

DIELECTRIC RELAXATION STUDY OF BINARY MIXTURES AT DIFFERENT TEMPERATURES

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Received: 07 Apr 2016 Revised and Accepted: 22 Jul 2016

ABSTRACT

Objective: The objective of this work is to study the intermolecular interaction and hydrogen bonding of the two binary mixtures at different temperatures which are determined from static dielectric constants and their excess properties.

Methods: Dielectric measurements have been carry out using a sensor which is based on frequency domain reflectometry technique. The excess dielectric properties, Kirkwood correlation factor and Bruggeman factor of the binary mixtures have also been calculated and reported in this paper.

Results: The positive and negative behavior of excess dielectric permittivity and variation in linear relation in Bruggeman factor suggests the presence of intermolecular interaction in the binary mixtures. The angular Kirkwood correlation factor confirms the parallel and antiparallel orientation of the dipoles in the mixtures.

Conclusion: The static dielectric constant of binary systems increases with the addition of the volume fraction of water and decreases with increase in temperature. From excess properties, it is confirmed that there is an intermolecular interaction between the studied binary systems. Such study is useful in drug-receptor interaction.

Keywords: Static dielectric constant, Excess dielectric properties, Kirkwood correlation factor, Bruggeman factor, Water-alcohol binary systems

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DOI: <http://dx.doi.org/10.22159/ijpps.2016.v8i9.12094>

INTRODUCTION

The thermodynamic properties of liquids such as dielectric constant, viscosity, density and refractive index are associated with the molecular interactions present in different binary mixtures. The deviation in these properties with composition gives significant data about the intermolecular interactions and the structure. There is a broad range of interactions is possible between the components of a mixture, such as a hydrogen bonding, molecular associations, charge transfer, dipole-dipole and dipole-induced dipole interactions [1].

The dielectric methods have been used to examine the well-known α or structural relaxation process over a broad frequency and temperature range. In recent times, special interest in the dynamic at high frequencies, in microwaves and sub-millimeter range has crop up due to the calculation of some theoretical and scaling approaches involved in the past. The static permittivity of polar liquids is closely related to its molecular structure. In past theories, this relation finds an evident phrase in the correlation orientation part which has been related to the fact that, under certain situation, the dipole orientation, an assembly of neighbored molecules, are not randomly scattered but may object to molecular order [2-6].

The dielectric permittivity shows the solvents capacity to reduce the field strength of the electric field surrounding the charged particle impressed in it. This reduction is then compared with the field strength of the charged particle in a vacuum. Macroscopic factors such as dielectric constant which is widely used for justification of solvents effects. It is one of the essential properties that must be known to develop theories of electrolyte solutions [7]. Dielectric permittivity is a key physicochemical factor, as it is related to many important physical and biological applications [8, 9]. The dielectric constant of a solvent is a relative measure of its polarization and its measurements are often used for estimation of characteristics of the liquid solutions [10]. This property can also be very useful as a support for competent design, stimulation of separation processes, sample preparation and chromatography techniques in analytical chemistry [11, 12]. In addition, the dielectric constant can be used to calculate the ionic activity coefficients of electrolyte solutions at any temperature and composition [13].

The parameters associated with the electrostatic forces at the site of actions are polarization, dipole moment and H-bond formation. These parameters could be properly studied in the binary mixtures interactions. In this hydrogen bonding is extremely important in affecting the properties of water and biological molecules. The hydrogen bond is said to be the 'bond of life.' The dual helix arrangement of DNA is formed and held together by hydrogen bonds. The nature of hydrogen bonds in proteins states their properties and behavior. Intramolecular hydrogen bonds (within the molecule) in proteins result in the creation of spherical proteins, e. g. enzymes or hormones. In contrast, intermolecular hydrogen bonds (between different molecules) have a tendency to give unsolvable proteins such as fibrous protein. Cellulose, a polysaccharide, molecules are detained together through hydrogen bonding, which supply plants with rigidity and protection in drug-receptor binding, hydrogen bonding often plays an important role. The aim of the present work was to determine the hydrogen bonding and intermolecular interaction between the water-ethanol and water-methanol binary mixture systems and its role in drug binding. The excess dielectric properties (ϵ^E), Kirkwood correlation factor (g^{eff}) and Bruggman factor (f_B) of the binary mixtures have also been also reported at 288, 298 and 308 K temperatures.

MATERIALS AND METHODS

The chemicals utilized in the current study are of spectroscopic grade with 99.9% purity and were used without further purification. The solutions were set by mixing ethanol and methanol with water at eleven different volume percentage of water as 0 to 100% in steps of 10%. The temperature controller arrangement with water bath has been used to sustain the constant temperature within the correctness limit of ± 1 °C. The sample cell is surrounded by a heat insulating container through which the water of steady temperature using a temperature controller system was circulated.

The static dielectric constants of the binary systems were measured using a FDR 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 couple of stainless steel rods, which convey an electromagnetic signal into the mixture. The field passes without

problems through the mixture ensuing in stable voltage output that acts as an easy sensitive measure of dielectric constant. Each measurement was repeated at least three times and the average value was taken as a dielectric constant. The precision of measurement in the dielectric constant was $\pm 3.0\%$.

The information related to the excess dielectric constant of the dual solutions was obtained from the excess properties [14] of the mixture. The excess permittivity is defined as

$$\epsilon^E = (\epsilon_0)_m - [(\epsilon_A \cdot X_A) + (\epsilon_B \cdot X_B)] \dots\dots\dots (3)$$

Where X is volume fraction and suffix m, A, B represents mixture, liquid A and liquid B respectively. The excess permittivity provides qualitative information about formation of new structure in the mixture as follows:

- i) $\epsilon^E = 0$: Indicates that solution A and B do not interact.
- ii) $\epsilon^E < 0$: Indicates that solution A and B interact in such a way that the effective dipole moment gets reduced.
- iii) $\epsilon^E > 0$: Indicates that solution A and B interact in such a way that the effective dipole moment increases.

The Kirkwood correlation factor [15] 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

$$\frac{4\pi N \mu^2 \rho}{9KT M} g = \frac{(\epsilon_0 - \epsilon_\infty)(2\epsilon_0 + \epsilon_\infty)}{\epsilon_0(\epsilon_\infty + 2)^2} \dots\dots\dots (5)$$

Where μ is dipole moment, ρ is density at temperature T, M is molecular weight, K is Boltzman constant, N is Avogadro's number, (ϵ_s) is static dielectric permittivity and ϵ_∞ is the dielectric permittivity 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 Kumbharkhane *et al.* [16, 17] two such equations used are as follows:

$$\frac{4\pi N}{9kT} \left(\frac{\mu^2_M \rho_M}{M_M} X_M + \frac{\mu^2_F \rho_F}{M_F} X_F \right) g^{eff} = \frac{(\epsilon_{0m} - \epsilon_{\infty sm})(2\epsilon_{0m} + \epsilon_{\infty sm})}{[\epsilon_{0m}(\epsilon_{\infty sm} + 2)^2]} \dots (6)$$

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

$$\frac{4\pi N}{9kT} \left(\frac{\mu^2_M \rho_M g_M}{M_M} X_M + \frac{\mu^2_F \rho_F g_F}{M_F} X_F \right) g^f = \frac{(\epsilon_{0m} - \epsilon_{\infty sm})(2\epsilon_{0m} + \epsilon_{\infty sm})}{\epsilon_{0m}(\epsilon_{\infty sm} + 2)^2} \dots (7)$$

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.

The static permittivity of two mixtures must lie somewhere between two extremes corresponding to the static permittivity of two liquids. In order to understand the dipole interaction in the mixture of two liquids a various mixture formula has been proposed [18, 19].

Bruggeman mixture formula [20, 21] can be used as first evidence of molecular interactions in a binary mixture. The useful volume of the solute gets tailored by solute-solvent interactions and is most excellent demonstrated by the non-linearity of Bruggeman formula. The static dielectric constant (ϵ_s) of the mixtures is linked to the Bruggeman mixture formula with the volume fraction of solute which shows the interaction between solvent and solute. This formula states that static dielectric permittivity of binary mixture

(ϵ_{sm}), solute (ϵ_{sA}) and solvent (ϵ_{sB}) can be correlated to volume fraction of solvent (V) which shows the interaction between solvent and solute in the mixture as;

$$f_B = \frac{(\epsilon_{sm} - \epsilon_{sB})}{(\epsilon_{sA} - \epsilon_{sB})} \left(\frac{\epsilon_{sA}}{\epsilon_{sm}} \right)^{1/3} = 1 - V$$

According to above equation linear relationship is expected in the Bruggeman factor (f_B) and (V). Any deviation from this linear relation indicates molecular interaction [22].

RESULTS

The variation in static dielectric constants (ϵ_s) of the ethanol-water and methanol-water binary mixtures at different temperatures is presented in fig. 1 and 2 respectively.

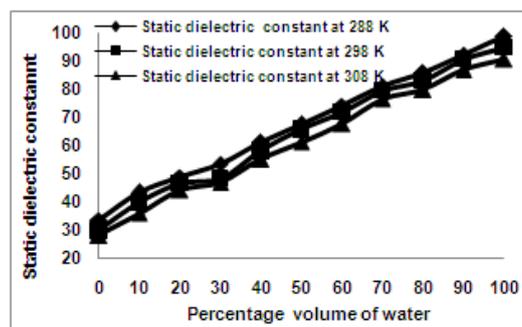


Fig. 1: Variation in static dielectric constant of ethanol with volume fraction of water at different temperatures

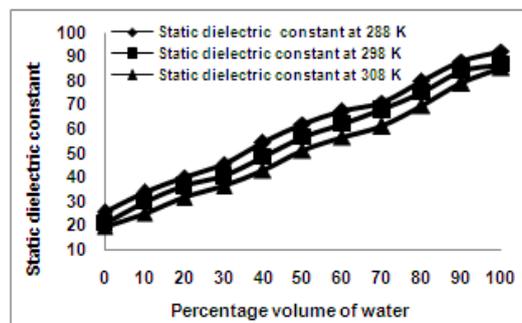


Fig. 2: Variation in static dielectric constant of methanol with volume fraction of water at different temperatures

The experimental data show that the dielectric permittivity of the binary solutions decreases with increase in temperature and increases with increase in volume fraction of water.

The excess permittivity (ϵ^E) provides significant information regarding the interaction between the polar-polar liquid mixtures. The excess dielectric permittivity of the binary mixtures was calculated using equation (3). The excess permittivity of the ethanol-water binary system for different temperatures is given in table 1.

The excess permittivity is nearly positive for the entire volume fraction range of the binary mixtures at 288 and 298K temperatures, and it is negative nearly for the entire volume fractions range at 308K temperature.

The excess permittivity of the methanol-water binary system for the three temperatures is given in table 2.

Table 1: Variation in excess dielectric constant of ethanol with volume fraction of water at different temperatures

Percentage volume of water in ethanol	excess dielectric constant (T=288 K)	excess dielectric constant (T=298K)	excess dielectric constant (T=308K)
00	0.0	0.0	0.0
10	1.50	1.95	-1.22
20	1.27	2.1	-1.44
30	0.30	-0.3	-2.90
40	1.94	1.05	-3.13
50	2.80	2.55	-1.27
60	1.77	1.35	-2.52
70	-1.09	0.75	-4.54
80	0.67	1.50	-2.40
90	2.60	3.90	0.12
100	0.0	0.0	0.0

Table 2: Variation in excess dielectric constant of methanol with volume fraction of water at different temperatures

Percentage volume of water in methanol	excess dielectric constant (T=288 K)	excess dielectric constant (T=298K)	excess dielectric constant (T=308K)
00	0.0	0.0	0.0
10	3.28	3.47	1.93
20	2.53	3.70	3.67
30	0.80	-1.07	0.12
40	1.48	2.15	1.94
50	1.42	3.37	1.84
60	1.66	2.85	2.27
70	2.10	4.07	4.62
80	0.14	1.3	1.55
90	0.41	2.27	2.41
100	0.0	0.0	0.0

The excess permittivity is positive for the entire volume fraction ranges of the binary solution for the studied temperatures.

The effective angular Kirkwood correlation factor (g^{eff}) values of the ethanol-water binary system at 288, 298 and 308K temperatures is represented graphically in fig. 3.

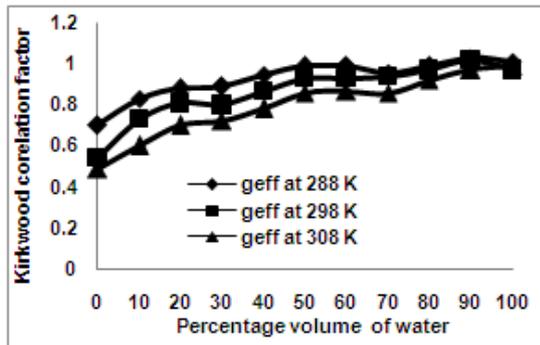


Fig. 3: Variation in Kirkwood correlation factor (g^{eff}) of ethanol with volume fraction of water at different temperatures

The $g^{eff} < 1$ up to 80% volume fraction of water in ethanol, and $g^{eff} > 1$ in water rich region for the studied temperatures.

The effective angular Kirkwood correlation factor (g^{eff}) values of the methanol-water binary system at 288, 298 and 308K temperatures is illustrated in fig. 4.

$g^{eff} < 1$ up to 50% volume fraction of water in methanol, and $g^{eff} > 1$ from 60 to 100% volume fraction of water in methanol.

The Bruggeman factor (f_B) values of ethanol-water and methanol-water binary systems at 288, 298 and the 308K temperature is given in fig. 5 and 6 respectively.

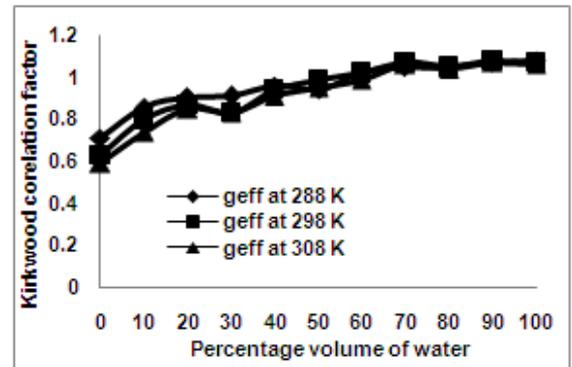


Fig. 4: Variation in Kirkwood correlation factor (g^{eff}) of methanol with volume fraction of water at different temperatures

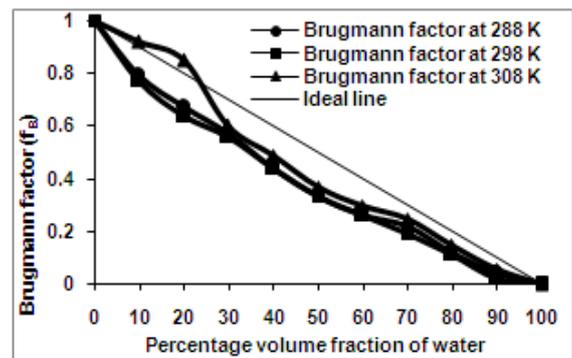


Fig. 5: Variation in Bruggeman factor (f_B) of ethanol with volume fraction of water at different temperatures

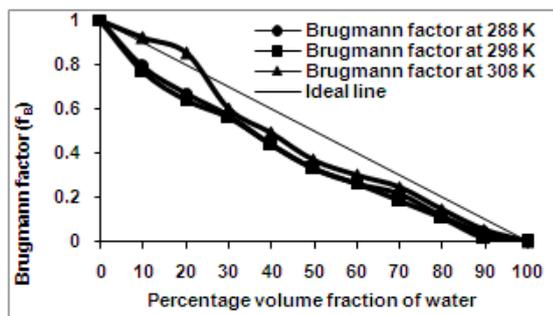


Fig. 6: Variation in Bruggman factor (f_B) of methanol with volume fraction of water at different temperatures

DISCUSSION

The dielectric permittivity of the dual solutions decreases with increase in temperature. This is due to the polarization. The decrease in permittivity with an increase in temperature might be due to rapid fall in orientation polarization because the increased thermal activity reduces the alignment of the permanent dipoles [23]. The dielectric permittivity of the mixtures increases with increase in volume fraction of water; this is due to decrease in carbon atoms number and size-shape of the composite molecules after hydrogen bonding interaction. This could be attributed to an increase in a number of dipoles in the complex, which may lead to an increase in the volume of the rotating molecules [24, 25].

The excess permittivity of the ethanol-water binary mixtures is nearly positive for the entire volume fraction range at 288 and 298K temperatures, which indicates that the ethanol-water solutions interact in such a way that the effective dipole moment increases. The positive excess permittivity (ϵ^E) suggest that the effective number of dipoles in the mixture might be greater than the corresponding average number in the pure liquids, maybe due to the formation of new structure leading to a higher macroscopic permittivity. The results are in agreement with the earlier results of Lone *et al.* [26]. The excess permittivity of the ethanol-water binary mixtures at 308K temperature is nearly negative for the entire volume fractions range. This suggests that the binary mixtures interact in such a way that the effective dipole moment gets reduced. The negative values of (ϵ^E) at this temperature may be probably due to the creation of less polar structure leading to a lower macroscopic permittivity. The negative deviations from perfect may be credited to a certain interaction between different molecules, and in particular to hydrogen bonding. From a molecular approach, the negative values of excess dielectric constant in water-aliphatic-alcohol mixtures, is the result of formation of hydrogen bonds between water which contains an-OH group and can act as a π -type donor and alcohol molecules, which have one acidic H atom on the-OH group and can act as a σ -acceptors. However, in pure alcohols, the linear n-mers formed give augment to a higher dipole moment which has been accredited to the fact that the O-H bond moment of these-aggregates is increased through reciprocal induction. The results are in good agreement with the earlier results of Yilmaz and Zhang *et al.* [27, 28].

The excess permittivity of the methanol-water binary system is positive for the entire volume fraction ranges at the studied temperatures indicates that the binary mixtures interacts in such a way that the effective dipole moment increases. This positive excess permittivity of the mixtures suggests any significant intermolecular interaction is effectively present at these temperatures.

The effective angular Kirkwood correlation factor $g^{\text{eff}} < 1$ up to 80% volume fraction of water in ethanol which indicates the antiparallel orientation of electric dipoles of the water molecules. The addition of ethanol to water, therefore, causes breaking of the antiparallel orientation of water molecules. The $g^{\text{eff}} > 1$ in water rich region that indicates the parallel orientation of electric dipoles in the ethanol molecules. The results are in good agreement with the earlier results of Hosamani *et al.* [29].

The effective angular Kirkwood correlation factor $g^{\text{eff}} < 1$ up to 50% volume fraction of water in methanol indicates the antiparallel orientation of electric dipoles of water molecules. Owing to this antiparallel organization and hydrogen bonding the excess dielectric constant in methanol rich region is positive. The addition of methanol to water, therefore, causes breaking of the antiparallel orientation of water molecules. $g^{\text{eff}} > 1$ from 60 to 100% volume fraction of water in methanol indicates parallel orientation of electric dipoles in the water molecules. That might indicate a strong interaction between methanol-water molecules. The results are in agreement with the earlier results of Hosamani *et al.* [29].

The Bruggeman factor (f_B) values of ethanol-water and methanol-water systems data shows that there is a deviation from the linear relation which gives the confirmation of strong intermolecular interactions between ethanol-water and methanol-water binary solutions.

CONCLUSION

The static dielectric constant of the ethanol-water and methanol-water systems decreases with increase in temperature and increases with the addition of volume fraction of water.

The excess permittivity of the ethanol-water binary system is positive at 288 and 298K temperatures and negative at 308K temperature. The excess permittivity of the methanol-water binary system is positive for entire volume fraction range of water at the studied temperatures.

In the mixture, the dipole pairs are formed and orient in the antiparallel direction in ethanol, methanol rich region and in a parallel direction in water-rich region.

The Bruggeman factor study shows the deviation from the linear relation which gives the strong evidence of molecular interactions in binary solutions.

The dipole moment, intermolecular interaction and hydrogen bonding study are useful in drug binding.

CONFLICT OF INTERESTS

Declared none

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How to cite this article

- VV Navarkhele. Dielectric relaxation study of binary mixtures at different temperatures. Int J Pharm Pharm Sci 2016;8(9):102-106.