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Measurement of static dielectric constants of aqueous solution of methanol for various temperatures

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ABSTRACT

Static dielectric constants of aqueous solution of methanol were measured at various temperatures. The static dielectric measurements have been achieved by using a sensor which is based on frequency domain reflectomery technique. The excess dielectric properties, Kirkwood correlation factor and Bruggman factor of the binary mixtures have also been calculated and reported. The behavior of excess dielectric permittivity shows positive - negative variations at the studied temperatures suggest the presence of intermolecular interactions in the mixture. The Kirkwood angular correlation factor confirms the parallel and antiparallel orientation of the dipoles in the mixture.

Keywords*:* Static dielectric constant; Excess dielectric properties; Kirkwood correlation factor; Bruggman factor; Water-methanol binary mixture.

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].

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 [2]. 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 [3]. The dielectric constant is an important physicochemical parameter, as it is related to many important physical and biological applications [4, 5]. 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 [6]. 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 [7, 8]. Additionally, dielectric constant can be used to calculate the ionic activity coefficients of electrolyte solutions at any temperature and composition [9].

The aim of the present work is to determine the hydrogen bonding between water and alcohol molecules. The excess dielectric properties (ε^E), Kirkwood correlation factor (g^{eff}) and Bruggman factor (f_B) of the binary mixtures have been also reported for 283,293 303 and313 k temperature to correlate these values with carbon chain length and intermolecular interactions.

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 methanol 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 ± 1°C. The sample cell is surrounded by a heat insulating container through which the water of constant temperature using a temperature controller system is circulated**.**

2.2 Measurement of dielectric constant

The static dielectric constants of the aqueous solution were measured using a 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 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 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 ± 3.0 %.

2.3 Measurement of excess permittivity

The information related to the excess permittivity of the aqueous solution was obtained from the excess properties [10] of the mixture. The excess permittivity is defined as

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

Where X is volume fraction and suffix m, A, B represents mixture, liquid A (Water) and liquid B (Methanol) respectively. The excess permittivity provides qualitative information about 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.

2.4 Measurement of Kirkwood correlation factor

The Kirkwood correlation factor [11] 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

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

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 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 [12, 13] 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.

2.5 Measurement of Bruggman factor

The static permittivity of two mixture must lie somewhere between two extremes corresponding to 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 [14, 15]

Bruggman mixture formula [16, 17] 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 Bruggman formula. The static dielectric constant ($\in_s$) of the mixtures is related to the Bruggman 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 ($\in_{sm}$), solute ($\in_{sA}$) and solvent ($\in_{sB}$) can be related to volume fraction of solvent (V) which indicates the interaction between solvent and solute in the mixture as;

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

According to above equation linear relationship is expected in the Bruggman factor **(**f_B) and (V). Any deviation from this linear relation indicates molecular interaction [18].

RESULTS AND DISCUSSION

Figure 1 illustrates the experimental results of static dielectric constants (ε_s) of the aqueous solution for different temperatures. The dielectric permittivity decreases with increase in temperature as well as increase in volume fraction of methanol. The decreases in dielectric permittivity with increase in temperature might be due to rapid fall in orientation polarization, because the increased thermal motion reduces the alignment of the permanent dipoles [19]. The decrease in dielectric permittivity with increase in volume fraction of methanol 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. The results are in agreement with the earlier results of Navarkhele et al [20].

The excess permittivity provides significant information regarding interaction between the polar-polar liquid mixtures. The excess dielectric permittivity of the binary mixtures was calculated using equation (3). The excess permittivity (ε^E) of the binary mixtures of water with methanol at 283, 293, 303 and 313 k are presented in figure 2 to 5 respectively. The excess permittivity is positive for the entire volume fractions range at 283 k, which indicates that water and methanol solutions interact in such a way that the effective dipole moment increases. It also suggests that any significant intermolecular interaction is effectively present at this temperature range.

At 293 k, the values of excess permittivity are negative in water and methanol rich region and positive at 30 to 70 % volume fraction range. The negative values of (ε^E) in water and methanol rich region are probably due to the creation of less polar structure leading to a lower macroscopic permittivity. The positive values of (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 [21].

The variation in excess permittivity (ε^E) is similar at 303 and 313 k temperature which is given in figure 4 and 5 respectively. According to this data, the excess permittivity is negative up to 50 % volume fraction and positive for rest of the volume fraction. The negative deviations from ideal may be attributed to a certain interaction between unlike molecules, and in particular to hydrogen bonding [22]. From a molecular point of view the negative values of excess permittivity in water-aliphatic – alcohol mixtures is the consequence 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 rise to a higher dipole moment which has been attributed to the fact that the O-H bond moment of this aggregate is increased through mutual induction [123, 24]

The Kirkwood angular correlation factor (g^{eff}) values for various compositions of the mixture and for the studied temperatures are represented graphically in figure. 6. The $g^{eff} > 1$, at 283 k temperature and for entire volume fraction range, indicates that in the mixture the dipole pairs have been formed in such a way that their orientation is parallel. The $g^{eff} < 1$, at 293, 303 and 313 k temperature for the entire volume fraction range, indicates that in the mixture the dipole pairs have been formed in such a way that their orientation is anti-parallel.

The Bruggman factor values for various compositions of the mixture and at various temperatures are represented graphically in figure 7. According to the data there is deviation from the linear relation which gives the evidence of molecular interactions in binary mixture of water and methanol.

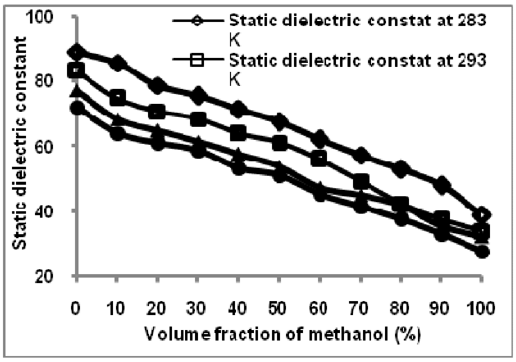

Fig. 1. Variation of static dielectric constant with volume fraction of methanol at different temperatures

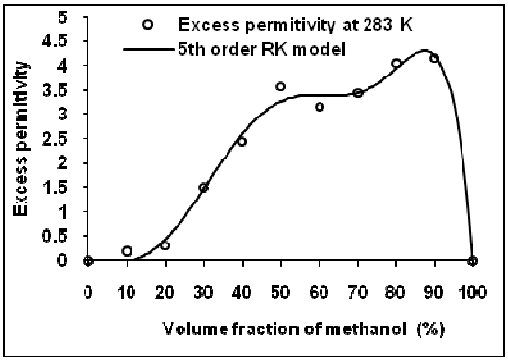

Fig. 2. Variation in excess dielectric constant with volume fraction of methanol at 283 k temperature

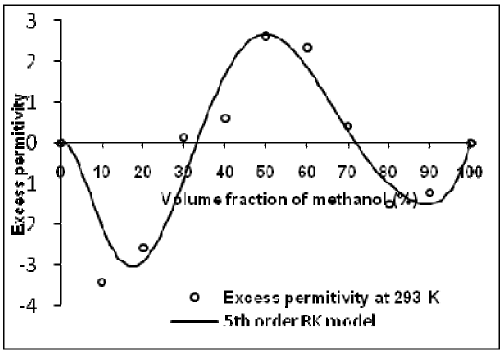

Fig. 3. Variation in excess dielectric constant with volume fraction of methanol at 293 k temperature

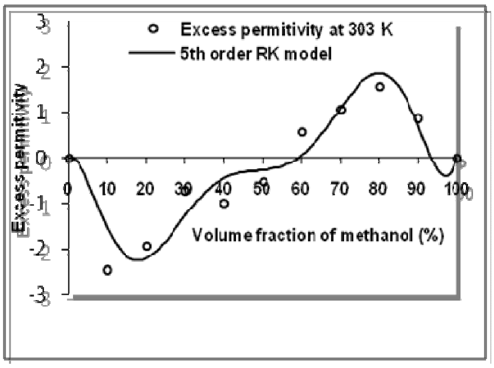

Fig. 4. Variation in excess dielectric constant with volume fraction of methanol at 303 k temperature

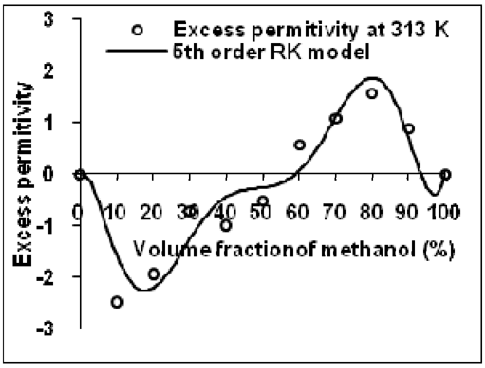

Fig. 5. Variation in excess dielectric constant with volume fraction of methanol at 313 k temperature

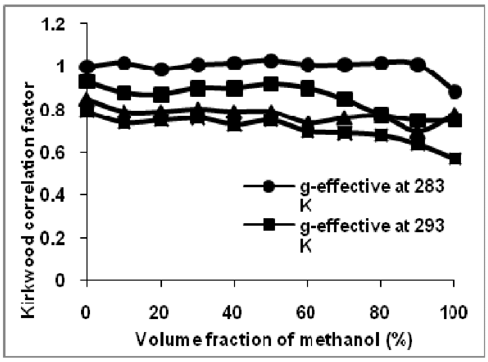

Fig. 6. Variation of Kirkwood correlation factor (g^{eff}) with volume fraction of methanol at different temperatures

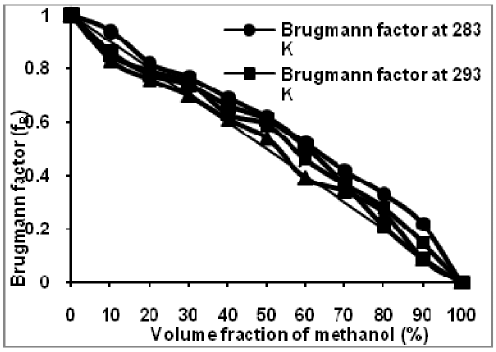

Fig. 7. Variation of Bruggman factor with volume fraction of methanol at different temperatures

CONCLUSION

The values of static dielectric constant of the aqueous solution are found to be in the range of 27 to 89 and decreases with the addition of methanol.

The excess permittivity is positive at lower temperature that is at 283 and 293k and in water rich region, indicates that the effective number of dipoles in the mixture might be greater than the corresponding average number in the pure liquids. The excess permittivity is negative at higher temperature that is at 303 and 313 k in methanol rich region, indicates that the presence of certain interaction between unlike molecules.

In the mixture the dipole pairs are formed and orient in parallel direction in water rich region and in antiparallel direction in methanol rich region which is confirmed from the (g^{eff}) values.

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

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