being an integer
We have,

$$
\begin{aligned}
\rho_n &= z_2 \tanh\left(\frac{n\alpha_d\lambda_d + 2jn\pi}{2}\right) \\
&= Z_2 \tanh\left(\frac{n\alpha_d\lambda_d}{2}\right)
\end{aligned}
\tag{6}
$$

where $\beta_d = 2\pi/\lambda_d$ is the phase shift constant.
α_d is attenuation constant in dielectric.

Table I. Values of ε', ε'', k', k'', X and Y and the parameters obtained by different methods.

Wt fraction W_2	ε'	ε''	X	$Y \times 10^4$	$K' \times 10^{-9}$	$K'' \times 10^{-9}$
		Molecule: 2-ethoxybenzonitrile		MW = 147.18		
0.00545	2.320	0.0144	0.3056	25.31	0.06559	10.5324
0.00743	2.344	0.0211	0.3094	37.97	0.09572	10.6394
0.00965	2.365	0.0287	0.3127	53.32	0.13005	10.7348
0.01217	2.380	0.0312	0.3151	58.60	0.14179	10.8040
		4-Ethoxybenzonitrile		MW = 147.18		
0.00861	2.301	0.0118	0.3024	19.17	0.05365	10.4436
0.01163	2.311	0.0142	0.3041	22.86	0.06429	10.4894
0.01359	2.318	0.0154	0.3053	24.79	0.06996	10.5223
0.01753	2.327	0.0166	0.3067	26.67	0.07555	10.5621
0.02058	2.334	0.0181	0.3078	28.97	0.08236	10.5955
		1-Bromo 2,4-Difluorobenzene		MW = 193.00		
0.01352	2.303	0.0040	0.3028	06.68	0.01827	10.4535
0.01774	2.316	0.0046	0.3049	07.52	0.02064	10.5126
0.02071	2.325	0.0050	0.3063	08.33	0.02288	10.5523
0.02196	2.331	0.0061	0.3073	10.16	0.02779	10.5790
		2,6-Difluorobenzaldehyde		MW = 142.11		
0.00796	2.3157	0.0108	0.3049	18.50	0.04889	10.5118
0.01012	2.3437	0.0129	0.3094	22.10	0.05839	10.6386
0.01180	2.3535	0.0132	0.3109	22.64	0.05993	10.6834
0.01396	2.3595	0.0134	0.3119	22.99	0.06094	10.7107
		2-Bromo 4-Fluoroanisole		MW = 205.03		
0.00995	2.3305	0.0073	0.3072	12.16	0.03302	10.5787
0.01221	2.3498	0.0093	0.3103	15.67	0.04238	10.6662
0.01513	2.3594	0.0127	0.3118	21.63	0.05759	10.7098
0.02060	2.3671	0.0133	0.3131	22.72	0.06045	10.7448

For low—loss medium, $\tanh x \approx \tan x \cong x$ and $z_2 = \lambda_d/\lambda_g$, so that,

$$\rho_n = z_2 \frac{n\alpha_d \lambda_d}{2} = \frac{\lambda_d}{\lambda_g} \frac{n\alpha_d \lambda_d}{2}$$

$$\rho_n = \frac{n\alpha_d \lambda_d^2}{2\lambda_g} \tag{7}$$

However, α_d in Eq. (7) is the sum of two parts; one due to dielectric attenuation and the other due to plunger resistance and other losses. To eliminate latter losses, a graph is plotted between several mean values of ρ_n and n. The slope of this graph gives the value of α_d given by,

$$\alpha_d = \frac{2\lambda_g}{\lambda_d^2} \frac{d(\rho_{\mathrm{mean}})}{dn} \tag{8}$$

The dielectric constant (ε') and dielectric loss (ε'') are given by[2]

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

$$\varepsilon'' = \frac{2}{\pi}\left(\frac{\lambda_0}{\lambda_d}\right)^2 \frac{\lambda_g}{\lambda_d}\left(\frac{d\rho_{\mathrm{mean}}}{dn}\right) \tag{9}$$
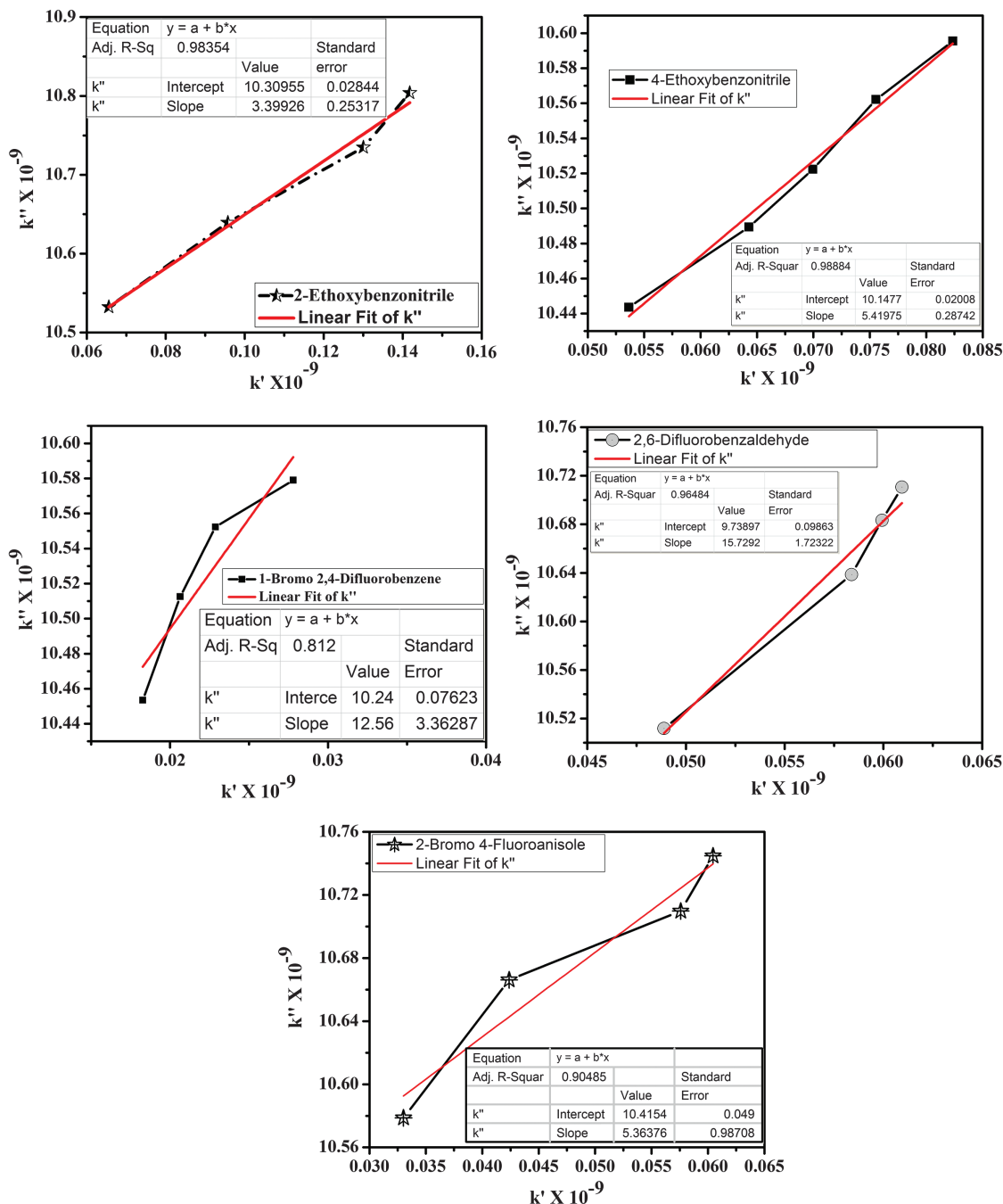

Fig. 3. Variation of k'' with k' for all samples.

Where, λ_0 is free space wavelength, λ_d is the wavelength in dielectric $\lambda_d = 2a$, the cutoff wavelength, a being waveguide inner broad dimension.

The following two methods are used to determine the molecular parameters, namely, dipole moment (μ) and relaxation time (τ).

2.2. Microwave Conductivity Method

The measurement of dipole moment (μ) and relaxation time (τ) of polar molecule in non-polar solvent from the study of microwave conductivity have been reported.[9] If any one of the two quantities "μ" and "τ" is known then the other one may be calculated. The method of finding both "μ" and "τ" without any pre-knowledge of any of the two quantities is proposed based on the concept of microwave conductivity as described below.

The Debye relations are

$$\varepsilon' = \frac{\varepsilon_\infty + 4\pi N d\mu^2(\varepsilon_0 + 2)(\varepsilon_\infty + 2)}{27KTM(1 + \omega^2\tau^2)} \qquad (10)$$

$$\varepsilon'' = \frac{4\pi W_2 N d\mu^2(\varepsilon_0 + 2)(\varepsilon_\infty + 2)\omega\tau}{27KTM(1 + \omega^2\tau^2)} \qquad (11)$$

The complex microwave conductivity is given as,

$$k^* = k' + jk''$$

where,

$$k' = \frac{\omega\varepsilon''}{4\pi} \qquad (12)$$

and

$$k'' = \frac{\omega\varepsilon'}{4\pi} \qquad (13)$$

Using this concept the Debye relations can be expressed as

$$k'' = k_\infty + \frac{k'}{\omega\tau} \qquad (14)$$

Where $k_\infty = \omega\varepsilon_\infty/(4\pi)$.

For the dilute solutions, the difference between ε_0, ε_∞ and ε' is negligible, therefore, by replacing ε_∞ by ε_0 in Eq. (11) and substituting the value of ε'' in Eq. (12), it can be written as,

$$k' = \frac{\omega W_2 N d\mu^2(\varepsilon_0 + 2)^2\omega\tau}{27KTM(1 + \omega^2\tau^2)} \qquad (15)$$

In the range of low concentrations used such that Debye relation can be approximated, the variation of k' and k'' with weight fraction W will be linear. Therefore, from Eq. (14), it can be seen that, the slope of the linear graph of k'' versus k' is equal to $(1/\omega\tau)$, from which "τ" can be obtained.

The slope of linear graph of k' versus W, plotted using Eq. (15) can be written as,

$$\mu = \frac{27KTM(1 + \omega^2\tau^2)}{\omega N d(\varepsilon_0 + 2)^2\omega\tau\mu^2} \qquad (16)$$

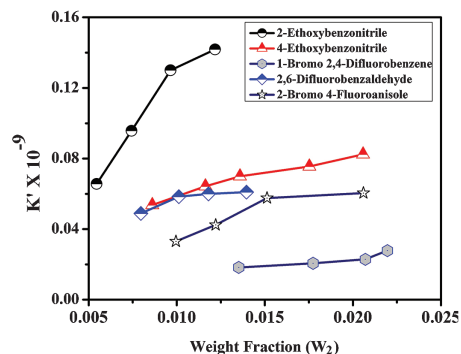Thus dipole moment (μ) can be determined.

Fig. 4. Variation of k' with weight fraction (W_2) for all samples in benzene solvent.

2.3. Gopalkrishna Method

The two parameters X and Y were calculated for each concentration of the solution using the formulae[11] given below

$$X = \frac{\varepsilon'^2 + \varepsilon' + \varepsilon''^2 - 2}{(\varepsilon' + 2)^2 + \varepsilon''^2} \qquad (17)$$

and

$$Y = \frac{3\varepsilon''}{(\varepsilon' + 2)^2 + \varepsilon''^2} \qquad (18)$$

The graph of Y plotted against X is a straight line, the slope of which is equated to $Y\omega\tau$ in order to obtain the value of relaxation time (τ).

Another graph of X plotted against W, the weight fraction of the solute is also a straight line, the slope of which is equated to the factor $[(4\pi N\mu^2 d)/(9KTM(1 + \omega^2\tau^2))]$ in order to evaluate the dipole moment (μ), where, d is density of the solvent.

2.4. Higasi Method

Using the concept of infinite dilution and by modifying Debye equation, Higasi determined the dipole moment of solute molecules in the dilute solutions. a_0 and a_∞ are the slopes of the straight lines obtained by plotting ε_0 plotted against W_2, and ε_∞ plotted against W_2, respectively. B is
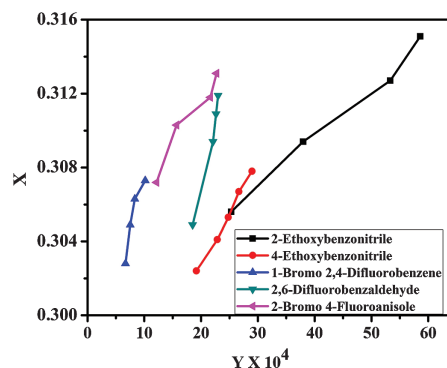

Fig. 5. Variation of X with Y for all samples in benzene solvent (Gopal-Krishna Method).
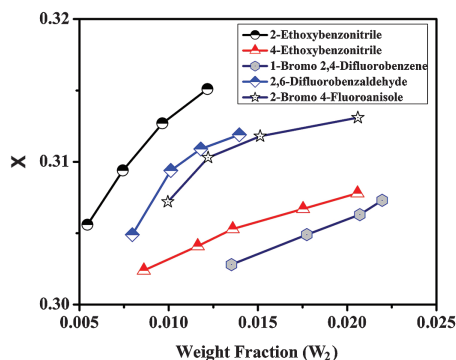
Fig. 6. Variation of X with weight fraction (W_2), for all molecules in benzene solvent.

a constant for the solute molecules of molecular weight M, dissolved in the non-polar solvent of density (ρ), given as

$$\mu = B(a_0 - a_\infty)^{1/2} \quad \text{Where} \tag{19}$$

$$B = \frac{1}{2(\varepsilon_0 + 2)} \left\{ \frac{27kTM}{N\pi\rho} \right\}^{1/2} \tag{20}$$

The static (ε_0) microwave (ε') and optical (ε_∞) dielectric constants and the dielectric loss vary linearly with concentration, and expressed in terms of weight fractions as

$$\varepsilon' = \varepsilon'_1 + a'W_2 \tag{21}$$

$$\varepsilon'' = \varepsilon''_1 + a''W_2 \tag{22}$$

$$\varepsilon_o = \varepsilon_{10} + a_o W_2 \tag{23}$$

$$\varepsilon_\infty (n_d)^2 = \varepsilon_1 + a_d W_2 \tag{24}$$

in which subscript 1 refers to the pure solvent and 2 refers to the solute, 0 refers to the static frequency and ∞ refers to the infinite or optical frequency measurements and W_2 is the weight fraction of the solute.

$$A = a''(a_0 - a_d) \tag{25}$$

$$B = (a_0 - a')(a' - a_d) - a''^2 \tag{26}$$

$$C = (a' - a_d)^2 + a''^2 \tag{27}$$

$$\alpha = 1 - \frac{2\tan^{-1}(A/B)}{\pi} \tag{28}$$

$$\tau_0 = \frac{\{A^2 + B^2\}^{1/2(1-\alpha)}}{\varpi C^{1/2(1-\alpha)}} \tag{29}$$

where microwave angular frequency (ω).

The distribution parameter (α) and relaxation time (τ_o) were calculated using above relations equations. A finite and significant value of distribution parameter (α) indicates existence of more than one relaxation process. Non-zero values of distribution parameter are obtained for dilute solutions of the molecules in benzene, which indicates that there is a large contribution of segment reorientation and group rotation to the relaxation processes, besides the overall rotation.[12]

2.5. Higasi et al. Method

In this method analyzing of the dielectric relaxation data is expressed in terms of two relaxation times $(\tau_1$ and $\tau_2)$, with one for molecular rotation and the other for intramolecular rotation. Debye equation for relaxation time (τ_1) and the dielectric relaxation time (τ_2) for over all rotation of the molecule.

$$\tau_1 = \frac{a''}{\varpi\{a' - a_d\}} \tag{30}$$

$$\tau_2 = (a_o - a')t/\varpi a'' \tag{31}$$

If a large separation exists between τ_1 and τ_2 then it indicates the presence of more than one relaxation time. Hence the mean relaxation time (τ_0) is given by

$$\tau_0 = \sqrt{\tau_1 \bullet \tau_2} \tag{32}$$

3. RESULTS AND DISCUSSION

The values of dielectric constant (ε'), dielectric loss (ε'') obtained by microwave plunger technique, the parameters k', k'', relaxation time (τ) and dipole moment (μ) obtained by microwave conductivity method for the polar dielectric solute all molecules in benzene solvent are given in the Table I. The values of dielectric constant (ε') and dielectric loss (ε'') of all molecules in dilute solution of benzene (C_6H_6) are in increasing order as function of concentration of polar solute. Figure 3 represents the variation of the parameter k'' with k' of the

Table II. Various slopes in different methods.

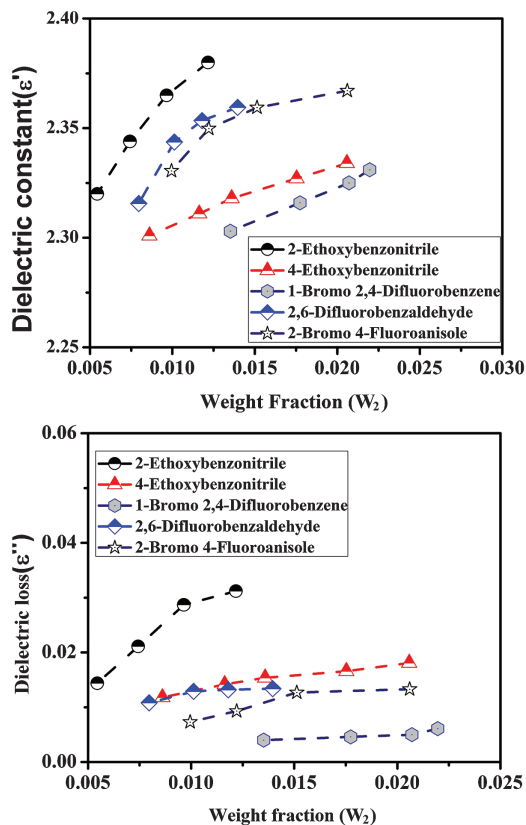| Molecule	Microwave conductivity		G.K. method		Higasi method			
	K' versus K''	W_2 versus $K' \times 10^{-9}$	Y versus X	W_2 versus X	a_o	a_d	a'	a''
2-Ethoxybenzonitrile	3.399	11.619	2.720	1.413	9.852	0.271	8.893	2.56
4-Ethoxybenzonitrile	5.422	2.272	5.637	0.444	3.771	0.949	2.755	0.51
1-Bromo 2,4-Difluorobenzene	12.563	0.985	12.104	0.514	3.233	0.163	3.193	0.217
2,6-Difluorobenzaldehyde	15.734	1.927	14.766	1.148	7.244	0.457	7.198	0.423
2-Bromo 4-Fluoroanisole	5.363	2.564	4.845	0.498	3.534	0.463	3.138	0.565

Fig. 7. Variation of Dielectric constant and dielectric loss with weight fraction (W_2).

microwave conductivity method for the polar solute all molecules dissolved in benzene (C_6H_6). It can be seen that, the variation is linear as expected all molecules. The slopes of 2-Ethoxy-benzonitrile, 4-Ethoxy-benzonitrile, 1-Bromo 2,4-Difluorobenzene, 2,6-Difluoro benzaldehyde, and 2-Bromo 4-fluoroanisole were 3.399, 5.422 12.563, 15.734 and 5.363 respectively. The value of dielectric relaxation time (τ) of all molecules as obtained by the reciprocal of the product of angular frequency (ω) and the slope, at the microwave frequency 9.08 GHz. Table I.

Figure 4 indicates the dependence of k' on the weight fraction of the solute W_2 for the all polar solutes dissolved in benzene (C_6H_6). It is evident that, the value of k' depends linearly on the weight fraction of 2-Ethoxy-benzonitrile, 4-Ethoxy-benzonitrile,

1-Bromo 2,4-Difluorobenzene, 2,6-Difluoro benzaldehyde, and 2-Bromo 4-fluoroanisole slopes of the line being 11.619×10^{-9}, 2.272×10^{-9}, 0.985×10^{-9}, 1.927×10^{-9}, 2.564×10^{-9} respectively. The electric dipole moment (μ) was 3.61 Debye as calculated using the Eq. (16).

Figure 5 shows variation of X with Y and Figure 6 shows variation X with weight fraction W_2, for all solvents in benzene solvent. The values the parameters X, Y (tabulated in Table I), the dielectric constant (ε' and ε'') and dipole moment (μ) obtained by Gopalkrishna method for all solvent in benzene solvent are listed in the Table II. From, the linear variation of parameter X with Y as stated in Gopal-krishna method for the polar solutes in benzene solvent. The value of dielectric relaxation time (τ) was calculated by depicting slopes. It can be seen that, the value of X increased linearly with weight fraction of the solute and the slope of the line calculated for different solvents and dipole moment (μ) is computed by Gopal-krishna method. Figure 7 describes the variation of dielectric constant and dielectric loss with weight fraction (W_2). It is observed that dielectric constant and loss increases with increases with weight fraction (W_2).

The slopes a_0, a', a'' and a_d of 2-Ethoxy-benzonitrile, 4-Ethoxy-benzonitrile, 1-Bromo 2,4-Difluorobenzene, 2,6-Difluoro benzaldehyde, and 2-Bromo 4-fluoroanisole of varying with benzene at room temperature are computed using the standard Higasi method and Higasi method et al. relations (as discussed above). The slopes a_0, a', a'' and a_d of these linear plots were determined and used to evaluate relaxation times, distribution parameter and dipole moments. The most probable relaxation time (τ_0) and distribution parameter (α) were determined by Higasi's method. Relaxation times τ_1 and τ_2 corresponding to group rotation and over all rotations calculated using equations proposed by Higasi et al. method. Three molecules are associated with a very small non-zero distribution parameter values while the remaining two molecules have slightly higher values (4-Ethoxy-benzonitrile, 1-2-Bromo 4-fluoroanisole). The detailed various results of all samples like distribution parameter (α), relaxation time (τ_0), τ_1 and τ_2 and dipole moments (μ) of the individual components are presented in Table III. Figure 8 depicts the modification of relaxation times all molecules by different methods.

Table III. Comparison of the evaluated dielectric parameters.

|	Microwave conductivity		G.K. method		Higasi method			Hagasi et al.	
Molecule	τ (ps)	μ (D)	τ (ps)	μ (D)	τ_0 (ps)	μ (D)	α	τ_1 (ps)	τ_2 (ps)
2-Ethoxybenzonitrile	5.16	3.61	6.44	3.67	5.04	3.63	0.05	5.20	6.57
4-Ethoxybenzonitrile	3.23	1.97	3.11	1.96	5.91	1.97	0.54	4.86	5.57
1-Bromo 2,4-Difluorobenzene	1.40	2.19	1.45	2.35	1.04	2.32	0.07	1.26	3.26
2,6-Difluorobenzaldehyde	1.11	2.96	1.19	3.03	1.02	2.98	0.03	1.10	1.90
2-Bromo 4-Fluoroanisole	3.27	2.41	3.62	2.43	2.75	2.39	0.26	3.70	2.29
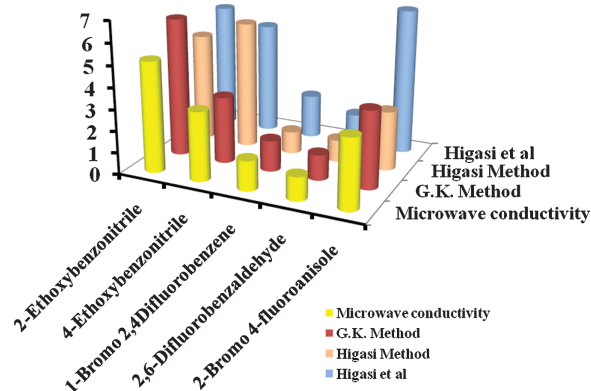
Fig. 8. Analysis of relaxation time obtained by various methods for all samples.

Thermodynamics of dipole relaxation is used to study the disturbances in the local structure. As per Eyring theory[12–15] the molecular rotation requires activation energy (ΔF_E) sufficient enough to overcome the energy barrier separating the two mean equilibrium positions with opposite directions of the dipole and hence the relaxation time (τ) is given by the rate expression. The free energy of activation ΔF_E is related to the relaxation time (τ) as

$$\Delta F_E = 2.303RT \log_{10}(KT\tau/h) \qquad (33)$$

The dielectric relaxation process involves only the rotational motion of the molecules. The calculated free energy of activation ΔF_E is tabulated in Table IV and Variation of ΔF_E by all four molecules is depicted in Figure 9 The free energy of activation (ΔF_E) of 2,6-Difluorobenzaldehyde is least (in the range 4.6–5.48 kJ/mol) and 2-Ethoxybenzonitrile is most (8.78–9.41 kJ/mol).

In the present study first two molecules of benzonitriles are position isomers having the same molecular weight and same polarizability (due to the $-OC_2H_5$ and -CN dipoles only), same angle of inclination (about 57°) about the bond but the location of $-OC_2H_5$ dipoles differ. It is seen that relaxation time "τ" decreases when the position (location) of the $-OC_2H_5$ dipole is shifted from *ortho* to *para* position. The "α" values for the two isomers of Ethoxybenzonitriles would have yielded the same
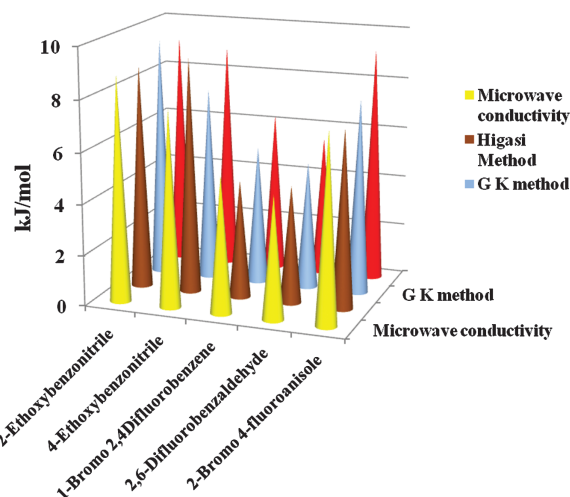

Fig. 9. Analysis of free energy of activation (ΔF_E) obtained by various methods for all samples.

value of "τ" but these values differ. This may be partly due to the fact that the mutual interaction between the dipoles –CN and $-OC_2H_5$ in the *ortho* position might hinder the free rotation of the molecule during the observed dielectric absorption. Similarly, parallel to the above discussion it is seen that the molecule 2,6-Difluorobenzene has higher polarizability value than the 1-Bromo 2,4-Difluorobenzene and hence has the shorter relaxation time "τ" value. Polarizability value of 2-Bromo, 4-fluoroanisole is in between that of 1-Bromo 2,4 Difluorobenzene and 2,6-Difluorobenzaldehyde but the molecule has a longer relaxation time "τ" value. Thus we conclude that, dipole moment (μ) and relaxation time (τ) values determined from different procedures agree well within the small errors. The most probable relaxation time "τ_0" (Higasi method) value is approximately nearer to the geometric mean of the τ_1, τ_2 (Higasi et al. method) as expected. The distribution parameter value is small but it differs in the cases where this parameter has slightly higher values.

4. CONCLUSION

From this study, one may conclude that microwave conductivity method, Higasi method, Gopal-Krishna method and Higasi et al. methods of Ethoxy-benzonitrile, 4-Ethoxy-benzonitrile, 1-Bromo 2,4-Difluorobenzene, 2,6-Difluoro benzaldehyde, and 2-Bromo 4-fluoroanisole in benzene solvents plays a significant role in the determination of dielectric parameters systematically. This work shows that the microwave plunger technique requiring a simple set up is a cost effective technique for the determination of complex permittivity of loss less and low loss dielectric liquids. On the basis of the observations, it was witnessed that the dielectric relaxation process could be treated as the rate process like the viscous flow process. Dielectric constant (ε'), dielectric loss (ε''), relaxation times (τ) and the dipole moments (μ), free energy of

Table IV. Comparison of the evaluated free energy of activation (ΔF_E).

Molecule	Microwave conductivity (kJ/mol)	Higasi method (kJ/mol)	G. K. method (kJ/mol)	Hagasi et al. (kJ/mol)
	Methods			
2-Ethoxybenzonitrile	8.849	8.789	9.411	9.165
4-Ethoxybenzonitrile	7.695	9.232	7.598	8.908
1-Bromo 2,4-Difluorobenzene	5.356	4.619	5.443	6.273
2,6-Difluorobenzaldehyde	4.829	4.619	5.003	5.489
2-Bromo 4-Fluoroanisole	7.425	6.997	7.676	7.212

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activation (ΔF_E) of the individual components are in fair agreement by different methods.

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