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Dielectric Constant, Density, and Refractive Index in Binary Mixtures of Ethanol with N,N-Dimethylformamide at 293.15 K

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Abstract

Experimental static dielectric constants, densities and refractive indices at 293.15 K temperature are reported for the binary liquid mixtures of ethanol with N,N-dimethylformamide (DMF) over entire volume fraction range. From the experimental dielectric data, excess dielectric constant, Kirkwood correlation factor, Bruggeman factor are estimated and reported in the study. From density and refractive index data various parameters like atomic polarization, permittivity at optical frequency, excess molar volume, molar refraction, polarizabilty, solvated radii, molar polarization and excess properties like excess density, excess refractive index, excess molar polarization, and excess molar volume were estimated and reported in the study to confirm intermolecular interaction and hydrogen

bonding in the binary mixture. The results show that the dielectric constants, densities and refractive indices of the binary mixtures increases with increase in percentage volume of DMF. The study shows the presence of molecular interactions and hydrogen bonding in the binary mixtures.

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INTRODUCTION

The physicochemical properties of pure liquids such as dielectric constant, viscosity, density and refractive index and their mixtures are essential for accurate design and optimal operation of many industrial processes. With the development of measuring techniques and instruments, these properties can now be obtained in an easy, fast and precise way, which allows systematic and accurate investigations of these properties [1]. The variation of these properties with composition and temperature gives important data about intermolecular interactions and the structure. There are a 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 [2].

In drug discovery and formulation, drug solubility in water organic solvent plays an important role and affects many pharmaceutical processes including design, synthesis, extraction, purification, absorption and distribution in body fluids. In most cases, aqueous solubility of a chemical compound as a medical is not enough to be applicable in pharmaceutical formulations and clinical administration.

Hence, different kinds of solubilization techniques including co solvency, complexation, micellization and salt formation have been applied to increase the solubility. However, in some cases, it is required to reduce solubility in the medium, for example, in crystallization process [3]. These methods not only influence the solubility of a compound, but can also alter its stability in the liquid medium [4, 5]. Co solvency is the most feasible method for this purpose, and the most common pharmaceutical cosolvent is ethanol. Maybe the changes in dielectric constant of the medium have a dominant effect on the solubility of ionizable solute in which higher dielectric constant can cause more ionization of the solute and results in more solubilization [6].

The particular system (ethanol + DMF) was chosen for study because both the liquids are common solvents and they are used in pharmaceutical industry for development and production of pesticides.

In the present study, the dielectric constant, density and refractive index of ethanol with DMF binary mixture have been reported over the entire volume fraction range at 293.15 K temperature. The atomic polarization, permittivity at higher frequency was also estimated and reported in this study. The excess parameters like, excess dielectric constant (ε^E), excess density (d^E), excess refractive index (n^E), excess molar polarization (P_m)^E, excess molar volume (V^E), the molar refraction, polarizability, solvated radii, molar polarization, effective Kirkwood correlation factor (g^{eff}), and Bruggeman factor (f_B) values were also estimated using appropriate equations to confirm intermolecular interactions and hydrogen bonding between the components of the mixtures.

EXPERIMENTAL

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 with DMFat eleven different volume percentages of ethanol plus DMF as 0 to 100% in steps of 10%.

Measurement of Dielectric Constant

The dielectric constants of the binary mixture were measured using a wet sensor make by Delta-T Devices Ltd. UK, which 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. The measurements were recorded with a calibrated meter which is

connected to the wet sensor through a cable. When probes of the sensor inserted into the mixture, pressing the read button on the meter, the dielectric constant reading will appear on it. There is facility to store the readings in the meter. Each measurement was repeated at least five times and the average value of that reading was taken as a dielectric constant of that mixture. The accuracy of measurement of the dielectric constant was $\pm 3\%$.

Measurement Refractive Index

The refractive index is a useful optical property exhibiting ionic or molecular behavior in a mixture and determine basically by the molecular structure, wavelength and temperature. The refractive index can offer valuable information concerning the molecular rearrangement on mixing and also a few useful properties like electronic polarizability [7]. The refractive indices values of the binary mixture of ethanol with DMF were measured using a digital pocket refractometer PAL–RI make by Atago–Japan. The apparatus measures the refractive index of liquids in the range of 1.3306 to 1.5284. The uncertainty in the measurement of refractive indices was ±0.0003.

Measurements of Density

Densities of the binary mixtures were measured using an Anton Paar oscillation U-tube densitometer (model DMA-35, Austria), calibrated with double-distilled water and air. The densities of pure liquids and their mixtures were carried at single temperature, since there is no facility for temperature variation for this model. The density values have a standard uncertainty of $\pm 10^{-3}$ g cm⁻³.

Molar refraction, Polarizabilty, Solvated Radii, Molecular Polarization, and Excess Molar Volume

From experimental densities (d) and refractive indices (n) of pure substances and mixtures, we have calculated the molar refraction (R) from the equation:

```
$$R = \left( {\frac{{{n}^{{2~}}} - 1}}{{{{n}^{2}}} + 2}} \right){{V}_{m}} = {{P}_{A}} + {{P}_{E}} = {{P}_{T}} = {{P}_{D}}\,,$$

(1)
```

where n is the refractive index of the liquid and $V_m = M/d$ is molecular volume, in this M and d is the molecular weight and the density of the pure liquids respectively. The right hand side of Eq. (1) is equal to the summation of both atomic polarization (P_A) and electronic polarization (P_B) and that is equal to the distortion polarization (P_D).

The atomic polarization (P_A) was calculated from the refractive indices (n) of pure substances and mixtures by the equation:

```
$${{P}_{A}} = 1.05{{n}^{2}}.$$
(2)
```

The permittivity at higher frequency $((\{\{\{\{\}\}\}\})))$ is the square of the refractive index and it was calculated by the equation:

```
${{\varepsilon }_{\infty }}_{{({\text{Permittivityathigher frequency}})}} = {{n}^{2}},$$ (3)
```

where n is the refractive index of the binary mixture.

The molecular dipole polarizability (α) was calculated from the experimental densities and refractive indices of pure substances and mixtures using Lorentz formula:

```
$$\alpha = \left( {\frac{{{{n}^{{2~}}} - 1}}{{{{n}^{2}} + 2}}} \right)\frac{{3{{V}_{m}}}}{{4\pi
N}},$$
```

(4)

where *n* is the refractive index of the binary mixture, and $V_m = M/d$ is molecular volume of the mixture.

Considering spherical form of the solvated molecules, the solvated radii of the pure solvents and binary mixtures were calculated using the equation:

```
\{V_{m}\} = \left( {\frac{4}{3}} \right) Pi {\{r}^{3}}.$
(5)
```

From experimental dielectric constants and densities of pure substances and mixtures the molecular polarization (P_m) was estimated using the equation

```
$\{P_{m}\} = \{V_{m}\} \setminus \{ \sqrt{xrepsilon - 1} \} \} \cdot ( \frac{rac{{\bar u}}}{right}, $
```

(6)

where ε and V_m is the static dielectric constant and molecular volume of the binary mixtures [8, 9].

Excess Parameters (Excess Density (d^E), Excess Refractive Index (n^E), Excess Molar Polarization (P_m)^E, and Excess Molar Volume (V)^E)

Excess density (d^E). The excess density was measured from the density data (d), and it was calculated using the equation:

```
$${{d}^{E}} = {{d}_{{{\text{mix}}}}} - ({{x}_{1}}{{d}_{1}} - {{x}_{2}}{{d}_{2}}),$$

(7)
```

where d_{mix} is the value of density of mixture, \(\{\{x}_{1}\},\;\{\x}_{2}\\\) and d_1 , d_2 are the mole fractions and densities of the first and second solvents, respectively.

Excess refractive index (n^E). From the experimental refractive index (n), the excess refractive index was calculated using the equation [8]:

```
 $$\{\{n\}^{E}\} = \{\{n\}_{\{\{\{\text{mix}\}\}\}\}\} - (\{\{x\}_{1}\}\{\{n\}_{1}\}\} - \{\{x\}_{2}\}\{\{n\}_{2}\}\}), $$ (8)
```

where $(\{\{n\}_{\{\{\text{mix}\}\}\}\})$ is the value of refractive index of the mixture $(\{\{x\}_{\{1\}\},\,\{\{x\}_{\{2\}\}\}})$ and $(\{\{n\}_{\{1\}\},\,\{\{n\}_{\{2\}\}\}})$ are the volume fractions and refractive indices of the first and second solvents, respectively.

Excess molar polarization $(P_m)^E$. The excess molar polarization $(P_m)^E$ of the binary mixture was calculated by the equation:

```
$${{({{P}_{m}})}^{E}} = {{({{P}_{m}})}_{m}} - [{{({{P}_{m}})}_{A}}{{{Phi }_{A}}} + {{({{P}_{m}})}_{B}}],$$

(9)
```

where P_m is the polarization of the mixture, $(P_m)_A$, $(P_m)_B$, are the molar polarization and \({{\Phi}}

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 $_{A}}\), (_{\Phi} _{B}}\) the volume fraction of solution A and B, respectively.$

Excess molar volume $(V)^E$. From the experimental density data of the binary mixtures, the excess molar volumes (V^E) , was calculated by the equation [10]:

```
$${{V}^{E}} = {{V}_{m}} - \mathop \sum \limits_{i = 1}^n \,{{{\Phi }}}_{i}}{{V}_{i}},$$
(10)
```

where V_m is the molar volume of the mixture, Φ_i and V_i represent volume fraction and molar volume of the component i, respectively.

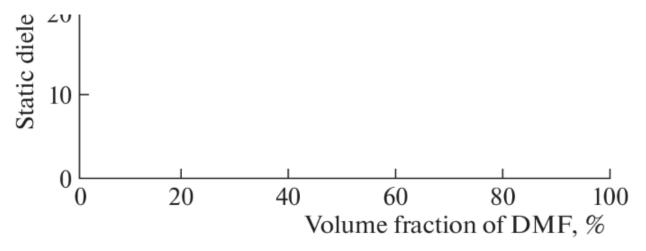
RESULTS AND DISCUSSION

Static Dielectric Constant

The experimental data of dielectric constant of the binary mixture of ethanol—DMF is reported in <u>Table 1</u> and illustrated graphically in <u>Fig. 1</u>. The dielectric constant of the mixture increases with an increase in volume fraction of DMF at the studied temperature. The increase in dielectric constant with an increase in volume fraction of DMF may be due to decrease in size and shape of the complex molecules after hydrogen bonding interaction. This could be attributed to the increase in the number of dipoles in the complex, which may lead to increase in the volume of the rotating molecules [11, 12].

Table 1. Variation in experimental values of static dielectric constant, density and refractive index of the binary mixture of ethanol with DMF at 293.15 K temperature

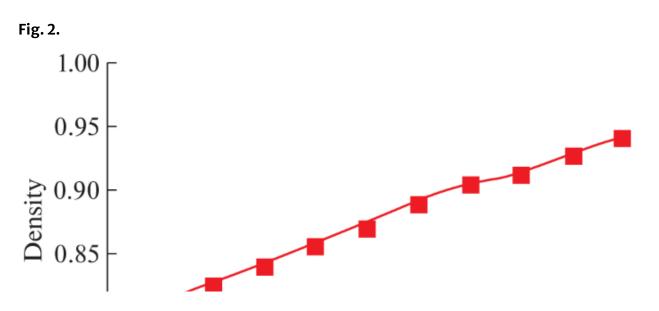


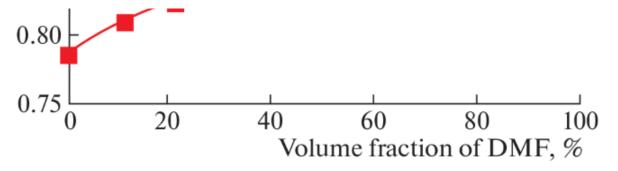


Variation in the static dielectric constant of the binary mixture of ethanol—DMF at 293.15 K temperature.

From <u>Fig. 1</u>, it is also observed that, the dielectric constant increases non–linearly with the concentration of DMF. In an ideal mixture of polar liquids, if the molecules are interacting, a non–linear variation in dielectric permittivity with concentration is expected, and the same is inferred from the figure. This confirms that the intermolecular association is taking place in the system [$\underline{13}$, $\underline{14}$].

The experimental density data of the binary mixture of ethanol—DMF is given in <u>Table 1</u> and shown graphically in <u>Fig. 2</u>. The density of the binary mixture increases with an increase in the percentage volume of DMF. In the binary mixture, with an increase in the concentration of DMF in ethanol, may strengthen the intermolecular bonds that results in new bonds between similar and dissimilar molecules, resulting in decreased volume of the mixture and consequently increased density. The results are in agreement of earlier results of Farid.

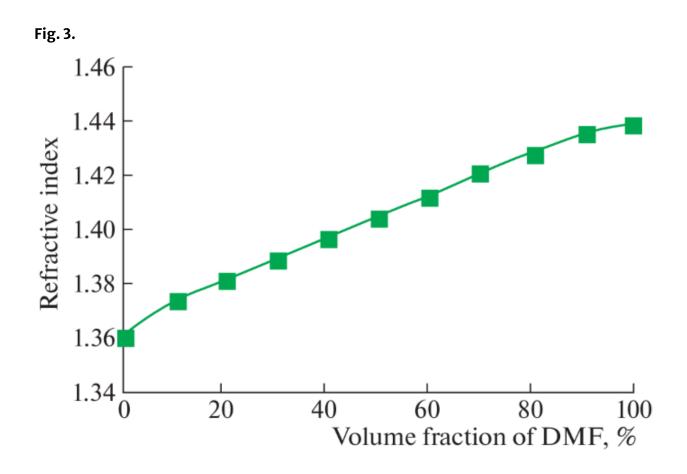




Variation in density of the binary mixture of ethanol-DMFat 293.15 K temperature.

It is also seen that there is nonlinear improvement of the density data of the binary mixture; this is because of the increment of DMF mass fraction in ethanol. Therefore, it is concluded that by adding the carboxyl group to the ethanol, the density of the binary mixture is increased [15].

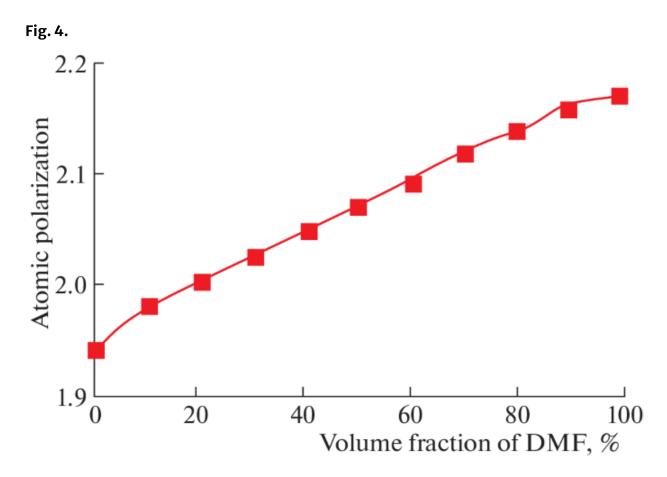
The refractive index of the binary mixture of ethanol with DMF is given in <u>Table 1</u> and graphically represented in <u>Fig. 3</u>. From <u>Fig. 3</u> it is noticed that the refractive index of the binary mixture increases with increasing the percentage volume of DMF, this may be due to increase in density and dielectric constant of the binary mixture.



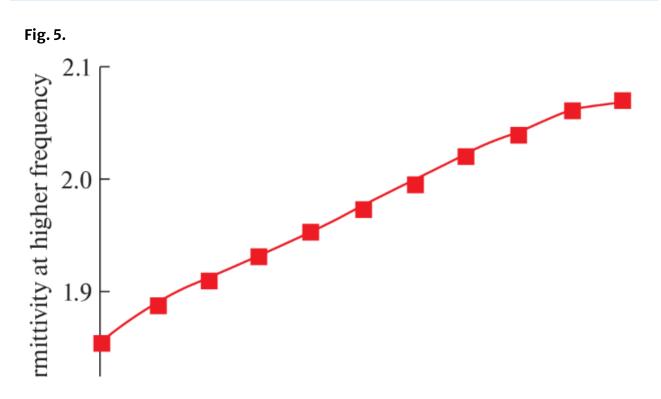
Variation in refractive index of the binary mixture of ethanol–DMF at 293.15 K temperature.

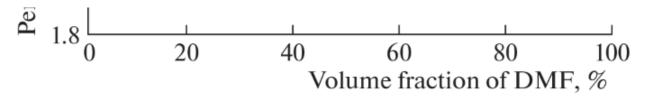
The estimated values of atomic polarization and permittivity at optical frequency of the binary mixture are given in <u>Table 2</u> and graphically represented in <u>Figs. 4 and 5</u>, respectively. From the said data, it is observed that the atomic polarization and optical permittivity increases with increasing percentage volume of DMF. The behavior of atomic polarization and permittivity at higher frequency is similar to that of static dielectric constant, density and refractive index.

Table 2. Variation in estimated values of atomic polarization, permittivity at optical frequency, excess dielectric constant, Kirkwood correlation factor and Bruggeman factor of the binary mixture of ethanol with DMFat 293.15 K temperature



Variation in estimated values of atomic polarization of the binary mixture of ethanol–DMF at 293.15 K temperature.





Variation in estimated values of permittivity at higher frequency of the binary mixture of ethanol–DMF at 293.15 K temperature.

Excess Dielectric Constant (ϵ^{E})

The information related to the excess dielectric constant of the binary solution was obtained from the excess properties [16] of the mixture. The excess dielectric constant is obtained by the equation:

```
$${{\varepsilon }^{E}} = {{({{\varepsilon }_{{\rm O}}})}_{m}} - [{{\varepsilon }_{A}}{{{X}_{A}}} + {{\varepsilon }_{{B}}}{{{X}_{{B}}}],$$

(11)
```

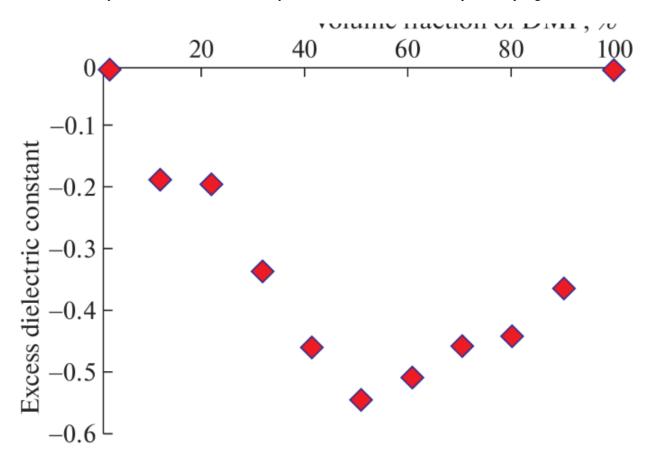
where X is the volume fraction and suffix m, A, B represents a mixture, liquid A (ethanol), and liquids B (DMF), respectively. Excess dielectric constant provides qualitative information about the formation of new structure in the mixture as follows:

- (i) $\varepsilon^E = 0$: indicates that solution *A* and *B* do not interact;
- (ii) ε^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.

Excess dielectric constant (ε^E) provides significant information regarding interaction between the polar-polar liquid mixtures. Excess dielectric constant of the binary mixtures was calculated using Eq. (11) and it is tabulated in Table 2 and graphically represented in Fig. 6.

Fig. 6.

Volume fraction of DMF %



Variation in estimated values of excess dielectric constant of the binary mixture of ethanol–DMF at 293.15 K temperature.

The excess dielectric constant is negative over entire volume fraction range of the binary mixture for the studied temperature. This indicates that in the mixture, the solutions interacts in such a way that the effective dipole moment decreases. The negative values of (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. The results are in agreement with earlier results of [17, 18].

Kirkwood Correlation Factor

The Kirkwood correlation factor given by Kirkwood [19] provides information regarding the orientation of the electric dipoles in polar liquids.

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

\$\$\frac{{4\pi N{{\mu }^{2}}\rho }}{{9KTM}}g = \frac{{({{\varepsilon }_{0}} - {{\varepsilon } _{\infty }})}}{{{\varepsilon }_{0}}} + {{\varepsilon }_{\infty }})}}{{{{\varepsilon }_{0}}}

```
{{{({{\varepsilon }_{\infty }} + 2)}}^{2}}}},$$
(12)
```

where \(\mu\) is dipole moment, \(\rho\) is density at temperature T, M is molecular weight, K is Boltzman constant, N is Avogadro's number, ε_s is the static dielectric permittivity, and \({{\varepsilon}} -{\infty }}\) 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 [20, 21] two such equations used are as follows:

```
 $\\left( \frac{\{\{\{m\}^{\{\{m\}^{\{\{m\}}\}}\}\{\{\{m\}^{\{\{m\}}\}\}\}\{\{\{m\}^{\{\{m\}}\}\}\}\{\{\{m\}^{\{\{m\}}\}\}\}\{\{\{m\}^{\{\{m\}}\}\}\}\{\{\{m\}^{\{\{m\}}\}\}\}\{\{\{m\}^{\{\{m\}}\}\}\}\}\{\{\{m\}^{\{\{m\}}\}\}\}\}\{\{\{m\}^{\{\{m\}}\}\}\}\}\} \\  \left( \{\{\{\alpha\}^{\{\{n\}}\}\}\}+\{\{\{\alpha\}^{\{\{n\}}\}\}\}\}\{\{\{m\}^{\{\{m\}}\}\}\}\}\{\{\{m\}^{\{\{m\}}\}\}\}\}\{\{\{m\}^{\{\{m\}}\}\}\}\}\}\{\{\{\{m\}^{\{\{m\}}\}\}\}\}\}\{\{\{m\}^{\{\{m\}}\}\}\}\}\}\{\{\{m\}^{\{\{m\}}\}\}\}\}\}\{\{\{m\}^{\{\{m\}}\}\}\}\}\} \\  \left( \{\{\{\alpha\}^{\{\{n\}}\}\}\}+\{\{\{\alpha\}^{\{\{n\}}\}\}\}\}\}\}\{\{\{m\}^{\{\{m\}}\}\}\}\}\}\}\{\{\{m\}^{\{\{m\}}\}\}\}\}\}\} \\  \left( \{\{\{\alpha\}^{\{\{n\}}\}\}\}\}\}\}\{\{\{m\}^{\{\{n\}}\}\}\}\}\}\}\{\{\{m\}^{\{\{n\}}\}\}\}\}\}\}\} \\  \left( \{\{\{\alpha\}^{\{\{n\}}\}\}\}\}\}\{\{\{m\}^{\{\{n\}}\}\}\}\}\}\}\{\{\{m\}^{\{\{n\}}\}\}\}\}\}\} \\  \left( \{\{\{\alpha\}^{\{\{n\}}\}\}\}\}\}\}\{\{\{m\}^{\{\{n\}}\}\}\}\}\}\}\}\{\{\{m\}^{\{\{n\}}\}\}\}\}\}\} \\  \left( \{\{\{\alpha\}^{\{n\}}\}\}\}\}\{\{\{m\}^{\{\{n\}}\}\}\}\}\}\}\}\}\{\{\{m\}^{\{\{n\}}\}\}\}\}\}\} \\  \left( \{\{\{\alpha\}^{\{n\}}\}\}\}\}\{\{\{m\}^{\{\{n\}}\}\}\}\}\}\}\}\{\{\{m\}^{\{\{n\}}\}\}\}\}\} \\  \left( \{\{\{\alpha\}^{\{n\}}\}\}\}\}\{\{\{m\}^{\{\{n\}}\}\}\}\}\}\}\{\{\{m\}^{\{\{n\}}\}\}\}\}\}\}\} \\  \left( \{\{\{\alpha\}^{\{n\}}\}\}\}\{\{\{n\}\}\}\}\}\}\}\{\{\{m\}^{\{\{n\}}\}\}\}\}\}\}\} \\  \left( \{\{\{\alpha\}^{\{n\}}\}\}\}\{\{\{n\}\}\}\}\}\}\}\{\{\{n\}^{\{n\}}\}\}\}\}\}\}\} \\  \left( \{\{\{\alpha\}^{\{n\}}\}\}\}\{\{\{n\}\}\}\}\}\}\}\{\{\{n\}^{\{n\}}\}\}\}\}\}\}\}\}\} \\  \left( \{\{\{\alpha\}^{\{n\}}\}\}\}\{\{\{n\}\}\}\}\}\}\{\{\{n\}^{\{n\}}\}\}\}\}\}\}\}\}\}\}\}  \{\{\{\alpha\}^{\{n\}}\}\}\{\{\{n\}\}\}\}\}\{\{\{n\}\}\}\}\}\}\{\{\{n\}^{\{n\}}\}\}\}\}\}
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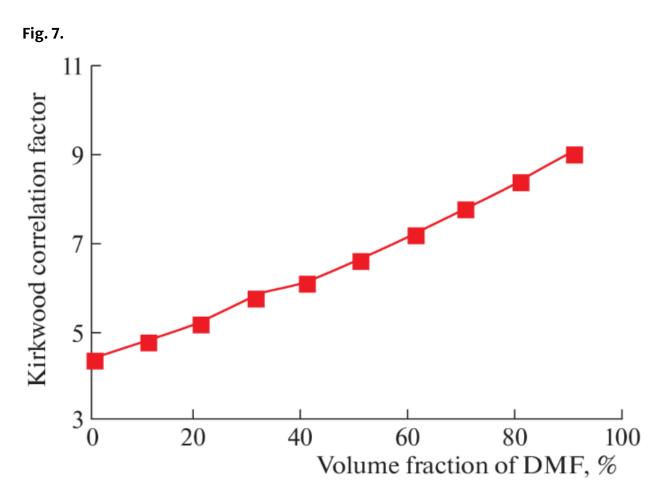
where $g^{\rm eff}$ is the Kirkwood correlation factor for the binary mixtures. $g^{\rm eff}$ varies between \({{g}_{M}}\) and \({{g}_{F}}\)

```
 $\\left( {\frac{\mu_{M}^{2}_{nn}}} \right) $$\Big( {\frac{\mu_{M}^{2}_{nn}_{g}_{M}}} \left( {\frac{\mu_{M}^{2}_{nn}}} \right) $$\Big( {\frac{\mu_{M}^{2}_{nn}_{g}_{M}}} \left( {\frac{\mu_{M}^{2}_{nn}}} \right) $$\Big( {\frac{\mu_{K}^{2}_{nn}_{g}_{nn}}} \left( {\frac{\mu_{K}^{2}_{nn}}} \right) $$\Big( {\frac{\mu_{K}^{2}_{nn}}} \left( {\frac{\mu_{K}^{2}_{nn}}} \right) $$\Big( {\frac{\mu_{K}^{2}_{nn}}} \right) $\Big( {\frac{\mu_{K}^{2}_{nn}}} \right) $$\Big( {\frac{\mu_{K}^{2}_{nn}}
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\(\{\{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.

In the mixture, the dipole pairs are formed and orient in parallel and antiparallel directions in the binary mixture that is confirmed from the Kirkwood correlation factor q^{eff} . The effective Kirkwood

correlation factor of the binary mixture of ethanol–DMF was calculated using $\underline{\text{Eq. (13)}}$ and presented in $\underline{\text{Table 2}}$, its variation with volume fraction is given in $\underline{\text{Fig. 7}}$. The g^{eff} values of the binary mixtures are greater than 1 for entire volume fraction range for the studied temperature; indicates that in the mixture the dipole pairs have been formed and their orientation is parallel in the entire volume fraction range of the binary mixture. The results are in agreement with earlier results of Hosamani et al. [17].



Variation in estimated values of effective kirkwood correlation factor of the binary mixture of ethanol–DMF at 293.15 K temperature.

Bruggeman Factor

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 was given by Bruggeman [22].

Bruggeman mixture formula given by Bottcher [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 (ε_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 (ε_{sm}), solute (ε_{sB}), and solvent (ε_{sA}) can be related to volume fraction of solvent (V) which indicates the interaction between solvent and solute in the mixture [24]

```
$${{f}_{{{\text{BM}}}}} = \left[ {\frac{{{{\varepsilon }_{{sm}}} - {{\varepsilon }_{{sB}}}}} {{{{\varepsilon }_{{sA}}}} - {{\varepsilon }_{{sB}}}}} \right]{{\left[ {\frac{{{{\varepsilon }_{{sA}}}}}} {{sA}}}}} \right]}^{{{\varepsilon }_{{sM}}}}} \right]}^{{1/3}}} = 1 - V,$$

(15)
```

where V is the volume fraction. In fact, mole fraction is a qualitative measure of the volume fraction of the solute. $\{\{\{varepsilon\}_{\{sM\}}\}\}, \{\{sA\}\}\}\}, \{sA\}\}\}$ are static dielectric constant values of mixture, solution A (solvent) and solution B (solute) respectively. 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. When both the solvent and the solute happen to be polar liquids, the Bruggeman equation has to be modified as;

```
$${{f}_{{{\text{BM}}}}} = 1 - [a - (a - 1)V~]~V,$$
(16)
```

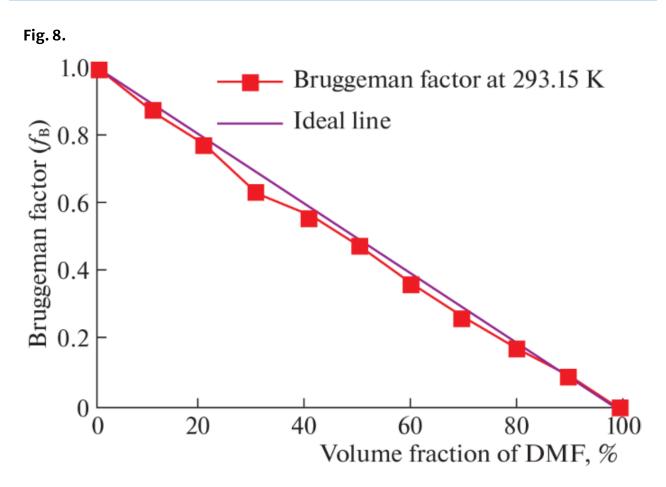
where *a* is the interaction factor. The relative change in value of *a* reveals the amount of interaction between solute and solvent as follows.

- (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 Brugemann mixture factor.

Bruggeman factor values f_B of ethanol–DMF binary mixtures have been evaluated using Eq. (15), given in Table 2 and graphically presented in Fig. 8. From Fig. 8 it is observed that, there is deviation from the

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linear relation of binary mixture has been taking place at the studied temperature, which gives the evidence of presence of molecular interaction and hydrogen bonding in the binary mixture. It is also observed that the values of a are less than 1 (a < 1), indicates that the effective microscopic volume of solvent (ethanol) gets less than the actual volume, and the solute (DMF) exerts an attractive microscopic force on the system.



Variation in estimated values of Bruggeman factor of the binary mixture of ethanol–DMF at 293.15 K temperature.

Molar Refraction, Polarizabilty, Solvated Radii, and Molecular Polarization

The calculated values of the molar refractions (R), polarizability (α), solvated radii (r), and molar polarization (P_m) were given <u>Table 3</u>. This show that, for this polar binary mixture, all these parameters are increasing and they are of the same nature to that of the refractive index. This means that as the refractive index increases, the solvent—solvent interaction increased and so the molar refraction, polarizabilities, molar volumes and solvated radii increase. The molar refraction is a measure of volume occupied with an atom or molecule and depends on the refractive index, it was

noticed that the molar refraction of the studied binary mixtures increases, as the molar volume and refractive index increase and vice versa. The results are in agreement with the earlier results of Farid.

Table 3. Variation in estimated values of molar refraction, polarizability, solvated radii and molar polarization of the binary mixture of ethanol with DMFat 293.15 K temperature

Excess Parameters

Excess density (d^E). The excess density of the binary mixtures was calculated using Eq. (7) and it is illustrated in Table 4. From the density data it is noted that the excess density is positive over the entire volume fraction range of the binary mixture at the studied temperature.

Table 4. Variation in estimated values of excess density, excess refractive index, excess molar polarization and excess molar volume of the binary mixture of ethanol with DMFat 293.15 K temperature

Excess refractive index (n^E). The excess refractive index was estimated using Eq. (8) and they are listed in Table 4. From the data, it is noticed that, the excess refractive index of this polar binary mixture is positive for entire volume fraction range at the studied temperature. The excess refractive indices and the solvent-solvent interaction processes depend on the nature of the solvent, its physical properties such as the dielectric constant, the dipole moment and the donor number. The results are in agreement with the earlier results of Farid.

From excess refractive index, it is also observed that, the maximum solvent—solvent interaction is achieved at 70% volume fraction of DMF. This may explain why doctors in medicine use a 70% mixture than any other percentage. Also this may explain why chemists use mixed solvents in their experiments. This means that we can choose or define a suitable composition of any mixture under investigation which has a maximum excess refractive index. The results are in agreement with the earlier results of Farid.

Excess molar polarization $(P_m)^E$. The excess molar polarization was determined using Eq. (9) and is given in Table 4. From the data, it is observed that the excess molar polarization is nearly positive over

entire volume fraction range of the binary mixture.

Excess molar volume (V)^E. The excess molar volumes were estimated using Eq. (10) and it is given in Eq. From the data it is seen that the values of excess molar volume are nearly positive for the ethanol-DMF binary mixture at the studied temperature. The positive behavior may be due to the specific interactions, like formation of hydrogen bonds, charge transfer complexes and other complex forming interactions including strong dipole-dipole interactions between the component molecules in the mixture, which may lead to the positive values of excess molar volume [18].

CONCLUSIONS

The static dielectric constants, densities, refractive indices, atomic polarization and permittivity at optical frequency of the binary mixtures increase with increasing volume fraction of DMF.

Excess dielectric constants negative over entire volume fraction range of the binary mixture at the studied temperature.

In ethanol–DMF binary mixture the dipole pairs are formed and orient in parallel direction which is confirmed from the (q^{eff}) values.

There is a deviation from the linear relations that was confirmed from the Buggeman factor study that gives strong evidence of presence of molecular interactions and hydrogen bonding in the binary mixtures.

Molar refraction, polarizability, solvated radii, molar polarization increases with increasing volume fraction of DMF.

Excess density, excess refractive index, excess molar volume and the excess molar polarization are nearly positive over entire volume fraction range of the binary mixture at the studied temperature.

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Ethics declarations

The authors declare that they have no conflicts of interest.

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