Available online at www.joac.info

ISSN: 2278-1862

Journal of Applicable Chemistry

2016, 5 (6): 1302-1306

(International Peer Reviewed Journal)

Dielectric Parameters and Intermolecular Interactions in Binary Mixture of Hydroxyl Groups in Polar Liquids

K.P. Tiwari

Department of Physics, Agra College, Agra-282002, **INDIA**

Email: drkptiwari@rediffmail.com

Accepted on 12th November 2016, Published online on 27th November 2016

ABSTRACT

A study of dielectric parameters like static dielectric constant, excess dielectric constant, dipole moment, relaxation time and Kirkwood correlation factor for the binary mixtures of ethylene glycol with ethanol of different concentration has been performed at microwave region to confirm the complex formation through hydrogen bonds. Dielectric behavior and dipole moment values of polar molecule binary mixtures were used to explore the molecular interactions between ethylene glycol and ethanol molecules at different concentrations. It is observed that relaxation time is very closely related with molecular parameters and molecular structure of these alcohols systematically change with number of carbon atoms and hydroxyl groups and their position in the molecules of polar liquids. We have developed the mixture of hydroxyl groups of binary compounds with specific concentrations and tried to study their dielectric properties and their molecular interactions. We have tried this prescription on various ionic, covalent and cross compounds also with different mixing proportions at certain temperature. This theory leads to explain the intermolecular behavior of crystals, which can be extended to interpret the molecular interactions of hydroxyl and amino groups in mixture of polar liquids. This approach has proved to be remarkably successful in the study of dielectric parameters of nano- materials. Certain industrial and technical applications are also suggested.

Keywords: Dielectric constant, Dipole moment, Kirkwood correlation factor, Relaxation time, hydrogen bond, Polar liquids.

INTRODUCTION

The dielectric and refracting properties of mixed binary crystals in mixed and complex compounds are found to be of great scientific and technological importance. Numerous attempts have been made to investigate various properties of mixed crystals in the recent past but all these studies are generally confined only to the ionic and covalent families [1, 2]. It is also noticed that dielectric relaxation and dipole moment studies of polar liquid in non-polar solvent are more important to interpret the solute-solute and solute – solvent interactions. Dielectric measurements are also useful to investigate the interaction properties of binary mixture of hydrogen bonded molecules [3]. The molecules of ethylene glycol exist with intra and intermolecular hydrogen bonding in dynamic equilibrium in pure liquid state. The molecules of ethyl alcohol also exist in linear polymeric chain structure with switch over mechanism due to breaking and making of H-bonds [4, 5]. The binary mixtures of ethylene glycol and ethyl alcohol can give rise to different confirmations and these confirmations can vary with the change in the concentration of the mixture constituents. The dielectric parameters of binary mixture of hydroxyl groups were investigated over the different concentrations at constant temperature.

MATERIALS AND METHODS

Theory: The well established isotropic one gap dielectric model for binary solids given by Penn [1], Van-Vechten [2] and frequency dependent dielectric theory of Phillips (8) lead to a generalized expression,

$$n^2 = 1 + (h\,\omega_\rho / Eg) \quad \text{................ (1)}$$

Where ω_ρ is the plasma frequency and Eg is the average energy gap.

In the dielectric studies of matter, one finds that the optical dielectric constant (ϵ_∞) of a compound is closely related to its optical refractive index(n) as [6, 7],

$$\epsilon_\infty = n^2 \quad \text{.................................. (2)}$$

The values of (n) for almost all compounds are experimentally measured. It is also noticed that excess dielectric constant($\epsilon_o^{\,\epsilon}$) of mixture of binary compounds is correlated with concentration as [3, 4, 11, 12],

$$\epsilon_o^{\,\epsilon} = (\epsilon_o - \epsilon_\infty)_m - [(\epsilon_o - \epsilon_\infty)_1\, x_1 + (\epsilon_o - \epsilon_\infty)_2\, x_2] \quad \text{...................... (3)}$$

Here X_1 and X_2 are the mixing proportions of respective compounds where as ϵ_o is static dielectric constant and ϵ_∞ is limiting dielectric constant for binary mixture and suffix m stands for mixture.

The excess dielectric constant provides qualitative information as follows [3, 4]:

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 in constituents of mixtures and may vary from multimers to less effective dipoles.
3. $\varepsilon^E > 0$ indicates that the mixture constituents interact in such a way that the effective number of dipoles increases.

On the basis of static dielectric constant the Kirkwood correlation factor g is determined theoretically for liquid mixture by following expression which gives the information [4] regarding the information of multimers and ordering of dipoles in pure liquid as,

$$\frac{4\pi Nd}{9KTM}\mathbf{g}\,\mathbf{u}^2 = (\varepsilon o - \varepsilon\infty)(2\varepsilon o - \varepsilon\infty)/(\varepsilon o(\varepsilon\infty + 2)2 \quad \text{....................(4)}$$

Here (u) is the dipole moment; (d) is the density of compound at temperature (T), (M) is the molecular weight,(k) is the Boltzmann Constant and (N) is the Avogadro's number. It is also noticed that

$$\mathbf{U}_l^2 = g\ \mathbf{u}_g^2$$

Here $\mathbf{U}_l$ is dipole moment of liquids, $\mathbf{u}_g$ dipole moment in gas phase and g is the correlation factor. This factor g provides the information about formation of multimers in liquids.

The dipole moment of individual polar molecules and their binary mixtures in dilute solutions of solvents were determined using Higasi's equation[13]

$$U_H = [27kT/4\pi N)\,(M/(\varepsilon_0+2)^2\, d_1]^{1/2}\,(a_0.a_\infty) \quad \text{.....................(5)}$$

Whereas the average relaxation time (τ_0) was calculated using Higasi's equation proposed for single frequency measurements with solute concentration variation in non-polar solvents.

For binary mixtures

$$M = (X_1M_1m/[(1-X_1)m_1] \quad \text{..............................(6)}$$

Where X is the mole fraction of the non-polar solvent, M, is the molecular weight of the non-polar solvent, m and m_1 are the weights of the polar solvent binary mixtures and the non-polar solvent respectively.

Experimental Measurements: The static dielectric constant (ε_o) have been measured using LCR meter where as dielectric constant (ε) and dielectric loss (ε'') at microwave region have been measured using microwave bench at 250 K. The high frequency limiting dielectric constant for the pure and binary mixtures is obtained by measuring refractive index (n) using Abbe's refractometer. Higasi's equation is used to compute relaxation time.

RESULTS AND DISCUSSION

The optical refractive index and high frequency dielectric constant of compounds vary due to variation in intermolecular interactions. It is noticed that Kirkwood correlation factor is a shape dependent parameter that helps in a quantitative interpretation of the liquid structure (Table 1).

Table-1: Dipole moment (u) and Kirkwood correlation factor (g) for ethylene glycol and ethanol

Hydroxyl Group Compounds	**u**	**g**
Ethylene glycol	2.20	1.62
Ethanol	1.80	2.67

The Kirkwood correlation values greater than unity of ethylene glycol, and the ethanol in their pure liquid state confirm that these molecules exist in hydrogen bonded linear structures with parallel dipole alignment in dynamical equilibrium. The dipole moment of the hydrogen bonded complexes will give information regarding structure and properties of molecules. The non– linear behavior of excess dielectric constant (ε^E) for binary mixtures against mole fraction(Xe) confirms that the structure of the molecules changes with the variation in mixture constituents (Table 2).

Table- 2. Static dielectric constant (ε_0) and excess dielectric constant (ε^E) for various binary mixtures of ethylene glycol and ethanol at different mole fractions (Xe).

Xe	ε_0	ε_∞	ε^E
0.100	13.43	1.67	-
0.225	18.20	1.84	-1.13
0.450	19.78	1.82	-1.30
0.650	19.87	1.87	-1.04
0.850	22.12	1.80	-1.08
1.000	23.92	1.83	-1.08

It is also noticed that non-zero (ε^E) shows that the addition of ethanol in ethylene glycol proves the 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 reduce due to the formation of heterogeneous species. The values of effective Kirkwood correlation factor (g_{eff}) of polar binary mixtures at different volume fraction of mixtures shows that the ε_0 decreases with the increase in concentration. A binary mixture of ethylene glycol with ethanol confirms the H- bond complex in these mixtures at different mole fractions, which vary with the variation in mixture constituent's concentration. Our results are in better agreement with other workers [13].

Table-3: Effective Kirkwood correlation factor (geff) and Kirkwood correlation factor (g) of ethylene glycol in ethanol at different volume fractions.

Volume fraction of ethylene glycol and ethanol	g_{eff}	g
0.100	1.59	0.96
0.225	1.63	0.93
0.450	1.89	0.99
0.600	2.12	0.91
0.850	2.16	0.96
1.000	2.54	1.00

APPLICATIONS

These results are useful to explain the intermolecular behavior of crystals, which can be extended to interpret the molecular interactions of hydroxyl and amino groups in mixture of polar liquids. This approach has proved to be remarkably successful in the study of dielectric parameters of nano- materials. This theory can be useful to define shape, size and nature of solute molecules. This theory is also useful to confirm the existence in hydrogen bond in binary mixtures.

ACKNOWLEDGEMENTS

The author is thankful to University Grants Commission, New Delhi for the financial assistance for this work under UGC major research project scheme.

REFERENCES

[1] D.R. Penn, Wave- Number dependent dielectric function of semiconductors, *Phys. Rev*, **1962,**128, 2093.

[2] J.A.Van-Vachten, Quantum Dielectric Theory of Electro-negativity in Covalent Systems, II. Ionization Potentials and Interband Transition Energies, *Phys. Rev*, **1969**, 187, 1007.

[3] R.J. Sengwa, A. More, N.M. Malhotra, *S.C. J. Poly. Sci, Part B*, **2005,** 43, 1123.

[4] R.J. Sengwa, Madhavi, S. Sankla, S. Sharma, Characterization of Heterogeneous Interaction Behaviour in Ternary Mixtures by Dielectric Analysis: The H-Bonded Binary Polar Mixture in Non-Polar Solvent, *Bull. Korean Chem. Soc*, **2006**, 27, 718.

[5] S. Kumar, P. Periyasamy, P. Jeevanadham, *Int., J.Chem Tech research*, **2011**, 3, 336-375**.**

[6] J. Shanker, G.D. Jain, Analysis of the dielectric properties of mixed alkali halide crystals, *Phys. Status Solidi B*, **1983**, 119, 185.

[7] J. Shanker, S.C**.** Sharma, Evaluation of Electronic Dielectric Constant and Fractional Ionic Character of Mixed Alkali Halide Crystals, *Phys. Status Solidi B*, **1986**, 136, 505.

[8] J.C.Phillips, Ionicity of the Chemical Bond in Crystals, *Rev. Mod. Phys*, **1970**, 42, 317**,**

[9] O.F.Mossotti, Analytical discussion of the influence with the action of a dielectric medium exists on the distribution of the electricity on the surfaces of electric bodies dispersed in it, *Mem. Soc. Italy Sci (Modena)*, **1850,** 74, 49.

[10] S.T. Pantelides, Mechanisms That Determine the Electronic Dielectric Constants of Ionic Crystals, *Phys. Rev. Lett*, **1975**, 35, 250 .

[11] K.K. Sarkar, S.C. Goyal, Quantum-dielectric behavior of $A^N B^{8-N}$ binary-Solids, *Phys. Rev,* **1980,** 21, 879**.**
[12] K.P. Tiwari, K.K. Sarkar, Correlation between electronic dielectric and refracting properties of binary solids, *Ind. Journ. Pure and appl. Physics*, **2007,** 73**,** 169.
[13] R.Sengwa, Dielectric behavior and relaxation in Poly water mixtures studied by timed domain refrectrometere, *J.Polymer International, (U.K.),* **2004,** 53,744-748.

AUTHOR ADDRESS

1. **Dr. K.P. Tiwari**
Department of Physics,
Agra College, Agra – 282002, India.
E-mail: drkptiwari@rediffmail.com