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Binary Interaction Study of Polar Liquids at Different Temperatures

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Abstract: Dielectric constant of binary mixtures has been carried out at low frequency at different temperatures. The liquids used in the study were ethanol, methanol and sodium chloride. To confirm interaction, orientation of the dipoles and intermolecular interaction between the mixtures the excess dielectric constant, Kirkwood correlation factor and Bruggeman factor of the mixtures have been calculated and reported in the study. The measurements have been carried out at 100 MHz frequency using a wet sensor. The dielectric constant of the binary mixtures increases with increasing the concentration of the NaCl and decreases with increase in temperature. The results also show the presence of intermolecular interaction in the mixtures.

Keywords*:* Dielectric constant; Excess properties; Binary mixtures; Alcohols- NaCl mixtures.

I. INTRODUCTION

The dielectric constant is a physical property, which is influenced by interatomic and intermolecular attractions. It is a measure of solvents efficiency for separating the electrolytes into the ions. Solvents with high dielectric constants encourage complete dissociation of the electrolytes where as in solvents of low dielectric constants, considerable ion pairing occur [1]. The behavior of electrolytes in solutions could be strongly affected by the dielectric constant of the medium and this property could be used as a predictive tool in practice. Mixed solvents have been employed in different fields including pharmaceutical and analytical sciences. The knowledge of dielectric constant of mixed solvents is required to predict the drugs solubility and chemical solubility in water – cosolvent mixture and the analytes behavior in analytical methods like capillary electrophoresis and ion chromatography [2].

Drug solubility in mixed solvents [3-5] acid dissociation constants of drugs [6], chemical stability of pharmaceuticals [7] and the concentration of a drug in plasma from mixed solvent vehicles could be explained considering dielectric constant of the solvent system. The effect of dielectric constants on acid conversion of sucrose [8], sedimentation rate of concentrated suspensions [9], oxidation–reduction function of a cytochromec protein [10] and photoisomerisation reaction [11] have also been reported. In addition, electroosmotic flow and electrophoretic mobility of analytes in capillary electrophoresis were explained using dielectric constants as an independent variable [12, 13]. A comprehensive review on the applications of dielectric analysis of pharmaceutical systems has been published by [14].

Accurate measurement of these properties can provide scientists and engineers with valuable information that allows them to properly incorporate the material into its intended applications or to monitor a process for improved quality control. The permittivity is the fundamental property of the material and is independent of the measurement technique. The interpretation of dielectric behavior of a material in terms of its molecular structure is a scientific objective. The dielectric properties are essential and useful in a vast area of physical and biological sciences, engineering technologies [15, 16].

In the present work, the dielectric constants of the binary mixtures have been reported at 293, 298 and 303K temperatures. To understand the behavior of electrolytes in mixtures the excess dielectric constant (ε^E), Kirkwood correlation factor (g^{eff}) and Bruggeman factor (f_B) have also been calculated from the dielectric constant and reported in the study.

II. EXPERIMENTAL

The chemicals used in the present investigation are of spectroscopic grade with 99.9% purity. One mole solution of Nacl was prepared by using standard procedure. The solutions were now prepared by mixing 1 mole solution of Nacl in ethanol and methanol, at eleven different volume percentages of Nacl solution with ethanol and methanol as 0 to 100% in steps of 10%. The temperature controller system with water bath has been used to maintain the constant temperature within the accuracy limit of ± 2°C. The sample cell is inserted into a constant temperature bath and the water of constant temperature using a temperature controller system is circulated.

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Measurement of dielectric constant

The static dielectric constants of the binary solutions were measured using a wet sensor. It is based on the principle of frequency domain reflectometry (FDR) technique. When power is applied to the sensor, it creates a 100 MHz frequency signal. This signal is then applied to a pair of stainless steel rods, which transmit an electromagnetic field in to the mixture. The field passes easily through the mixture resulting in stable voltage output that acts as a simple sensitive measure of the dielectric constant. Each measurement was repeated at least five times and the average value of that reading was taken as a dielectric constant of that solution.

Study of excess dielectric constant

The information related to the excess dielectric constant of the binary mixtures was obtained from the excess properties [17] of the mixture. The excess dielectric constant is defined as:

$$\varepsilon^{E} = (\varepsilon_{O})_{m} - [(\varepsilon_{A} \cdot X_{A}) + (\varepsilon_{B}.X_{B})] \qquad (1)$$

Where X is the volume fraction and suffix m, A, B represents a mixture, liquid A (ethanol or methanol) and liquids B (1 mole NaCl solution) respectively. Excess dielectric constant provides qualitative information about the formation of new structure in the mixture as follows:

i) $\varepsilon^E = 0$: indicates that solution A and B do not interact.

ii) $\varepsilon^E < 0$: indicates that solution A and B interact is in such a way that the effective dipole moment gets reduced.

iii) $\varepsilon^E > 0$: indicates that solution A and B interact in such a way that the effective dipole moment increases.

Study of Kirkwood correlation factor

The Kirkwood correlation factor [18] provides information regarding the orientation of the electric dipoles in polar liquids.

For a pure polar liquid, the Kirkwood correlation factor "g" may be obtained by the expression

$$\frac{4\pi N\mu^2\rho}{9KTM} g = \frac{(\varepsilon_0 - \varepsilon_\infty)(2\varepsilon_0 + \varepsilon_\infty)}{\varepsilon_0(\varepsilon_\infty + 2)^2} \qquad \textbf{(2)}$$

Where μ is dipole moment, ρ is density at temperature T, M is molecular weight, K is Boltzman constant, N is Avogadro's number, ($\in_s$) is the static dielectric constant and ε_∞ is the dielectric constant at high frequency, often represented by the square of the refractive index.

Modified forms of this equation have been used to study the orientations of electric dipoles in the binary mixtures are given by [19, 20] two such equations used are as follows:

$$\frac{4\pi N}{9kT}\left(\frac{\mu^2{}_M\rho_M}{M_M}X_M + \frac{\mu^2{}_F\rho_F}{M_F}X_F\right)g^{eff} = \frac{(\varepsilon_{0m} - \varepsilon_{\infty m})(2\varepsilon_{0m} + \varepsilon_{\infty m})}{[\varepsilon_{0m}(\varepsilon_{\infty m} + 2)^2]} \qquad (3)$$

Where "g^{eff}" is the Kirkwood correlation factor for a binary mixture. g^{eff} varies between g_M and g_F.

$$\frac{4\pi N}{9kT}\left(\frac{\mu^2{}_M\rho_M g_M}{M_M}X_M + \frac{\mu^2{}_F\rho_F g_F}{M_F}X_F\right)g^{f} = \frac{(\varepsilon_{0m} - \varepsilon_{\infty m})(2\varepsilon_{0m} + \varepsilon_{\infty m})}{\varepsilon_{0m}(\varepsilon_{\infty m} + 2)^2}) \qquad (4)$$

g_M and g_F are assumed to be affected by an amount "g^f" in the mixture. $g^f = 1$ for an ideal mixture and deviation from unity may indicate the interaction between the two components of the mixture.

Study of Bruggeman factor

Static dielectric constant of two mixture must lie somewhere between two extremes corresponding to static dielectric constant of two liquids. In order to understand the dipole interaction in the mixture of two liquids a various mixture formula has been proposed [21]. Bruggeman mixture formula [22, 23] can be used as first evidence of molecular interactions in the binary mixture. The effective volume of the solute gets modified by solute – solvent interactions and is best illustrated by the non-linearity of Bruggeman formula. The static dielectric constant ($\in_s$) of the mixtures is related to the Bruggeman mixture formula with the volume fraction of solute which indicates the interaction between solvent and solute. This formula states that static dielectric permittivity of binary mixture ($\in_{sm}$), solute ($\in_{sB}$) and solvent ($\in_{sA}$) can be related to volume fraction of solvent (V) which indicates the interaction between solvent and solute in the mixture and it is given by [24]

$$FBM = \left(\frac{\varepsilon sm - \varepsilon sB}{\varepsilon sA - \varepsilon sB}\right)\left(\frac{\varepsilon sA}{\varepsilon sm}\right)^{1/3} = 1 - V \qquad (5)$$

Where 'V' is the volume fraction. In fact, mole fraction is a qualitative measure of the volume fraction of the solute. εsm, εsA and $\varepsilon sB$are static dielectric constant values of mixture, solution A (solvent) and solution B (solute) respectively.

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According to above equation linear relationship is expected in the Bruggeman factor **(**F_{BM}) and (V). Any deviation from this linear relation indicates molecular interaction [25]. When both the solvent and the solute happen to be polar liquids, the Bruggeman equation has to be modified as;

$$FBM = 1 - [a - (a - 1)V\,]\,V \qquad (6)$$

Where 'a' is the interaction factor. The relative change in value of 'a' reveals the amount of interaction between solute and solvent as follows:

i) a >1: indicates that the effective microscopic volume of solvent gets more than the actual volume . The solute exerts a repulsive force on the system.

ii) a <1: indicates that the effective microscopic volume of solvent gets less than the actual volume. The solute exerts an attractive microscopic force on the system.

iii) a =1: indicates that there is no change in effective microscopic volume of the system and that corresponds to the ideal Bruggeman mixture factor.

III. RESULTS AND DISCUSSION

The variation in experimental values of dielectric constants of ethanol – NaCl and methanol – NaCl binary mixtures is presented graphically in Fig. 1 and 2 respectively.

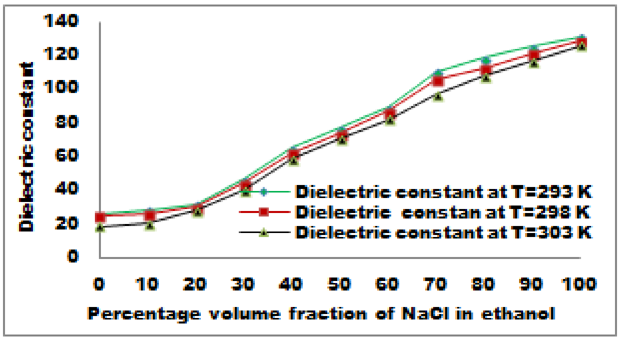

Fig. 1. Variation in dielectric constant of ethanol -NaCl binary mixture at different temperatures.

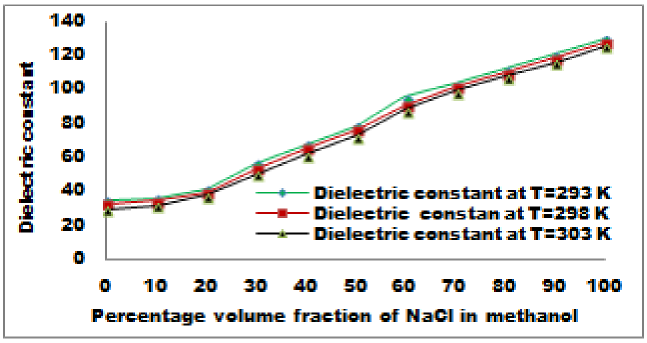

Fig. 2. Variation in dielectric constant of methanol -NaCl binary mixture at different temperatures.

From the experimental values it is noted that the dielectric constant (ε_s) of binary mixtures increases with increase in percentage volume of NaCl and decreases with increase in temperature. The increase in dielectric constant with percentage volume of NaCl may be due to the extent of ion association in the electrolytes (Wang and Anderko, 2001) and decrease in dielectric constant with temperature may due to rapid fall in orientation polarization, because an increased thermal motion reduces the alignment of the permanent dipoles [26].

From Figs. 1 and 2, it is also observed that, the dielectric constant of binary mixture increases with increase in volume fraction of NaCl for entire volume fraction range at the studied temperatures. The increase in dielectric constant may be due to decrease in size and shape of the complex molecules. This could be attributed to the increase in the number of dipoles in the complex, which may lead to an increase in the volume of the rotating molecules [27, 28]

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Excess (ε^E) dielectric constant provides significant information regarding interaction between the polar-polar liquid mixtures. Excess dielectric constant of ethanol – NaCl and methanol – NaCl binary mixtures was calculated using equation (1) and graphically illustrated in Fig. 3 and 4 respectively.

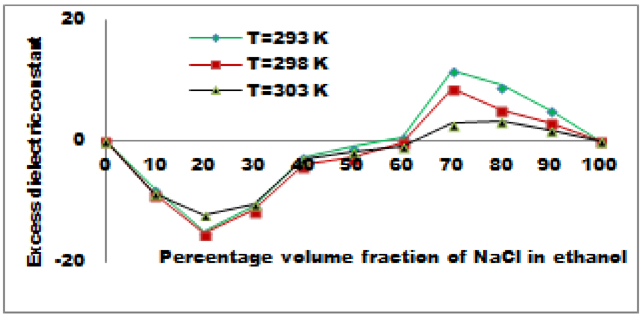

Fig. 3. Variation in excess dielectric constant of ethanol -NaCl binary mixture at different temperatures

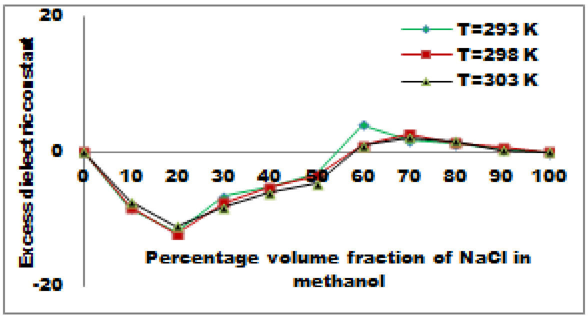

Fig. 4. Variation in excess dielectric constant of methanol -NaCl binary mixture at different temperatures.

From excess dielectric constant figures it is seen that, the excess dielectric constant is negative in ethanol and methanol rich region for the studied temperatures. This indicates that in ethanol and methanol rich region, the mixture of ethanol – NaCl and methanol – NaCl solutions interacts in such a way that the effective dipole moment decreases. The negative values of excess dielectric constant (ε^E) suggest that the effective number of dipoles in the mixture might be smaller than the corresponding average number in the pure liquids, probably due to the creation of new structure leading to a lower macroscopic permittivity. From excess dielectric constant figures it is also noted that, the excess dielectric constant (ε^E) is positive in NaCl rich region at the studied temperatures. This indicates that in Nacl rich region, the mixture of ethanol – NaCl and methanol – NaCl solutions interacts in such a way that the effective dipole moment increases. The positive values of excess dielectric constant (ε^E) suggest that the effective number of dipoles in the mixture might be greater than the corresponding average number in the pure liquids, probably due to the creation of new structure leading to a higher macroscopic permittivity [29, 30]. The Kirkwood angular correlation factor (g^{eff}) for various concentrations of the mixtures of ethanol – NaCl and methanol – NaCl at 295, 298, and 303K are illustrated graphically in Fig. 5 and 6 respectively.

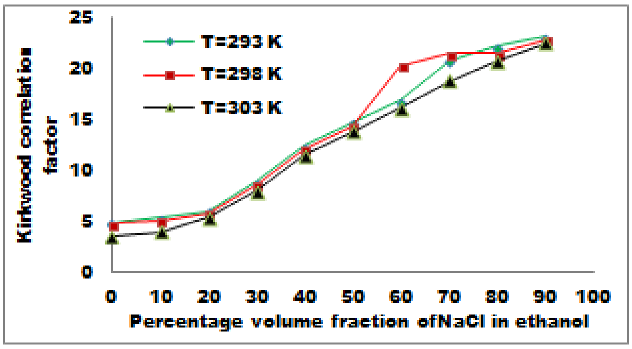

Fig. 5. Variation in Kirkwood correlation factor of ethanol -NaCl binary mixture at different temperatures.

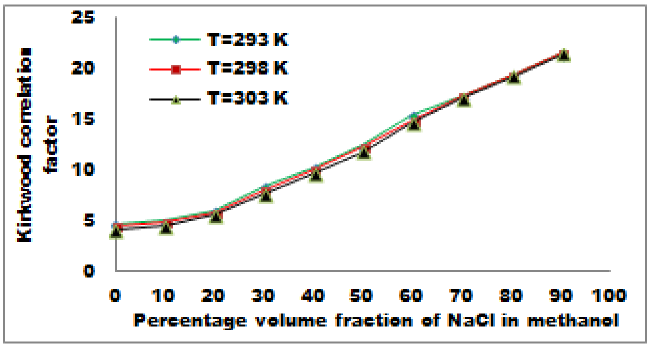

Fig. 6. Variation in Kirkwood correlation factor of methanol -NaCl binary mix ture at different tempera tures

From Figures it is observed that, the g^{eff} values of the binary mixtures are greater than 1 ($g^{eff} > 1$), for entire volume fraction range and at the studied temperatures; which indicates that in the binary mixtures the dipoles pairs have been formed in such a way that their orientation is parallel for entire volume fraction of NaCl [31,32]. Bruggeman factor values of ethanol – NaCl and methanol – NaCl at 295, 298, and 303K temperatures are given in Fig. 7 and 8 respectively.

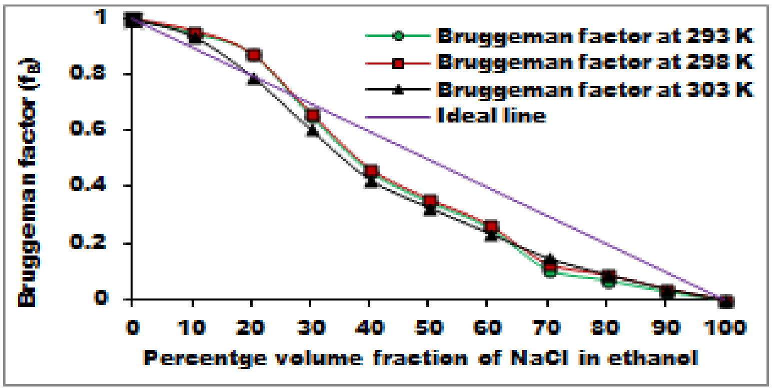

Fig. 7. Variation in Burggeman factor of ethanol - NaCl binary mix ture at different tempera tures.

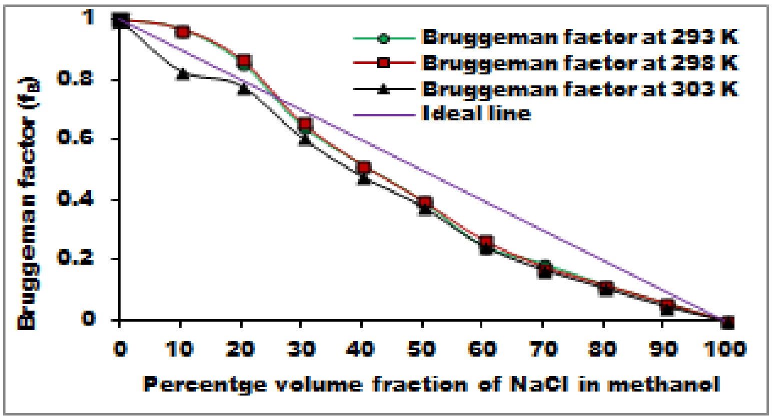

Fig. 8. Variation in Burggeman factor of methanol -NaCl binary mix ture at different temperatures

From Figures, it is noted that, there is a deviation from the linear relation for both the binary mixtures, which gives the evidence of presence of molecular interaction in the binary mixtures. It is also observed that the values of ‘a’ are smaller than 1 (i.e. $a < 1$), indicates that the effective microscopic volume of solvents (ethanol and methanol) gets less than the actual volume, and the solute (NaCl) exerts an attractive microscopic force on the system [32].

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IV. CONCLUSION

The dielectric constant of both the binary mixtures increases with increasing the percentage volume of NaCl. Excess permittivity is negative in ethanol, methanol rich region and positive in NaCl rich region. In the mixture, the dipole pairs are formed and orient in parallel direction for entire volume fraction range of NaCl which is confirmed from the (g^{eff}) values. The Bruggman factor shows there is deviation from the linear relation for both the binary solutions that gives the evidence of molecular interactions in mixtures and NaCl exerts an attractive microscopic force on the system.

Conflicts of interest: There are no conflicts to declare.

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Captions to the Figures

Fig. 1. Variation in dielectric constant of ethanol -NaCl binary mixture at different temperatures.
Fig. 2. Variation in dielectric constant of methanol -NaCl binary mixture at different temperatures.
Fig. 3. Variation in excess dielectric constant of ethanol –NaCl binary mixture at different temperatures.
Fig. 4. Variation in excess dielectric constant of methanol -NaCl binary mixture at different temperatures.
Fig. 5. Variation in Kirkwood correlation factor of ethanol -NaCl binary mixture at different temperatures.
Fig. 6. Variation in Kirkwood correlation factor of methanol -NaCl binary mixture at different temperatures.
Fig. 7. Variation in Burggeman factor of ethanol - NaCl binary mixture at different temperatures.
Fig. 8. Variation in Burggeman factor of methanol -NaCl binary mixture at different temperatures.

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