Dielectric Relaxation Studies of 2-Alkoxyethanol with o-Anisidine in benzene using frequency domain (X –band) technique

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ABSTRACT

The dielectric relaxation studies have been carried out on binary and ternary systems of 2-alkoxyethanols (2-methoxyethanol, 2-ethoxyethanol and 2-butoxyethanol) with *o*-Anisidine in dilute solution benzene of various molar ratios (1:0,3:1, 2:1, 1:1, 1:2, 1:3 and 0:1) over the frequency at 9.68 GHz in room temperature by using X-Band microwave technique were studied. The dielectric parameters like ε_0,ε',ε'' and ε_∞ are calculated. In addition, the dielectric relaxation times $\tau_{(1)}$,$\tau_{(2)}$ and $\tau_{(0)}$ have been calculated by employing Higasi's method and activation energies $\Delta f\tau$ and $\Delta f\eta$ have been determined using dielectric data. The most likely association between free hydroxyl groups of 2-alkoxyethanols with the aniline group of *o*-Anisidine was studied. The results show that the proton donating ability of 2-alkoxyethanols is decreasing in the order: 2-butoxyethanol >2-ethoxyethanol > 2-methoxyethanol and play an important role in determination of the strength of hydrogen bond is formed.

Key words: Dielectric Relaxation, 2-alkoxyethanols, o-Anisidine and X-Band Microwave Benches.

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INTRODUCTION

Dielectric approach is a powerful tool for the determination of molecular structure. Recently dielectric relaxation behavior of mixtures of polar Molecules under varying conditions of complexation, temperature and environmental factors has evoked considerable interest. The influence of association through hydrogen bonds on the structure of liquids and their relaxation behavior has been studied for a long time[1-4]. Based on the results, models of relaxation process in liquid mixtures have been formulated. The study of association of two polar molecules due to hydrogen bonding from the dielectric relaxation measurements at microwave frequencies are scare[5-8]. Microwave dielectric relaxation studies are useful to investigate molecular and intermolecular motions, solute-solute interaction, solute –solvent interactions and their molecular conformations. In the last two decades, dielectric relaxation behavior of binary mixture of industrial and biological useful associating polar solvents [9-

14]. Hydrogen bond constitutes a very interesting class of intermolecular interactions, which are of extreme importance in many fields of chemistry and molecular biology. "Hydrogen Bonding in Biological Structures" can be used in many ways by biophysicists.The study of the H-bonds of the type O=H --- O=C occupies a position of considerable importance as it relates to the study of biopolymers [15]. Thus the study and knowledge of dielectric properties of the mixtures of o-anisidine with three 2-alkoxyethanol such as In the present work, an attempt has been made to study the nature of molecular interactions in 2-alkoxyethanols with o-Anisidine in benzene using Dielectric frequency domain technique 2-methoxy ethanol, 2-ethoxy ethanol and 2-butoxy ethanol in non-polar solvents is expected to provide useful and vital process parameters for industrial interest. Keeping both the industrial and scientific interests in mind, all attempts have been made in the present work to study the hydrogen bonding between of 2-alkoxyethanol with the o-Anisidine. This study is expected to provide better understanding of the nature of molecular interaction process.

MATERIALS AND METHODS

o-Anisidine, benzene were purchased from E-Merck. 2-methoxy ethanol, 2-ethoxy ethanol and 2-butoxy ethanol were purchased from Sigma Aldrich and used without purification. The static dielectric constants where measured by heterodyne beat method at 303K using a commercial instrument, Dipole meter (supplied by Mittal enterprises – New Delhi). The refractive indexes of all the solutions have been measured by an Abbe's refractometer. The measurement of dielectric constant at an angular frequency (ε_0) and the dielectric constant (ε') and dielectric loss (ε'') have been measured using X-band (9.68 GHz) microwave benches at room temperature. The Viscosities were measured with help of Oswald's viscometer at 303K. The mole ratio of the binary and ternary mixtures of the o-anisidine: alkoxyethanol were always adjusted, in the ratio of 1:0,3:1, 2:1, 1:1, 1:2,1:3 and 0:1 however, keeping the solute concentration in benzene to be constant.

EVALUATION OF DIELECTRIC PARAMETERS

According to Higasi's[9] method, the average relaxation time $\tau_{(1)}$ is described by

$$\tau_{(1)} = \frac{a''}{\omega(a' - a_\infty)}$$

While the overall dielectric relaxation τ_2 and the mean relaxation time τ_0 is given by,

$$\tau_{(2)} = \frac{(a_0 - a')a''}{\omega a''}$$

$$\tau_{(0)} = \sqrt{\tau_{(1)} \times \tau_{(2)}}$$

Where, ω is the angular frequency, a_0, a', a'' and $a_\infty$are defined by the following equations

$$\varepsilon_0 = \varepsilon_{01} + a_0 w_2$$

$$\varepsilon' = \varepsilon_1' + a' w_2$$

$$\varepsilon_\infty = \varepsilon_{1\infty} + a_\infty w_2$$

In which subscript '1' refers to the pure solvent and subscript '2' refers to the solute subscript '0' refers to the static frequency measurements and w_2 is the mass fraction of the solute.

The molar free energies have been calculated using the Eyring's [16] equation,

$$\tau = \left(\frac{h}{kT}\right)\exp\left(\frac{\Delta F_\tau}{RT}\right)$$

$$\eta = \left(\frac{Nh}{V}\right)\exp\left(\frac{\Delta F_\eta}{RT}\right)$$

Where, h is the Plank's constant, k is the Boltzmann constant, N is the Avogadro number, V is the molar volume and Δf_τ, Δf_η are the molar free energies for the dielectric relaxation process and the viscous flow process, respectively.

RESULT AND DISCUSSION

The systems were binary and ternary mixtures of proton donor 2-alkoxyethanols (2-methoxyethanol, 2-ethoxyethanol and 2-butoxyethanol) with proton acceptors (*o*-Anisidine) in dilute solution of benzene of various molar ratios. (i.e, 1:0, 3:1, 2:1, 1:1, 1:2, 1:3 and 0:1) at 9.68 GHz in room temperature were carried out. The dielectric parameters like ε_0,ε',ε'' and ε_∞ are calculated and the dielectric relaxation times are $\tau_{(1)}$,$\tau_{(2)}$ and $\tau_{(0)}$ calculated by using Higasi's method. The activation energies $\Delta F\tau$ and $\Delta F\eta$ for all the systems studied by using dielectric parameters are given the table 1. From the table reveals that the dielectric parameters, dielectric relaxation times and the activation energies are higher value for binary mixture of 2-alkoxyethanols (2-methoxyethanol, 2-ethoxyethanol and 2-butoxyethanol) with benzene (1:0 ratio) system than that of o-Anisidine with benzene (0:1 ratio) system. The above statement suggests that the 2-alkoxyethanols molecules are heavier than that of o-Anisidine molecules. In the case of the ternary systems of 2-alkoxyethanols with *o*-Anisidine are significantly higher than that of binary systems because the hydrogen bond formed between hydrogen atom in the O-H group of 2-alkoxyethanols molecules and nitrogen of o-Anisidine show in Fig 1. Fig 2-3 shows the other possibility of intermolecular H-bond between, 2-alkoxyethanols and *o*-Anisidine molecules of the same species.

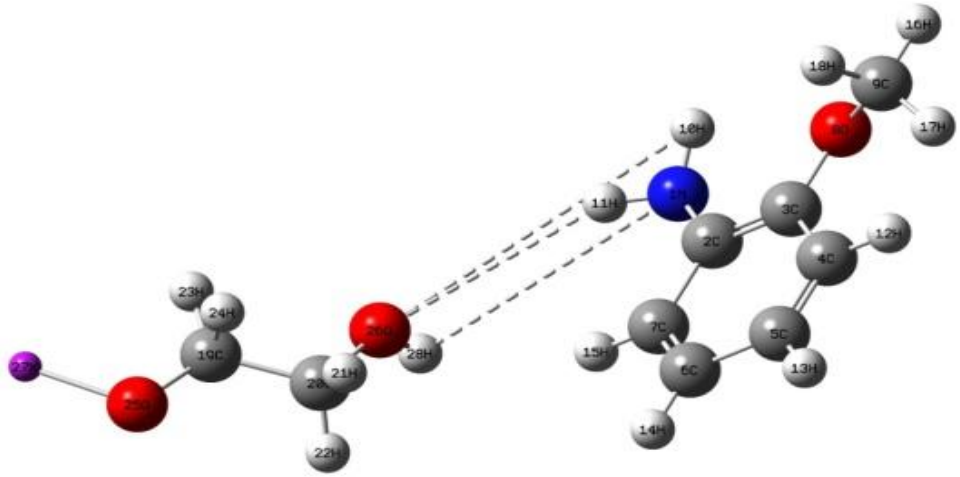

Fig. 1: Hydrogen bonding between 2-alkoxyethanols with *o*-Anisidine.

(X= CH_3 (2-ME), C_2H_5 (2-EE) and C_4H_9 (2-BE))

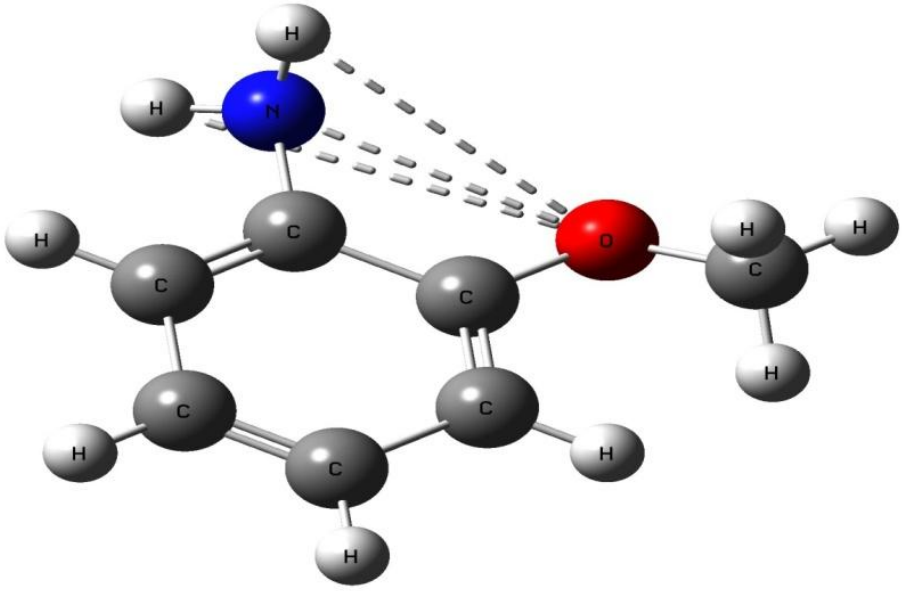

Fig. 2: Intramolecular hydrogen bonding between *o*-Anisidine of the same species.

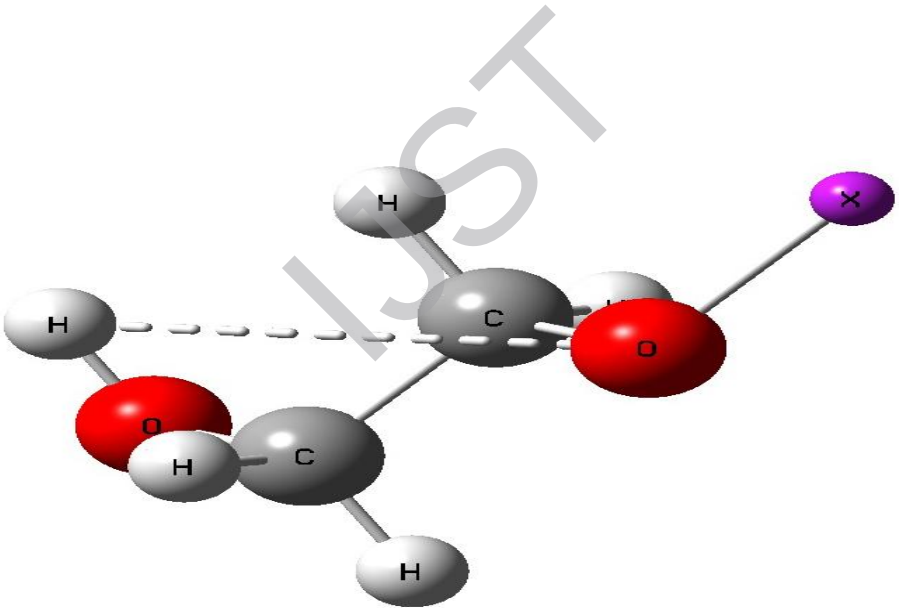

Fig. 3: Intramolecular hydrogen bonding between 2-alkoxyethanols of the same species(X= CH_3 (2-ME), C_2H_5 (2-EE) and C_4H_9 (2-BE))

Table 1 shows, that the values of τ_2 is significantly higher than the values of τ_1 for the binary and ternary mixtures of 2-alkoxyethanols (2-methoxyethanol, 2-ethoxyethanol and 2-butoxyethanol) with *o*-Anisidine in benzene for all the systems studied. The results of above statement suggest that the contribution of intermolecular or overall molecular relaxation τ_2 is longer than that the individual molecular relaxation τ_1. This observed result in this study is in the close agreement with Kalaivani et al., 2009[17].The value of relaxation

time increase with increasing chain length of 2-alkoxy ethanol and acidity of *o*-Anisidine [18-.19].

Table 1.Value of Dielectric constants,Relaxation times and Activation energy for various weight fractions, 2-alkoxyethanol with o-Anisidine in benzene

Ratio	Weight fraction	ε_0	ε'	ε''	ε_∞	Relaxation Time (ps)			Activation energy (KJ/mol)	
						Higasi's Method			$\Delta f\tau$	$\Delta f\eta$
						τ_1	τ_2	τ_0		
2-methoxyethanol										
1:0	0.3012	2.3141	2.2142	0.0812	2.1342	35.12	38.15	40.24	11.87	12.01
1:3	0.3542	2.4123	2.2948	0.1012	2.1523	45.23	55.23	51.24	12.34	13.58
1:2	0.4231	2.4852	2.3122	0.1231	2.1586	48.21	57.21	54.21	12.78	13.75
1:1	0.5213	2.5124	2.3545	0.1345	2.1602	50.12	58.12	57.12	13.12	13.98
2:1	0.6213	2.4945	2.3312	0.1269	2.1654	47.23	56.21	55.32	12.97	13.65
3:1	0.7124	2.4874	2.3214	0.1124	2.1698	46.21	54.21	53.14	12.67	13.24
0:1	0.2541	2.2531	2.1842	0.0712	2.514	31.24	37.23	38.12	10.24	11.25
2-ethoxyethanol										
1:0	0.3212	2.3451	2.2674	0.8422	2.1674	37.24	41.23	43.12	11.98	12.48
1:3	0.3812	2.4345	2.3124	0.1124	2.1612	48.12	57.25	55.21	12.62	13.87
1:2	0.4423	2.5214	2.3542	0.1421	2.1685	50.25	59.32	57.54	12.86	13.93
1:1	0.5521	2.5854	2.3745	0.1542	2.1721	52.75	61.24	60.84	13.23	14.12
2:1	0.6147	2.5441	2.3542	0.1312	2.1845	51.21	59.21	58.21	13.12	13.78
3:1	0.7321	2.5124	2.3314	0.1234	2.1912	49.14	57.24	55.21	12.98	13.45
0:1	0.2541	2.2531	2.1842	0.0712	2.514	31.24	37.23	38.12	10.24	11.25
2-butoxyethanol										
1:0	0.3425	2.3678	2.2874	0.8765	2.1689	39.87	45.41	46.24	12.14	13.21
1:3	0.5123	2.4752	2.3451	0.1324	2.1721	50.24	59.14	58.64	12.85	14.12
1:2	0.4821	2.5745	2.3874	0.1527	2.1788	52.24	60.27	60.24	13.12	14.25
1:1	0.5874	2.6123	2.4021	0.1634	2.1812	54.25	64.87	63.14	13.64	14.98
2:1	0.6754	2.5874	2.3754	0.1421	2.1897	52.14	62.45	60.12	13.31	14.21
3:1	0.7523	2.5721	2.3621	0.1314	2.1956	50.34	60.14	58.24	13.11	14.08
0:1	0.2541	2.2531	2.1842	0.0712	2.5140	31.24	37.23	38.12	10.24	11.25

The result also shows that the molecular association between *o*-Anisidine and 2-alkoxyethanol is maximum at 50:50 mol% ratio and then decreases at other mol%. From this we conclude that the 1:1 complex is dominant in *o*-Anisidine with 2-alkoxyethanol systems. Further τ values get increases as the chain length of the 2-alkoxy ethanol increases. It indicates that τ depends upon viscosity also. The average relaxation time (τ_0) is 74 ps at 1:1 molar ratio for X-band frequency of 9.68 GHz.Our present study of microwave dialectic relaxation $\Delta f\tau$ showed in table a very low value indicating that there is no group rotation in these complexes. Smyth[20] pointed out that the relaxation time of proton donor increases as the acceptor ability of the solvent environment increases. Similarly for a given proton acceptor the relaxation time must increase with the proton donor ability of the donor solute.

Our results are in accordance with this conclusion. From the measurement of free energy of activation for dielectric relaxation $\Delta F\tau$ and the free energy of activation for viscous flow $\Delta F\eta$ for all systems studied it is clear that the free energy of activation for dielectric relaxation $\Delta F\tau$ in lesser then the free energy of a activation flow $\Delta F\eta$ since the relaxation time involves rotation motion only. Whereas the viscosity involves both rational and translational motion for 2-alkoxyethanol with *o*-Anisidine. As the chain length of 2-alkoxyethanol increases the average relaxation time gets increase which was shown in fig:-4 respectively.

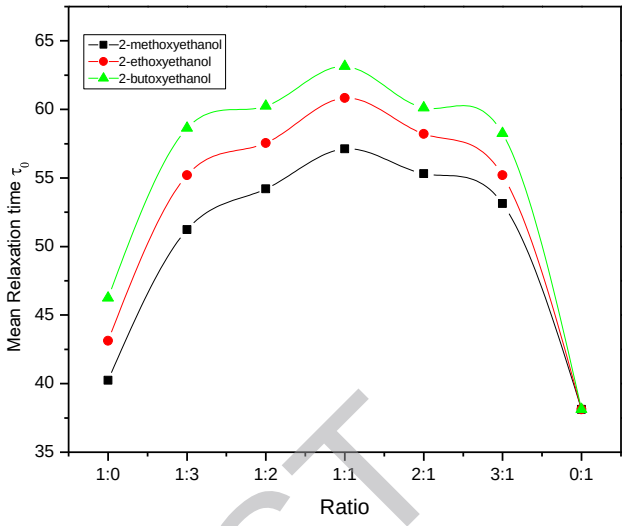

Fig.4: Variation of mean relaxation time with ratio of 2-alkoxyethanol and o-anisidine

CONCLUSION

In this conclusion, the hydrogen bonded complexes of 2-alkoxyethanol with o-Anisidine have been studied in dilute solution of benzene using dielectric relaxation method. The dielectric parameters, dielectric relaxation times and activation energies have been reported and discussed of all studied systems. This study, it may be concluded that the proton donating ability of 2-alkoxyethanol are varying with substitution of methyl group and provide a valuable information of solute-solute interaction system of the specified complexes.

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