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Static Dielectric Constants, Densities, Refractive Indices and Related Properties of Binary Mixtures at Various Temperatures Under Atmospheric Pressure

Navarkhele A.V.[2], Navarkhele V.V.[*1]

[1]Department of Physics, Dr. Babasaheb Ambedkar Marathwada University, Aurangabad - 431 004, India
[2]Chanabasweshwar College of Pharmacy Latur
Email: [1]vvn_bamu@yahoo.co.in

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Abstract

Experimental dielectric constants at (293.15, 298.15, 303.15) K, densities and refractive indices at 293.15 K are reported for water- ethanol and water- n-butanol binary mixture systems over the entire volume fraction range and atmospheric pressure. From the experimental dielectric data, the excess dielectric constant, effective Kirkwood correlation factor, Bruggeman factor and from density and refractive index data various parameters and their excess properties like excess density, excess refractive index, excess molar polarization, and excess molar volume were estimated and reported in the study. The static dielectric constant of the studied binary mixtures decreases with increase in temperature and volume fraction of the solutes. The density values are decreasing and refractive indices are increasing with increasing volume fraction of ethanol and n-butanol in water. Excess molar volumes values of ethanol and n-butanol are negative over the entire volume fraction range shows the presence of intermolecular interaction and hydrogen bonding in both the binary mixtures.

Keywords*: Static dielectric constant; density; refractive index; excess properties; polar binary mixtures.*

1. Introduction

The dielectric constant of the material is a measure of solvent's efficiency for separating the electrolytes into the ions; this physical property is influenced by interatomic and intermolecular attractions. Solvents with high dielectric constants encourage complete dissociation of the electrolytes whereas in solvents of low dielectric constant considerable ion pairing occur [1]. The variation in this physical property with composition, frequency and temperature gives important data about intermolecular interactions, hydrogen bonding and the molecular 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].

Ethanol is an alcohol produced from grains and agricultural products. It is a clear, colorless alcohol made from a variety of biomass materials. Ethanol is also called as ethyl alcohol, grain alcohol which dissolves in water and organic compounds readily. It is an important solvent and extractant that is widely used in the production of beverages. It is also an ingredient in number of beauty and personal care products. It has excellent solubility to many organic compounds. The solute n- butanol is also known as 1- butanol or butyl alcohol produced by fermentation of sugars derived from corn or petrochemical process. It is also used in a number of beverages, food and in an artificial food flavoring. It is also used in plastic, polymers, lubricants, synthetic rubber and brake fluids. The knowledge of the thermophysical properties of these liquids and their corresponding liquid mixtures has been employed in different fields including pharmaceutical and analytical sciences and they affect many pharmaceutical processes like design, synthesis, extraction, purification, absorption and distribution in body fluids [3]. However, reports are available about the thermophysical properties of ethanol and n-butanol with other compounds. Dielectric constants of water, methanol, ethanol, butanol and acetone: measurement and computational study was reported using low pass filter by M. Mohsen- Nia et al [4]. Excess properties of alcohol - water systems at 298.15 K were also reported by Hülya Yilmaz [5]. Dielectric and acoustic properties of binary liquid mixtures of cyclohexane with n-butanol at 308 K temperature were reported by Maharolkar et al [6].

Here we present the static dielectric constants ($\in s$) of the binary mixtures of water - ethanol and water - n-butanol at 293.15, 298.15 & 303.15 K temperatures and densities (ρ), refractive indices (n) at 293.15 K temperature over the entire volume fraction range. The related properties like excess dielectric constant (ε^E), effective Kirkwood correlation factor (g^{eff}), Bruggeman factor (f_B) , atomic polarization, electronic polarization, permittivity at higher frequency, molar volume, molar refraction, polarizability, solvated radii, molar polarization, deviation in molar refractivity, and the excess properties like excess density (d^E), excess refractive index (n^E), molar polarization $(P_m)^E$, excess molar volume (V^E), were estimated from the experimental data using appropriate equations to confirm molecular interactions, hydrogen bonding between the components of the mixtures.

*Corresponding Author

2. Materials and Methods

2.1 Chemicals and Sample Preparations

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 water and n-butanol with water at eleven different stages of a mixture of water plus ethanol and water plus n-butanol as 0 to 100% in steps of 10%. All mixtures were prepared just before the measurement.

2.2 Measurement of Dielectric Constant

The static dielectric constants of the binary mixtures were measured using a wet sensor make by Delta-T Devices Ltd. UK, which is based on the principle of frequency domain reflectometry technique. The measurements were recorded with a calibrated meter which is connected to the wet sensor. Measurement of each sample was repeated at least five times and the average value of that reading was taken as a dielectric constant of that mixture. The details of the apparatus have been described in our earlier paper [7]. The uncertainty in measurement of the dielectric constant is ± 3%. 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 used in the measurement system was surrounded by a heat protecting container through which the water of stable temperature was circulated using a temperature controller system**.**

2.2.1 Study of Excess Permittivity (ε^{E})

Excess dielectric constant- permittivity provides qualitative information about the formation of new structure in the binary mixtures and that may be obtained from the excess properties of the mixtures [8]. Excess dielectric constant is estimated by the equation:

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

In above equation Φ is the volume fraction and suffix m, A, B represents a mixture, liquid A (water) and liquids B (ethanol) first system and A (water) and liquids B (n-butanol) second system respectively. Excess permittivity provides qualitative information about the formation of new structure in the mixtures as follows:

i) $\boldsymbol{\varepsilon^{E}} = 0$: indicates that solution A and B do not interact or it is pure liquid.

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

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

2.2.2 Study of Kirkwood Correlation Factor

The Kirkwood correlation factor (g) provides information about the orientation of the electric dipoles in polar liquids [9]. The modified form of Kirkwood correlation factor that is, effective Kirkwood correlation factor (g^{eff}) given by [10, 11] was estimated by the equation:

$$\frac{4\pi N}{9kT}\left(\frac{\mu^{2}{}_{M}\rho_{M}}{M_{M}}X_{M} + \frac{\mu^{2}{}_{F}\rho_{F}}{M_{F}}X_{F}\right)g^{eff} = \frac{(\varepsilon_{0m} - \varepsilon_{\infty m})(2\varepsilon_{0m} + \varepsilon_{\infty m})}{[\varepsilon_{0m}(\varepsilon_{\infty m} + 2)^{2}]} \quad (2)$$

Where "g^{eff}" is the Kirkwood correlation factor for the binary mixtures.

2.2.3 Study of Bruggeman Factor

Molecular interactions in polar binary mixtures can be confirmed from the Bruggeman mixture formula. The static dielectric constant (ε_{sm}) of two binary mixtures is related to this formula with the volume fraction of solute (ε_{sB}) that proves the interaction between the solute (ε_{sB}) and solvent (ε_{sA}) of the mixtures by the equation [12]:

$$f_{BM=}\left[\frac{\varepsilon_{sm} - \varepsilon_{sB}}{\varepsilon_{sA} - \varepsilon_{sB}}\right]\left[\frac{\varepsilon_{sA}}{\varepsilon_{sm}}\right]^{\frac{1}{3}} = 1 - V, \quad (3)$$

In the above equation (V) is the volume fraction. According to this equation a linear relationship is expected in Bruggeman factor **(**f_{BM}) and (V), and deviation from this linear relation indicates presence of molecular interaction and hydrogen bonding in the mixtures. When both solute and solvent are polar liquids, the Bruggeman equation has to be modified as:

$$f_{BM} = 1 - [a - (a - 1)V\,]\,V, \quad (4)$$

In the above equation (a) is the interaction factor.

2.3 Measurement Refractive index

The refractive indices values of the studied binary mixtures were measured using digital pocket refractometer PAL- RI, make by Atago-Japan. The apparatus measures the refractive index in the range of 1.3306 to 1.5284**.** The uncertainty in the measurement of refractive indices given by the manufacturer is of ± 0.0003.

2.4 Measurements of Density

The 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 a single temperature, since there is no facility of temperature variation for the said model. The density values have a standard uncertainty given by the manufacturer is of $\pm 10^{-3}$ g·cm^{-3}.

2.5 Molar Refraction, Atomic Polarization, Permittivity at Higher Frequency, Polarizabilty, Solvated Radii, Molecular Polarization and Deviation in Molar Refraction

From experimental densities (d) and refractive indices (n) of pure substances and mixtures, the molar refraction (R) is calculated from the equation [13, 14]:

$$\boldsymbol{R} = \left(\frac{\mathbf{n^{2}-1}}{\mathbf{n^{2}+2}}\right)\mathbf{V} = \mathbf{P_{A}} + \mathbf{P_{E}} = \mathbf{P_{T}} = \mathbf{P_{D}} \quad (5)$$

Where "n" is the refractive index of the liquid and V = (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 equation (5) is equal to the summation of both atomic polarization (P_A) and electronic polarization (E_P) 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 [15]:

$$P_A = 1.05\ n^2 \quad (6)$$

The permittivity at higher frequency (ε_∞) is the square of the refractive index and it was calculated by the equation:

$$\varepsilon_\infty = n^2 \quad (7)$$

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- Lorentz formula [16]:

$$\left(\frac{n^2-1}{n^2+2}\right) = \left(\frac{4}{3}\right)\Pi n'\alpha \quad (8)$$

Where $n' = \frac{N}{V}$, N is Avogadro's number, and V is molar volume, (n) is the refractive index of the binary mixture.

Considering spherical form of the solvated molecules, the solvated radii of the pure solvents and binary mixtures were calculated using the equation [17]:

$$V = \left(\frac{4}{3}\right)\Pi r^3 \quad (9)$$

From experimental dielectric constants and densities of pure substances and mixtures the molecular polarization (Pm) was estimated using the equation [18]:

$$P_m = V\left(\frac{\varepsilon-1}{\varepsilon+2}\right) \quad (10)$$

Where (ε) and (V) is the static dielectric constant and molecular volume of the binary mixtures.

From the experimental density and refractive index data, the deviation in molar refraction was calculated using the well-known equation [19]:

$$\Delta_R = R_m - \sum_i \emptyset_i R_i \qquad \text{where i= 1, 2,} \quad (11)$$

In the above equation (R_m) is the molar refractivity of the mixtures (φi) and (Ri) are volume fraction and molar refractivity of pure liquids 1 and 2 respectively.

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

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

$$d^E = d_{mix} - (\Phi_1 d_1 - \Phi_2 d_2) \quad (12)$$

Where d_{mix} are the values of densities of mixtures, Φ_1, Φ_2 d_1, d_2 are the volume fractions and densities of the first and second liquids respectively.

The excess refractive index (n^E) was estimated from the experimental refractive index (n) using the equation:

$$n^E = n_{mix} - (\Phi_1 n_1 - \Phi_2 n_2) \quad (13)$$

Where n_{mix} are the values of refractive indices of the mixtures and Φ_1, Φ_2, n_1 , n_2 are the volume fractions and refractive indices of the first and second liquids respectively.

The excess molar polarization $(P_m)^E$ of the binary mixtures was determined by the equation:

$$(P_m)^E = (P)_m - \left[(P_m)_A \cdot \Phi_A + (P_m)_B . \Phi_B\right] \quad (14)$$

Where (P_m) is the polarization of the mixtures, $(P_m)_A$, $(P_m)_B$, the molar polarization and $\boldsymbol{\Phi_A}$, $\boldsymbol{\Phi_B}$ the volume fraction of liquid A and B respectively.

From the experimental density data of the binary mixtures, the excess molar volume $(V)^E$ was estimated by using the equation [20]:

$$V^E = V - \sum_{i=1}^{n} \Phi_i V_i \qquad \text{Where i} = 1, 2 \text{ ----} \quad (15)$$

Where V is the molar volume of the mixtures, Φ_i represents volume fraction and V_i is the molar volume of the components 1 and 2 respectively.

3. Results and Discussion

3.1 Static Dielectric Constant

The experimental values of the static dielectric constant of the binary mixtures of water - ethanol and water - butanol are given in Table 1 and graphically illustrated in Figure 1 and 2 respectively. The dielectric constants of the binary mixtures decrease with an increase in temperature (the decrease in dielectric constant with increase in temperature is around 0.20 to 0.55 per degree Celsius for ethanol and 0.15 to 0.40 per degree Celsius for n- butanol respectively) and volume fraction (the decrease in dielectric constant with an increase in volume fraction is around 0.30 to 0.60 for 1 % volume fraction of ethanol and 0.50 to 0.65 for 1 % volume fraction of n- butanol respectively) of ethanol and n-butanol in water for the studied temperatures. The decrease in dielectric constant with an increase in temperature may be due to rapid fall in orientation polarization, because the increased thermal motion reduces the alignment of the permanent dipoles [21]. The decrease in dielectric constant with an increase in volume fraction may be due to increase in size and shape of the complex molecules after hydrogen bonding interaction. This could be attributed to the decrease in the number of dipoles in the complex**,** which may lead to decrease in the volume of the rotating molecules [22, 23].

From Figure 1 and 2 it is also observed that, variation in dielectric constants is non- linear with increasing concentration of ethanol and butanol in water. In mixtures of polar liquid, if molecules are interacting a non-linear variation in dielectric constant with concentration was observed, and the same is confirmed from Figure 1 and 2. The variation in R- square values of dielectric constant of the studied binary mixtures of water - ethanol and water - butanol at different temperatures is graphically illustrated in Figure 3 and 4 respectively**.** From Figures, it is observed that there is non-linear variation in dielectric constants with concentration. This proves that the intermolecular association is taking place in the studied polar binary systems. Similar results have been reported by Lone et al for methanol – ethanol binary mixtures using TDR method, in that study they have claimed such type of non linear variation in dielectric constant [24]. Similar results were reported by Navarkhele et al on the binary mixture study of formamide with butylene glycol using high frequency TDR

technique, in that study the authors have reported the non-linear variation in the binary mixtures with concentration [25].

Table 1 *Variation in experimental values of static dielectric constants of water - ethanol and water – n-butanol binary mixture systems at different temperatures.*

Ethanol Volume (%)	Static dielectric constant T=293.15K	Static dielectric constant T=298.15K	Static dielectric constant T=303.15K
00	81.46	79.72	77.81
10	78.21	75.36	73.41
20	72.42	70.05	67.81
30	66.05	64.34	62.17
40	60.92	59.01	56.54
50	54.89	52.26	50.43
60	48.04	46.92	45.14
70	42.77	41.38	39.88
80	37.68	36.12	34.54
90	32.51	30.76	29.24
100	27.16	25.80	23.95
n-butanol volume (%)			
00	81.46	79.72	77.81
10	75.26	73.36	71.14
20	69.02	67.05	65.04
30	62.41	60.74	58.59
40	56.08	54.14	52.10
50	49.55	47.65	46.00
60	43.10	41.52	40.21
70	37.10	35.75	34.65
80	31.45	30.45	29.16
90	26.11	25.21	23.65
100	20.52	19.68	17.94

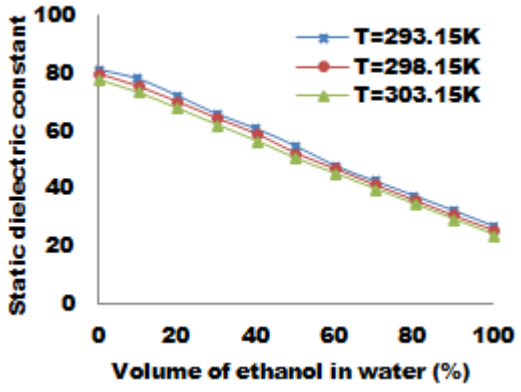

Figure 1*. Variation in static dielectric constant of the binary mixture of water - ethanol at different temperatures.*

The experimental density data of water - ethanol and water- butanol binary mixtures at 293.15 K temperature is given in Table 2. The density of the binary mixtures decreases with an increase in volume fraction of ethanol and n-butanol in water. This may be due to the addition of the concentration of ethanol and n-butanol in water, that may weaken the intermolecular bonds and may results in new bonds between similar and dissimilar molecules, that may increase the volume of the mixture consequently density is reduced. Similar results have been recorded by Nasim et al for the binary mixtures of poly(ethylene glycol) 300 + 1,2-ethanediol, 1, 2-propanediol, 1,3- propanediol, 1,3-butanediol, or 1,4-butanediol [26]

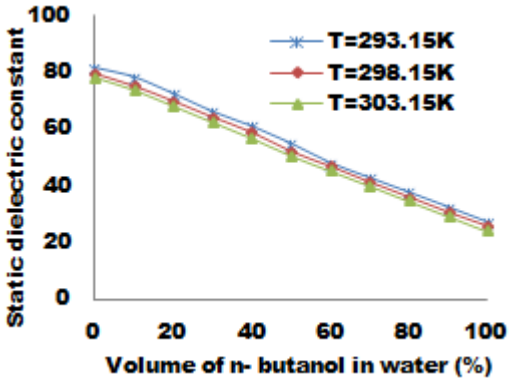

Figure 2*. Variation in static dielectric constant of the binary mixture of water - n-butanol at different temperatures.*

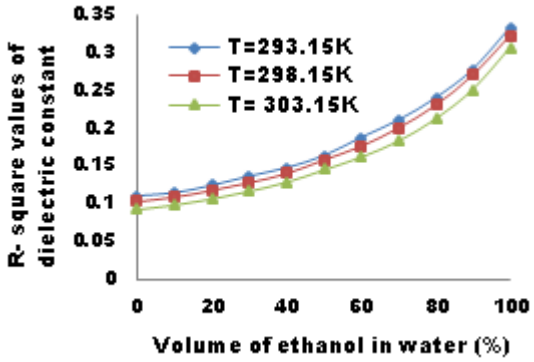

Figure 3 *Variation in R- square values of dielectric constants of the binary mixture of water - ethanol at different temperatures.*

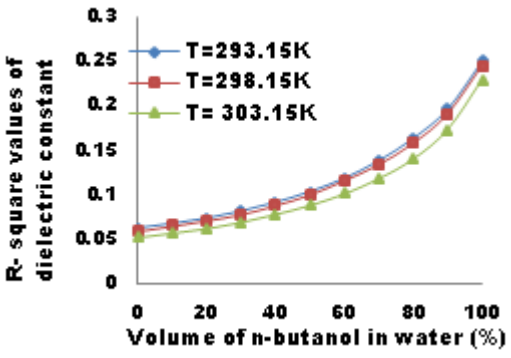

Figure 4 *Variation in R- square values of dielectric constants of the binary mixture of water - n-butanol at different temperatures.*

From density data, it is also seen that, there is nonlinear improvement in the density data of the binary mixtures; this is because of the increment of mass fraction of ethanol and n-butanol. It is observed that by adding hydroxyl groups to water over the entire volume fraction range, the density of the binary mixture is reduced Similar results have been

observed by Nasim et al for the binary mixtures of poly(ethylene glycol) 300 + 1,2-ethanediol, 1, 2-propanediol, 1,3- propanediol, 1,3-butanediol, or 1,4-butanediol [26].

The refractive index gives valuable information regarding molecular rearrangement on mixing. The refractive indices values of the binary mixtures of water - ethanol and water - butanol are given in Table 2. From the experimental data, it is observed that the refractive indices of both the binary mixture increases with an increasing volume fraction of ethanol and butanol in water. This may be due to decrease in density and number of dipoles per unit volume in the binary mixtures.

Table 2 *Variation in experimental values of densities and refractive indices of water- ethanol and water – n-butanol binary mixture systems at 293.15 K temperature.*

Ethanol Volume (%)	Density T=293.15K	Refractive index T=293.15K
00	0.9981	1.3338
10	0.9766	1.3363
20	0.9555	1.3392
30	0.9341	1.3418
40	0.9129	1.3445
50	0.8918	1.3474
60	0.8657	1.3500
70	0.8494	1.3527
80	0.8281	1.3556
90	0.8070	1.3582
100	0.7862	1.3612
n-butanol Volume (%)		
00	0.9981	1.3338
10	0.9782	1.3383
20	0.9590	1.3449
30	0.9400	1.3515
40	0.9211	1.3581
50	0.9021	1.3647
60	0.8831	1.3713
70	0.8640	1.3779
80	0.8450	1.3844
90	0.8261	1.3910
100	0.8071	1.3980

3.2 Excess Dielectric Constant (ε^E)

Excess dielectric constant of both the binary mixtures was calculated using equation (1) and it is tabulated in Table 3. The excess dielectric constant of water-ethanol binary mixtures is positive in water rich region that is 0 to 50% volume fraction of ethanol and negative in ethanol rich region that is 60 to 100% volume fraction of ethanol for the studied temperatures. The positive trend of (ε^E) indicates that, in the mixtures the solutions interacts in such a way that the effective dipole moment increases. The positive values of excess dielectric constant suggest that the effective number of dipoles in the mixture is greater than the corresponding average number in pure liquids; this may be due to the formation of new structure leading to a higher macroscopic permittivity. Similar results have been reported by Navarkhele et al in dielectric relaxation study of formamide-propylene glycol using time domain reflectometry, in the study the authors have reported that, the values of (ε^E) are negative up to 55% of mole fraction of PLG and positive for the rest of the mole fraction of PLG in the liquid mixtures [27].

Table 3 *Variation in estimated values of excess dielectric constants of water- ethanol and water – n-butanol binary mixture systems at different temperatures.*

Ethanol Volume (%)	Excess dielectric constant T=293.15K	Excess dielectric constant T=298.15K	Excess dielectric constant T=303.15K
00	0.00	0.00	0.00
10	2.18	1.02	0.98
20	1.82	1.11	0.72
30	0.88	0.79	0.51
40	1.88	0.85	0.27
50	0.58	-0.50	-0.45
60	-0.84	-0.44	-0.35
70	-0.68	-0.59	-0.22
80	-0.34	-0.46	-0.18
90	-0.08	-0.43	-0.09
100	0.00	0.00	0.00
n-butanol Volume (%)			
00	0.00	0.00	0.00
10	-0.10	-0.35	-0.68
20	-0.25	-0.66	-0.79
30	-0.76	-0.96	-1.25
40	-1.00	-1.56	-1.76
50	-1.44	-2.05	-1.87
60	-1.79	-2.17	-1.67
70	-1.70	-1.94	-1.25
80	-1.25	-1.23	-0.75
90	-0.50	-0.47	-0.27
100	0.00	0.00	0.00

Negative values of excess dielectric constant of water - ethanol and water with n-butanol binary mixtures show that, in the mixture the solutions interacts in such a way that the effective dipole moment decreases. Negative trend of (ε^E) indicates that the effective number of dipoles in the mixture might be smaller than the corresponding average number in the pure liquids that indicates the formation of new structure leading to a lower macroscopic permittivity. Similar results have been reported in the study of p-fluorophenylacetonitrile–methanol binary mixtures using time-domain reflectometry technique by Hosamani et al, in that study the authors are reported that when the values of (ε^E>1) the excess permittivity is positive, and (ε^E < 1) the excess permittivity is negative [28].

3.3 Kirkwood Correlation Factor

The estimated effective Kirkwood correlation factor values of water- ethanol and water-butanol binary mixtures were estimated using equation (2) and tabulated in Table 4 and graphically illustrated in Figure 5 and 6 respectively. From Figures 5 and 6 it is also observed that, there is small bump in (g^{eff}) values at 40% volume fraction of ethanol and n- butanol in water, that may be an experimental error. From Figure 5 and 6 it is also observed that the effective

Kirkwood correlation factor values of both the binary mixtures are greater than 1 (g^{eff} >1) over the entire volume fraction range. This indicates that in the mixtures the dipole pairs have been formed and their orientation is parallel over the entire volume fraction range of the binary mixtures for the studied temperatures. In the study of p-fluorophenylacetonitrile–methanol binary mixtures using time-domain reflectometry technique by Hosamani et al reported that when the values of g^{eff} >1, the dipoles are formed and their orientation is parallel and when g^{eff} <1, their orientation is antiparallel [28].

Table 4 *Variation in estimated values of effective Kirkwood correlation factor of water- ethanol and water – n-butanol binary mixture systems at different temperature.*

Ethanol Volume (%)	Kirkwood correlation factor T=293.15 K	Kirkwood correlation factor T=298.15 K	Kirkwood correlation factor T=303.15 K
00	5.00	4.95	4.91
10	5.13	5.02	4.97
20	5.12	5.04	4.95
30	5.07	5.02	4.93
40	5.11	5.03	4.90
50	5.08	4.91	4.81
60	4.95	4.91	4.80
70	4.98	4.89	4.78
80	5.03	4.90	4.75
90	5.10	4.89	4.71
100	5.16	4.97	4.66
n-butanol Volume (%)			
00	4.98	4.95	4.91
10	4.99	4.95	4.87
20	5.01	4.94	4.87
30	4.99	4.94	4.84
40	5.00	5.05	4.80
50	5.00	4.88	4.78
60	4.99	4.88	4.80
70	5.05	4.94	4.86
80	5.20	5.11	4.96
90	5.50	5.39	5.11
100	5.96	5.79	5.31

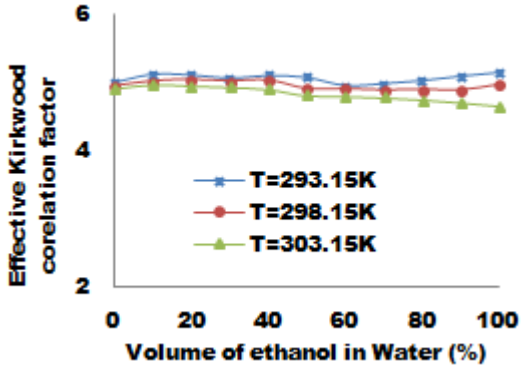

Figure 5*. Variation in estimated values of effective Kirkwood correlation fator of the binary mixture of water - ethanol at different temperatures.*

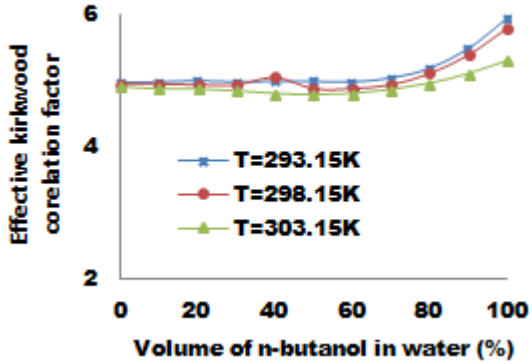

Figure 6*. Variation in estimated values of effective Kirkwood correlation fator of the binary mixture of water - n-butanol at different temperatures.*

3.4 Bruggeman Factor

Bruggeman factor values of water - ethanol and water-butanol binary mixtures were estimated using equation (3) that is noted in Table 5, and graphically illustrated in Figure 7 and 8 respectively. From figures it is observed that, there is deviation from the linear relation has been taking place in both the studied binary mixtures for the three different temperatures, which give the evidence of presence of molecular interaction and hydrogen bonding in the binary mixtures.

Table 5 *Variation in estimated values of Bruggeman factor of water- ethanol and water - n-butanol binary mixture systems at different temperatures.*

Ethanol Volume (%)	Bruggeman factor T=293.15K	Bruggeman factor T=298.15K	Bruggeman factor T=303.15K
00	1.00	1.00	1.00
10	0.95	0.93	0.93
20	0.86	0.85	0.85
30	0.76	0.76	0.76
40	0.68	0.68	0.67
50	0.58	0.56	0.56
60	0.45	0.46	0.47
70	0.35	0.35	0.36
80	0.25	0.24	0.25
90	0.13	0.12	0.13
100	0.00	0.00	0.00
n-butanol Volume (%)			
00	1.00	1.00	1.00
10	0.92	0.91	0.91
20	0.84	0.83	0.83
30	0.75	0.74	0.74
40	0.66	0.65	0.65
50	0.56	0.55	0.55
60	0.45	0.45	0.46
70	0.35	0.34	0.36
80	0.24	0.24	0.25
90	0.13	0.13	0.14
100	0.00	0.00	0.00

Table 6 *Estimated values of molar volume (V), molar refraction (R), polarizability (α), solvated radii (r), molar polarization (Pm), deviation in molar refractivity (Δ_R) , atomic polarization (P_A), electronic polarization (P_E) and permittivity at higher frequency (ε_∞) of water- ethanol and water – n-butanol binary mixture systems at 293.15K temperature.*

Ethanol Volume (%)	V (cm^3/mol)	R (cm^3/mol)	α (10^{-24}) cm/molecule	(r) A^0	(Pm) (cm^3/mole)	Δ_R	(P_A)	(P_E)	ε_∞
00	18.049	3.720	1.47	1.62	17.400	0.000	1.86	1.85	1.77
10	21.319	4.424	1.75	1.72	20.521	-0.221	1.87	2.54	1.78
20	24.726	5.171	2.05	1.80	23.729	-0.399	1.88	3.28	1.79
30	28.296	5.959	2.36	1.89	27.048	-0.536	1.89	4.06	1.80
40	32.026	6.793	2.69	1.96	30.499	-0.627	1.89	4.89	1.80
50	35.930	7.679	3.04	2.04	34.035	-0.666	1.90	5.77	1.81
60	40.254	8.661	3.43	2.12	37.840	-0.609	1.91	6.74	1.82
70	44.329	9.604	3.80	2.19	41.359	-0.591	1.92	7.68	1.82
80	48.857	10.664	4.22	2.26	45.163	-0.456	1.92	8.73	1.83
90	53.611	11.778	4.67	2.33	48.569	-0.267	1.93	9.84	1.84
100	58.598	12.971	5.14	2.40	52.274	0.000	1.94	11.02	1.85
n-butanol Volume (%)									
00	18.049	3.720	1.47	1.62	17.400	0.000	1.86	1.85	1.77
10	24.152	5.039	1.99	1.79	23.214	-0.525	1.88	3.15	1.79
20	30.485	6.473	2.56	1.93	29..198	-0.935	1.89	4.57	1.80
30	37.070	8.007	3.17	2.06	35.344	-1.246	1.91	6.08	1.82
40	43.922	9.647	3.82	2.18	41.653	-1.450	1.93	7.11	1.84
50	51.066	11.402	4.52	2.30	48.095	-1.540	1.95	9.44	1.86
60	58.518	13.277	5.26	2.40	54.626	-1.509	1.97	11.30	1.88
70	66.306	15.283	6.06	2.51	61.218	-1.347	1.99	13.28	1.89
80	74.436	17.419	6.90	2.60	67.760	-1.056	2.01	15.40	1.91
90	82.931	19.703	7.81	2.70	74.080	-0.616	2.03	17.67	1.93
100	91.846	22.164	8.78	2.79	79.611	0.000	2.05	20.11	1.95

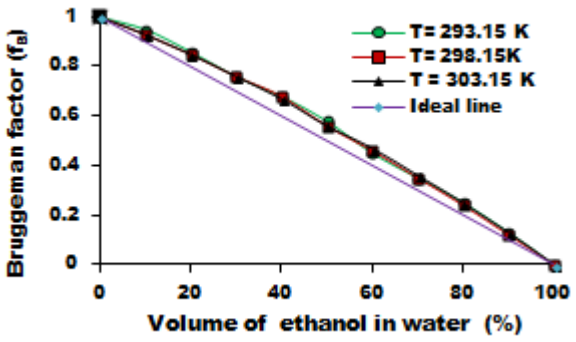

Figure 7*. Variation in estimated values of Bruggeman factor of the binary mixture of water – ethanol at different temperatures.*

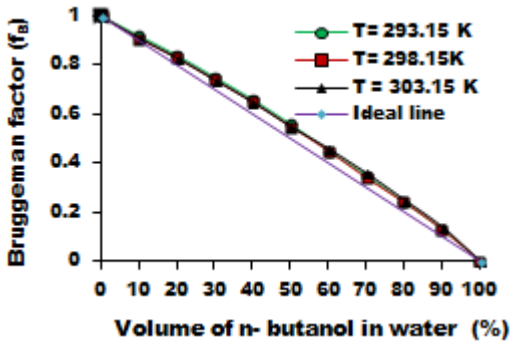

Figure 8*. Variation in estimated values of Bruggeman factor of the binary mixture of water – n-butanol at different temperatures.*

3.5 Molar Volume (V), Molar Refractions (R), Polarizabillty (α), Solvated Radii (r), Molar Polarization (P_m), Deviation in Molar Refraction (Δ_R), Atomic Polarization (P_A), Electronic Polarization (P_E) and Permittivity at Higher Frequency ($\mathcal{E}_\infty$)

The calculated values of the molar volume (V), molar refractions (R), polarizabillty (α), solvated radii (r), molar polarization (P_m), deviation in molar refraction (Δ_R), atomic polarization (P_A), electronic polarization (P_E) and permittivity at higher frequency ($\mathcal{E}_\infty$) of water-ethanol and water- butanol binary mixtures are given in Table 6. From the data it is observed that, all these parameters are increasing with volume fraction of ethanol and n-butanol in water and their trend is similar to that of refractive index. This means that as the refractive index increases, the solute-solvent interaction increases and so the molar volume, molar refraction, polarizabilities, molar volumes, solvated radii, atomic polarization, electronic polarization and permittivity at higher frequency increase. Since 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 refractions of the studied binary mixtures increases as the molar volume and refractive index increase and the same is noticed from Table 6 and 2. Similar results have been reported by Farid for selected binary protic-protic, aprotic-aprotic, and aprotic-protic systems at temperatures from 298.15 K to 308.15 K, in that study the author reported that, as the refractive index increases the solute-solvent interaction increases and so the molar volume, molar refraction, polarizabilities, solvated

radii and molar polarization increases. In the same study the author also reported that the molar refraction is a measure of volume occupied with an atom or molecule and depends on the refractive index and temperature, it was noticed that the molar refractions of the studied binary mixtures increases as the molar volume and refractive index increase. [13].

3.6 Excess Density, Excess Refractive Index, Excess Molar Polarization and Excess Molar Volume

The estimated values of excess density excess (d^E), excess refractive index (n^E), excess molar polarization **(**$P_m)^E$ and excess molar volume (V^E) of water-ethanol and water-butanol binary systems are tabulated in Table 7. From the Table it is observed that, excess density values are negative over the entire volume fraction range of the binary mixtures at the studied temperature. This may be due to increase in molar volume of the binary mixtures.

Table 7 *Variation in estimated values of excess density* $(d)^E$*, excess refractive index* $(n)^E$*, excess molar polarization* $(P_m)^E$ *and excess molar volume*(V^E) *of water- ethanol and water – n-butanol binary mixture systems at 293.15 K temperature.*

Ethanol Volume (%)	$(d)^E$	$(n)^E$	$(P_m)^E$	(V^E)
00	0.0000	0.0000	0.000	0.00
10	-0.0003	-0.00031	-0.366	-0.71
20	-0.0002	-0.00022	-0.645	-1.16
30	-0.0004	-0.00043	-0.814	-1.37
40	-0.0004	-0.00044	-0.850	-1.37
50	-0.0003	-0.00035	-0.802	-1.20
60	-0.0052	-0.00526	-0.484	-0.88
70	-0.0003	-0.00037	-0.452	-0.61
80	-0.0004	-0.00048	-0.136	-0.31
90	-0.0005	-0.00039	-0.217	-0.08
100	0.0000	0.00000	0.000	0.00
n-butanol Volume (%)				
00	0.0000	0.00000	0.000	0.00
10	-0.0008	-0.00192	-0.407	-1.17
20	-0.0009	-0.00174	-0.644	-1.91
30	-0.0008	-0.00156	-0.719	-2.25
40	-0.0006	-0.00138	-0.631	-2.25
50	-0.0005	-0.00120	-0.410	-1.99
60	-0.0004	-0.00102	-0.100	-1.55
70	-0.0004	-0.00084	0.270	-1.02
80	-0.0003	-0.00076	0.591	-0.52
90	-0.0001	-0.00058	0.690	-0.14
100	0.0000	0.00000	0.000	0.00

From Table 7, it is also observed that the excess refractive indices of both the binary mixture are negative over the entire volume fraction range at the studied temperature. The excess refractive indices and the binary mixtures interactions depend on the nature of the solvent and its physical properties such as the dielectric constant, dipole moment and the donor number. The results are in agreement with the earlier results of Farid, in the same study the author Farid reported that the values of excess refractive indices indicates maximum solvent- solvent interaction and depends mainly on the different physical properties of the solvents such as the dielectric constant, dipole moment donor number, chemical structure.

The estimated values of excess molar polarization of both the binary mixtures are given in Table 7. From the data it is noticed that for water- ethanol binary mixtures the excess molar polarization is negative over the entire volume fraction range and for water- butanol binary mixture it is negative in water rich region and positive in n-butanol rich region.

The estimated values of excess molar volume of water-ethanol and water - butanol binary mixtures are given in Table 7 and graphically illustrated in Figure 9 and 10 respectively.

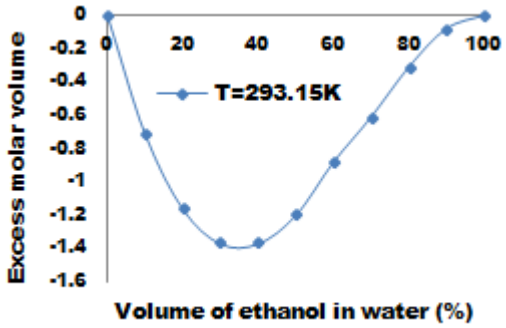

Figure 9*. Variation in estimated values of excess molar volume of the binary mixture of water – ethanol at 293.15K temperature.*

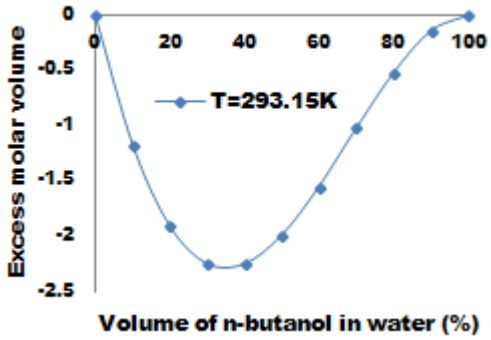

Figure 10*. Variation in estimated values of excess molar volume of the binary mixture of water – n-butanol at 293.15K temperature.*

From figures it is observed that, the values of excess molar volumes are negative over the entire volume fraction range for both the binary mixtures at the studied temperature. The negative behavior of excess molar volume over the entire concentration range may be due to the volume contraction after mixing. Excess molar volume is generally used as a signal of non-ideal behavior of real mixtures. Negative values of excess molar volumes show strong intermolecular interaction and formation of hydrogen bonds, charge transfer complexes and other complex forming interactions including strong dipole-dipole interactions between the component molecules in the mixtures. In the study of Density, Viscosity, Refractive Index, and Speed of Sound in Binary Mixtures of Pyridine and 1-Alkanols (C6, C7, C8, C10) at 303.15 K by A. Ali,

the authors had reported similar results. In the study the authors reported that, the negative deviations in $\mathbf{V^E}$ values over the entire composition range for all the binary systems suggest the presence of strong interactions between pyridine and 1-alkanol molecules and that the strength of interaction follows the order: 1-hexanol > 1-heptanol > 1-octanol >1-decanol. [29].

4. Conclusions

The static dielectric constant of binary mixtures decreases with increase in temperature and volume fraction of ethanol and n-butanol in water.

The variation in R- square values in dielectric constant of the studied binary mixtures show a non-linear variation with concentration, that shows the intermolecular association is taking place in the studied binary systems.

Densities of the studied binary mixtures decrease and the refractive indices increase with increase in volume fraction of ethanol and n-butanol in water.

Excess dielectric constant of water - ethanol binary mixture is positive in water rich region and negative in ethanol rich region. In case of water- butanol binary mixtures the excess dielectric constant is negative over the entire volume fraction range of n- butanol.

In both the studied binary mixtures the dipole pairs are formed and they orient in parallel direction over the entire volume fraction range of ethanol and n-butanol in water that is confirmed from the (g^{eff}) values.

The Bruggeman factor study of both the binary mixture systems shows that there is deviation from linear relations, which gives strong evidence of presence of molecular interactions and hydrogen bonding in the binary mixture systems.

Molar volume, molar refraction, polarizability, solvated radii, molar polarization, atomic polarization, electronic polarization, optical permittivity values increases with increasing volume fraction of ethanol and n-butanol in water.

Excess density, excess refractive index, and excess molar volume values of the binary mixtures is negative over the entire volume fraction range of ethanol and n-butanol. In water- butanol binary mixtures the excess molar polarization values are negative in water rich region and positive in butanol rich region.

Negative values of excess molar volume over entire volume fraction range of the studied binary systems confirm the presence of intermolecular interaction and hydrogen bonding between the binary systems.

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Nomenclature

Symbol	***Variable***
D	*Density*
d^E	*excess density*
f_{BM}	*Bruggeman factor*
g^{eff}	*effective Kirkwood correlation factor*
n	*Refractive index*
n^E	*excess refractive index*
P_A	*Atomic polarization*
P_E	*Electronic polarization*
P_M	*molar polarization*
$P_m{}^E$	*excess molar polarization*
R	*Molar refraction*
r	*Solvated radii*
V	*Molar volume*
V^E	*excess molar volume*
Greek	
Δ_R	*Deviation in molar refraction*
α	*Polarizabilty*
ε	*Dielectric constant*
ε_∞	*Permittivity at higher frequency*
$\boldsymbol{\varepsilon^E}$	*excess dielectric constant*
Superscript	
E	*Excess*
eff	*Effective*
Subscripts	
BM	*Bruggeman*
M	*Molar*
A	*Atomic*
E	*Electronic*
∞	*Higher Frequency*
Abbrevations	
r^2	*Coefficient of determination*

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