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Research Article

DIELECTRIC STUDIES OF BINARY MIXTURES OF ALKOXY ETHANOLS AND ANILINE AT 9.85 GHz MICROWAVE FREQUENCY

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ABSTRACT
Using Surber's technique of measuring reflection coefficient from the air-dielectric boundary of liquid , the dielectric constant ($\in'$), dielectric loss ($\in''$) of 2-Alkoxyethanols with aniline and their binary mixtures for different mole fraction of aniline have been measured at 9.85 GHz microwave frequency at 22^0c. The values of Density (ρ), viscosity (η), Sq refractive index (n_D^2) of binary mixtures as well those of pure liquids are reported. The excess square refractive index (Δn_D^2), viscosity ($\Delta\eta$) and activation energy (ΔEa) of viscous flow have been estimated. These parameters are used to explain the formation of complex in the systems. It is found that the values of dielectric constant ($\in'$) of 2-Methoxyethanol (2-ME), 2-Etoxyethanol (2-EE), 2-Butoxyethanol (2-BE) goes on decreasing due to the presence of additional – CH_2 group.

Key Words: *Dielectric Parameters, Polarization, Binary Mixture, Complex Formation*

INTRODUCTION
2-Alkoxyethonals are monoalkyl ethers of ethylene glycol, known as "cellosolves" are very interesting class of solvent having oxy (-O-) & hydroxyl (-OH-) group in the same molecule. The presence of both groups may form intra and intermolecular hydrogen bonds between –O- and –OH- group of same and different molecules (Sengwa *et al.*, 2006).
Aniline is an organic compound consisting of a phenyl group attached to an Amino group having various applications in the field of medicine, dye industry etc. Therefore to obtain more information regarding the dielectric behavior of 2-Methoxyethanol (2ME), 2-Etoxyethanol (2EE), 2-Butoxyethanol (2BE)] with aniline, this work is undertaken. The dielectric constant ($\in'$) dielectric loss ($\in''$) relate to the inability of the molecules reorient themselves with an alternating electric fields and are both affected by molecular size, composition and relative orientation of functional groups within the molecules. Therefore dielectric investigation of solutions containing varing amount of interacting molecules help to detect the formation and composition of complexes in them.

MATERIALS AND METHODS
Pure samples of 2-Methoxyethanol (2ME), 2-Etoxyethanol (2EE),2-Butoxyethanol (2BE) and Aniline of AR grade were procured from Spectrochem. Pvt ltd. Mumbai and M/s S.D. fine Chemicals, Mumbai, were used without further purification. The binary mixtures of 2ME+Aniline, 2EE+Aniline and 2BE+Aniline, were prepared and kept for six hours in well-stoppered bottles to ensure good thermal equilibrium. The density (ρ) and viscosity (η) of pure components and their mixtures were measured by using pyknometer and Oswald's viscometer respectively. The refractive indices at sodium 'D' line were measured by using Abbe's refractrometer.
The dielectric parameters were measured by using Surber's technique (Sisodia and Raghuwanshi, 1990; Narwade *et al*., 2005) of measuring reflection coefficient from the air-dielectric boundary of liquid at 9.85 GHz microwave frequency at 22^0c.
The free energy of activation (Ea) is obtained by using relation (Hill *et al*., 1968)

$$\eta = \left(\frac{hN}{V}\right) exp\left(\frac{Ea}{RT}\right)$$

And the values of polarization were obtained using formula (Chelkowski, 1980; Job, 1928).

$$P_{12} = \left(\frac{\epsilon' - 1}{\epsilon'' + 2}\right)\left[\frac{M1X1 - M2X2}{\rho}\right]$$

Where, M_1 and M_2 are the molecular weights X_1 and X_2 are the molar concentrations of the constituents of mixture and ρ the density of the mixture.

The excess values of permittivity ($\Delta\varepsilon'$ and $\Delta\varepsilon''$),excess viscosity ($\Delta\eta$), excess squre of refractive index (Δn^2_D) and the excess activation energy (ΔE_a) for Alkoxy ethanol's +Aniline system are calculated by using the relation of the form

$$\Delta Y = Y_m - (X_1Y_1 + X_2Y_2)$$

Where, ΔY is the excess parameter and Y refers to the above mentioned quantities. The subscripts m ,1 and 2 used in the equation are respectively for the mixture, component 1 and component 2. X_1 and X_2 are the mole fraction of the two components in the liquid mixture.

RESULTS AND DISCUSSION

The values of density (ρ), viscosity (η), squre of refractive index (n_D^2), dielectric constant (∈′), loss factor (∈″), loss tangent (Tan δ), activation energy (E_a), and molar polarization (P_{12}) with increasing mole fraction (X) of Aniline in the binary mixture of 2-ME, 2-EE, 2-BE. are listed in table-1,2,3.

Variation of dielectric constant (ε') with molar concentration (X) of Aniline in the mixture is depicted in fig.(1). According to Job ,(1928) if the relationship observed between dielectric constant (ε') and mole fraction (X) for one of the components is not linear in the binary mixture. There is an occurrence of complexation and the curve of dielectric constant (ε') against mole fraction (x) shows a change in slope at the mole fraction corresponding to the complex. In the present investigation, the change in slope occurs for the mole fraction of aniline at X = 0.4 for 2ME + Aniline, at X = 0.5 for 2EE + Aniline and X = 0.6 for 2BE + Aniline indicates that the formation of complexes in the mixture. The same nature is observed in the curve of dielectric loss (**ε"**) against mole fraction of aniline as shown in fig, (2).

Table 1: Values of dielectric parameters of binary liquid mixtures of 2MEandaniline at 22^0c

s. n.	X	Density ρ	Viscosity η c.p.	Squre of R.I. n^2_D	ε'	ε"	Tan δ	E_a	P_{12}
1	0.0000	0.95339	1.54696	1.96394	9.061011	2.36471	0.26097	3.41783	58.1713
2	0.1100	0.96451	1.85462	2.03210	8.10959	2.10536	0.25961	3.52346	56.8525
3	0.2239	0.97384	2.10094	2.10432	7.77267	2.05637	0.26456	3.59608	56.8695
4	0.3418	0.98288	2.36799	2.16890	7.162209	1.87952	0.26242	3.66577	56.0570
5	0.4639	0.98676	2.59801	2.23445	6.624956	1.72793	0.26082	3.71975	55.5175
6	0.5905	0.99515	2.86305	2.29486	6.38018	1.65744	0.25977	3.77632	55.4062
7	0.7219	1.00325	3.12139	2.35929	6.149616	1.60560	0.26108	3.82663	55.6741
8	0.8583	1.00681	3.42223	2.44296	5.794783	1.48776	0.25674	3.88802	55.4243
9	1.0000	1.00870	3.71494	2.51222	5.601826	1.37761	0.24592	3.92800	55.8902

Fig.(3) shows the variation of Tanδ with mole fraction of aniline. Two maximas and a minima were observed for the systems 2ME + Aniline, 2EE + Aniline, 2BE + Aniline. Same type of behavior was

obtained by Deogaonkar *et al.,* (1977). They suggests that the formation of adduct complex is at the minima.

Table 2: Values of dielectric parameters of binary liquid mixtures of 2EEandaniline at 22^0c

s.n.	X	Density ρ	Viscosity η c.p.	n^2_D	ε'	ε''	Tan δ	E_a	P_{12}
1	0.0000	0.99885	3.24089	1.97233	7.568574	1.95597	0.25843	3.848514	61.93623
2	0.13165	1.01521	4.88161	2.06373	7.027055	1.858145	0.26442	4.087058	59.52917
3	0.26132	0.01773	5.72674	2.12771	6.624956	1.759954	0.26565	4.180042	58.25389
4	0.38904	0.01814	5.88367	2.18966	6.38018	1.686815	0.26438	4.195785	57.56672
5	0.51487	0.01795	6.24700	2.25552	6.149661	1.615967	0.26277	4.230679	56.90347
6	0.63884	0.01785	6.90024	2.2888	6.078725	1.62899	0.26798	4.288596	56.84842
7	0.76099	0.01658	4.87118	2.37776	6.009105	1.623672	0.27020	4.085812	56.85338
8	0.88136	0.01522	4.42446	2.43048	5.799663	1.55109	0.26744	4.029798	56.2336
9	1.0000	0.01366	3.78876	2.51222	5.699663	1.53785	0.26516	3.939471	56.53693

Table 3: Values of dielectric parameters of binary liquid mixtures of 2BEandaniline at 22^0c

s.n.	X	Density ρ	Viscosity η c.p.	n^2_D	ε'	ε''	Tan δ	E_a	P_{12}
1	0.0000	0.90037	3.04221	2.00924	4.56626	1.15115	0.25210	3.81167	71.28832
2	0.1705	0.91097	3.34470	2.07815	4.34677	1.08679	0.25002	3.86687	65.93675
3	0.3242	0.92931	3.47871	2.14238	4.47651	1.13494	0.25353	3.88975	63.57216
4	0.4634	0.94252	3.55453	2.20142	4.61283	1.18213	0.25626	3.90230	61.77491
5	0.5901	0.95563	3.71603	2.26153	4.7072	1.19355	0.25355	3.92818	59.80357
6	0.7058	0.97249	3.82869	2.30095	4.90704	1.25896	0.25656	3.94557	58.45691
7	0.8120	0.98570	3.71505	2.38393	5.06597	1.29624	0.25587	3.92803	57.11649
8	0.9097	0.99728	3.69689	2.45235	5.12061	1.29373	0.252650	3.92517	55.35278
9	1.0000	1.0149	3.69728	2.51222	5.47349	1.38634	0.25328	3.92523	54.92745

Such type of behavior may be due to the presence of -O- and –OH- group in 2-ME, 2-EE, 2-BE which is responsible for multiple complexation in the mixture which shows the wobbling nature of curve.

The values of excess dielectric constant (Δε'), fig. (4) are found to be negative. This indicates that 2-Alkoxyethonals and aniline interacts in such a way that the total effective dipoles get reduced forming multimers in the binary mixtures (Corradini *et al.,* 1995) has suggested that the minimum in Δε' values are corresponding to the stable adduct complexation. The 2ME + Aniline, 2EE + Aniline and 2BE + Aniline mixture exhibit the minimum in Δε' values at $X_A \approx 0.46$, $X_A \approx 0.51$, $X_A \approx 0.59$ respectively which is a reliable indication of the formation of complex at these concentration. The negative peak values for 2ME < 2EE < 2BE attributed as the presence of an additional $–CH_2$ group due to which hydrogen bond connectivity between unlike molecules (alkoxyethanols and aniline) becomes stronger.

The values of excess viscosity (Δη), excess activation energy (ΔE_a) are positive indicating strong interactions between 2-Alkoxyethanols with Aniline molecules.

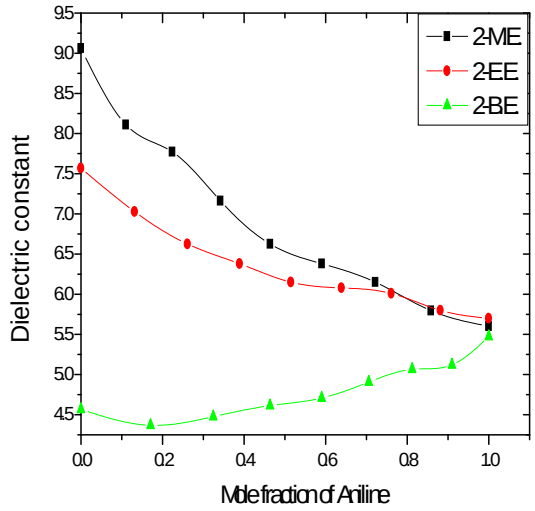

Figure1: Variation of dielectric constant versus mole fraction of

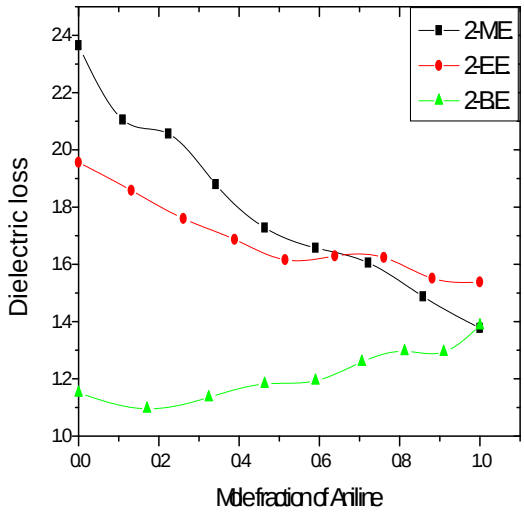

Figure 2: Variation of dielectric loss versus mole fraction of aniline

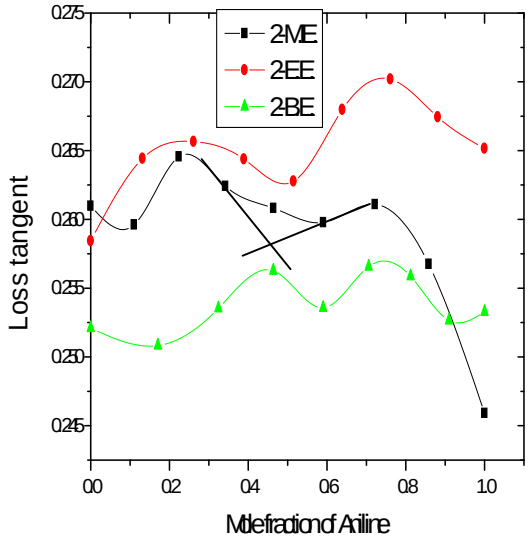

Figure 3: Variation of loss tangent versus mole fraction of aniline

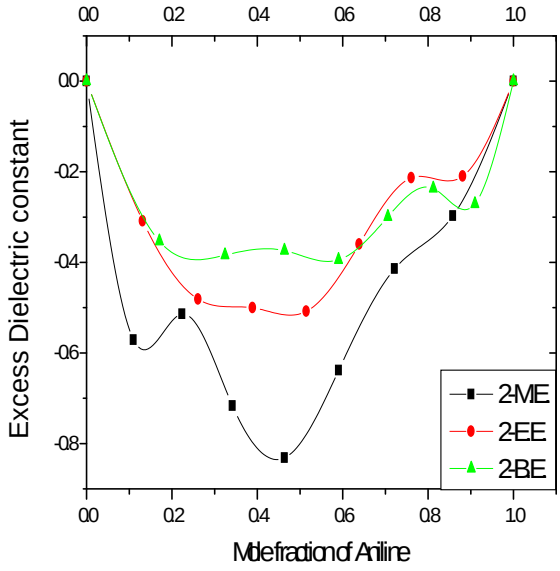

Figure 4: Variation of excess dielectric constant versus mole fraction of aniline

CONCLUSIONS

Values of dielectric parameters, viscosity, activation energy, excess dielectric parameters have been reported for different mole fractions of Aniline in the binary mixture of 2ME + Aniline, 2EE + Aniline, 2BE + Aniline. These studies suggest the strong interaction between 2-Alkoxyethanols with Aniline molecules.

It is found that the values of dielectric constant ($\in'$) of 2ME = 9.061011, 2EE=7.568574,and 2BE=4.56626 goes on decreasing due to the presence of additional $-CH_2$ group[(1)]. This confirms that the dielectric constant values decreases by increasing carbon atoms number (Yilmaz, 2002)

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