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Molecular Interactions and Dielectric Relaxation in the Mixtures of Amines with 2–Fluorobenzoic Acid in 1, 4–Dioxane

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Abstract: ***For the present study, the estimation of the static dielectric constants (ε_0), dielectric constant (ε') at an angular frequency and dielectric loss (ε'') of methyl, ethyl and propyl amines with 2-fluorobenzoic acid in 1,4-dioxane were carried using Klystron microwave bench at frequency 9.43GHz. Using the dielectric parameters, the overall relaxation time (τ_1) and group rotation relaxation time (τ_2) of the polar solute molecules and average relaxation times (τ_0) were also determined using Higasi and Gopalakrishna method employing Debye's equations. The obtained results revealed that, out of five different molar ratios, relaxation time (τ) is maximum at 1:1 molar concentration for all the systems due to inter and intramolecular interactions through hydrogen bonding. In addition, the dipole moment, activation viscous flow (Δf_η) and dielectric relaxation (Δf_τ) due to molar free energy also been discussed.***

Keywords: ***Dielectric relaxation, amines, 2–fluorobenzoic acid, molecular interactions***

I. INTRODUCTION

In recent decade, dielectric relaxation studies create interests among the researchers in both time domain [1-4] and frequency domain [5-8] methods. Since studying dielectric relaxation between the mixtures playing important role to understand H bonding via inter and intra molecular interactions. Dielectric relaxation spectroscopy will also be helpful in recognizing molecular interactions and dynamics among the molecules. [9]. Dielectric relaxation spectroscopy is portrayed the estimation of relaxation parameters that are related to the occurrence of dipoles in molecules. In the present study, mixtures of methylamine, ethylamine and propylamine with 2-fluorobenzoic acid in 1,4-dioxane is studied. Aliphatic amines have been chosen for the investigation because of its numerous applications, amines are largely used in pharmaceutical field as a pain killers, decongestant, water purification and in day to day life amines found applications in pest control, tanning of leather, man-made dyes and azo-dyes [10,11]. In industries, amines are used as neutralization of chemical reactions because of its basic in nature also used in developing chemicals for crop protection [12]. Such an important amines are mixed with 2-fluorobenzoic acid because hydrogen accepting ability and involving in noncovalent interactions are better in fluorine atom, likely C–F⋯F–C, C–F⋯π, and C–F⋯O [13]. Diederich et.al., examined that, the substitution of fluorine atom in the pharmaceuticals in addition, identified interactions through the active sites of protein by means of C–F⋯H–N, C–F⋯C=O, and C–F⋯H–Cα interactions [15]. Moreover, the ability of accepting H-bond by the fluorine atom was also elaborately studied in the existence of strong H-bond donating atoms [16-22]. The significance of such C–H⋯F interactions being feeble, C–H⋯N hydrogen bond have been realized [13]. 1,4-doxane is a polar solvent used to dissolve aliphatic amines with 2-fluorobenzoic acid in five different molar ratios (1:3, 1:2, 1:1, 2:1, 3:1) at room temperature.

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II. MATERIALS AND METHODS

A. Materials

Analar grade chemicals of Methylamine, Ethylamine, Propylamine, 1,4-dioxane and 2– fluorobenzoic acid were purchased from E-Merck and Aldrich chemicals respectively. The obtained chemicals are directly used for the study without any further purification.

B. Dielectric Relaxation Method

The mixtures of methylamine, ethylamine and propylamine with 2-fluorobenzoic acid in 1,4-dioxane have been prepared in five various molar concentrations (1:3, 1:2, 1:1, 2:1, 3:1) at room temperature and Dielectric parameters such as static dielectric constant (ε_0) was measured with the help of heterodyne beat technique using a dipole meter and other Dielectric parameters like Dielectric constant (ε') and the corresponding loss (ε'') were measured in the microwave atmosphere with a Klystron microwave bench at X-band with frequency 9.43 GHz [23]. Using the obtained data of dielectric parameters, dielectric relaxation times also have been calculated. In general, dielectric relaxation time is of three categories, they are namely mean relaxation time (τ_0), average relaxation time (τ_1) and overall relaxation time (τ_2). Which are calculated using Higasi and Gopalakrishna method.

As well, dipole moment, activation energy of viscous flow (Δf_η) and dielectric relaxation time (Δf_τ) for free energy due to molar concentrations were also obtained. The refractive index and viscosities of the mixtures were obtained using Abbe's refractrometer and Oswald's viscometer respectively. For the selected mixtures, maximum deviation taken place at the equimolar ratio of the solutes, this deviation perhaps due to the formation of 1:1 complexes [24, 25].

III. GENERAL THEORY

A. Dielectric Parameters by Higasi's method

The dielectric parameters of polar molecules in dilute solutions are obtained by the following equations [26].

$$\left.\begin{aligned} \varepsilon_0 &= \varepsilon_{10} + a_0\omega_2 \\ \varepsilon' &= \varepsilon_1' + a'\omega_2 \\ \varepsilon'' &= \varepsilon_1'' + a''\omega_2 \\ \varepsilon_\infty &= \varepsilon_{1\infty} + a_\infty\omega_2 \end{aligned}\right\} \qquad \text{………. (1)}$$

Here the numbers in the suffix 1 and 2 are assigned to the solvent and solute respectively, similarly 0 and ∞ referred to the measurement at zero and very high frequency in the static field respectively. ω_2 represented as solute concentration in mole fraction [27, 28].

Debye equation for relaxation time are expressed according to Higasi method [29] for dilute solution of solutes in a solvent is expressed as

$$\frac{a'-a_\infty}{a_0-a_\infty} = \frac{1}{1+\omega^2\tau^2} \qquad \text{………. (2)}$$

$$\frac{a''}{a_0-a_\infty} = \frac{1}{1+\omega^2\tau^2} \qquad \text{………. (3)}$$

Where, a′, a″, a_0 and a_∞ were obtained from the Eqn. 1, ω and τ refers to the angular frequency and molecular relaxation time respectively. Combining equation (2) and (3) the subsequent two independent equations are obtained.

$$\left.\begin{aligned} \tau_1 &= \frac{1}{\omega}\frac{a''}{a'-a_\infty} \\ \tau_2 &= \frac{1}{\omega}\frac{a_0-a'}{a''} \\ \tau_3 &= \sqrt{\tau_1 . \tau_2} \end{aligned}\right\} \qquad \text{………. (4)}$$

Where, τ_1 is average relaxation time, τ_2 is overall relaxation time and τ_3 is a geometric mean relaxation time.

According to Eyring [30], the molecular rotation needed sufficient activation energy to prevail over the energy barrier split two mean balancing positions with opposed directions of the dipole therefore the relaxation time (τ) is represented by the rate equation.

$$\tau = \frac{h}{kT}\exp\left(\frac{\Delta F_\tau}{RT}\right) \qquad \text{………. (5)}$$

$$\eta = \frac{Nh}{V}\exp\left(\frac{\Delta F_\eta}{RT}\right) \qquad \text{………. (6)}$$

Where, F_τ and F_η are molar activation energy for relaxation and viscosity respectively. k is Boltzmann constant, V is molar volume, h is Planck's constant, T is the absolute temperature and R is gas constant.

B. Dielectric Parameters by Gopalakrishna's method

Gopalakrishna's method adopted Debye's theory of dielectric relaxation [31]. Debye proposed equation for dielectric constant of complex a dielectric medium (ε*) that is expressed as,

$$\frac{\varepsilon^*-1}{\varepsilon^*+2} = \frac{\varepsilon_\infty-1}{\varepsilon_\tau+2} + \frac{4\pi N_1\mu^2}{9kT}\frac{1}{1+j\omega\tau} \qquad \text{………. (7)}$$

Where, N_1 is represented for the no. of molecules/unit volume, ε_∞ is the optical permittivity, and ω the angular frequency. Substituting the value of ε^* given in the above equation and explicitly represented as real and imaginary parts, we get,

$$\frac{\varepsilon'^2+\varepsilon'+\varepsilon''^2-2}{(\varepsilon'+2)^2+\varepsilon''^2} = \frac{\varepsilon_\infty-1}{\varepsilon_\tau+2} + \frac{4\pi N_1\mu^2}{9kT}\frac{1}{1+\omega^2\tau^2}\frac{3\varepsilon''}{(\varepsilon'+2)^2+\varepsilon''^2} = \frac{4\pi N_1\mu^2}{9kT}\frac{\omega\tau}{1+\omega^2\tau^2} \qquad \text{… … . . (8)}$$

On putting;

$$X = \frac{\varepsilon'^2+\varepsilon'+\varepsilon''^2-2}{(\varepsilon'+2)^2+\varepsilon''^2} \qquad \text{………. (9)}$$

$$Y = \frac{3\varepsilon''}{(\varepsilon'+2)^2+\varepsilon''^2} \qquad \text{………. (10)}$$

And

$$P = \frac{\varepsilon_\infty-1}{\varepsilon_\tau+2} \text{ then } X = P + \frac{Y}{\omega\tau} \qquad \text{………. (11)}$$

Where, P is as a constant over the solution concentration. It may be due to the errors committed during the experimental observations in determining ε' and ε". The slope of the curve Y vs X, the values of relaxation time of molecules are expressed as

$$\tau = \frac{\lambda_0}{2\pi c}\left(\frac{dY}{dX}\right) \qquad \text{………. (12)}$$

To find the dipole moment (μ) of the solution, equation (11) can be written as

$$X = P + \frac{4\pi N_1\mu^2 w d_{12}}{9kTM(1+\omega^2\tau^2)} \qquad \text{………. (13)}$$

$$N_1 = \frac{(Nd_{12}W)}{M}$$

Where, M is molecular weight, N is Avogadro number, W is the weight fraction of the solution and d_{12} is the density of the solutions and the varying density with respect to w may be given by the expression,

$$d_{12} = d_0(1+\alpha\omega)$$

Where, d_0 is the solvent density. At varying concentrations, the graph between X and w can be taken as a linear line with its slope dw dX as kd_0. From this, the values of dipole moment can be determined using the relation given below

$$\mu^2 = \frac{9kTM}{4\pi N d_0}\left(1+\left(\frac{dY}{dX}\right)^2\right)\frac{dX}{d\omega} \text{ ..(14)}$$

The values of ε' and ε'', τ, and μ thus determined are reported in Tables 1-4.

IV. RESULT AND DISCUSSION

This study is aimed to obtain dielectric data, which were analyzed in the view of molecular interactions between solute and solvent molecules. Aliphatic amines; methylamine, ethylamine and propylamine with 2–fluorobenzoic acid are independently mixed up at the equal molar concentration in a polar solvent 1,4-dioxane. Table 1–4 provided the values of dielectric parameters such as ε_0, ε′ and ε″, the relaxation time due to internal rotation, overall rotation of the molecules and the most probable mean relaxation time (τ_0). Table 4 also provided the values of dipole moment, the activation energy due to the dielectric relaxation time (ΔF_τ) and viscous flow of proton donors with proton acceptors in 1,4–Dioxane.

The values of dielectric parameters are obtained are for the title compunds are observed to be nearly in concurrence with the Debye theory of dielectric absorption in the region of microwaves at frequency (9.43GHz). The values of ε′ and ε″ decreases with increasing carbon chain-length of the molecule (proton acceptor). Lingyun Zhao *et.al* [32] pointed out the influence of chain length in molecular interactions in lipids and Robinson *et.al* [33] observed that similar frequency absorption is strongly dependent on chain-length in ethyl esters. The decrease tendency is attributed the number of dipoles in the complex and it is believed that the absorption is due to rotation of the whole molecule [34]. The values of relaxation time (τ_1, τ_2 and τ_0) increases with increasing effective radius of the rotating component. The obtained values of mean relaxation time raising with increasing chain length of proton acceptor (ie., aliphatic amines) are in the decreasing order of propylamine, ethylamine, and methylamine. The increase in the relaxation time has the possibility to the increase in viscosity and increasing molar size with the increase in the chain length.

Table 1. Value of dielectric parameters and relaxation times of methylamine with 2-fluorobenzoic acid at various weight fractions in 1, 4-dioxane

Ratio	W_2	□□	□′	□″	□□	Relaxation Time (in10^{-12}s)			
						Higasi's Method			Gopalakrishna's Method
						□□	□□	□□	□
1:3	0.0175	3.0698	2.6328	0.3651	2.1742	17.316	19.896	18.562	19. 177
1:2	0.0202	3.1864	2.6405	0.3939	2.1803	18.602	23.034	20.700	
1:1	0.0257	3.2349	2.6411	0.4146	2.1824	19.660	23.806	21.634	
2:1	0.0311	3.1154	2.6367	0.3940	2.1857	19.108	20.195	19.644	
3:1	0.0339	3.0471	2.6205	0.3642	2.1861	18.558	19.472	19.010	

Table 2. Value of dielectric parameters and relaxation times of ethylamine with 2-fluorobenzoic acid at various weight fractions in 1, 4-dioxane

Ratio	W_2	□□	□′	□″	□□	Relaxation Time (in10^{-12}s)			
						Higasi's Method			Gopalakrishna's Method
						□□	□□	□□	□
1:3	0.0207	3.1062	2.6338	0.3687	2.1750	17.479	21.299	19.295	18.978
1:2	0.0230	3.1841	2.6369	0.3918	2.1771	18.527	23.217	20.740	
1:1	0.0278	3.2442	2.6389	0.4140	2.1803	19.638	24.304	21.847	
2:1	0.0325	3.1465	2.6338	0.3938	2.1827	19.089	21.640	20.324	
3:1	0.0349	3.0652	2.6205	0.3642	2.1863	18.570	20.300	19.416	

Table 3. Value of dielectric parameters and relaxation times of propylamine with 2-fluorobenzoic acid at various weight fractions in 1, 4- dioxane

Ratio	W_2	□□	□′	□″	□□	Relaxation Time (in10^{-12}s)			
						Higasi's Method			Gopalakrishna's Method
						□□	□□	□□	□
1:3	0.0238	3.0652	2.5863	0.3623	2.1827	20.384	21.974	21.164	

1:2	0.0258	3.1291	2.5900	0.3781	2.1887	21.440	23.696	22.540	
1:1	0.0299	3.1883	2.5960	0.3873	2.1913	21.716	25.420	23.495	21.215
2:1	0.0339	3.1108	2.5910	0.3732	2.1948	21.539	23.147	22.329	
3:1	0.0360	3.0652	2.5824	0.3513	2.1957	20.968	22.846	21.887	

The mixture selected for the study is ternary systems of primary amines (methyl, ethyl and propyl) with proton donor 2–fluorobenzoic acid using 1,4–dioxane as solvent. Especially, the value of relaxation time (***τ)*** of the mixtures pointed out that the participation of intermolecular relaxation or overall molecular relaxation is superior in association to intramolecular interactions [35]. Tables 1–3 provided the values of relaxation time and found increasing trend with regard to the chain length [36] of primary aliphatic amines with 2-fluorobenzoic acid. The higher value of relaxation time for all the systems may be attributable to the increase in the effective radius of the rotating unit. Higher value is observed for propyl amine because of its larger size in comparison to methylamine and ethylamine molecules with 2–fluorobenzoic acid. The values of dielectric parameters (ie., ε_0, ε' and ε''), relaxation times (τ_1, τ_0 and τ_2) pointed out that there is a complex formation in the form of intermolecular hydrogen bond between the $H^{+\delta}$ of 2–fluorobenzoic acid and $N^{\delta-}$ of the amino group presented in aliphatic amines due to inter and intra molecular hydrogen bonding.

Table 4. Dipole moment (μ), Activation energy of primary amines with 2-Fluorobenzoic acid in 1,4-Dioxane at 1:1 ratio

System	**Dipole moment**		**Activation Energy**	
	Higasi's Method	**Gopalakrishna's Method**	**□f□□**	**□□f□**
Methyl amine + 2-Fluorobenzoic acid	5.0540	5.7410	13.12	15.23
Ethyl amine + 2-Fluorobenzoic acid	4.8582	5.3951	14.34	17.04
Propyl amine + 2-Fluorobenzoic acid	4.4933	5.9506	16.12	18.76

In the present study, 2–fluorobenzoic acid is chosen as one of the prime component of the mixture because interactions involving halogens have been comprehensively explored in terms of both the elementary perception and fields of applications. [37-39]. The attribution of interactions associating the fluorine atom is still in the discussion [40] because fluorine is the smallest halogen and it is the most electronegative element, with a radius as small as that of hydrogen, and contains low energy orbitals. Together with its low polarizability, these factors mean that covalently bound fluorine has a low tendency to involve in the intramolecular OH···F, CH···F and CH···O interactions are also be taken place, contributing to the stabilization of the different configuration, and dominating the comprehensive hydrogen bonding properties of the OH group [15, 41]. In primary amines, nitrogen is sp^3 hybridized so it has four sp^3 hybrid orbitals. In that, two of them are overlie among *s* orbitals from hydrogens to create N–H single bonds along with two sigma bonds. In addition, sp^3 hybridized orbitals is also overlie by a sp^3 hybridized orbital from carbon to form two C–N sigma bond. The lone pair electrons on nitrogen atom are limited in the last sp^3 hybridized orbital. As a result of sp^3 hybridization, the nitrogen has a tetrahedral shape [42]. In addition, primary amine is that they can make H-bonds among each other along with dipole-dipole interactions and Van der Waals dispersion forces. Hydrogen bonds can form the lone pair between the electronegative nitrogen atom and somewhat positive hydrogen atom in other molecule. Hence, complex formation is more when chain length of primary amines as a result of the noticeable amount of Van der Waals dispersion forces among the larger molecules.

Khan et.al studied molecular interactions between acrylates with 2-substituted benzoic acids [43, 44] and revealed that the relaxation time is invariably higher than either of the polar solutes in the solvent and the values of τ are in the range of 13 to 23 ps. The results obtained in the present study are in agreement with the earlier investigations. The molecular association between aliphatic amines and 2–fluorobenzoic acid is maximum at equal molar concentration and then decreases at the rest of other molar concentrations. From this, we conclude that, the 1:1 complexes are showing predominant effect in all the selected systems in the form of hydrogen bonding. The possibility of hydrogen bonding observed between solute-solute and solute-solvent. Under solute-solute interaction, amino group of aliphatic amines forms hydrogen bonding with OH group of 2-fluorobenzoic acid. Even more remarkable sustainable interactions are the nonbonding F···O interactions also possible in 2-fluorobenzoic acid. For the selected mixtures there is a possibility of solute solvent interaction between hydrogen attached in amino group of aliphatic amines with oxygen present in the polar solvent 1,4-dioxane.

The molar activation free energy of viscous flow (ie., ΔFη) and the free energy of relaxation time (ie., ΔFτ) are determined.

In addition, dipole moments of the selected systems are also calculated using Higasi and Gopalakrishna method. And the values are given in Table−4. Form the observation, the values of $\Delta F\eta$ are found to be higher than the values of $\Delta F\tau$. This is evident that the fact of the process of viscous flow, this involved in both transnational and rotational forms of motion, faced better interference from bystander than dielectric relaxation, which took place only by rotation [45]. The values of relaxation time of a proton donor are rising as the capability of acceptor when increasing the solvent environment. Likewise, for the selected proton acceptor, the value of relaxation time is supposed to be in the increase trend along with the capability of proton donor in the solute [46].

V. CONCLUSION

The systems of primary aliphatic amines (methyl, ethyl and propyl) with 2−fluorobenzoic acid in 1,4−dioxane have been studied with the help of dielectric relaxation time method proposed by Higasi and Gopalakrishna. The dielectric parameters were measured in X-band microwave region. The complex formations in the mixtures have predicted with the values of relaxation time, and they are varies with the different mole ratios and found to be maximum at 1:1 ratio. The interactions among the title molecules are interpreted by means of hydrogen bonding. Hydrogen bonding occurred between the nitrogen in the amino group of amines and hydrogen in the carboxyl group of 2−fluorobenzoic acid. The possibilities of solute-solute and solute-solvent interactions are discussed and the strength of interactions are found to be increased when the chain length of amines increases.

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