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STUDY OF SOLUTE-SOLVENT INTERACTION THROUGH DIELECTRICS AND DENSITIES PROPERTIES OF 2-BUTOXYETHANOL IN 2-ETHOXYETHNOL AT DIFFERENT TEMPERATURE

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ABSTRACT

The excess molar volume (v^E), static dielectric deviation ($\Delta\epsilon$), molar refraction (R_m), excess molar refraction (ΔR_m), Bruggeman factor (f_B), Mean molar polarizability (α), and polarity have been calculated from experimental measured density (ρ), static dielectric constant (ϵ) and refractive index (n) data of the binary mixtures of 2-Butoxyethnol (2-BE) with 2-Ethoxyethnol (2-EE) measured over the entire range of composition at 288.15, 298.15, 308.15 and 318.15 K. The excess properties were fitted to the Redlich-Kister (RK) polynomial equation to derive the adjustable parameters (A_j) and corresponding standard deviations (σ).Results regarding the intermolecular hydrogen bonding are discussed.

KEYWORDS

2-Butoxyethnol; 2-Ethoxyethnol; Polarity; Mean molecular polarizability.

INTRODUCTION

In chemical process industrial materials are normally handled in fluid from and as a consequence. The physical, chemical and thermodynamic properties of fluids assume importance. On the other hand excess thermodynamic functions and deviations of non thermodynamic ones of binary liquid mixtures are fundamental for understanding the intermolecular interaction between molecules in these types of mixtures. These functions have also been used as a qualitative and quantitative guide to predict the extent of complex formation in this kind of mixtures [1].

This work is a part of our program to provide data for the characterization of the molecular interactions between solvent in binary system [2-4]. The study of binary mixtures of 2-BE with 2-EE are very interesting because these system show the effect of the simultaneous presence of the ether and hydroxyl group. We report static dielectric constant (ϵ), density (ρ) and refractive index (n) of pure 2-Butoxyethnol and 2-Ethoxyethanol as well as for the binary mixture constituted by these two chemicals at temperatures of 288.15, 298.15, 308.15 and 318.15 K. From

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these experimental results excess molar volume (v^E), static dielectric deviation ($\Delta\epsilon$), molar refraction (R_m), excess molar refraction (ΔR_m), Bruggeman factor (f_B), Mean molecular polarizability (α), and polarity of the mixtures over the entire mole fraction ranges were calculated. Excess properties were fitted to the Redlich-Kister (RK) type equation to obtain their coefficients and standard deviations. Literature survey showed that no measurements have been previously reported for the mixture studied in this paper.

MATERIALS AND METHODS

Materials: The chemicals used in the present investigation are of spectroscopic grade & were used without further purification. The solutions were prepared by mixing 2-EE with 2-BE at 11 different volume percentage of 2-EE, 0 to100% in steps of 10 %.The measured values are included in Table 1 along with literature values show good agreement [5].

Apparatus: Density of pure components and their mixtures were measured using the single arm capillary pyknometer having a bulb volume approximately 2 cm^3 and internal diameter of the capillary of about 0.265mm.The temperature was controlled to ±0.01K with circulating thermostat water. The maximum error in the density measurements was ±0.00001gcm^{-3}

Static dielectric constant of pure components and their mixtures was measured indigenous developed instrument.

Refractive index of pure components and their mixtures were measured with Abbe refractometer. The values of refractive index were obtained using sodium D line .The temperature was controlled to ±0.01K with circulating thermostat water to the jacketed sample vessel. Caliberation was performed periodically using double distilled water. The maximum error in the refractive index measurements was ±0.001

Table 1

Comparison of Experimental and Literature Values of Densities (ρ), refractive indices (n) and static dielectric constants (ε) for pure 2-BE and 2-ME at T= (288.15 to 318.15) K.

Liquid	T/K	ρ/g.cm^{-3}		n		ϵ	
		Exp.	Lit.[5]	xptl.	Lit.	Exp.	Lit.
2-BE	288.15	0.90448	0.90448	1.421	1.4198* (293.15 K)	8.74	9.2*(283.15)
	298.15	0.89778	0.89630	1.416	-	8.37	-
	308.15	0.88166	0.8810	1.411	-	8.01	-
	318.15	0.85775	-	1.407	-	7.65	-
2-EE	288.15	0.93471	0.93478	1.409	14080* (293.15 K)	13.25	-
	298.15	0.92639	0.92573	1.404	-	12.66	-
	308.15	0.90850	0.91674	1.400	-	12.09	-
	318.15	0.88160	-	1.395	-	11.51	-

** R.C. Weast, Handbook of Chemistry and Physics 87th Edition, CRC Press Florida, 2006-2007.*

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RESULT AND DISCUSSION

The values of static dielectric constant (ϵ), density (ρ), refractive index (n) for the solutions of different concentration are presented in tables 2, 3 and 4 respectively.

Table 2

Static dielectric constant for pure components and their binary mixtures at T= (288.15 to 318.15) K.

Mole fraction of 2-EE	288.15 K	298.15 K	308.15 K	318.15 K
0.00000	8.74	8.37	8.01	7.65
0.10629	9.28	8.88	8.50	8.11
0.21110	10.01	9.57	9.16	8.72
0.31447	10.37	9.91	9.48	9.04
0.41643	10.73	10.26	9.81	9.35
0.51700	11.08	10.59	10.12	9.66
0.61621	11.26	10.76	10.30	9.81
0.71409	11.63	11.11	10.62	10.12
0.81066	11.99	11.46	10.96	10.43
0.90596	12.53	11.97	11.44	10.90
1.00000	13.25	12.66	12.09	11.51

Table 3

Density (ρ/g.cm^{-3}) for pure components and their binary mixtures at T= (288.15 to 318.15) K.

Mole fraction of 2-EE	288.15 K	298.15 K	308.15 K	318.15 K
0.00000	0.90448	0.89778	0.88166	0.85775
0.10629	0.90983	0.90177	0.88520	0.86076
0.21110	0.91081	0.90267	0.88602	0.86150
0.31447	0.91210	0.90385	0.88707	0.86246
0.41643	0.91361	0.90524	0.88833	0.86360
0.51700	0.91530	0.90679	0.88973	0.86487
0.61621	0.91710	0.90844	0.89126	0.86626
0.71409	0.91890	0.91011	0.89285	0.86771
0.81066	0.92043	0.91155	0.89440	0.86912
0.90596	0.92322	0.91460	0.89721	0.87100
1.00000	0.93471	0.92639	0.90850	0.88160

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Table 4

Refractive index (n) for pure components and their binary mixtures at T= (288.15 to 318.15) K.

Mole fraction of 2-EE	288.15 K	298.15 K	308.15 K	318.15 K
0.00000	1.421	1.416	1.411	1.407
0.10629	1.419	1.414	1.410	1.405
0.21110	1.418	1.413	1.409	1.404
0.31447	1.416	1.411	1.407	1.402
0.41643	1.415	1.410	1.406	1.401
0.51700	1.414	1.409	1.405	1.400
0.61621	1.413	1.408	1.404	1.399
0.71409	1.412	1.407	1.403	1.398
0.81066	1.411	1.406	1.402	1.397
0.90596	1.410	1.405	1.401	1.396
1.00000	1.409	1.404	1.400	1.395

From table 2 it can be seen that with an increasing concentration of 2-EE in 2-BE, the static dielectric constant values are increases for all four temperatures. These values, of static dielectric constant are decreased with increase in temperature. This type of results contribution for several factors such as:

-The 2-EE has large permanent dipole moments also have large static dielectric constant, because the dielectric polarization depends primarily on the ability of their dipoles to reorient in an applied electrical field.

-As the concentration of 2-EE increases in the solution, the alignment of dipoles along the field also increases due to this effect static dielectric constant increases.

- The increase in temperature, the alignments of dipoles along the field also decrease due to thermal demonstration. This caused gradually decreased in static dielectric constant.

-This may be possible due to the increase in the molar volume, the increase in the effective length of the dipole caused by the temperature increases, and also due to the thermal agitation and partly because of the sample viscosity decrease.

The increase in static dielectric constant of these alkoxyalkanol systems, with increasing mole fraction of 2-EE in mixture, indicates the formation of hydrogen bonding due to the influence of ions resulting (complex formation) between two molecules.

The density of these binary mixtures increases with increasing mole fraction of the 2-EE indicates that the molar volume of binary solution decreases because influence of Hydrogen bonding with 2-BE molecules.

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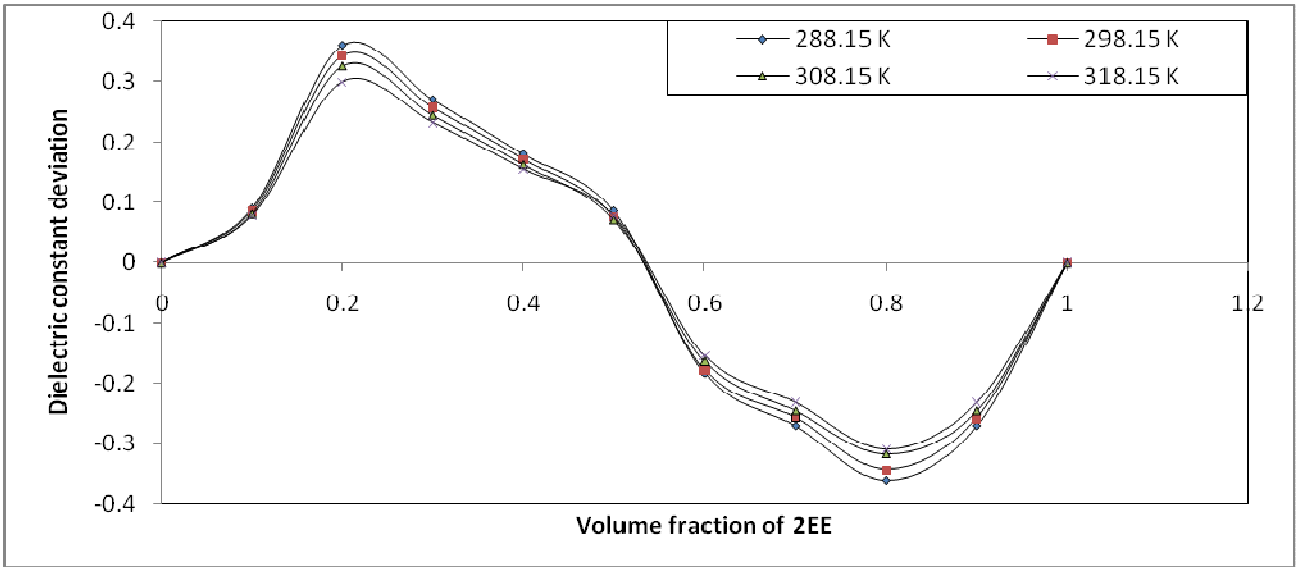
Refractive index of these binary mixtures decreases as mole fraction of 2-EE increases in mixture; because electronic polarization decreases.

Information related to solute-solvent interaction may be obtained by deviation from eq. 3, from figure1. Shows the static dielectric constants are dependence on 2-EE mole fraction (x) in the solutions at 288.15K to 318.15K. This dependence is strongly nonlinear, and results seem to be good example for illustration of a possible error extension in the estimation (even rough) of the static dielectric constants of liquid mixtures, assuming the static dielectric constants of the mixture partners.

$$\Delta A = A_{Mix} - (A_1 X_1 + A_2 X_2) \ldots\ldots (1)$$

Where, ΔA represents the static dielectric constant deviations ($\Delta\varepsilon$). A_1, A_2 and A_{mix} represent the static dielectric constant of pure liquids 1, 2 and that of the mixtures and X_1 and X_2 are mole fraction of pure liquids 1, 2 and their mixture at 288.15K to 318.15K respectively. The deviation parameters contains the structural information due to interaction between 1 and 2 .If ΔA is zero over the all concentration, this represents there is no interaction between 1 and 2 liquids. The deviations of $\Delta\varepsilon$ are shown in fig 1. From the fig. 1 it is observed that static dielectric constant deviations ($\Delta\varepsilon$) were found to be positive and negative this indicates the intermolecular interaction takes please in mixtures.

Figure 1
Variation of static dielectric deviation ($\Delta\varepsilon$) as a function of Mole fraction of 2-EE in the binary mixtures at 288.15-318.15 K.



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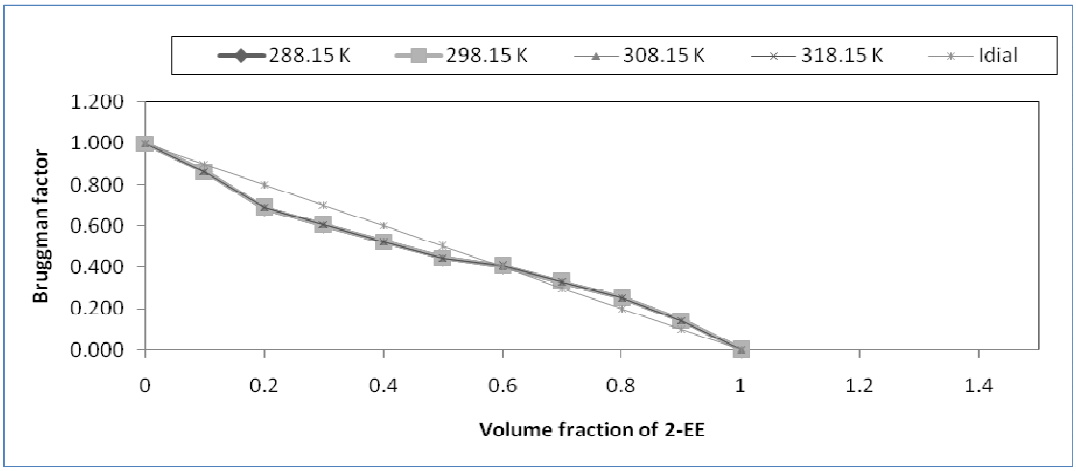
The modified Bruggeman equation[6] is another parameter, which may be, used as an indicator of liquid A and B interactions. The Bruggeman factor f_B is given by

$$f_B = \left(\frac{\varepsilon_m - \varepsilon_B}{\varepsilon_A - \varepsilon_B}\right)\left(\frac{\varepsilon_A}{\varepsilon_m}\right)^{(1/3)} = 1 - V \quad \ldots\ldots \quad (2)$$

Where V is Volume fraction, in fact, volume fraction V is a qualitative measure of volume of the solute. ε_m, ε_A and ε_B respectively are the values of static dielectric constant corresponding to mixture, solvent and solute. The Bruggeman plots of volume fraction of 2-EE versus f_B for 2-BE+2-EE mixtures are given in figure 2. It can be seen from this figure that f_B is not linear function of volume fraction of 2-EE because there are difference between ideal molar volume and resultant molar volume of pure components and their binary mixtures. The nonlinearity of the curves indicates heterointeraction, which may be due to hydrogen bonding of -OH group of 2-BE with –OH group of 2-EE.Similar interpretation were given by Sivagurunathan et al[7]

Figure 2

Variation of Bruggeman factor (f_B) as a function of Mole fraction of 2-EE in the binary mixtures at 288.15 -318.15 K.



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The excess molar volume [8-9] have been calculated as

$$V^E = \left[\frac{X_1M_1 + X_2M_2}{\rho}\right] - \left[\frac{X_1M_1}{\rho_1} + \frac{X_2M_2}{\rho_2}\right] \ldots. (3)$$

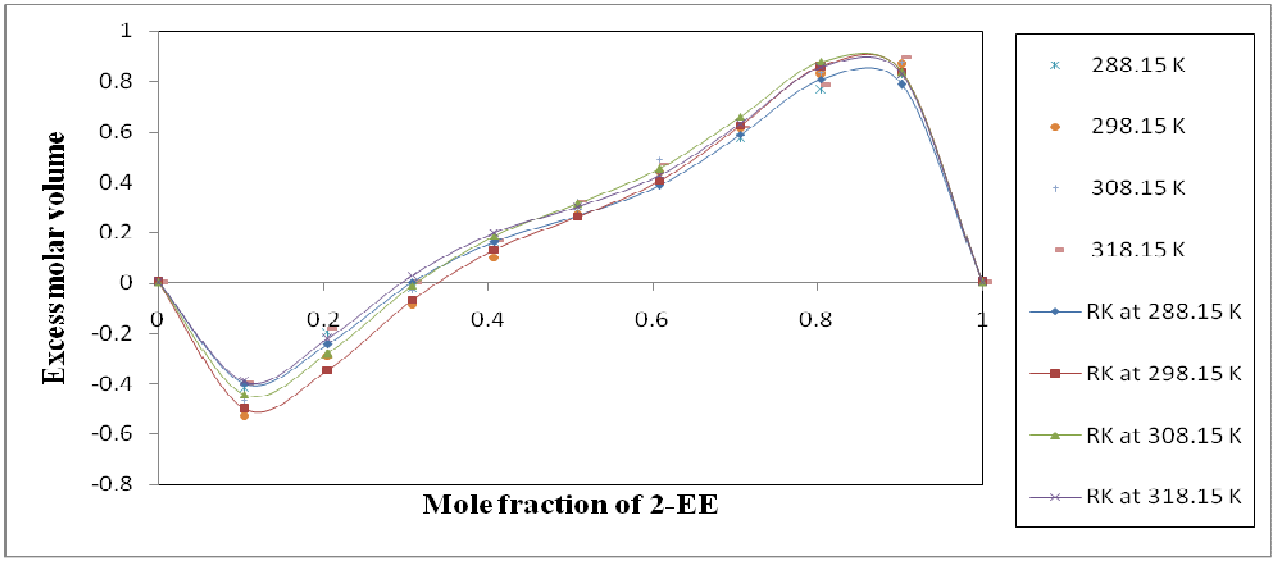
Where ρ is the density of the mixture, X_i, M_i and ρ_i are the mole fraction, the molar mass and the density of component i respectively.

The v^E are shown graphically in figure 3. Shows that its values for 2-ME in 2-BE binary mixtures are negative up to ≈ 30% 2-EE and positive above the 30%. The negative and positive values of V^E are the results of contributions from several factors such as:

- The negative v^E are indicated excess molar volume increases. So the strong intermolecular interaction takes placed up to ≈ 30% of 2-EE.While positive excess molar volume indicated weak intermolecular interaction takes placed above ≈ 30% 2-EE in mixture
- Structural changes such as changes in the correlation of molecular orientation and formation of new chemical species through hydrogen bonding or electron donor acceptor interactions between same function group.

Figure 3

Variation of Excess molar volumes (V^E) as a functionof Mole fraction of 2-EE in the binary mixtures at 288.15 -318.15 K.



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With the aim of gathering further information about the specific intermolecular interactions in studied binary mixture, we have investigated the molar refraction R_m defined by Lorenz-Lorenz equation [10]:

$$R_m = \frac{n^2 - 1}{n^2 + 2} v^m \quad \ldots\ldots\ldots\ldots (4)$$

where v_m is the molar volume of liquids. It must be remembered that R_m is a computed property strictly related to the electronic mean molecular Polarizability, α, of a real system (ether pure species or mixed components) by the equation:

$$\alpha = \frac{R_m \, 3 \varepsilon_0}{N_A} \quad \ldots\ldots\ldots\ldots (5)$$

where N_A is the Avogadro constant, ϵ_0 is the permittivity of free space and α is the mean Polarizability of the liquids.

Generally, the Polarizability α consists of two contributions, the first one measuring the ability with which the molecules will be deformed by an electric field, and other due to the orientation of the molecules dipoles under the action of this field . The more important are the orientation effects. Since we measured the refractive index in the optical region, the Polarizability should not include orientation effects. Therefore, the molar refraction should not more depend on temperature over a small temperature range, as can be seen in figure 4.The R_m values obtained for the 2-BE+2-EE solution lies in range 33.1386 cm^3 $mole^{-1}$ (pure 2-BE at 288.15K) to 23.8481 cm^3 $mole^{-1}$ (pure 2-EE at 288.15 K).From figure 4 reproduces the experimental trend of R_m versus mole fraction of 2-EE at 288.15K to 318.15 K..The mean molar Polarizability values are tabulated in table 5. From table 5 it is observed that, the contribution of electronic polarizability at small temperature interval also small.

Table 5

Mean molecular polarizability (α/cm^3mol^{-1}) for pure components and their binary mixtures at T= (288.15 to 318.15) K.

Mole fraction of 2-EE	288.15 K	298.15 K	308.15 K	318.15 K
0.00000	1.314E-24	1.313E-24	1.322E-24	1.347E-24
0.10629	1.269E-24	1.266E-24	1.279E-24	1.301E-24
0.21110	1.233E-24	1.231E-24	1.244E-24	1.265E-24
0.31447	1.195E-24	1.193E-24	1.205E-24	1.226E-24
0.41643	1.160E-24	1.158E-24	1.170E-24	1.190E-24
0.51700	1.125E-24	1.123E-24	1.135E-24	1.155E-24
0.61621	1.090E-24	1.089E-24	1.100E-24	1.119E-24
0.71409	1.056E-24	1.054E-24	1.066E-24	1.084E-24
0.81066	1.022E-24	1.021E-24	1.032E-24	1.050E-24
0.90596	9.878E-25	9.863E-25	9.967E-25	1.015E-24

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1.00000	9.454E-25	9.433E-25	9.533E-25	9.721E-25

The excess molar refractions have been calculated as

$$\Delta R_m = R_m - (x_1 R^1{}_m + x_2 R^2{}_m) \ldots\ldots\ldots (6)$$

where $R^1{}_m$ and $R^2{}_m$ are molar refraction of the mixed pure components. The molar refraction of pure component i is calculated using

$$R^i{}_m = \frac{n^2{}_i - 1}{n^2{}_i + 2} V^m{}_i \ldots\ldots\ldots\ldots\ldots\ldots (7)$$

The results of the analysis of ΔR_m are plotted in figure 5, where curve at 288.15 K to 318.15 K. The excess molar refraction ΔR_m as calculated from equation (7) represents the electronic perturbation due to orbital mixing of the molecules. Figure 5 shows that ΔR_m values are negative up to 50% of 2-EE and positive above 50% of 2-EE for the binary mixtures.

Figure 4

Variation of molar refraction (R_m) as a function of Mole fraction of 2-EE in the binary mixtures at 288.15 -318.15 K.

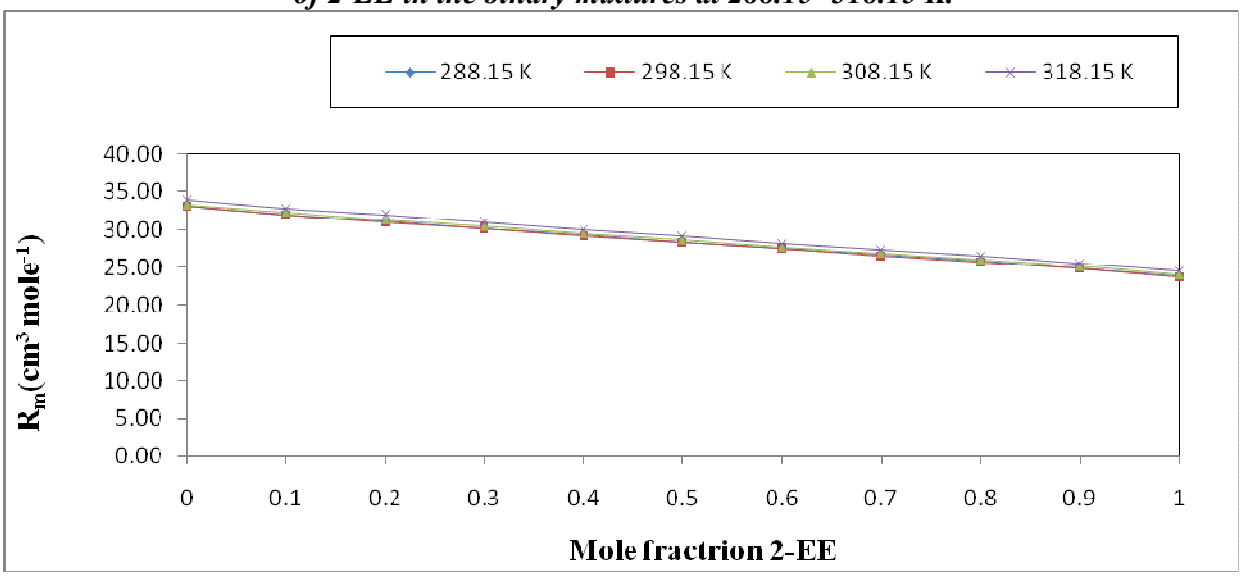

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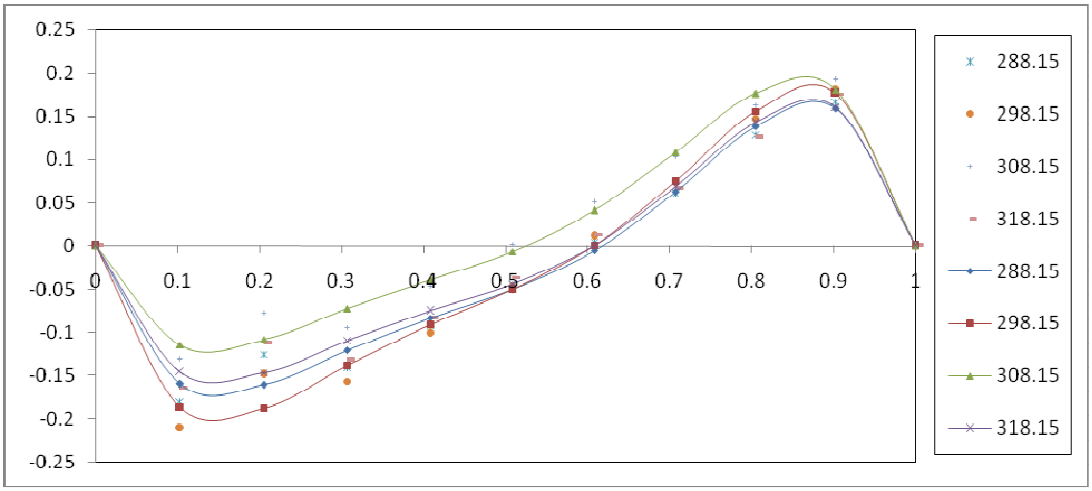
Figure 5

Variation of excess molar refraction (ΔR_m) as a function of Mole fraction of 2-EE in the binary mixtures at 288.15 -318.15 K.



From the William L. Marshall Equation 8 presented here describes the dielectric constant (ε) expressed as dielectric susceptibility (ε-1) to be isothermally proportional to the density (ρ) raised to a Constant power, given in logarithmic form [11]

$$\log(\varepsilon - 1) = A + B \log \rho \text{.....(8)}$$

Where A gives the information of polarity i.e. the ability of dipoles alignment along the field direction resulting in the mixture/pure liquids and B gives the information about the nature of liquids.

The constants A and B are calculated from equation (8).The polarity plot of log density verses log (ϵ-1)for 2-BE+2-EE pure components and their mixtures are give in figure 6.It can be seen from this figure that constants A and B values are gradually goes on increased. From table 6 it is observed that polarity goes on increases as well as there is small difference in B values it means these pure components and binary mixture are belongs same class.

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Figure 6
Variation of Log (ϵ-1) as a function of log density in the binary mixtures at 288.15 -318.15 K.

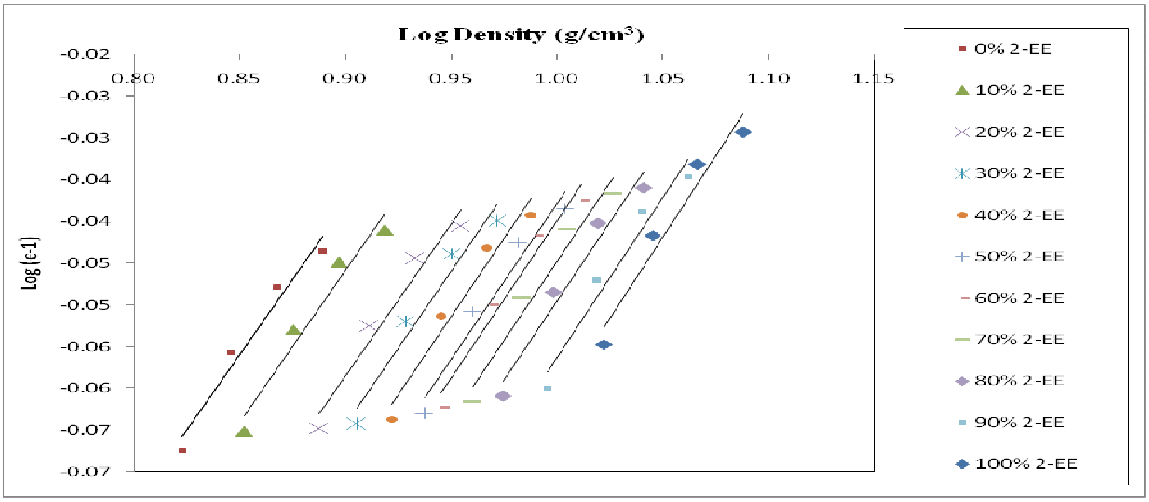

Table 6
Intercept A and B for pure components and their binary mixtures.

Mole fraction of 2-EE	A	B
0.00000	0.353	0.350
0.10629	0.375	0.365
0.21110	0.386	0.364
0.31447	0.396	0.369
0.41643	0.404	0.371
0.51700	0.411	0.374
0.61621	0.417	0.377
0.71409	0.422	0.378
0.81066	0.428	0.379
0.90596	0.440	0.383
1.00000	0.447	0.385

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For each mixture, the excess or deviation properties (v^E and ΔR_m) were fitted to Redlich-Kister equation (RK).

$$Y^E = X_1 X_2 \sum_{j=0}^{3} A_j (2X-1)^J \quad \ldots\ldots\ldots (8)$$

$$\sigma = \sqrt{\frac{\left[\sum (v^E_{mcal} - v^E_{m\exp t})^2\right]}{(n-1)}} \quad \ldots\ldots\ldots (9)$$

Where Y^E refers to an excess properties (v^E and ΔRm) for 1-2 binary pair; and X_i is the mole fraction of the *i*th component; Aj represents the coefficients and n is the number of experimental data points. Aj coefficients and standard error for all parameters were tabulated in table 7 and table 8 shows the 95% confidence interval (±) for same parameters

Table 7

Aj coefficients and standard error for excess molar volume and excess molar refraction.

Excess properties	A_j coefficients					Standard Error
	Temp.	A_0	A_1	A_2	A_3	
Excess molar volume	288.15 K	1.0269	1.8720	1.8539	10.0202	3.45E-02
	298.15 K	1.0054	2.3781	1.4719	10.8907	3.49E-02
	308.15 K	1.2114	2.3444	1.6052	10.3202	3.62E-02
	318.15 K	1.1754	1.9139	2.0357	10.3569	4.77E-02
Excess molar refraction	288.15 K	-0.2138	0.6970	0.3514	2.3591	1.87E-02
	298.15 K	-0.2163	0.8349	0.2785	2.6193	1.99E-02
	308.15 K	-3.77E-02	0.7336	0.6530	2.0589	1.79E-02
	318.15 K	-0.1874	0.6855	0.4432	2.2550	2.02E-02

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Table 8

Standard error and 95% confidence intervals of estimated Aj coefficients for excess molar volume and excess molar refraction.

Excess properties		Temp.	A_j Coefficients			
			A_0	A_1	A_2	A_3
Excess molar volume	Standard error	288.15 K	1.0269	1.8720	1.8539	10.0202
		298.15 K	1.0054	2.3781	1.4719	10.8907
		308.15 K	1.2117	2.3444	1.6052	10.3202
		318.15 K	1.1754	1.9139	2.0357	10.3569
	95% confidence interval (±)	288.15 K	0.1874	0.7369	0.8634	1.91961
		298.15 K	0.1896	0.7454	0.8735	1.94194
		308.15 K	0.1967	0.7732	0.9060	2.01428
		318.15 K	0.2588	1.0177	1.1925	2.65111
Excess molar refraction	Standard error	288.15 K	-0.2138	0.6970	0.3514	2.3591
		298.15 K	-0.2163	0.8349	0.2785	2.6193
		308.15 K	-3.77E-02	0.7336	0.6530	2.0589
		318.15 K	-0.1874	0.6855	0.4432	2.2550
	95% confidence interval (±)	288.15 K	0.1017	0.4000	0.4688	1.0422
		298.15 K	0.1081	0.4251	0.4981	1.1074
		308.15 K	9.72E-02	0.3820	0.4476	0.9951
		318.15 K	0.1095	0.4304	0.5043	1.1212

CONCLUSION

In this work, static dielectric constant , density and refractive index have been measured for the binary mixture of 2-BE+2-EE.static dielectric deviation, excess molar volume , molar refraction, excess molar refraction, Bruggeman factor (f_B), Mean molar polarizability (α), and polarity of the mixtures have been also been measured. From the variation of these parameters with composition and the effect of hydrogen bonding in new species were discussed from the point of view of intermolecular interactions in these mixtures.

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