ISSN No-2031-5063 Vol.1,Issue.I/July 11pp.1-4

Research Paper - Physics

Comparative study of Dielectric behavior of binary mixtures of ethylene glycol with benzene and ethanol

Dr.G.Meenakshi
Department of Physics,
KMCPGS, Pondicherry.

T.Beena, Ramya Rajan M.P., Dr.L.Sudha,
Department of Physics, SRM University ,
Ramapuram, Chennai.

Dielectric relaxation and dipole moment of ethylene glycol (ROCH2CH2OH) with benzene and ethanol of different concentrations were studied at microwave frequency of 21.4 GHz at 300K. Different dielectric parameters like dielectric constant (ε) and dielectric loss(ε") at microwave frequency, static dielectric constant (ε0) and optical dielectric constant (ε∞) of these molecules and their binary mixtures of different concentration were measured. The average relaxation time (τ0), relaxation time corresponding to overall molecular reorientation (τ1) and group rotations (τ2) were determined using Higasi's single frequency measurement. It has been observed that relaxation time is very closely related with molecular parameters such as size, shape and nature of the solute molecule. The excess inverse relaxation time was determined to confirm the existence of hydrogen bond in the binary mixtures in non polar solvent. The dipole moment of the binary mixtures was evaluated using Higasi's and Guggenheim's equations. The evaluated values of dipole moments and computed dipole moment values using a simple mixing equation of the polar molecules binary mixtures were used to explore the effect of non-polar solvent environment on molecular interactions between ethylene glycol with benzene and alcohol molecules.

Introduction

Microwave dielectric relaxation and dipole moment studies of polar liquid in non polar solvent are expected to throw more light on the solute –solute and solute –solvent interactions. Several investigators have extensively investigated the interaction properties of binary mixtures of hydrogen bonded molecules by dielectric measurements. The molecules of ethylene glycol ((ROCH2CH2OH) exist with intra and intermolecular hydrogen bonding in dynamic equilibrium in pure liquid state1 .The molecules of ethyl alcohol (C2H5OH) also exist in linear polymeric chain structure with switch over mechanisms due to breaking and making of H-bonds 2,3.The binary mixtures of ethylene glycol with benzene and ethyl alcohol can give rise to different conformations and these confirmation can vary with the change in the concentration of the mixture constituents. The dielectric behaviour of ethylene glycol was investigated in benzene solution over the entire concentration.

Experimental Details

Materials:

Ethylene glycol and ethyl alcohol were obtained from E-Merck grade .Benzene of LR grade was obtained from Qualigens fine Chemicals, India.

Dielectric measurements:

Dielectric constant (ε)and dielectricloss(ε")at microwave frequency, have been measured using Microwave bench(k-band) at 300K . The static dielectric constant (ε0) have been measured using LCR meter. The high frequency limiting dielectric constant (ε∞ =n2) was taken as the square of the refractive index n2 for the pure and binary system are obtained from Abbe's refractometer. The dielectric relaxation time (τ) was calculated by Higasi's method. The densities were determined using 10ml specific gravity bottle and weightings were carried out by using electronic balance.

Data analysis

Excess dielectric constant : The excess dielectric constant (ε E) for binary mixtures is -defined as

$$\varepsilon E = (\varepsilon 0 - \varepsilon\infty)m - [(\varepsilon 0 - \varepsilon\infty)1X1 + (\varepsilon 0 - \varepsilon\infty)2X2]$$

where X is the mole fraction and subscripts m,1 and 2 represents the binary mixtures and components 1 and 2 of the binary mixture respectively.

The excess dielectric constant provides qualitative information4 as follows:

1. $\varepsilon E = 0$ indicates that the mixture constituents do not interact
2. $\varepsilon E < 0$ indicates that the mixture constituents interact so as to reduce the total number of effective dipoles (this suggests that the constituents of the mixtures may vary from multimers regarding to less effective dipoles) and
3. $\varepsilon E > 0$ indicates that the mixture constituents interact in such a way that the effective number of dipoles increases.

Kirkwood correlation factor . The Kirkwood correlation factor g is also a parameter ,which gives the information4 regarding the formation of multimers and ordering of dipoles in pure liquid .In a pure liquid g is given by the expression

$$\frac{4\pi Nd\, g\mu^2}{9kTM} = \frac{(\varepsilon 0 - \varepsilon\infty)(2\varepsilon 0 + \varepsilon\infty)}{\varepsilon 0(\varepsilon\infty + 2)}$$

Where μ is the dipole moment d is the density at temperature T ,M is the molecular weight,k is the Boltzmann constant and N is the Avagadro's number.

Distribution parameter α and the average relaxation time (τ0) were calculated by using Higasi's equation proposed for single frequency measurements in the dispersion region with solute concentration variation in non polar solvent.

The dipole moment of individual polar molecules and their binary mixtures in dilute solutions of non polar solvents were determined using Higasi's equation

$$\mu H = [(27kT/4\pi N)(M/(\varepsilon 1 + 2)^2 d1\,]1/2 \quad (a0 - a\infty)^{1/2}$$

where ε1 and d1 are the values of dielectric constant and the density of non polar solvents respectively and T,the absolute temperature .For binary mixtures ,solute of polar molecules A and B ,M, the molecular weight of the solute is given by the relation

$$M = (X1\, M1\, m/[(1-X1)m1\,]$$

Where X is the mole fraction of the non polar solvent, M ,the molecular weight of the non polar solvent ,m and m1 are the weights of the polar solvents binary mixtures and the non polar solvent respectively.

Result and Discussion

The dipole moment of the hydrogen bonded complexes will give information regarding structure and properties of the molecules. The linear correlation factor g is

a shape dependent parameter that helps in a quantitative interpretation of the liquid structure.

The Kirkwood correlation values(Table 1)greater than unity of ethylene glycol , benzene and ethanol in their pure liquid state confirms that these molecules exist in hydrogen bonded linear structures with parallel dipole alignment in dynamical equilibrium. The ethanol molecule has switch over mechanism in their linear H-bonded polymeric structure .

Table 1 values of dipolement μ and Kirkwood correlation factor for ethylene glycol ,ethanol

Sample	μ	g
Ethylene glycol	2.23	1.69
ethanol	1.85	2.77

The table 2 shows the values of ε0 , ε∞ and ε E of ethylene glycol –ethanol binary mixtures o against the mole fraction of ethanol. The non linear behaviour of against Xe confirms that the structures of the molecules in the binary mixtures changes with the variation

Table 2 Values of static dielectric constant(ε0)and excess dielectric constant (ε E) for various binary mixtures of ethylene glycol and ethanol at different mole fraction

Xe	ε_0	ε_8	ε^E
0.000	17.43	1.97	-
0.246	18.50	1.94	-1.17
0.468	19.98	1.92	-1.37
0.676	20.87	1.90	-1.06
0.848	22.32	1.88	-1.09
1.000	24.12	1.86	-

in mixtures constituents concentration. The findings of non zero ε E shows that the addition of ethanol in ethylene glycol acts as

Table 3 values of effective averaged Kirkwood correlation factor geff and Kirkwood correlation factor gf for ethylene glycol in ethanol.

Volume fraction of ethanol	geff	gf
0.0	1.59	1.00
0.2	1.68	0.95
0.4	1.99	0.99
0.6	2.16	0.907
0.8	2.22	0.96
1.0	2.60	1.00

Table 4 Values of static dielectric constant(ε0)and excess dielectric constant (ε E) for various binary mixtures of ethylene glycol at different mole fraction of benzene Xb

Xb	ε_0	ε_8	ε^E
0.000	14.94	1.96	-
0.246	12.45	1.99	-0.99
0.468	10.98	2.05	-1.20
0.676	8.36	2.09	-1.54
0.848	5.07	2.13	-1.23
1.000	3.54	2.18	-

homogeneous structure breakers and simultaneously there is a formation of complexes between these molecules through H-bonds. The observed negative values of ε E of the mixtures also confirms the effective number of dipoles reduces due to the formation of heterogeneous species. The values of effective Kirkwood correlation factor geff (Table 3)of polar binary mixtures at different volume fraction of ethanol are recorded.

The table 4 shows the values of ε0 , ε∞ and ε E of ethylene glycol –benzene binary mixtures against the mole fraction of benzene . Addition of the benzene acts as a structures breaker of the polar molecules H-bonded structures. In polar solvent or mixture rich in benzene solvent ,the molecules of benzene penetrate into the H-bonded homogeneous polar molecules structures, due to which the structures elongation takes place and hence there is large change in ε0 values at lower concentration Xb.It is found that the ε0 decreases with increases in concentration. Binary mixtures of ethylene glycol with ethanol and ethylene glycol with benzene confirms the H–bond complex in these mixtures, which vary with the variation in mixture constituents' concentration.

References

1.Purohit,H.D.;Sengwa,R.J.J.Mol.Liq 1990,47,53
2.Sengwa,R.J.;Abhilasha;More,N.M.Polymer 2003 ,44, 2577
3.Sengwa,R.J.;Abhilasha;More,N.M. Malhothra S.C.J.Polymer Sci.Part B Polymer Phys.2005,43,1123
4. Sengwa,R.J.;Madhvi,Sonu Sankla,and Shoba Sharma;Bull .Korean Chem.Soc.2006 ,27,718
5.Kumar.S.,Periyasamy.p.,Jeevanandham.P.,Int.J.Chem Tech research 2011,3, 336-375
6. Sengwa,R.J.;Madhvi and Abhilasha .J.Mol.Liq., 2006, 123 ,92
7.Choudhari,A.Choudhari,h.c.andMalhothra Bull .Korean Chem.Soc.2004,25,1403
8.Purohit,H.D.;Sengwa,R.J.J.Mol.Liq 1989,40,237
9.Purohit,H.D.;Sengwa,R.J.J.Mol.Liq 1988,39,43
10. Sengwa,R.J.J.Mol.Liq 1994,62,139

* * * * * * * *