Dielectric Relaxation Studies of Binary Liquid Mixtures of a   few Glycols with 1,4-Dioxane

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Abstract: The dielectric relaxation and dipole moment of different concentration binary mixtures of Ethylene glycol, Propylene glycol and Butylene glycol with dilute solutions of 1,4-Dioxane at 33°C. The dielectric relaxation of binary mixtures of polar liquids in non polar solvents at microwave frequencies has been attempted such studies provide meaningful information regarding intermolecular and intramolecular association between the solutes and solvent molecules. The static dielectric constants (ε_0) of glycols like ethylene glycol, propylene glycol and butylene glycol in dilute solutions of 1,4-Dioxane were determined at 303K. The measuring frequency of the dipole meter was 2MHz. X-band and J-band microwave benches operating at 9.52GHz and 7.72GHz were used for determination dielectric permittivity (ε') and dielectric loss factor (ε''). The values of molecular relaxation time (τ_0) and dipole moment (μ) for the different composition of binary mixtures are determined. The comparative values of relaxation time (τ_0) of the two bands (X-Band) and (J-Band) for various binary mixture molecular conformation of these system.
Keywords: Dielectric relaxation, Dipole moment, Hydrogen bonding, Binary mixtures.

Introduction

Microwave dielectric relaxation studies are useful to investigate molecular and intramolecular 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 [1-6] in their pure liquid state and also in non-polar solvents under varying conditions of compositions has evoked considerable interest. It helps in formulating adequate models of liquid relaxation and also in obtaining information about the relaxation processes and formation of molecular interactions in their binary mixtures. Mono alkyl ethers of ethylene glycol, propylene glycol and butylene glycol are commercially known as cellosolves. These are used as industrial solvents, surfactants, detergents and wetting agents. The molecules of these compounds have hydrogen bonding sites and can enter into intra and inter molecular hydrogen bonding giving rise to several different

conformations. In pure liquid state, the molecules of mono alkyl ethers of ethylene glycol, propylene glycol and butylene glycol exist in hydrogen bonded linear structure in dynamical equilibrium [6].The Kirkwood correlation factor(g) values lower than unity with anti parallel ordering of their dipole moment. The values of microwave dielectric relaxation time depend upon the molecular size, shape and intermolecular interactions. The molecular reorientation intermolecular associated liquid requires breaking and reforming of hydrogen bonds in an alternating electric field. Therefore, it is a great interest to study the dielectric behavior different concentration at binary mixtures of the molecules of EG, PG and BG in non polar solvents, to understand the effect of non polar solvent environment on hydrogen bonded binary mixtures with their constituent's concentration variation. Furthermore, the effect of the number of carbon atoms, i.e., chain length, on dielectric relaxation times and the effect of non polar solvent environment on the molecular

dynamics can be explored by measurement of various dielectric parameters.

Earlier in this laboratory dielectric behavior of mono alkyl ethers of EG and of DEG in benzene and carbon tetrachloride solvents [7-10] and mono alkyl ethers of EG and of DEG in their pure liquid state [11-12] were carried out for their molecular conformation in pure liquid state and also in different non polar solvent environment.

For small size polar molecules in non polar solvents, the dielectric measurements at single microwave frequency in the X-band frequency region of their dielectric dispersion frequency range provide fair results regarding their molecular relaxation.

In the present paper, dielectric relaxation study of different concentration at the binary mixtures of the EG, PG and BG were carried out in dilute solutions of non polar solvent 1, 4-Dioxane. The dielectric parameters i.e., relaxation time, distribution parameter, free energy of activation and dipole moment of binary mixtures were determined for their molecular conformations in binary mixtures are,
1. Ethylene glycol+1,4-Dioxane
2. Propylene glycol+1,4-Dioxane
3. Butylene glycol+1,4-Dioxane

Materials and methods:

Mono alkyl ethers of EG, PG and 1,4-Dioxane of puriss AR grade were obtained from Spectrochem Pvt.Ltd Mumbai(India). 1,4-Dioxane was used as solvent. BG of AR grade were obtained from Fluka Company Japan.

The dielectric constant (ε') and dielectric loss factor (ε'') have been measured by using the (X-band) and (J-band) microwave bench at 303K. The static dielectric constant(ε_0) at 2MHz have been measured by WTW Dipole meter DM 01 type based on the principle of heterodyne beat method. It seemed, therefore appropriate to carryout dielectric investigations on glycols such as EG, PG and BG using (X-J band) microwave bench. Refractive index of the binary system was determined using the Abbe's refractometer with sodium D light as source. High frequency of dielectric constant ($\varepsilon_\infty = n_D^2$) for the pure and binary system are obtained from refractometer measurements.

Densities were determined using 10ml specific gravity bottle and weightings were carried out by using Anamed electronic balance. The losses due to evaporation of the sample were minimized. Ostwalt's viscometer was used to determined the viscosity of the liquids and liquid mixtures. The time of flow was measured with help of a Rocar stop watch with an accuracy of 0.1 sec.

The dielectric relaxation time (τ) was calculated by Higasi's method (14). Assuming ε_0, ε', ε'' and ε_∞ vary linearly with weight fraction W_2 of the solute, one obtains,

$$\left. \begin{array}{l} \varepsilon_0 = \varepsilon_1 + a_0 W_2 \\ \varepsilon' = \varepsilon_1 + a'_0 W_2 \\ \varepsilon'' = a'' W_2 \\ \varepsilon_\infty = \varepsilon_{1\infty} + a_\infty W_2 \end{array} \right\} \quad (1)$$

The Debye equation interms of a_0, a', a'' and a_∞ yields two independent equations

$$\tau_{(1)} = \frac{a''}{\omega(a' - a_\infty)} \quad (2)$$

$$\tau_{(2)} = \frac{a_0 - a'}{\omega a''} \quad (3)$$

Where $\tau_{(1)}$ stands for the molecular relaxation time of the complex as a whole and $\tau_{(2)}$ indicates the relaxation of the base molecule.

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

may be called the mean relaxation time. The free energy activation for dielectric relaxation (ΔF_τ) and viscous flow (ΔF_η) have been calculated using Eyring's equation (15)

$$\tau = \frac{h}{KT} \exp\left[\frac{\Delta F\tau}{RT}\right] \quad (4)$$

$$\eta = \frac{NA h}{V} \exp\left[\frac{\Delta F\eta}{RT}\right] \quad (5)$$

Where, h is planck,s constant, K is Boltzmann constant, N is Avagadro number and V is the molar volume.

Result and discussion

The dipole moment of the hydrogen bonded complexes will give information regarding structure and properties of the molecules (16). In the present study like EG, PG and BG are chosen for the study of molecular interaction with the non polar solvent. The dipole moment of the binary liquid systems were calculated by Onsager method.
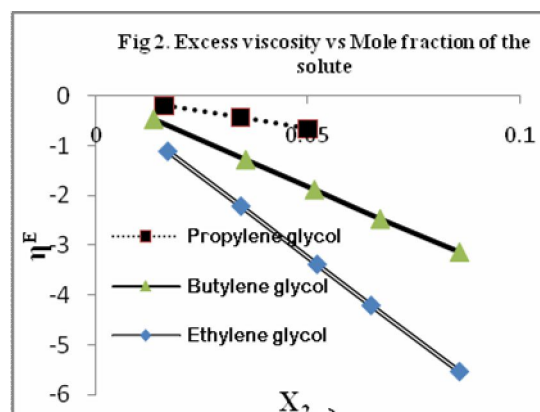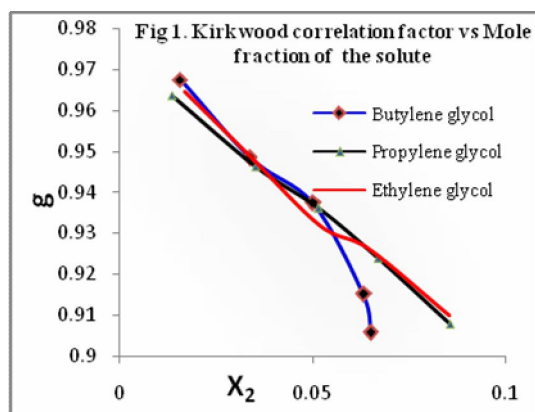
The values are reported in the tables (1). In Onsager method, as the concentration of the solute increases the dipole moment values are decreases from many literatures it is found that Onsager′s equation

gives more satisfactory result (17). The linear correlation factor 'g' is a shape dependent parameter that helps in a quantitative interpretation of the liquid structure. In the case of these glycols with 1,4-Dioxane systems concentration increases 'g' values are decreases. The 'g' values decreases with the dilution can be explained by assuming conversion of α-multimers to β-multimers on dilution of an associated liquid with a non polar solvent, the value of 'g' undergoes a change, signifying the change in the nature of multimerization.

Table – 1:

Variation of $\varepsilon_{12}, \varepsilon_{\infty}, \mu_{(D)}$, g, V^E and η^E with Mole fraction of glycols with 1,4 – Dioxane system

System	Mole Fraction of solute X_2	Static dielectric constant ε_{12}	Dielectric constant at infinite dilution ε_{∞}	Onsager method $\mu(D)$	Linear correlation factor (g)	Excess molar volume (V^E) x $10^{-6} m^3 mol^{-1}$	Excess viscosity (η^E) x 10^{-3} Nsm^{-2}
Ethylene Glycol	0.0160	2.3496	2.0036	2.6674	0.9671	0.6958	-0.1978
	0.0340	2.4732	2.0050	2.4421	0.9482	0.6931	-0.4381
	0.0500	2.5909	2.0064	2.3881	0.9372	0.6579	-0.6535
	0.0630	2.7672	2.0078	2.2173	0.9149	0.6344	-0.8628
	0.0650	2.8922	2.0093	2.0162	0.9055	0.4996	-0.7900
Propylene Glycol	0.0135	2.3543	2.0022	2.7822	0.9636	0.8378	-0.4714
	0.0352	2.5230	2.0050	2.6298	0.9462	0.8206	-1.2827
	0.0514	2.6222	2.0093	2.4720	0.9361	0.8183	-1.8832
	0.0669	2.7418	2.0121	2.4346	0.9238	0.8009	-2.4706
	0.0856	2.8984	2.0135	2.4205	0.9076	0.7898	-3.1334
Butylene Glycol	0.0169	2.3449	2.0022	2.6708	0.9646	1.1583	-1.1224
	0.0341	2.4983	2.0036	2.6189	0.9486	1.0476	-2.2188
	0.0520	2.6582	2.0050	2.5893	0.9319	1.0471	-3.3806
	0.0647	2.7141	2.0064	2.4526	0.9262	0.9189	-4.2002
	0.0855	2.8708	2.0078	2.4125	0.9100	0.7767	-5.5209

Fig 1. Kirkwood correlation factor vs Mole fraction of the solute

Fig 2. Excess viscosity vs Mole fraction of the solute

The above concept was discussed by Garabadu and Swain (18). The excess molar volumes V^E at different concentration for the binary systems were calculated. The V^E values are found to be positive in all the three systems studied and indicate that the expansion factors dominate over the contractive factors.

Excess viscosities are negative over the entire composition range for all the three systems. The negative excess viscosity behavior of these mixtures may be due to change in the liquid associated structure of glycols.

This indicates that dispersion forces are dominant similar results were reported by Mariano et.al (19). From the results of (η^E) values of the molecular interaction is found in the following order BG > PG > EG. The graph connecting excess viscosity (η^E) and mole fraction (X_2) of the solute are given in fig (2).

The dielectric relaxation of binary mixtures of polar liquids in non-polar solvents at microwave frequencies has been attempted by many workers because such studies provide meaningful information regarding intermolecular and intra molecular association between the solutes and solvent molecules (20). The (X – Band) and (J – Band) microwave benches operating at 9.52 GHz and 7.72 GHz. The two bands regarding molecular conformation of these systems.

Ab intio molecular orbital calculations (21) confirmed that the most stable conformers is gauche, stabilized by formation of inter (or) intramolecular hydrogen bond between the two hydroxyl groups above these systems. Thus only one hydroxyl group EG, PG and BG can interact with neighbouring molecule through H-bond (22), the conformation of the EG, PG and BG chain in 1,4 – Dioxane solution with more dilution.

Table – 2:
Variation of Relaxation Time (Higasi's method) Glycols with 1,4 – Dioxane system (X – J band)

System	Mole Fraction of solute X_2	Relaxation time by Higasi's method					
		J-Band (4- 8 GHz)			X-Band (8- 12 GHz)		
		(τ_1) ps	(τ_2) ps	(τ_0) ps	(τ_1) ps	(τ_2) ps	(τ_0) ps
Ethylene Glycol	0.0160	09.3000	11.1483	04.8396	29.6913	5.0687	12.2678
	0.0340	01.4025	45.8630	08.0201	25.9781	10.7454	16.7076
	0.0500	01.3370	83.7550	10.7394	24.0399	17.7729	20.6702
	0.0630	08.4635	25.1511	14.5899	21.0384	25.9454	23.3635
	0.0650	08.6264	31.5861	16.5070	21.0300	31.9198	25.9089
Propylene Glycol	0.0135	22.9828	01.7422	06.3277	19.1249	8.3798	12.6595
	0.0352	01.5862	59.2444	09.6941	13.5332	16.2040	14.8085
	0.0514	02.8930	57.3968	12.8860	16.7979	17.3365	17.0651
	0.0669	03.1551	67.4377	14.5868	26.4839	13.9459	19.2183
	0.0856	04.1083	76.2632	17.7007	23.3852	21.9907	22.6772
Butylene Glycol	0.0135	02.6149	23.3132	07.8079	37.8193	4.73860	13.3870
	0.0352	01.7424	66.4162	10.7576	32.1395	9.48663	17.4612
	0.0514	02.8528	77.1447	14.8350	17.6649	21.9248	19.6799
	0.0669	03.7545	94.2274	18.8091	20.9398	23.3852	22.1287
	0.0856	04.7706	96.6427	21.4721	22.9114	26.7839	24.7721

The gauche conformation of the $OCH_2 - CH_2O$ group predominantly stabilized. Further there exists a specific interaction between oxyethylene, oxypropylene and oxybutylene and it has been suggested that the oxygen – oxygen distance is closely related to the interaction. This favours the formation of an gauche conformer of $OCH_2 - CH_2O$ group of EG, PG and BG molecules with 1,4-dioxane the formation of intermolecular (or) intramolecular H-bonds (23).

In the present investigation the relaxation time (τ) was calculated by Higasi's method. The value of distribution parameter (α) of the binary systems (EG – DX, PG – DX and BG – DX) were determined. Similar results were discussed by many workers (24).The distribution parameter (α) values are lies between 0 and 1. It has been suggested by many workers (25-26) that if a system has non – zero values of 'α' then the relaxation mechanism may be resolved into two separate processes.

The significant α values of the mixtures also suggest that beside the molecular reorientation in the mixture, there is a large probability of the group rotations due to breaking and reforming of hydrogen bonds in dilute solutions. (i.e.,) τ_1, may be due to individual molecular rotation where as τ_2 may be due to over all intermolecular rotations. From both the X – band (8-12 GHz) and J-band (4-8 GHz) analysis, it is found that the relaxation time is higher in X – band than the J-band for each binary system.

It reveals that the most probable relaxation time τ is lower in the J-band when compared to X-band. Hence if the frequency is lower, τ is also lower and if the frequency is higher, τ is also higher. This result was supported by Srivastava and Viji (25). The concentration increases relaxation time (τ_0) increases in two bands (X-J band). Nearly linear increase in the values of τ_0 with X_2.

This suggested that there is significant variation in the size and the characteristics in dilute solution of 1,4 – Dioxane. Further from our results, we can come to the conclusions that the relaxation time values increase with increasing viscosity of the medium.
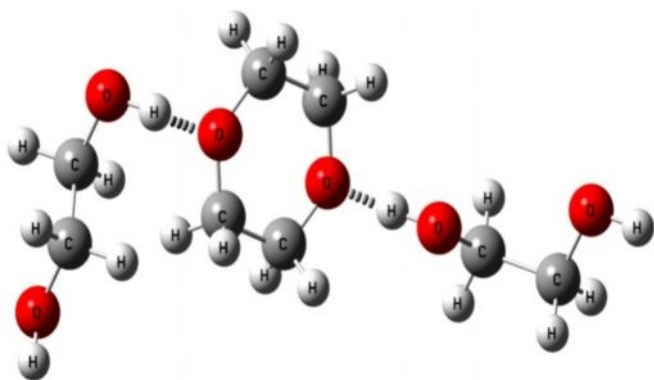

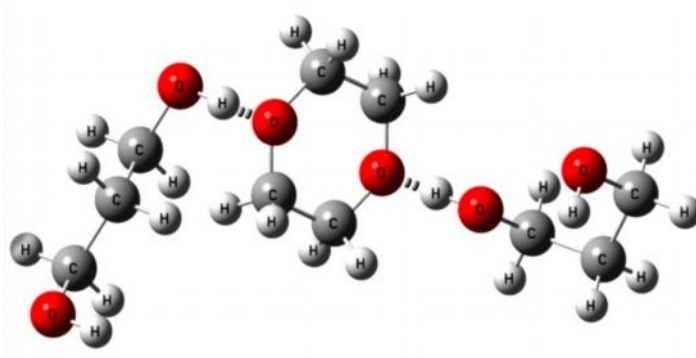**Fig 3. Formation of H-bonding in Ethylene glycol+1,4-Dioxane**

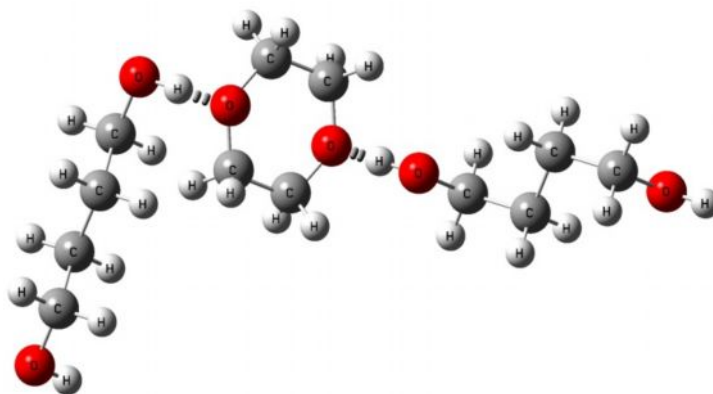**Fig 4. Formation of H-bonding in Propylene glycol+1,4-Dioxane**

Fig 5. Formation of H-bonding in Butylene glycol+1,4-Dioxane

Table – 3:
Activation energies of Glycols + 1,4-Dioxane at 303 K

System	X_2	Activation Energy for Relaxation ($\Delta F\tau$) KJ/mol		Activation Energy for Viscous flow ($\Delta F\eta$) KJ/mol
		X-band	J-band	
Ethylene glycol	0.0160	10.9579	08.6144	14.3851
	0.0340	11.7362	09.8871	14.4205
	0.0500	12.2725	10.6227	14.4242
	0.0630	12.5811	11.3947	14.4520
	0.0650	12.8416	11.7058	14.5561
Propylene glycol	0.0135	11.0372	09.2899	14.4238
	0.0352	11.4322	10.3647	14.4841
	0.0511	11.7896	11.0818	14.5326
	0.0669	12.0890	11.3944	14.5558
	0.0856	12.5059	11.8817	14.6584
Butylene glycol	0.0169	11.1779	09.8195	14.3403
	0.0341	11.8474	10.6270	14.4291
	0.0520	12.1488	11.4367	14.4955
	0.0647	12.4443	12.0347	14.5408
	0.0855	12.7286	12.3681	14.6477

From the measurement of free energy of activation for dielectric relaxation ΔF_τ and free energy of activation for viscous flow ΔF_η for all systems studied. It is clear that the free energy of activation for dielectric relaxation ΔF_τ is always less than the free energy of activation for viscous flow ΔF_η. Since the relaxation time involves rotational motion only. Whereas, the viscosity involves both rotational and translational forms of motion (26).

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