

Measurements of Density, Dynamic Viscosity, Refractive Index and excess properties to Investigate Molecular Interactions in the Binary Mixture of Ethyl Benzoate and 2-Butanol from 303.15 K to 313.15 K

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Abstract

The thermochemical characteristics of binary mixture of ethyl benzoate (EB) and 2-Butanol (2-BuOH) over the entire composition range at temperatures between 303.15 K and 313.15 K under atmospheric pressure have been measured. Excess molar volume V^E , excess Gibbs energies of activation of viscous flow ΔG^{*E} , excess viscosity deviations $\Delta\eta$ and, and deviation in refractive indices Δn_D , were calculated then fitted to the Redlich-Kister polynomial equation. In the chemical and biochemical industries, these results can be used to create detailed theoretical models for the design of various technological processes. The values estimated by theoretical procedure and the experimental one showed good agreement. The intermolecular interactions have been used to explain the deviations for excess characteristics.

Keywords: Ethyl benzoate, 2-Butanol, thermophysical characteristics, excess properties, Redlich-Kister equation.

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Introduction

Renewable energy sources that adhere to the fundamentals of "green" chemistry are becoming more and more necessary due to the rising environmental pollution by the usage of fossil fuels and the depletion of their reserves as defined by Anastas and Warner [1]. It is a significant task to go from the current economy, which is dependent on fossil fuels to a sustainable biobased economy. With regard to the creation of energy as well as a variety of chemical materials, biomass has emerged as a promising, carbon-neutral replacement for fossil fuels.

[2] The production of the biomass result in a significant effect on In many significant chemical, industrial, and biological processes, understanding of the fluctuation of the thermodynamic characteristics of mixed solvent systems and their dependency on temperature and mole fraction is of significant importance[3]. The understand of the nature and potency of molecular interactions between the component molecules can be accomplished through the study of excessfunctions such as excess molar volume, deviation in viscosity, excess free energy of activation of viscous flow, and deviation in refractive index, etc. of binary liquid mixtures. When at least two solvent molecules join force to produce a liquid mixture, changes in free volume, energy, and molecular orientation have a major impact on the intermolecular interactions and correspond with changes in the thermodynamic parameters [4]. This research is a continuation of our previous work on binary liquid mixture physicochemical measurements [5]. The great variety of esters used in flavoring, fragrance, synthetic essences, and cosmetics has increased interest in the thermophysical study of esters. Esters have a significant role as solvents in the plastic, paint, and pharmaceutical industries [6]. The study of liquid mixtures with esters as one of the components has recently attracted more attention [7]. These studies are very important because they provide information on the structural alterations by mixing in pure ester with other solvents. Among the different types of esters, ethyl benzoate (EB) an aromatic ester, a polar solvent ($\mu = 1.8$ D), not a strongly associated liquid and is used as a perfume scent. It acts as a food flavoring agent. It is an active component of artificial fruit flavors. Further, it is used in cosmetics and personal care products as fragrance ingredients and preservatives [8, 9]. On the other hand, a number of authors have reported the thermophysical properties of pure 2-butanol with Allyl Chloride and Formamide at different temperatures and pressures [10, 11]. Many chemical molecules can be synthesized using alkanols. In general, alkanols are used in a variety of industrial products, including perfumes, cosmetics, paint, varnish, medicines, explosives, gasoline, fats, waxes, resin, plastics, rubber, and detergents. [12]. There is no study on the thermophysical properties of ethyl benzoate (EB) and 2-butanol (2-BuOH) mixture. Our aim with this project is to collect unique, highly accurate data on the density, viscosity, and refractive index of a mixture of ethyl benzoate (EB) and 2-butanol as a function of composition because this study is important for understanding the molecular interactions between associated and un-associated molecules. The objective of this work is to measure densities, viscosities and refractive indices of

the binary system {(EB) (1) + 2-BuOH (2)} at atmospheric pressure and temperature range from 303.15 K to 313.15 K at intervals of 5 K to get a better understanding of the nature of molecular orientation processes. These data have been used to calculate the excess properties, excess molar volume V^E , deviation in viscosity $\Delta\eta$, excess Gibb's free energy of activation for viscous flow ΔG^{*E} and deviation in refractive index Δn_D . The Redlich- Kister polynomial equation has been employed to correlate the excess properties.

1. EXPERIMENTAL SECTION

1.1. Chemicals

Table 1 regroups the source and purity of ethyl benzoate (EB) and 2-Butanol (2-BuOH) used in this work. No further purification of the chemicals was performed. The chemicals used in the present study were analyzed for densities, viscosities, refractive indices, and all the obtained values were compared with the literature data [13-32]. These values agree well with the data in the published literature as shown in Table 2. This agreement gives verification of the results obtained by the apparatus.

Table 1: Pure component specifications: suppliers, CAS number, specified purity.

| Chemical name | Supplier | CAS N° | Mass fraction purity (Supplier) |
|---------------------|----------------|---------|---------------------------------|
| Ethyl benzoate (EB) | Acrös organics | 93-89-0 | 99+% |
| 2-Butanol (2-BuOH) | Sigma Aldrich | 78-92-2 | ≥ 99 % |

Table 2: Comparison of experimental density, ρ , dynamic viscosities, η and refractive indices, n_D , of the pure components with the corresponding literature values at T= (293.15, 298.15, 303.15, 308.15, and 313.15) K and at $p = 1 \times 10^5$ Pa.

| | | ρ (g.cm ⁻³) | | η (mPa.s) | | nD | |
|-----------|-------------|------------------------------|--------------|----------------|------------|--------|-------------|
| Component | Temperature | Exp. | Lit. | Exp. | Lit. | Exp. | Lit. |
| 2-BuOH | 293.15 | 0.0000 | 0.80657 [13] | 0.0000 | 3.742 [16] | 0.0000 | 1.3971 [18] |
| | | | 0.8067 [14] | | | | |
| | 298.15 | 0.80354 | 0.80228 [13] | 3.0652 | 3.093 [16] | 1.3956 | 1.3954 [18] |
| | | | 0.8024 [14] | | | | |
| | | | | | 3.035 [17] | | |

| | | | | | | | |
|----|--------|--------|--------------|--------|------------|--------|--------------|
| | 303.15 | 0.7993 | 0.79799 [13] | 2.5451 | 2.579 [16] | 1.3949 | 1.3928 [18] |
| | | | 0.7984 [14] | | | | |
| | 308.15 | 0.795 | 0.79372 [13] | 2.128 | 2.147 [16] | 1.3923 | 1.3890 [18] |
| | | | 0.79405 [15] | | 2.111 [17] | | |
| | 313.15 | 0.7934 | 0.78943 [13] | 1.7934 | 1.826 [16] | 1.3905 | |
| | | | 0.78965 [15] | | | | |
| EB | 293.15 | 0.0000 | 1.04486[19] | 0.0000 | 2.21[20] | 1.0000 | 1.5056[20] |
| | | | 1.04622[20] | | 1.9776[19] | | 1.5053[19] |
| | 298.15 | | 1.04124[19] | 1.9974 | 1.9430[19] | 1.5025 | 1.5025 [19] |
| | | | 1.0413[21] | | 1.9543[23] | | 1.5027[29] |
| | | | 1.04142[22] | | | | 1.5034[30] |
| | | | 1.0423[23] | | | | 1.50328 [31] |
| | | | 1.04163[24] | | | | |
| | 303.15 | | 1.06393[19] | 1.8088 | 1.8123[19] | 1.5007 | 1.5007 [19] |
| | | | 1.038[25] | | 1.811 [20] | | 1.5012 [20] |
| | | | 1.0421[26] | | 1.756 [27] | | 1.5009 [32] |
| | | | 1.0371[27] | | | | |
| | 308.15 | | 1.03232[19] | 1.6451 | 1.6490[19] | 1.4988 | 1.4988 [19] |
| | | | 1.0325[27] | | 1.623[22] | | 1.49863[32] |
| | | | 1.0381[26] | | 1.633[28] | | 1.4985 [24] |
| | | | | | | | 1.49863[28] |

| | | | | | |
|--------|-------------|--------|------------|--------|-------------|
| 313.15 | 1.02772[19] | 1.4676 | 1.5093[19] | 1.4966 | 1.4966 [19] |
| | 1.0279[27] | | 1.463[27] | | 1.4997[32] |
| | 1.0328[26] | | 1.4619[23] | | |

In order to decrease evaporation losses, the binary liquid mixtures were carefully created by mixing known masses of pure liquids in glass vials (12 mL). All mixtures were measured on the same day using freshly produced solutions for each composition. A 0.01 mg accurate. OHAUS Discovery analytical balance was used to weigh all of the mixes. As soon as the samples with different compositions were created, the values were measured. [33].

1.2. Apparatus and procedure

1.2.1. Density and viscosity measurements

Using an SVM 3001 Stabinger viscometer (Anton Paar) with density and viscosity repeatability of $0.00005 \text{ g}\cdot\text{cm}^{-3}$ and 0.1%, respectively, and temperature stability of 0.005 K, the density and dynamic viscosity of the pure liquids and their binary mixture were measured at temperature $T = (303.15, 308.15, \text{ and } 313.15) \text{ K}$ and under atmospheric pressure. The instrument was calibrated in accordance with the procedure advised by the supplier. Uncertainties arising from the measurement protocol have been taken into account. It was found that the nominal uncertainties in density measurements were $u(\rho) = 0.05 \text{ g}\cdot\text{cm}^{-3}$. The instrument can measure simultaneously density in the range of $(0 \text{ to } 3) \text{ g}\cdot\text{cm}^{-3}$ and viscosity $(0.2 \text{ to } 30000) \text{ mm}^2\cdot\text{s}^{-1}$ in a temperature range of $(273.15 \text{ to } 343.15) \text{ K}$. The measured densities and viscosities were compared to literature values.

1.2.2. Refractive indices measurements

The refractive indices of the pure liquids and their binary combination were measured using a digital refractometer (RFM T series, Bellingham & Stanley Ltd., UK) at the required temperatures and atmospheric pressure. Before each measurement session, the refractometer was calibrated using distilled deionized water. Standard errors for temperature and refractive index are approximately $\pm 0.1 \text{ K}$ and $\pm 2 \times 10^{-4}$ units, respectively. A zero sample was measured to calibrate the refractometer after a prism had been washed with doubly distilled water and dried with a clean paper towel.

2. RESULTS AND DISCUSSION

Measurements of Density, Dynamic Viscosity, Refractive Index and excess properties to Investigate Molecular Interactions in the Binary Mixture of Ethyl Benzoate and 2-Butanol from 303.15 K to 313.15 K

The experimental densities, viscosities and refractive indices of the binary system {EB (1) + 2-Butanol (2)} at the temperature range $T = (303.15 - 313.15)$ K at intervals of 5 K under atmospheric pressure over the entire composition range are listed in Table 3.

Table 3: Experimental densities, ρ , dynamic viscosities, η , refractive indices, nD and calculated excess molar volume, V^E , viscosity deviations, $\Delta\eta$, excess Gibbs energies of activation of viscous flow, ΔG^{*E} , and deviation in refractive indices, ΔnD of the binary mixture {EB (1) + 2-Butanol (2)} at $T = (303.15, 308.15 \text{ and } 313.15)$ K and under atmospheric pressure.

| x_1 | ρ | x_1 | η | x_1 | nD | V^E | $\Delta\eta$ | ΔG^{*E} | ΔnD |
|-------------|-----------------------|--------|---------|--------|--------|---------------------------------------|--------------|------------------------|-------------|
| | (g.cm ⁻³) | | (mPa.s) | | | (cm ³ .mol ⁻¹) | (m.Pa.s) | (J.mol ⁻¹) | |
| T= 303.15 K | | | | | | | | | |
| 0.1001 | 0.8327 | 0.1001 | 1.9318 | 0.1001 | 1.4094 | 1.021 | -1.59 | -1388.9 | 0.0044 |
| 0.2000 | 0.8632 | 0.2000 | 1.6620 | 0.2000 | 1.4233 | 1.057 | -1.67 | -1566.1 | 0.0077 |
| 0.2999 | 0.8930 | 0.2999 | 1.5275 | 0.2999 | 1.4369 | 0.827 | -1.61 | -1592.0 | 0.0107 |
| 0.3991 | 0.9186 | 0.3991 | 1.4726 | 0.3991 | 1.4483 | 0.754 | -1.48 | -1503.0 | 0.0115 |
| 0.4998 | 0.9423 | 0.4998 | 1.4635 | 0.4998 | 1.4591 | 0.688 | -1.30 | -1340.8 | 0.0116 |
| 0.5992 | 0.9639 | 0.5992 | 1.4833 | 0.5992 | 1.4689 | 0.590 | -1.09 | -1137.6 | 0.0108 |
| 0.7017 | 0.9836 | 0.7017 | 1.5231 | 0.7017 | 1.4776 | 0.594 | -0.86 | -899.4 | 0.0086 |
| 0.8007 | 1.0029 | 0.8007 | 1.5878 | 0.8007 | 1.4861 | 0.358 | -0.60 | -638.0 | 0.0066 |
| 0.9018 | 1.0206 | 0.9018 | 1.6804 | 0.9018 | 1.4940 | 0.203 | -0.32 | -338.0 | 0.0037 |
| T= 308.15 K | | | | | | | | | |
| 0.1000 | 0.8289 | 0.1000 | 1.6687 | 0.1001 | 1.4077 | 1.407 | -1.84 | -1718.3 | 0.0047 |
| 0.2001 | 0.8602 | 0.2001 | 1.4532 | 0.2000 | 1.4215 | 1.304 | -1.85 | -1845.1 | 0.0079 |
| 0.3000 | 0.8883 | 0.3000 | 1.3687 | 0.2999 | 1.4352 | 1.211 | -1.72 | -1783.9 | 0.0110 |
| 0.3991 | 0.9138 | 0.3991 | 1.3008 | 0.3991 | 1.4465 | 1.089 | -1.59 | -1708.5 | 0.0117 |
| 0.5575 | 0.9374 | 0.5575 | 1.2868 | 0.4998 | 1.4572 | 2.569 | -1.27 | -1389.9 | 0.0117 |
| 0.5994 | 0.9593 | 0.5994 | 1.3435 | 0.5992 | 1.4669 | 0.800 | -1.13 | -1237.2 | 0.0108 |

| | | | | | | | | | |
|--------|--------|--------|--------|--------|--------|-------|-------|--------|--------|
| 0.7011 | 0.9796 | 0.7011 | 1.3852 | 0.7017 | 1.4757 | 0.658 | -0.88 | -969.4 | 0.0087 |
| 0.8006 | 0.9982 | 0.8006 | 1.4469 | 0.8007 | 1.4842 | 0.476 | -0.61 | -678.4 | 0.0066 |
| 0.9023 | 1.0165 | 0.9023 | 1.5352 | 0.9018 | 1.4918 | 0.190 | -0.32 | -350.0 | 0.0035 |

T= 313.15 K

| | | | | | | | | | |
|--------|--------|--------|--------|--------|--------|------|-------|---------|--------|
| 0.0999 | 0.8243 | 0.0999 | 1.4427 | 0.1000 | 1.4062 | 1.89 | -2.05 | -2044.9 | 0.0051 |
| 0.2000 | 0.8485 | 0.2000 | 1.3065 | 0.2001 | 1.4202 | 2.59 | -1.96 | -2033.7 | 0.0085 |
| 0.3000 | 0.8837 | 0.3000 | 1.1936 | 0.3000 | 1.4329 | 1.58 | -1.86 | -2047.8 | 0.0106 |
| 0.4057 | 0.9092 | 0.3996 | 1.1910 | 0.3991 | 1.4442 | 1.61 | -1.64 | -1812.2 | 0.0114 |
| 0.4988 | 0.9326 | 0.4988 | 1.1777 | 0.5575 | 1.4548 | 1.25 | -1.44 | -1641.0 | 0.0051 |
| 0.5992 | 0.9542 | 0.5992 | 1.1979 | 0.5994 | 1.4645 | 1.08 | -1.19 | -1383.7 | 0.0104 |
| 0.7007 | 0.9745 | 0.7007 | 1.2609 | 0.7011 | 1.4736 | 0.88 | -0.91 | -1044.3 | 0.0087 |
| 0.8008 | 0.9923 | 0.8008 | 1.3050 | 0.8006 | 1.4820 | 0.76 | -0.64 | -752.3 | 0.0066 |
| 0.9011 | 1.0112 | 0.9011 | 1.4031 | 0.9023 | 1.4900 | 0.31 | -0.32 | -375.0 | 0.0038 |

2.1. Volumetric studies

Values of experimental densities, ρ , for {EB (1) + 2-Butanol (2)} binary system at various composition at the temperature range $T = (303.15 - 313.15)$ K at intervals of 5 K are regrouped in Table 3. One can see from Table 3 that ρ values increase with the ethyl benzoate concentrations but their magnitude decreases with increasing temperature. This trend revealed the dissociation of the dipoles in the liquid mixture and it reflects the existence of interactions between the molecular constituents depending on the composition, temperature and molecular shapes and sizes of the components. These experimental data were employed to compute the excess molar volume V^E by using the below equation

$$V^E = \frac{(x_1 M_1 + x_2 M_2)}{\rho} - \frac{x_1 M_1}{\rho_1} - \frac{x_2 M_2}{\rho_2} \quad (1)$$

Where x_1 , M_1 and ρ_1 are mole fraction, molar mass and density respectively of pure components 1 and 2. ρ is the density of the binary mixture.

Furthermore, the composition dependence of the V^E values of {EB (1) + 2-BuOH (2)} binary

system at T = (303.15, 308.15 and 313.15) K were fitted with the Redlich- Kister type equation:

$$Y^E = x_1 (1 - x_1) \sum_{k=0}^m A_k (1 - 2x_1)^k \quad (2)$$

Where $Y^E \equiv V^E$ or $\Delta\eta$ or ΔnD or ΔG^{*E} and x_1 is the mole fraction of EB, A_k are adjustable parameters obtained by least-squares method, and k is the degree of the polynomials. In each case, the optimum number of coefficients was ascertained from an examination of the variation of standard deviation σ with:

$$\sigma = \left[\frac{\sum (Y_{\text{exp}} - Y_{\text{cal}})^2}{(n - p)} \right]^{1/2} \quad (3)$$

Where Y_{exp} and Y_{cal} are the experimental and calculated values of the property Y , respectively, and n and p denote the number of experimental points and number of parameters retained in the respective equations. Table 4 presents the values of the parameters A_k together with the standard deviation σ . The number of coefficients reported was chosen to achieve the best correlation obtained.

Table 4: Coefficients of Redlich–Kister equation A_k , and standard deviations σ , for excess molar volumes, V^E , deviation in viscosity, $\Delta\eta$, deviation in refractive indices, ΔnD , and excess Gibb's free energy, ΔG^{*E} , for the liquid mixture {EB (1) + 2-BuOH (2)} at T= (303.15, 308.15 and 313.15) K and under atmospheric pressure.

| Properties | A1 | A2 | A3 | A4 | A5 | σ |
|-----------------|-----------|----------|-----------|---------|----------|----------|
| T= 303.15 K | | | | | | |
| V^E | 0.975 | 0.686 | 1.844 | -2.274 | - | 0.051 |
| $\Delta\eta$ | -2.9 | 1.5 | -1.3 | 1.2 | -1.0 | 0.005 |
| ΔnD | 0.0468 | -0.0114 | -0.0074 | 0.0118 | 0.0083 | 0.0002 |
| ΔG^{*E} | -3534.706 | 1846.648 | -1264.258 | 529.372 | -430.460 | 4.897 |
| T= 308.15 K | | | | | | |
| V^E | 3.195 | 2.865 | -5.601 | -6.360 | - | 0.616 |

| | | | | | | |
|-----------------|-----------|----------|----------|---------|-----------|--------|
| $\Delta\eta$ | -2.4 | 1.2 | -0.3 | 0.9 | -1.6 | 0.016 |
| Δn_D | 0.047 | -0.012 | -0.003 | 0.008 | 0.001 | 0.0003 |
| ΔG^{*E} | -3334.788 | 1704.682 | -194.095 | 488.492 | -1554.839 | 22.148 |

T= 313.15 K

| | | | | | | |
|-----------------|-----------|----------|----------|---------|----------|--------|
| V^E | 1.352 | -1.166 | 4.046 | -0.592 | - | 0.292 |
| $\Delta\eta$ | -1.8 | 0.9 | -0.6 | 0.9 | -0.3 | 0.017 |
| Δn_D | 0.035 | -0.018 | 0.078 | 0.020 | -0.095 | 0.0021 |
| ΔG^{*E} | -2895.150 | 1398.025 | -395.196 | 964.844 | -374.063 | 39.399 |

V^E values of {EB (1) + 2-BuOH (2)} binary system at the temperature range T= (303.15, 308.15 and 313.15) K at intervals of 5 K under atmospheric pressure are plotted in Fig.3.

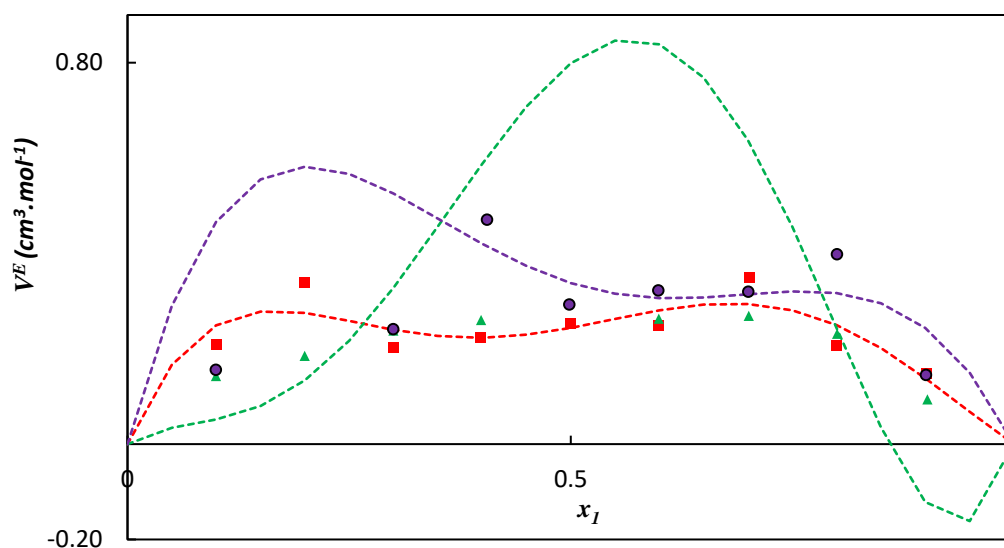


Fig. 1: Excess molar volume, V^E , against the mole fraction of EB, x_1 , for the binary mixture {EB (1) + 2-BuOH (2)} at T = (303.15, 308.15 and 313.15) K and under atmospheric pressure. ■ 303.15 K, ▲ 308.15K, ● 313.15K. ---, values derived from the Redlich-Kister equation (Eq. 2) using the coefficients listed in Table 4.

An examination of Fig. 1 illustrates that V^E values have positive signs which is attributed to the

decrease in the hydrogen bond interaction between the molecules of alcohol. The V^E values in our current study are positive in frequently. This type of V^E behavior can be attributed to:

(i) The absence of hydrogen bonds or in other term the dissociation of 2-BuOH resulting an increase in the volume. (ii) The difficulty in fitting the of one component into the other (iii) The presence of physical or non-specific effects including dispersion forces or weak dipole–dipole interactions.

2.2. Viscometric properties

Based on the experimental values of dynamic viscosity , η , the viscosity deviation , $\Delta\eta$, can be calculated as:

$$\Delta\eta/(mPa.s) = \eta - \sum_{i=1}^n x_i \eta_i \quad (4)$$

Where x_i , and η_i are mole fraction and dynamic viscosity of pure component i , respectively. η is dynamic viscosity of the mixture.

The excess Gibbs energy of activation of viscous flow, ΔG^{*E} , is given by:

$$\Delta G^{*E}/(Jmol^{-1}) = RT[(\ln(vM) - \sum^n x_i \ln(v_i M_i))] \quad (5)$$

Where v is the kinematic viscosity of the mixture, v_i is the kinematic viscosity of pure component i , ΔG^{*E} : is the excess Gibbs energy of activation of viscous flow, M is the molar mass of the mixture, n : is the number of components in the mixture.

Values of η , $\Delta\eta$ and ΔG^{*E} are included in Table 3. Viscosity changes nonlinearly with increasing temperature and composition as displayed in Fig. 4. This kind of behavior might be explained by the presence of particular forces in the mix. The exponential rise of the viscosity decrease with increasing temperature.

$\Delta\eta$ and ΔG^{*E} values of the binary system {EB (1) + 2-BuOH (2)} are depicted graphically in Fig. 2 and Fig. 3, respectively. Deviation in viscosity and excess Gibbs energy of activation were fitted to Redlich–Kister equation (Eq. 2). The adjustable parameters and standard deviations are given in Table 4.

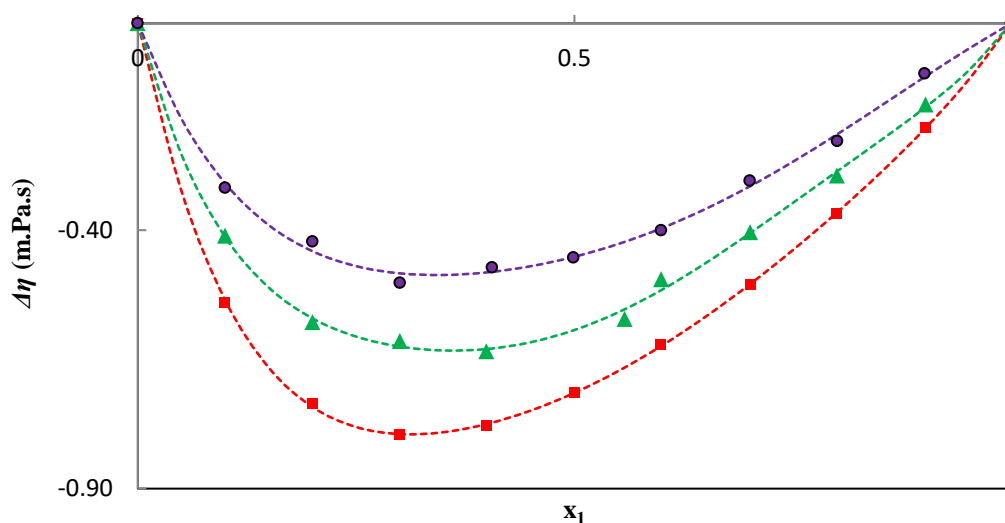


Fig. 2: Deviation in viscosity, $\Delta\eta$, against the mole fraction of EB, x_1 , for the binary mixture {EB (1) + 2-BuOH (2)} at $T = (303.15, 308.15 \text{ and } 313.15) \text{ K}$ and under atmospheric pressure. ■ 303.15 K, ▲ 308.15K, ● 313.15K. ---, values derived from the Redlich-Kister equation (Eq. 2) using the coefficients listed in Table 4.

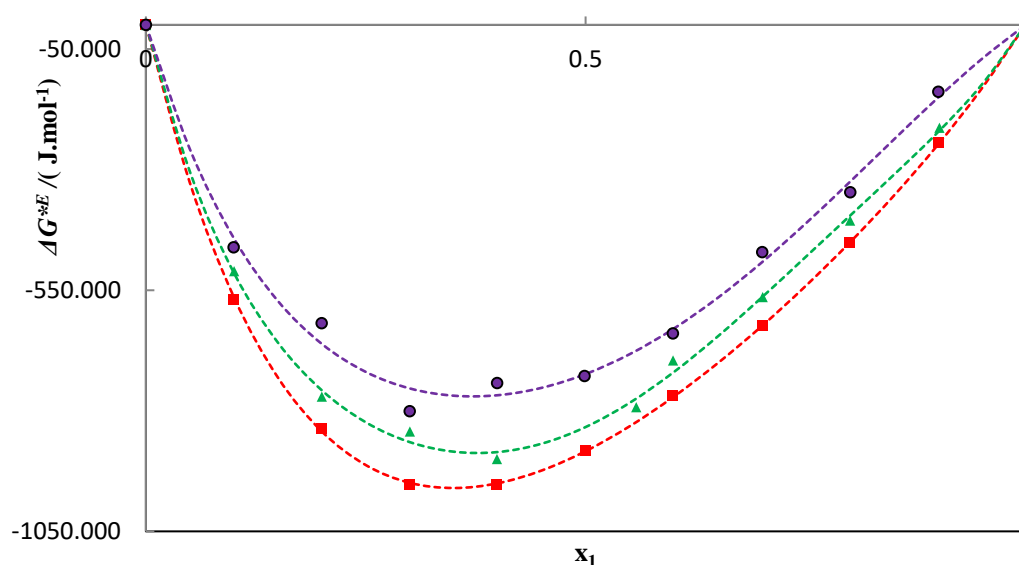


Fig. 3: Excess Gibbs energy of activation of viscous flow, ΔG^{*E} , against the mole fraction of EB, x_1 , for the binary mixture {EB (1) + 2-BuOH (2)} at $T = (303.15, 308.15 \text{ and } 313.15) \text{ K}$ and under atmospheric pressure. ■ 303.15 K, ▲ 308.15K, ● 313.15K. ---, values derived from the Redlich-Kister equation (Eq. 2) using the coefficients listed in Table 4.

The values of viscosity deviations are compared with those obtained from the Redlich–Kister polynomial equation in figure 2. $\Delta\eta$, exhibit a large negative values at $T = (303.15, 308.15 \text{ and } 313.15) \text{ K}$.

313.15) K over the whole composition range, According to Fortand Moore [36] the deviation in viscosity tends to get stronger as the interaction increases. A qualitative evaluation of the strength of the intermolecular interactions is provided by the difference in viscosity variation.

The following factors can be used as a general framework for explaining the deviation in viscosities [37]. (i) The different sizes and shapes of the molecules that make up the components and the loss of dipolar association in pure components may help to reduce viscosity; (ii) certain interactions between unlike components, like the formation of hydrogen bonds and charge-transfer complexes, may increase viscosity in mixtures compared in pure components. While the latter effect causes a positive divergence in viscosity, the former impact causes a negative deviation. This negative trend of $\Delta\eta$, would imply that the mixture is less viscous than the corresponding ideal mixtures.

Meyer et al. [38] state that excess Gibbs energy of activation for viscous flow, like viscosity deviations can be used to detect molecular interactions. A perusal of Fig.3 shows that the values of ΔG^{*E} on mixing are negative for the whole composition range of EB with 2-BuOH at T = (303.15, 308.15 and 313.15) K. The dependence is not uniform. The negative values of ΔG^{*E} , suggest the dominance of dispersion interaction between EB and 2- butanol molecules.

2.3. Refractive index

The refractive indices of the binary mixture {EB (1) + 2-BuOH (2)} at the temperature range T = (303.15 - 313.15) K at intervals of 5 K under atmospheric pressure over the whole composition range are gathered in Table 3 and plotted in Fig. 4. Refractive index deviations Δn_D can be calculated as:

$$\Delta n_D = n_D - (x_1 n^*_{D1} + (1 - x_1) n^*_{D2}) \quad (6)$$

n_{D1}

n_{D2}

Where n_D , the refractive index of the mixture, $n^*_{D,i}$, is that corresponding to the pure component i and x_1 is the mole fraction of component 1 in the mixture. The results were fitted by Eq. (2) and the adjustable parameters and standard deviations are regrouped in Table 4.

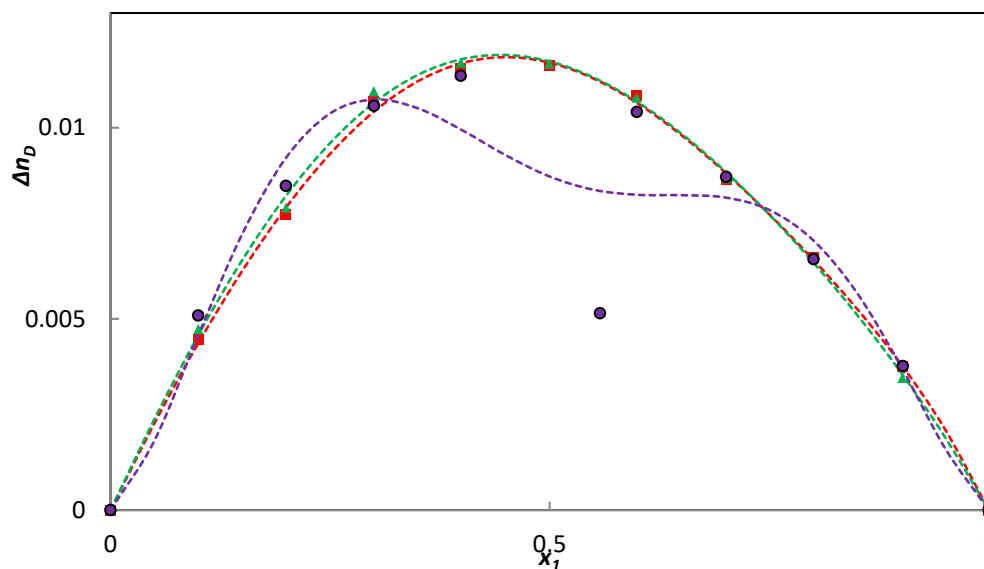


Fig. 3: Deviation in refractive index, Δn_D , against the mole fraction of EB, x_1 , for the binary mixture {EB (1) + 2-BuOH (2)} at $T = (303.15, 308.15 \text{ and } 313.15) \text{ K}$ and under atmospheric pressure. ■ 303.15 K, ▲ 308.15 K, ● 313.15 K. ---, values derived from the Redlich-Kister equation (Eq. 2) using the coefficients listed in Table 4.

As seen from Fig. 3, when the temperature and composition increase, the values of refractive indices decrease. Redlich and Kister [39, 40], have reported that the strong specific forces between molecules are the result of the positive values of refractive index deviations. According to Chaudhary and Kumar [41]: negative values are indicative of weak forces or breaking association of the components of the mixture while positive values are sign of formation of significant interactions. In our study, the obtained positive values of Δn_D indicate the dipole-dipole interaction which predominate.

Conclusion

The molecular interactions between the components of the binary system {EB (1) + 2-BuOH (2)} are identified through thermodynamic studies. Densities, viscosities, and refractive indices have been measured. The excess properties of this solution were correlated using the Redlich-Kister polynomial equation. The values excess Gibb's free energy of activation and deviation in viscosity are found to be negative. The excess molar volume values and deviation in refractive indices are positive over the entire range of composition at all temperatures for the liquid mixture system considered in the present study, except at $T = 298.15 \text{ K}$ in which VE changed from positive to negative. This is a clear indication of the presence of special interaction in the mixture. The difference in the molecular size and shape of the liquid molecules and average degree of association are also important factors that influence the trend of the excess properties.

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DECLARATION OF INTEREST

There is no conflict of interest.

NOMENCLATURE

ρ : Density (g/cm^3).

ΔnD : Deviation in refractive index.

η : Dynamic viscosity ($\text{mPa} \cdot \text{s}$).

$\Delta\eta$: Dynamic viscosity deviation ($\text{mPa} \cdot \text{s}$).

ΔG^E : Excess Gibbs free energy of activation flow (J/mol).

V^E : Excess molar volume (cm^3/mol).

REFERENCES

1. Anastas, P.T.; Warner, J.C. Green Chemistry: Theory and Practice; Oxford University Press: New York, NY, USA, 2000.
2. Isikgor, F.H.; Becer, C.R. Lignocellulosic biomass: A sustainable platform for the production of bio-based chemicals and polymers. *Polym. Chem.* 2015, 6, 4497–4559. [CrossRef]
3. Raju, R., Ravikumar, S., Sivakumar, K., Bhanuprakash, P., Pandiyan, V., 2021. Investigation on thermodynamic properties and spectroscopic studies of binary mixtures of 1, 2, 4-trichlorobenzene with alkyl acetates (C1-C5) at $T = (303.15 \text{ to } 318.15) \text{ K}$. *Chemical Data Collections* 36 100781.
4. Kumar, D. B. K., Reddy, K. R., Rao, G. S., Sandhyasri, P.B., Begum, Z., Rambabu, C., 2013. Measurements of some physical properties of binary liquid mixtures (N-methyl-2-pyrrolidone + an aliphatic ester) at several temperatures and data processing of viscosity and ultrasonic speed. *Journal of Molecular Liquids* 183 31–44
5. Zaoui-Djelloul Daouadji Manel, Belfar Mohammed Lakhder, Allaoui Messaouda, Mekhelfi Tarak, Bouguerra Amina, Belkhalifa Hakim, Maameri Messaouda and Maamri Ilhem, Study of Molecular Interactions in the Binary Mixture of Ethyl Benzoate and 2- Butanol by Density, Dynamic Viscosity and Refractive Index Measurements at 298.15 K , *Transylvanian Review: Vol 30, No. 1, May 2022*.

7. Y.-W. Sheu and C. H. Tu, "Densities and viscosities of binary mixtures of ethyl acetoacetate, ethyl isovalerate, methyl benzoate, benzyl acetate, ethyl salicylate, and benzyl propionate with ethanol at $T = (288.15, 298.15, 308.15, \text{ and } 318.15) \text{ K}$," *Journal of Chemical and Engineering Data*, vol. 51, no. 2, pp. 545–553, 2006.
8. J. N. Nayak, M. I. Aralaguppi, and T. M. Aminabhavi, "Density, viscosity, refractive index, and speed of sound in the binary mixtures of 1,4-dioxane + ethyl acetoacetate, + diethyl oxalate, + diethyl phthalate, or + dioctyl phthalate at 298.15, 303.15, and 308.15 K," *Journal of Chemical and Engineering Data*, vol. 48, no. 6, pp. 1489–1494, 2003.
9. Miller, S. A.; Leadbeater, N. E. Direct, rapid, solvent-free conversion of unactivated esters to amides using lithium hydroxide as a catalyst. *RSC Adv.* 2015, 5 (113), 93248-93251.
10. Camp, D.; Harvey, P. J.; Jenkins, I. D. The effect of solvent polarity on the rate of the Mitsunobu esterification reaction. *Tetrahedron* 2015, 71 (23), 3932-3938
11. Akihiro Wakisaka, Shunsuke Mochizuki, and Hitomi Kobara, "Cluster Formation of 1-Butanol–Water Mixture Leading to Phase Separation," *Journal of Solution Chemistry*, Vol. 33, Nos. 6/7, June/July 2004.
12. Mohammad Shafiqur Rahman, Muhammad A. Saleh, Faisal Islam Chowdhury, M. Shamsuddin Ahmed, M. Mehedi Hasan Rocky, Shamim Akhtar Density and viscosity for the solutions of 1-butanol with nitromethane and acetonitrile at 303.15 to 323.15 K, *Journal of Molecular Liquids* 190 (2014) 208–214
13. Sastry, S. S., Babu, S., Vishwam, T., Tiong, H. S., 2014. Excess parameters for binary mixtures of alkyl benzoates with 2-propanol at different temperatures. *J Therm Anal Calorim* 116:923–935.
14. Outcalt, S. L.; Laesecke, A.; Fortin, T. J. Density and Speed of Sound measurements of 1- and 2-Butanol. *J. Mol. Liq.* 2010, 151, 50– 59.
15. Nain, A. K. Densities and Volumetric Properties of Binary Mixtures of Formamide with 1-Butanol, 2-Butanol, 1,3- Butanediol and 1,4-Butanediol at Temperatures between 293.15 and 318.15 K. *J. Solution Chem.* 2007, 36, 497–516.
16. Alaoui, F.; Montero, E.; Bazile, J. P.; Comuñas, M. J. P.; Galliero, G.; Boned, C. Liquid Density of 1-Butanol at Pressure up to 140 MPa and from 293.15 K to 403.15 K. *Fluid Phase Equilib.* 2011, 301, 131–136.
17. Nain, A. K. Molecular Interactions in Binary Mixtures of Formamide with 1-Butanol, 2-Butanol, 1,3-Butanediol and 1,4-Butanediol at Different Temperatures: An Ultrasonic and Viscometric Study. *Fluid Phase Equilib.* 2008, 265, 46–56.
18. José J. Cano-Gómez, Gustavo A. Iglesias-Silva, Pasiano Rivas, Christian O. Díaz-Ovalle,
19. and Felipe de Jesús Cerino-Córdova, Densities and Viscosities for Binary Liquid Mixtures of Biodiesel + 1-Butanol, + Isobutyl Alcohol, or + 2-Butanol from 293.15 to 333.15 K at 0.1 MPa, *J. Chem. Eng. Data* 2017, 62, 10, 3391–3400.
20. E. Jiménez*, M. Cabanas, L. Segade, S. García-Garabal, H. Casas. Excess volume, changes of refractive index and surface tension of binary 1,2-ethanediol + 1-propanol or 1-butanol

- mixtures at several temperatures, *Fluid Phase Equilibria* 180 (2001) 151–164.
21. Zaoui-Djelloul Daouadji Manel, Belfar Mohammed Lakhder, Mekhelfi Tarak Bouguerra Amina, Boudrae Chaima, Bouafia Wiam, Belkhalifa Hakim, Density, Dynamic
 22. Viscosity and Refractive of the Binary Mixture of Ethyl Benzoate with ethyl acetate from 293.15 K to 313.15k, 2022 ;8(1) 2664 -2684.
 23. Nikos G. Tsierkezos, Antonis E. Kelarakis, Ioanna E. Molinou (2000) Densities, Viscosities, Refractive Indices, and Surface Tensions of 4-Methyl-2-Pentanone + Ethyl Benzoate Mixtures at (283.15, 293.15, and 303.15) K. *J. Chem. Eng. Data* 45:5, 776-779 <https://doi.org/10.1021/je0000423>
 24. Lien, P. J., Lin, H., Lee, M. J., Venkatesu, P., 2003. Excess Molar Enthalpies of Dimethyl Carbonate with o-Xylene, m-Xylene, p-Xylene, Ethylbenzene, or Ethyl Benzoate at 298.15 K. *J. Chem. Eng. Data* 2003, 48, 110-113
 25. <https://doi.org/10.1021/je020120h>
 26. Yaw-Wen Sheu and Chein-Hsiun Tu. 2005 Densities, Viscosities, Refractive Indices, and Surface Tensions for 12 Flavor Esters from T 288.15 K to T 358.15 K. *J. Chem. Eng. Data* 2005, 50: 5, 1706-1710. <https://doi.org/10.1021/je050170x>
 27. D. Venkatesan, D. Joshua Amarnath, and K. Saravanakumar. Thermophysical Properties of Binary Mixtures of Diisopropyl Ether with Methyl Benzoate, Ethyl Benzoate, and Benzyl Acetate at Various Temperatures. *Russian Journal of Physical Chemistry A*, 2020, Vol. 94,
 28. No. 8, pp. 1573–1580. DOI: 10.1134/S0036024420080300
 29. A.M. Blanco, J. Ortega, B. Garcia and J.M. Leal. Studies on densities and viscosities of binary mixtures of alkyl benzoates in n-heptane. *Thermochimica Acta*, 222 (1993) 127-136
 30. T.M. Aminabhavi, T.S.M. Phayde, S.R. Khinnavar, B. Gopalakrishna, C.H. Keith, *J. Chem. Eng. Data* 39 (1994) 251–260.
 31. T. Madhu Mohan • S. Sreehari Sastry • V.R.K. Murthy . Thermodynamic, Dielectric and Conformational Studies on Hydrogen Bonded Binary Mixtures of Propan-1-ol with Methyl Benzoate and Ethyl Benzoate. *J Solution Chem* (2011) 40: 131–146 DOI 10.1007/s10953-010-9634-6
 32. Manapragada V. Rathnam • Sharad Mankumare, Kirti Jain • M.S.S. Kumar. Densities, Viscosities and Speeds of Sound of Binary Mixtures of Ethyl Benzoate + Hydrocarbons at (303.15, 308.15 and 313.15) K. *J Solution Chem* (2012) 41:475–490
 33. Santiago Aparicio, Rafael Alcalde, Begoña García, and José M. Leal. Thermophysical Behavior of n-Alkane + Alkylbenzoate Mixed Solvents. Measurements and
 34. Properties Modeling. *Ind. Eng. Chem. Res.* 2005, 44, 19, 7575–7583
 35. Aminabhavi, T. M., Raikar, S. K., Balundgi, R. H., 1993. Densities, Viscosities, Refractive Indices, and Speeds of Sound in Methyl Acetoacetate + Methyl Acetate, + Ethyl Acetate, + n-Butyl Acetate, + Methyl Benzoate, and + Ethyl Benzoate at 298.15, 303.15, and 308.15 K. *J. Chem. Eng. Data* 38, 441-445 <https://doi.org/10.1021/je00014a014>
 36. Begoña García, Santiago Aparicio, Ana M. Navarro, Rafael Alcalde, and José M. Leal.

- Measurements and Modeling of Thermophysical Behavior of (C1 - C4) Alkylbenzoate/(C1 - C11) Alkan-1-ol Mixed Solvents. J. Phys. Chem. B 2004, 108, 15841-15850
37. Sheu, Y.-W., Tu, C.-H. Refractive Indices and Surface Tensions of Binary Mixtures of Isoamyl Acetate, Ethyl Caproate, Ethyl Benzoate, Isoamyl Butyrate, Ethyl Phenylacetate, and Ethyl Caprylate with Ethanol at (288.15, 298.15, 308.15, and 318.15) K. J. Chem. Eng. Data 51 (2006) 496. <https://doi.org/10.1021/je0601208>
39. Rathnam, M.V., Mohite, S., Kumar, M.S.S. Viscosity, Density, and Refractive Index of Some (Ester + Hydrocarbon) Binary Mixtures at 303.15 K and 313.15 K. J. Chem. Eng. Data 50 (2005) 325. <https://doi.org/10.1021/je0400052>
40. D. Venkatesan, Joshua Amarnath D., T. Srinivasa Krishna, Piyashi Biswas, Ranjan Dey. Densities, viscosities and excess parameters of octanol with alkyl (C1 – C4) acetates at varying temperatures. Journal of Molecular Liquids 299 (2020) 112221.
41. <https://doi.org/10.1016/j.molliq.2019.112221>
42. Lien, P. J., Lin, H., Lee, M. J., Venkatesu, P., 2003. Excess Molar Enthalpies of Dimethyl Carbonate with o-Xylene, m-Xylene, p-Xylene, Ethylbenzene, or Ethyl Benzoate at 298.15 K. J. Chem. Eng. Data 2003, 48, 110-113 <https://doi.org/10.1021/je020120h>
43. R. Rajalakshmi, S. Ravikumar, K. Sivakumar, V. Pandiyan. Excess thermodynamic properties of intermolecular interactions in binary liquid mixtures of furfural with alkyl acetates (C1-C5) at different temperatures. Chemical Data Collections 24 (2019) 100299.
44. Fort, R.J., Moore, W.R., 1966. Viscosities of binary liquid mixtures. Trans. Faraday Soc. 62, 1112–1119.
45. Pikkarainan, L., 1983. Densities and viscosities of binary mixtures of N,N-dimethylacetamide with aliphatic alcohols. J. Chem. Eng. Data 28, 344–347.
46. Meyer R, Meyer M, Metzger J, Peneloux A (1971) J Chim Phys 62: 406
47. Redlich, O., Kister, A.T.: Algebraic representation of thermodynamic properties and the classification of solutions. J. Ind. Eng. Chem. 40, 345–348 (1948) <https://doi.org/10.1021/ie50458a036>
48. M. Chandra Sekhar, T. Madhu Mohan, T. Vijaya Krishna, A. Venkatesulu, K. Siva Kumar. Density, Refractive Index, Speed of Sound and Computational Studies of Intermolecular Interactions in Binary Mixtures of 2-Chloroaniline with Butanols (1-Butanol, 2-Butanol) at T 5 (303.15–318.15) K. J Solution Chem DOI 10.1007/s10953-015-0306-4
49. Neha Chaudhary, Anil Kumar Nain. Volumetric, ultrasonic, viscometric and refractive index studies of molecular interactions in binary mixtures of 1-butyl-3-methylimidazolium tetrafluoroborate with methyl acrylate at temperatures from 293.15 to 318.15 K. Journal of Molecular Liquids 297 (2020) 111890. <https://doi.org/10.1016/j.molliq.2019.111890>