



Dielectric study of binary mixtures at 298K temperature

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ABSTRACT

Static dielectric constants and excess properties of three binary systems were studied at 298K temperature. The dielectric measurements have been carryout by using a sensor which is based on frequency domain reflectometry technique. To determine the intermolecular interaction and hydrogen bonding, the excess dielectric properties, Kirkwood correlation and Bruggeman factor of the binary mixtures have also been calculated and reported. The behavior of excess dielectric permittivity and Bruggeman factor suggest the presence of molecular interaction in the binary mixtures. The angular Kirkwood correlation factor confirms the parallel and antiparallel orientation of the dipoles in the binary mixtures.

Keywords: Dielectric constant; Excess dielectric constant; Kirkwood correlation factor; Bruggeman factor; Binary solutions.

INTRODUCTION

It is well known that the thermophysical properties, of liquid systems such as dielectric constant, viscosity, density and refractive index among others, are strictly related to the molecular interactions present in different binary liquid mixtures. The variation in these properties with composition gives important data about intermolecular interactions and the structure. There is wide range of possible interactions between the components of a mixture, such as hydrogen bonding, molecular associations, charge transfer, dipole-dipole and dipole induced dipole interactions [1]. Dielectric techniques have been used to observe the well-known α or structural relaxation process over a broad frequency and temperature range. Recently, special interest in the dynamic at high frequencies, in the microwaves and sub-millimeter range has arisen due to the prediction of some theoretical and scaling approaches elaborated in the past. The static permittivity of bipolar liquid is closely related to its molecular structure. In former theories this relation finds an obvious expression in the orientation correlation factor which has been related to the fact that, under certain conditions, the dipole orientation, an ensemble of neighbored molecules, are not randomly distributed but may be object to molecular order [2-7].

The dielectric constant indicates the solvents ability to reduce the field strength of the electric field surrounding the charged particle impressed in it. This reduction is then compared with to the field strength of the charged particle in vacuum [8]. Macroscopic parameters such as dielectric constant have extensively used for explanation of solvents effects. The dielectric constant is one of the fundamental properties that must be known to utilize theories of electrolyte solutions [9]. The dielectric constant is an important physicochemical parameter, as it is related to many important physical and biological applications [10, 11]. The dielectric constant of a solvent is a relative measure of its polarity and its measurements are often used for evaluation of characteristics of the liquid solutions [12]. This property can also be very useful as a support for efficient design, stimulation of separation processes, sample

preparation and chromatography techniques in analytical chemistry [13, 14]. Additionally, dielectric constant can be used to calculate the ionic activity coefficients of electrolyte solutions at any temperature and composition [15].

The aim of the present work is to determine the hydrogen bonding and intermolecular interaction between three binary systems. 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 298K temperature.

EXPERIMENTAL SECTION

2.1. Materials

The chemicals used in the present investigation are of spectroscopic grade with 99.9% purity and were used without further purification. The solutions were prepared by mixing ethanol, methanol and acetone with water at eleven different volume percentage of water 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 $\pm 1^\circ\text{C}$. The sample cell is surrounded by a heat insulating container through which the water of constant temperature using a temperature controller system was circulated.

2.2. Measurement of dielectric constant

The static dielectric constants of the alcohol-water binary systems were measured using a fixed frequency 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 transmits an electromagnetic signal into the mixture. The field passes easily through the mixture resulting in stable voltage output that acts as a simple sensitive measure of dielectric constant. Each measurement was repeated at least three times and average value of that reading was taken as a dielectric constant. The accuracy of measurement in the dielectric constant was $\pm 3.0\%$.

2.3. Study of excess permittivity

The information related to the excess permittivity of the binary solutions was obtained from the excess properties [16] of the mixture. The excess permittivity is defined as

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

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.

2.4. Study of Kirkwood correlation factor

The Kirkwood correlation factor [17] 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

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

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 [18, 19] two such equations used are as follows:

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

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

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

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.

2.5. Study of Bruggeman factor

The static dielectric constant of two the mixtures must lie somewhere between two extremes corresponding to static dielectric constant of the two liquids. In order to understand the dipole interaction in the mixture of two liquids a various mixture formula has been proposed [20, 21]

Bruggeman mixture formula [22, 23] can be used as first evidence of molecular interactions in 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 (ϵ_s) of the mixtures is related to the Bruggeman mixture formula with volume fraction of solute which indicates 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 related to volume fraction of solvent (V) which indicates the interaction between solvent and solute in the mixture as;

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

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 [24].

RESULTS AND DISCUSSION

The experimental results of static dielectric constants, excess dielectric constant, and Kirkwood correlation factor of water- acetone, water - methanol and water – ethanol binary solutions is shown in Table 1, 2 and 3 respectively. The dielectric permittivity of the binary solutions decreases with increase in volume fraction of acetone, methanol and ethanol. This may be due to increase in carbon atoms number and size- shape of the complex molecules after hydrogen bonding interaction. This could be attributed to decrease in number of dipoles in the complex, which may lead to decrease in volume of the rotating molecules [25, 26]

The excess dielectric constant (ϵ^E) provides significant information regarding interaction between the polar-polar liquid mixtures. The excess dielectric permittivity of the binary systems was calculated using equation (3). The excess permittivity is positive nearly for the entire volume fraction range of water- acetone, water –methanol and water - ethanol binary systems at the studied temperature, which indicates that the binary solutions interact in such a way that the effective dipole moment increases. The positive excess permittivity (ϵ^E) also 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 [27, 28]. This positive excess permittivity of the mixtures also suggests any significant intermolecular interaction is effectively present at studied temperature range.

The effective angular Kirkwood correlation factor (g^{eff}) values of water- acetone, water - methanol and water – ethanol binary systems is shown in Table 1, 2 and 3 respectively. $g^{\text{eff}} > 1$ in water rich region for three binary systems. This indicates parallel orientation of electric dipoles in acetone, ethanol and methanol molecules. The $g^{\text{eff}} < 1$ in acetone, methanol and ethanol rich region indicates anti-parallel orientation of electric dipoles of water molecules. The addition of acetone, methanol and ethanol to water therefore causes breaking of anti-parallel orientation of water molecules [29, 30].

The Bruggman factor (f_B) of water-acetone, water-methanol and water-ethanol binary systems at 298K temperatures is graphically presented in Figure 1, 2, and 3 respectively. According to the given data there is deviation from the linear relation which gives the evidence of strong molecular interactions between the binary systems of acetone, ethanol and methanol solutions.

Table 1 Variation in static dielectric constant, excess dielectric constant and Kirkwood correlation factor of water-acetone mixture at 298K temperature

Percentage volume of acetone in water	Static dielectric constant	Excess dielectric constant	Kirkwood correlation factor
00	89.68	0	1.01
10	82.40	-0.04	1.00
20	78.40	3.19	1.03
30	70.40	2.48	1.01
40	64.32	3.58	1.01
50	56.64	3.14	0.98
60	50.56	4.29	0.98
70	42.40	3.37	0.92
80	34.88	3.08	0.87
90	25.12	0.56	0.69
100	17.32	0.0	0.48

Table 2 Variation in static dielectric constant, excess dielectric constant and Kirkwood correlation factor of water – methanol mixture at 298K temperature

Percentage volume of methanol in water	Static dielectric constant	Excess dielectric constant	Kirkwood correlation factor
00	85.50	0	1.06
10	81.67	2.04	1.02
20	74.92	1.16	1.00
30	71.55	3.66	0.95
40	64.57	2.56	0.90
50	59.17	3.03	0.88
60	52.20	1.98	0.83
70	43.82	-0.56	0.74
80	41.85	3.33	0.77
90	35.77	3.12	0.71
100	26.77	0.0	0.54

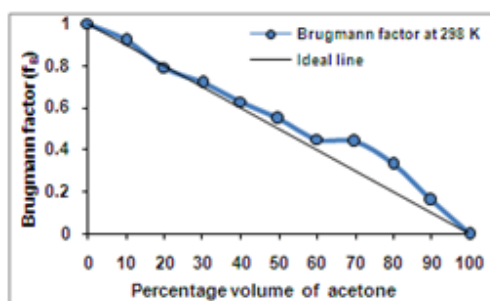


Figure 1 Variation in Bruggman factor (f_B) of water with volume fraction of acetone at 298K temperature

Table 3 Variation in static dielectric constant, excess dielectric constant and Kirkwood correlation factor of water-ethanol mixture at 298K temperature

Percentage volume of ethanol in water	Static dielectric constant	Excess dielectric constant	Kirkwood correlation factor
00	90.81	0.0	1.02
10	87.92	3.95	1.06
20	80.32	3.19	1.04
30	72.48	2.19	1.01
40	66.08	2.63	1.00
50	60.32	3.71	1.00
60	51.68	0.91	0.94
70	43.20	0.27	0.86
80	40.96	4.87	0.94
90	31.52	2.27	0.80
100	22.40	0.0	0.60

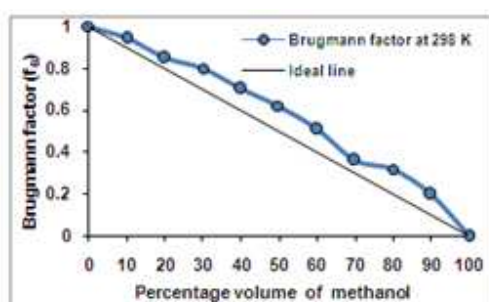


Figure 2 Variation in Bruggman factor (f_B) of water with volume fraction of methanol at 298K temperature

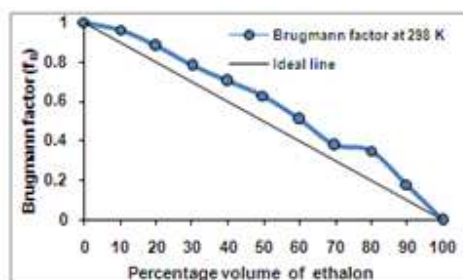


Figure 3 Variation in Bruggman factor (f_B) of water with volume fraction of ethanol at 298K temperature

CONCLUSION

The static dielectric permittivity of the binary systems decreases with increase in volume fraction of acetone, methanol and ethanol for the studied temperature.

The excess permittivity is positive nearly for the entire volume fraction range of water- acetone, water –methanol and water - ethanol binary systems at the studied temperature, which indicates that the binary solutions interact in such a way that the effective dipole moment increases.

In the binary systems the dipole pairs are formed and orient in parallel direction in water rich region and anti-parallel direction in acetone, methanol and ethanol rich region.

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

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