Densities, Viscosities, and Refractive Indices, of Binary Mixture of Ethyl Benzoate with Ethyl Acetate from 293.15 K to 313.15 K

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Abstract
In the present paper, thermochemical properties such densities, ρ, viscosities, η, and refractive indices, n_D, of binary mixture of ethyl benzoate (EB) with ethyl acetate (EA) over the whole composition range at temperatures between 293.15 and 313.15 K under atmospheric pressure have been measured. Based on the measurements, excess molar volume, V^E, viscosity deviations, $\Delta\eta$, excess Gibbs energies of activation of viscous flow, ΔG^{*E}, and deviation in refractive indices, Δn_D were calculated then fitted to the Redlich–Kister polynomial equation to obtain the coefficients. The experimental results for the binary mixture at 298.15 K and the pure components at different temperatures were comparable to those found in previous research. The properties were explained in terms of the predominant molecular interactions in the mixtures.
Keywords: Ethyl benzoate, ethyl acetate, thermophysical properties, excess properties, Redlich-Kister equation.

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INTRODUCTION

Compounds that include carbon have been crucial to our society's modernization [1] Esters are among these substances and have several applications in biological, medicinal and chemical industry. Esters are used extensively across industry as an essential solvent in a wide variety of applications [2]; for this purpose, enormous quantities are manufactured commercially. Esters exist as dipolar associates in their pure liquid state, available with an aliphatic and/or aromatic structures with molecular formulas, $R(CH_2)_{n-1}COOR'$[3]. Ethyl acetate (EA) is an organic solvent widely used for broad applications in manufacturing, pharmaceutical, or food industry, mainly as a solvent for paints, lacquers, printing inks, varnishes, in the production of enamels, plastics, rubber and an extraction solvent in the manufacture of pharmaceuticals [4]; in addition in glues, nail Polish removers, decaffeinating tea and coffee, and cigarettes [5]. It is used as an additive for oxygenated fuels [6], desirable in spark-ignition (SI) engines [7] as well as a cosolvent to improve the viability of biodiesel production [8]. EA is used in food industry as a synthetic flavouring and in the pharmaceutical industry as an extraction solvent in the production of pharmaceuticals [4]. Aromatic esters like ethyl benzoate (EB) are highly in demand as solvent in technological applications such as perfumery, pesticides, [9, 10] artificial essences, paint, plastic industries [9], cosmetic [9, 11], dye carriers in fibers industry [11]. This characteristic is due to the existence of the polarizable aromatic π-electron system adjacent to the dipolar -COO as well as the hydrophobic and aprotic nature of these esters [11]. In general, alkyl benzoates are a good hydrogen bonding acceptors and their packing is disrupted upon mixing [12]. These two esters EB and EA were selected because of their importance in the engineering process. According to a survey of the literature, Kendall and Wright [13] measured the density and viscosity of the binary system {EB (1) + EA (2)} at T=298.15 K as well as pure components with unknown purity. To the best of our knowledge, no investigation has been done on density and viscosity over the whole composition range of the binary mixture {EB (1) + EA (2)} at temperatures T = (293.15 - 313.15) K at intervals of 5 K under atmospheric pressure. There hasn't been any prior research on refractive index. In continuation of our work for binary mixtures containing EB [14], we report the results on density ρ, viscosity η and refractive index n_D, for the mixture of ethyl benzoate (EB) with ethyl acetate (EA) in the temperature between 293.15 and 313.15 K, at intervals of 5 K for the liquid region and under atmospheric pressure for the whole composition range. From these results, excess molar volume, V^E, viscosity deviations, $\Delta\eta$, excess Gibbs energies of activation of viscous flow, ΔG^{*E}, and deviation in refractive indices, Δn_D have been calculated then fitted to the Redlich–Kister polynomial equation. This study is helpful in understanding about the molecular interactions between non-associated molecules with each other.

1. EXPERIMENTAL SECTION

1.1. Chemicals

Table 1 regroups the source and purity of ethyl benzoate (EB) and ethyl acetate (EA) 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 [15-40]. 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)	Acrōs organics	93-89-0	99+%
Ethyl acetate (EA)	Honeywell	141-78-6	≥ 99.5%

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 = 1×10^5 Pa.

Component	T(K)	ρ (g.cm^{-3})		η (mPa.s)		n_D	
		Exp.	*Lit.*	*Exp.*	*Lit.*	*Exp.*	*Lit.*
Ethyl benzoate	293.15	1.04486	1.04622[22]	1.9776	2.21[22]	1.5053	1.5056[22]
	298.15	1.04124	1.0413[15] 1.04142[16] 1.0423[17] 1.04163[18]	1.9430	1.936[19] 1.9543[17]	1.5025	1.5027[24] 1.5034[25] 1.50328 [26] 1.5026 [18]
	303.15	1.03693	1.03707[9] 1.038[19] 1.0421[20] 1.0371[21]	1.8123	1.811 [9] 1.811 [22] 1.756 [21]	1.5007	1.5012 [22] 1.5009 [27]
	308.15	1.03232	1.0325[21] 1.0381[20] 1.0326[17] 1.03255[18]	1.6490	1.623[16] 1.633[23]	1.4988	1.49863[27] 1.4985 [18] 1.49863[23]
	313.15	1.02772	1.0279[21] 1.0328[20] 1.0279[17]	1.5093	1.463[21] 1.4619[17]	1.4966	1.4997[27]
Ethyl acetate	293.15	0.90140	0.90070[30]	0.3794	-	1.3729	1.3728[34]

298.15	0.89500	0.89445[28] 0.8954[29] 0.8944[1]	0.3819	0.4135[30]	1.3702	1.3706[35] 1.3698[29] 1.36986[36] 1.37[37]
303.15	0.88709	0.8885[40] 0.8885[1]	0.3397	0.379[31]	1.3684	1.368[38] 1.3681[39]
308.15	0.87989	0.88205[28] 0.8827[1]	0.2915	0.361[31]	1.3662	1.3646[28]
313.15	0.79287	0.8763[1]	0.3076	0.3429[32] 0.3426[33]	1.3643	1.3621[37]

The binary liquid mixtures were well mixed for suitable volumes and prepared by mixing known masses of pure liquids in glass vials (12 mL) by taking utmost precautions to minimize evaporation losses. The solutions of each composition were prepared fresh and all the properties were measured the on same day. All mixtures were weighed using an OHAUS Discovery analytical balance with an accuracy of 0.01 mg. The values were gauged as soon as the samples with various compositions were prepared [29].

1.2. Apparatus and procedure

1.2.1. Density and viscosity measurements

The density and dynamic viscosity of the pure liquids and their binary mixture were determined at temperature T= (293.15, 298.15, 303.15, 308.15, and 313.15) K and under atmospheric pressure by using an SVM 3001 Stabinger viscometer (Anton Paar) with density and viscosity repeatability of 0.00005 $g{\cdot}cm^{-3}$ and 0.1%, respectively, and temperature stability of 0.005 K. 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 (ρ) = 0.05 $g{\cdot}cm^{-3}$. The instrument can measure simultaneously density in the range of (0 to 3) $g{\cdot}cm^{-3}$ and viscosity (0.2 to 30000) $mm^2{\cdot}s^{-1}$ in a temperature range of (273.15 to 343.15) 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 mixture were measured at the atmospheric pressure and the required temperatures by using a digital refractometer (RFM T series, Bellingham & Stanley Ltd, UK). The refractometer was calibrated with distilled deionized water before each measurement session. The standard uncertainty of temperature and refractive index are approximated to be ± 0.1 K and ± 2 × 10^{-4} units, respectively. The refractometer was calibrated by cleaning a prism with doubly distilled water, followed by wiping it with a clean paper towel and measuring a zero sample.

2. RESULTS AND DISCUSSION

The experimental densities, viscosities and refractive indices of the binary system {EB (1) + EA (2)} at the temperature range T = (293.15 - 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, n_D 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, Δn_D of the binary mixture {EB (1) + EA (2)} at T= (293.15, 298.15, 303.15, 308.15 and 313.15) K and under atmospheric pressure.

x_1	ρ (g.cm^{-3})	x_1	η (mPa.s)	x_1	n_D	V^E ($cm^3.mol^{-1}$)	$\Delta\eta$ (m.Pa.s)	ΔG^{*E} (J.mol^{-1})	Δn_D
T= 293.15 K									
0.0000	0.9014	0.0000	0.3794	0.0000	1.3729	0	0	0	0
0.1001	0.9240	0.1001	0.4977	0.1001	1.3928	-0.266	-0.042	275.1	0.007
0.1995	0.9430	0.1995	0.5982	0.1999	1.4116	-0.360	-0.100	335.7	0.012
0.3001	0.9601	0.3001	0.7347	0.3001	1.4271	-0.371	-0.124	442.4	0.014
0.3999	0.9757	0.4000	0.8581	0.4004	1.4425	-0.394	-0.160	422.8	0.017
0.5005	0.9904	0.5005	1.0205	0.5006	1.4522	-0.437	-0.159	441.2	0.013
0.6008	1.0037	0.6008	1.2087	0.6014	1.4665	-0.431	-0.131	447.7	0.014
0.7000	1.0140	0.7000	1.3858	0.7000	1.4828	-0.194	-0.112	379.2	0.017
0.8001	1.0259	0.8001	1.6170	0.8003	1.4886	-0.250	-0.041	341.7	0.010
0.9012	1.0370	0.9012	1.8919	0.9011	1.4972	-0.283	0.072	304.4	0.005
1.0000	1.0449	1.0000	1.9776	1.0000	1.5053	0	0	0	0
T= 298.15 K									
0.000	0.8950	0.000	0.3819	0.000	1.370	0	0	0	0

0		0		0	2				
0.0990	0.9083	0.0990	0.4432	0.1001	1.3872	0.796	-0.093	6.7	0.0038
0.1999	0.9369	0.1999	0.5570	0.1999	1.4096	-0.305	-0.137	153.4	0.0129
0.3001	0.9545	0.3001	0.6752	0.3001	1.4224	-0.367	-0.175	234.1	0.0125
0.4004	0.9707	0.4004	0.7942	0.4004	1.4392	-0.412	-0.213	235.9	0.0160
0.5006	0.9853	0.5006	0.9422	0.5006	1.4531	-0.407	-0.221	256.5	0.0167
0.6014	0.9987	0.6014	1.1037	0.6014	1.464	-0.377	-0.217	240.2	0.0142
0.7000	1.0108	0.7000	1.2876	0.7000	1.475	-0.338	-0.187	219.3	0.0122
0.8003	1.0219	0.8003	1.4706	0.8003	1.4853	-0.261	-0.161	136.8	0.0092
0.9011	1.0324	0.9011	1.7111	0.9011	1.4945	-0.185	-0.077	95.1	0.0051
1.0000	1.0412	1.0000	1.9430	1.0000	1.5025	0	0	0	0
T= 303.15 K									
0.0000	0.8871	0.0000	0.3397	0.0000	1.3684	0	0	0	0
0.0998	0.9067	0.0998	0.4282	0.1001	1.3888	0.146	-0.058	180.9	0.0065
0.2000	0.9289	0.2000	0.5207	0.1999	1.4085	-0.208	-0.114	254.3	0.0124
0.2993	0.9488	0.2993	0.6221	0.3001	1.4238	-0.501	-0.158	285.2	0.0138
0.4000	0.9652	0.4000	0.7373	0.4004	1.4381	-0.521	-0.191	292.8	0.0142
0.5007	0.9800	0.5007	0.8780	0.5006	1.4519	-0.494	-0.199	309.6	0.0141
0.6009	0.9936	0.6009	1.0219	0.6014	1.4634	-0.448	-0.203	268.5	0.0117
0.7001	1.0057	0.7001	1.1868	0.7000	1.4742	-0.367	-0.184	223.3	0.0088
0.8001	1.0170	0.8001	1.3711	0.8003	1.4845	-0.267	-0.147	159.5	0.0052
0.9015	1.0276	0.9015	1.5462	0.9011	1.4927	-0.150	-0.121	26.8	-0.0006
1.0000	1.0369	1.0000	1.8123	1.0000	1.5070	0	0	0	0

T= 308.15 K									
0.0000	0.8799	0.0000	0.2915	0.0000	1.3662	0	0	0	0
0.0994	0.8907	0.0994	0.4018	0.1001	1.3869	1.208	-0.025	414.1	0.0074
0.1996	0.9240	1.1998	0.4782	0.1995	1.4045	-0.426	-1.442	-3640.6	0.0119
0.3000	0.9378	0.3000	0.5875	0.3001	1.4202	0.070	-0.111	488.2	0.0142
0.4088	0.9600	0.4088	0.6998	0.4000	1.4354	-0.456	-0.147	447.8	0.0162
0.5001	0.9724	0.5001	0.8170	0.5005	1.4507	-0.276	-0.153	443.8	0.0181
0.6013	0.9850	0.6009	0.9478	0.6008	1.4592	-0.056	-0.159	380.8	0.0133
0.6979	1.0002	0.6979	1.0904	0.7006	1.4696	-0.383	-0.149	299.6	0.0105
0.8000	1.0122	0.8000	1.2543	0.8001	1.4813	-0.302	-0.123	201.2	0.0090
0.9007	1.0227	0.9007	1.4318	0.9012	1.4902	-0.157	-0.082	87.5	0.0045
1.0000	1.0323	1.0000	1.6490	1.0000	1.4988	0	0	0	0
T= 313.15 K									
0.0000	0.7929	0.0000	0.3076	0.0000	1.3643	0	0	0	0
0.0996	0.8829	0.0996	0.3792	0.1001	1.3858	-7.809	-0.048	-40.0	0.0083
0.2001	0.9107	0.2001	0.4762	0.1995	1.4043	-7.745	-0.072	142.0	0.0136
0.3014	0.9370	0.3014	0.5499	0.3001	1.4172	-7.675	-0.120	110.4	0.0132
0.4005	0.9545	0.4005	0.6494	0.4000	1.4328	-6.794	-0.140	157.3	0.0156
0.5007	0.9680	0.5007	0.7670	0.5005	1.4429	-5.518	-0.142	205.2	0.0124
0.6010	0.9831	0.6010	0.8971	0.6008	1.4589	-4.596	-0.133	217.9	0.0151
0.6991	0.9953	0.6991	1.0094	0.7006	1.4689	-3.473	-0.138	143.6	0.0119
0.8002	1.0029	0.7810	1.1605	0.8001	1.4790	-1.753	-0.086	186.2	0.0088
0.9019	1.0143	0.9019	1.3211	0.9012	1.4883	-0.639	-0.070	53.4	0.0048

1.000 0	1.0277	1.000 0	1.5093	1.000 0	1.496 6	0	0	0	0

For clarity and comparison, we have plotted experimental values of density and viscosity with those reported by Kendall and Wright [13] at 298.15 K and graphically presented in Figs. 1 and 2

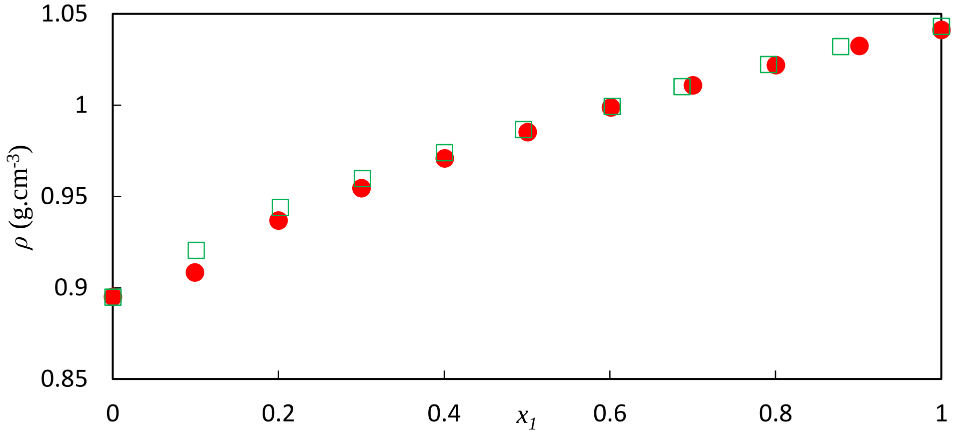

Fig. 1 Comparison of density for the {EB (1) + EA (2)} system at 298.15 K and atmospheric pressure: ●, this work; □, Ref. [13].

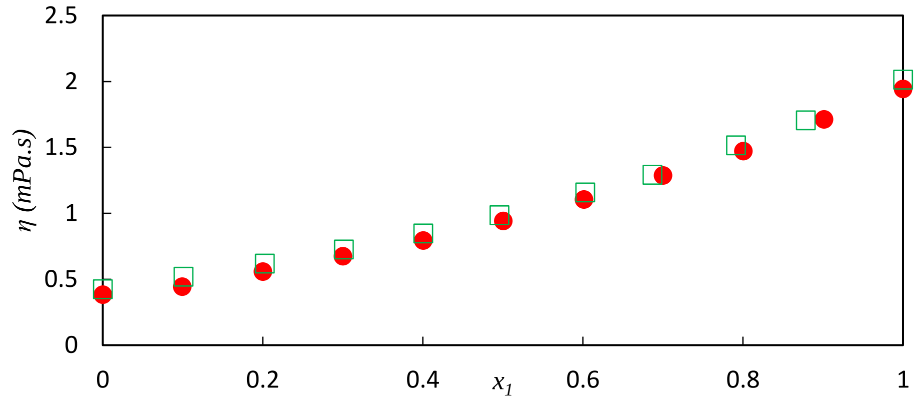

Fig. 2 Comparison of viscosity for the {EB (1) + EA (2)} system at 298.15 K and atmospheric pressure:●, this work;□, Ref. [13].

One can observe from Fig.s 1 and 2 that Kendall and Wright's investigations [13] reveal similarities in the behavior of these properties for the binary system under study in this work. The slight deviation observed may be due to the purity of the liquids and/or the use of different measurement techniques as well as the accuracy of the solution preparation.

2.1. Volumetric studies

Values of experimental densities, ρ for {EB (1) + EA (2)} binary system at various composition at the temperature range T = (293.15 - 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_I, M_1 and ρ_I are mole fraction, molar masse 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 = (293.15, 298.15, 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 Δn_D or ΔG^{*E} and x_I 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

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

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, Δn_D, and excess Gibb's free energy, ΔG^{*E}, for the liquid mixture {EB (1) + EA (2)} at T= (293.15, 298.15, 303.15, 308.15 and 313.15) K and under atmospheric pressure.

Properties	A1	A2	A3	A4	A5	σ

T= 293.15 K						
V^E	-1.8	0.8	2.9	-1.1	-8.0	0.058
$\Delta\eta$	-0.6	0.0	-0.2	1.2	2.2	0.014
ΔG^{*E}	1811.656	-258.580	-117.953	697.617	3457.203	27.932
Δn_D	0.058	0.003	0.110	-0.024	-0.166	0.002
T= 298.15 K						
V^E	-1.4	2.8	-8.0	-12.5	23.1	0.194
$\Delta\eta$	-0.9	-0.1	0.1	0.3	-0.3	0.009
ΔG^{*E}	1004.087	-299.201	528.320	1143.756	-1926.729	21.517
Δn_D	0.0631	-0.0168	0.0119	0.0274	-0.0393	0.002
T= 303.15 K						
V^E	-2.0	1.5	-1.2	-5.4	6.8	0.026
$\Delta\eta$	-0.8	-0.039	0.2	-0.5	-0.8	0.007
ΔG^{*E}	1183.022	-108.019	402.188	-1357.388	-593.623	13.854
Δn_D	0.054	-0.024	0.024	-0.039	-0.083	0.001
T= 308.15 K						
V^E	-0.6	3.2	-12.9	-16.2	33.3	0.404
$\Delta\eta$	-0.6	-0.2	-1.3	0.0	2.5	0.023
ΔG^{*E}	1841.810	-811.693	-1700.568	-1810.791	5933.584	40.965
Δn_D	0.066	-0.023	-0.045	0.011	0.080	0.001
T= 313.15 K						
V^E	-23.2	17.0	-6.4	47.2	-45.2	0.406
$\Delta\eta$	-0.6	-0.002	0.3	-0.2	-0.6	0.014
ΔG^{*E}	728.186	187.672	951.909	426.708	-2631.425	50.424
Δn_D	0.056	-0.006	0.047	-0.036	-0.033	0.00149

V^E values of {EB (1) + EA (2)} binary system at the temperature range T = (293.15 - 313.15) K at intervals of 5 K under atmospheric pressure are plotted in Fig.3.

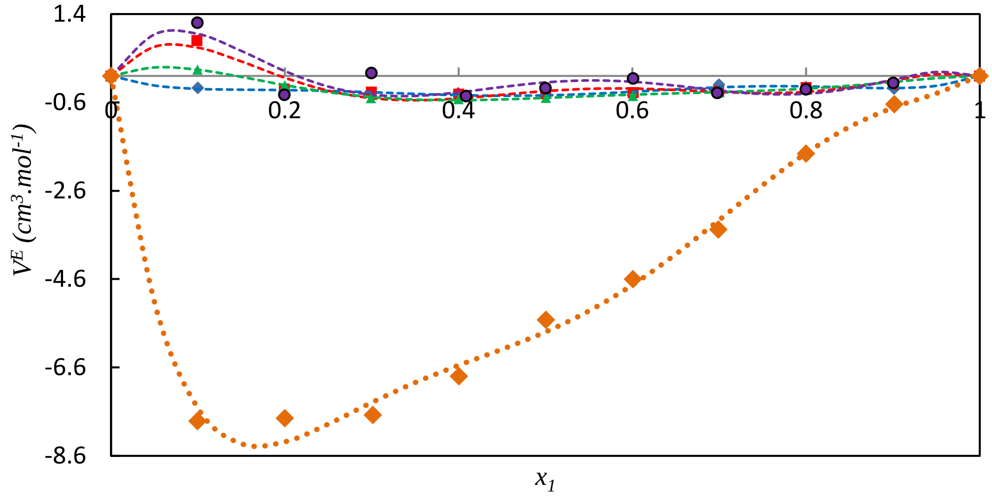

Fig. 3: Excess molar volume, V^E, against the mole fraction of EB, x_1, for the binary mixture {EB (1) + 2-BuOH (2)} at T = (293.15, 298.15, 303.15, 308.15 and 313.15) K and under atmospheric pressure. ♦ 293.15K, ■ 298.15 K, ▲303.15K, ●308.15K, ♦313.15K. ---, values derived from the Redlich-Kister equation (Eq. 2) using the coefficients listed in Table 4.

A close look of Fig. 3 show that excess molar volume V^E exhibit a different trends, a sigmoidal nature having both positive and negative values at T = (293.15, 298.15, 303.15, 308.15) K, a large negative V^E values at 313.15 K, and the dependence is not uniform. As is widely known, the magnitude of excess molar volume V^E may be discussed in terms of several opposing effects which may be chemical, physical and structural contributions [14, 4]. At lower ethyl benzoate concentrations, excess molar volumes of EB with EA were shown to be initially positive, leading to volume expansion brought on by the dissolution of molecular association of one or both of the components in the solution and then moved over to negative values (Fig. 3) involving a contraction of volume witch indicate of strong specific or chemical interactions between the constituents. The large negative values of V^E especially at 313.15 K indicate the possibility of Keesom dipole-dipole Van der Walls forces which arise due the dipole moments of EB (μ = 2.00 D) and EA (μ = 1.38 D). It is evident that the nature or type of interaction depends on the nature of the binary mixture components. This assumption was also considered by Nayeem *et al.* [4, 41] and Rajagopal and Chenthilnath [42]. The structural effect may also be ascribed, arising from the geometrical fitting of one component into another due to the differences in shape and size between components which implies negative V^E and positive ΔG^{*E} values. The expansion on volume at lower concentration and very high of EA explain the presence of dispersion forces (Physical contribution) due to dissociation or breaking bonds between the same molecules (EB-EB and EA-EA). The unavailability of free hydrogen atom provides assurance that there are no hydrogen bonding. In short, the chemical or specific interactions and structural contributions are predominant over the physical (dispersion) contribution which makes EB and EA move closer resulting in negative V^E [4].

2.2. *Viscometric properties*

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

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

Where *xi*, and η_i are mole fraction and dynamic viscosity of pure component *I*, respectively. η is dynamic viscosity of the mixture.

$$\Delta G^{*E} \Big/ (Jmol^{-1} = RT[(\ln(\upsilon M) - \sum x_i \ \ln{(\upsilon_i M_i)}] \tag{5}$$

$$M = \sum_{i=1}^{n} x_i \ \ M_i \tag{6}$$

$$\eta = \upsilon * \rho \tag{7}$$

In the above Eqs. (5-7), ρ is the density, ν is the kinematic viscosity of the mixture, ν_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, *R* is the gas constant, *T* is the absolute temperature, x_i is the mole fraction in component i, *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.

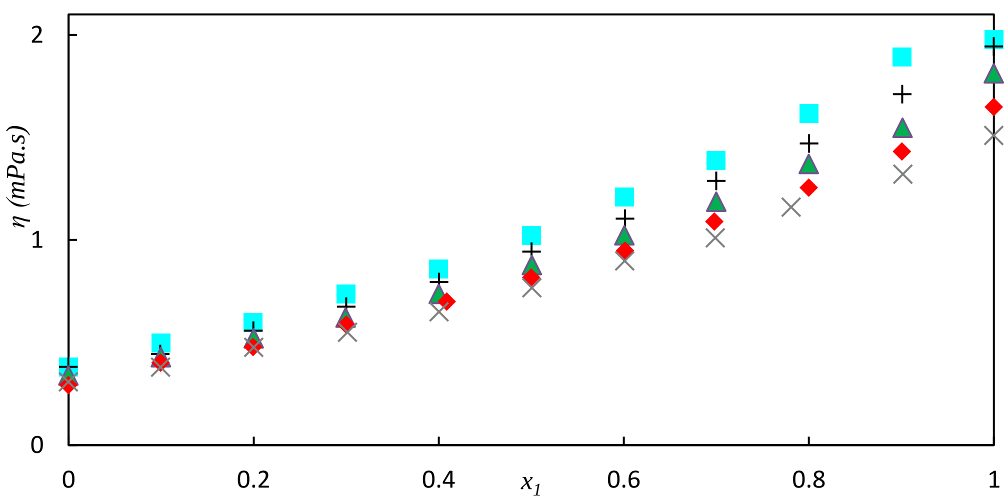

Fig. 4: Plot of viscosity, η, against the mole fraction of EB, x_1, for the binary mixture {EB (1) + EA (2)} at T = (293.15, 298.15, 303.15, 308.15 and 313.15) K and under atmospheric pressure. ♦ 293.15K, ■ 298.15 K, ▲303.15K, ●308.15K, ♦313.15K.

$\Delta\eta$ and ΔG^{*E} values of the binary system {EB (1) + EA (2)} are depicted graphically in Fig. 5 and Fig. 6, 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.

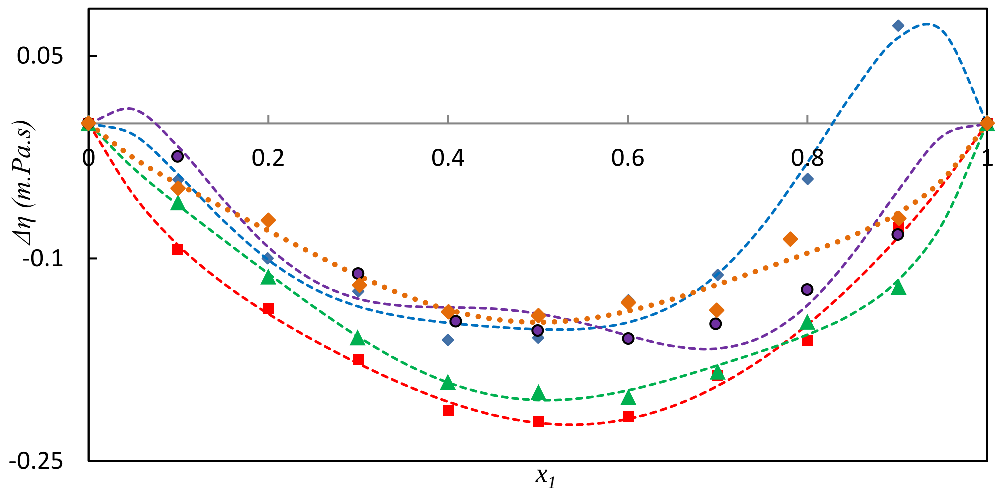

Fig. 5: Deviation in viscosity, $\Delta\eta$, against the mole fraction of EB, x_1, for the binary mixture {EB (1) + EA (2)} at T = (293.15, 298.15, 303.15, 308.15 and 313.15) K and under atmospheric pressure. ♦ 293.15K, ■ 298.15 K, ▲303.15K, ●308.15K, ♦313.15K. ---, values derived from the Redlich-Kister equation (Eq. 2) using the coefficients listed in Table 4.

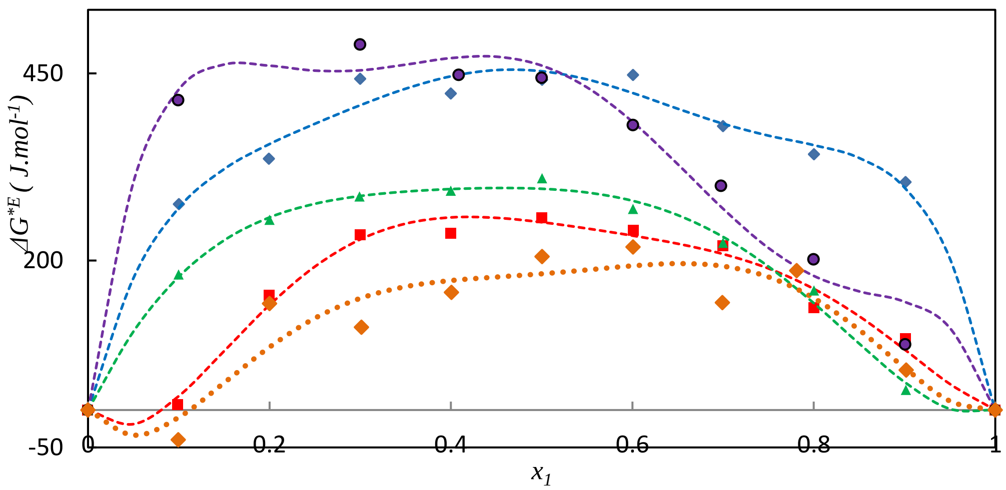

Fig. 6: Excess Gibbs energy of activation of viscous flow, ΔG^{*E}, against the mole fraction of EB, x_1, for the binary mixture {EB (1) + EA (2)} at T = (293.15, 298.15, 303.15, 308.15 and 313.15) K and under atmospheric pressure. ♦ 293.15K, ■ 298.15 K, ▲303.15K, ●308.15K,

♦313.15K.---, values derived from the Redlich-Kister equation (Eq. 2) using the coefficients listed in Table 4.

From Fig.5, $\Delta\eta$ exhibit a large negative values at T = (298.15, 303.15and 313.15) K over the whole composition range, whereas at T = 293.15 K beyond x_1 = 0.8 and at T = 308.15 K up to x_1 = 0.1 with maxima at 0.05 and 0.95, respectively. According to Benson et al. [43], the strength of the interactions between the different components of the mixture (like and unlike molecules) helps to identify the trend of $\Delta\eta$. Vogel and Weiss [44] state that positive values of $\Delta\eta$ suggest strong specific interactions between unlike molecules whereas weaker interactions imply negative deviation of $\Delta\eta$ as well as the existence of the dispersion forces and absence of complex formation [45]. Therefore, the large negative values indicate the dissociation of the associated entities of like molecules in the mixture. This Behavior is indicative of the presence of an associated component in the mixture where the stability of (solute + solvent) complexes is negligible or nonexistent. [45]; whereas the positive deviation may be attributed to the Keesom dipole-dipole Van Der Walls forces. We can summarized the qualitative estimation of the strength of the intermolecular interactions given by the trend of $\Delta\eta$ as follows: (i) Specific effects between the different entities (unlike molecules) such as dipole –dipole interaction lead to an increase in viscosity in the mixture producing positive deviation in viscosity (ii) A decrease in viscosity may be caused by differences in the size and shape of the component molecules as well as the loss or weak of dipolar interaction in pure components leading to positive values of $\Delta\eta$.

A perusal of Fig.6 shows that the values of ΔG^{*E} are positive over the whole composition range except for T = 298.15 K and T = 313.15 K where an S shape was observed. The dependence is also not uniform. The positive deviation of ΔG^{*E} at about $x_1 \approx 0.1$ corresponds to the existence of intermolecular interaction through dipole-dipole forces between the component molecules of the liquid mixture. However, the negative values may be ascribed to the dominance of dispersion forces in the mixture under study. These conclusions are in accordance with those reported by Reed and Taylor [46] who claimed that specific interactions between the different entities in a mixture lead to positive deviation of ΔG^{*E} while dispersion forces imply negative values of ΔG^{*E}.

2.3. Refractive index

The refractive indices of the binary mixture {EB (1) + EA (2)} at the temperature range T = (293.15 - 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. 7. Refractive index deviations Δn_D can be calculated as:

$$\Delta n_D = n_D - (x_1 n_{D1}^* + (1 - x_1) n_{D2}^*) \qquad (8)$$

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.

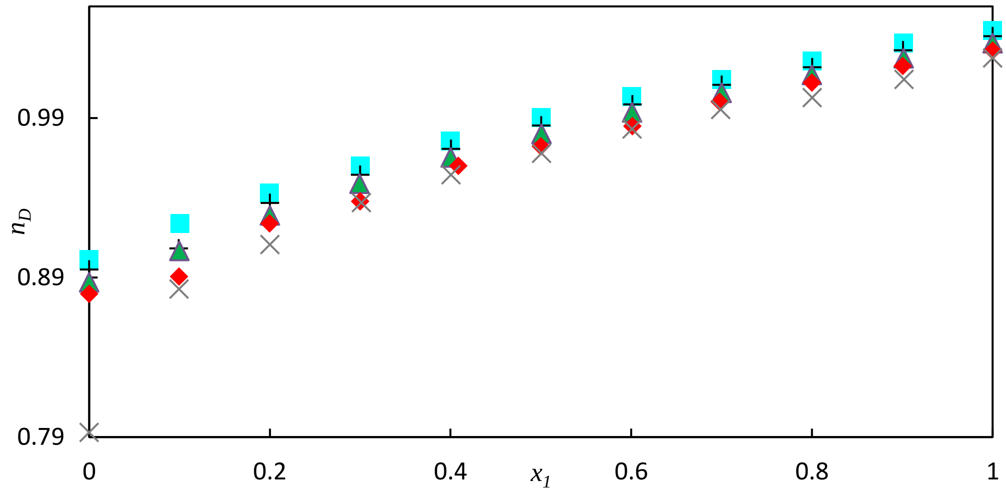

Fig. 7: Plot of refractive index, n_D, against the mole fraction of EB, x_1, for the binary mixture {EB (1) + EA (2)} at T = (293.15, 298.15, 303.15, 308.15 and 313.15) K and under atmospheric pressure. ♦ 293.15K, ■ 298.15 K, ▲303.15K, ●308.15K, ♦313.15K.

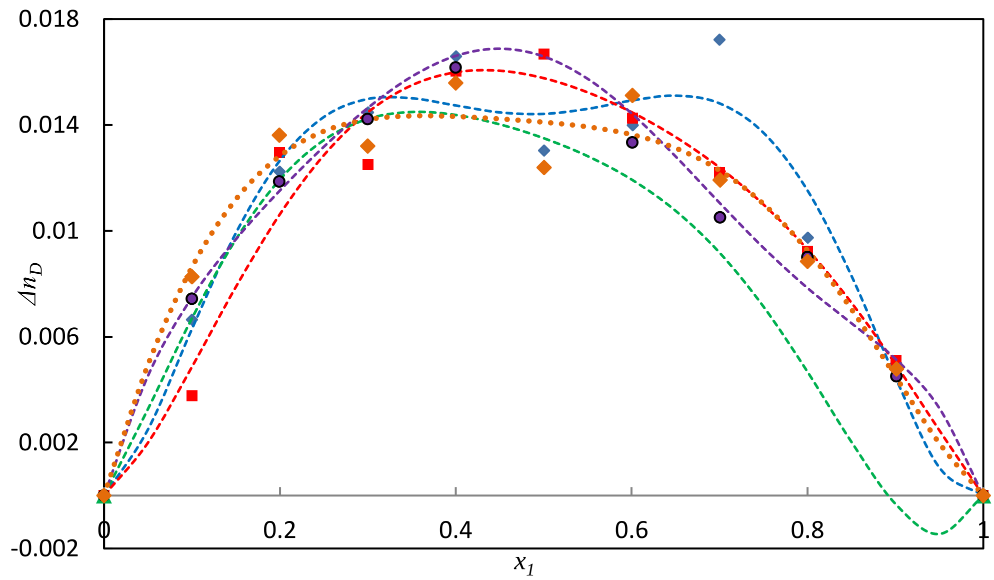

Fig. 8: Deviation in refractive index, Δn_D, against the mole fraction of EB, x_1, for the binary mixture {EB (1) + EA (2)} at T = (293.15, 298.15, 303.15, 308.15 and 313.15) K and under atmospheric pressure. ♦ 293.15K, ■ 298.15 K, ▲303.15K, ●308.15K, ♦313.15K. ---, values derived from the Redlich-Kister equation (Eq. 2) using the coefficients listed in Table 4.

As seen from Fig. 7, the values of refractive indices decrease with increasing temperature and composition. According to Redlich and Kister [47, 48], strong specific forces between molecules are the result of the positive values of refractive index deviations. The same assumptions were stated by Chaudhary and Kumar [49]: positive values are sign of formation of significant interactions while negative values are indicative of weak forces or breaking association of the components of the mixture. In the present case, the obtained positive values of Δn_D indicate the dipole-dipole interaction which predominate

CONCLUSION

This paper has reported the experimental data of density, , viscosity, and refractive index, for the pure components of EB and EA and their binary mixture {EB (1) + EA (2)} at the temperature range T = (293.15 - 313.15) K at intervals of 5 K under atmospheric pressure over the whole composition range. From these data, excess properties were derived and fitted by using the Redlich-Kister equation. Various trends were observed. The sign and magnitude of these properties indicate the presence of dipole-dipole forces as well as the dissolution of the polymers of pure EB and pure EA on mixing. We can confirm that the molecular interactions are affected by size, shape and the degree of association.

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DECLARATION OF INTEREST

There is no conflict of interest.

NOMENCLATURE

ρ: Density (g/cm^3).

Δn_D: Deviation in refractive index.

η: Dynamic viscosity (mPa. s).

$\Delta\eta$: Dynamic viscosity deviation (mPa. s).

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

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

REFERENCES

1. Indra Bahadura, Nirmala Deenadayalub, Deresh Ramjugernath. Effects of temperature and concentration on interactions in methanol + ethyl acetate and ethanol + methyl acetate or ethyl acetate systems: Insights from apparent molar volume and apparent molar isentropic compressibility study. *Thermochimica Acta*, 577 87– 94 (2014). https://doi.org/10.1016/j.tca.2013.12.016

2. R. Gerald Arokiaraj, R. Raju, S. Ravikumar, K. Sivakumar, P. Bhanuprakash, V. Pandiyan. Excess thermodynamic properties and FTIR studies of binary mixtures of aniline with esters at different temperatures. Chemical Data Collections **37** 100807 (2022) https://doi.org/10.1016/j.cdc.2021.100807

3. Nandhibatla V. Sastry, Rakesh R. Thakor, Mitesh C. Patel. Excess molar volumes, viscosity deviations, excess isentropic compressibilities and deviations in relative permittivities of (alkyl acetates (methyl, ethyl, butyl and isoamyl) + n-hexane, + benzene, + toluene, + (o-, m-, p-) xylenes, + (chloro-, bromo-, nitro-) benzene at temperatures from 298.15 to 313.15 K. Journal of Molecular Liquids 144 (2009) 13–22

4. Sk. Md Nayeem, Sk. Nyamathulla, Imran Khan, D. Krishna Rao. Investigation of molecular interactions in binary mixture (benzyl benzoate + ethyl acetate) at T = (308.15, 313.15, and 318.15) K: An insight from ultrasonic speed of sound and density. Journal of Molecular Liquids. Volume 218, June 2016, Pages 676-685. http://dx.doi.org/10.1016/j.molliq.2016.02.045

5. Hamid Reza Rafiee, Farshid Frouzesh, Shokofeh Miri. Volumetric properties for binary mixtures of ethyl acetate, vinyl acetate and tert-butyl acetate with 1-propanol and iso-butanol at T = (293.15–313.15) K and P = 0.087 MPa. Journal of Molecular Liquids 213 (2016) 255–267

6. P.V.V.S. Rama Rao, T.S. Krishna, D. Ramachandran. Effect of temperature on molecular interaction of ethyl acetate with ionic liquid 1-butyl-3-methylimidazolium exafluorophosphate. J. Chem. Thermodynamics 141 (2020) 105906. https://doi.org/10.1016/j.jct.2019.105906

7. Francis Oppong, Cangsu Xu, Xiaolu Li, Zhongyang Luo. Esters as a potential renewable fuel: A review of the combustion characteristics. Fuel Processing Technology 229 (2022) 107185 https://doi.org/10.1016/j.fuproc.2022.107185

8. Nattee Akkarawatkhoosith, Amaraporn Kaewchada and Attasak Jaree. Production of Biodiesel from Palm Oil under Supercritical Ethanol in the Presence of Ethyl Acetate. Energy Fuels 2019, 33, 5322−5331. doi: 10.1021/acs.energyfuels.9b00641

9. D. Vijayalakshmi, C. Narasimha Rao, M. Gowrisankar, K. Sivakumar, P. Venkateswarlu. Densities, viscosities and speeds of sound of binary mixtures of ethyl benzoate with toluene, and isomeric chlorotoluenes at different temperatures. Journal of Molecular Liquids 197 (2014) 272–286

10. S. Sreehari Sastry, Shaik Babu, T.Vishwam, K.Parvateesam, Ha.SieTiong. Excess parameters for binary mixtures of ethyl benzoate with 1-propanol, 1-butanol and 1-pentanol at T = 303, 308, 313, 318, and 323K. Physica B 420 (2013) 40–48. https://doi.org/10.1016/j.physb.2013.03.028

11. Santiago Aparicio, Rafael Alcalde, Maria J. Davila, Begona Garcıa, and Jose´ M. Leal. Properties and Structure of Aromatic Ester Solvents. J. Phys. Chem. B 2007, 111, 4417-4431 doi: 10.1021/jp068560t

Zaoui–Djelloul Daouadji Manel et al.
Densities, Viscosities, and Refractive Indices, of Binary Mixture of Ethyl Benzoate with Ethyl Acetate from 293.15 K to 313.15 K

12. T. Madhu Mohan, S. Sreehari Sastry, V.R.K. Murthy. Investigations on Binary Mixtures of Propan-2-ol with Methyl Benzoate and Ethyl Benzoate. J Solution Chem (2011) 40:1847–1862 DOI 10.1007/s10953-011-9763-6

13. James Kendall and Alexander Olland Wright. The viscosity of liquids. Iv. Ideal mixtures of the types ether-ether and ester-ester. J. Am. Chem. Soc. 42 (1920) 1776–1779

14. Zaoui-Djelloul Daouadji M, Belfar M, Mekhelfi T, Allaoui M, Bouguerra A, Belkhalfa H, Maamri M, Maamri I. 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 (2022); *Transylvanian Review.* 30(1): 15951-15959. http://www.transylvanianreviewjournal.com/ojsfolder/index.php/TR/article/view/894

15. 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

16. 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

17. 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, No. 8, pp. 1573–1580.* **DOI:** 10.1134/S0036024420080300

18. 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

19. T.M. Aminabhavi, T.S.M. Phayde, S.R. Khinnavar, B. Gopalakrishna, C.H. Keith, J. Chem. Eng. Data 39 (1994) 251–260.

20. 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

21. 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
DOI 10.1007/s10953-012-9802-y

22. 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

23. Santiago Aparicio, Rafael Alcalde, Begoña García, and José M. Leal. Thermophysical Behavior of *n*-Alkane + Alkylbenzoate Mixed Solvents. Measurements and Properties Modeling. *Ind. Eng. Chem. Res.* 2005, 44, 19, 7575–7583 https://doi.org/10.1021/ie0502281

24. 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
25. Begonã 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
26. 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
27. 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
28. Nandhibatla V. Sastry, Sunil R. Patel, Saurabh S. Soni. Excess molar volumes, excess isentropic compressibilities, excess viscosities, relative permittivity and molar polarization deviations for methyl acetate+, ethyl acetate+, butyl acetate+, isoamyl acetate+, methyl propionate+, ethyl propionate+, ethyl butyrate+, methyl methacrylate+, ethyl methacrylate+, and butyl methacrylate + cyclohexane at T = 298.15 and 303.15 K. Journal of Molecular Liquids 183 (2013) 102–112. https://doi.org/10.1016/j.molliq.2013.04.015
29. 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. https://doi.org/10.1016/j.molliq.2019.112221
30. R. K. Wanchoo, JyotI Narayan, G. K. Raina. Excess properties of (2-propanol + ethylacetate or benzene) binary liquid mixture. Chem. Eng. Comm. 1989, Vol. 81, pp. 145-156
31. Asra Banu Syeda, Ranjith Kumar Bachu, Amara Jyothi Koppula, Sathyanarayana Boodida, and Satyanarayana Nallani. Volumetric and Transport Properties of Binary Liquid Mixtures of Phenylacetonitrile with Aliphatic Esters at Temperatures of (303.15 to 313.15) K. J. Chem. Eng. Data 2010, 55, 2, 1067–1071. https://doi.org/10.1021/je900525f
32. Saravanakumar, K., Baskaran, R. & Kubendran, T.R. The variation of viscosity, refractive indices, compressibility, intermolecular free length, and excess molar volume of the acetophenone—ethyl acetate solutions at 303.15–323.15 K. Russ. J. Phys. Chem. 86, 1947–1952 (2012). https://doi.org/10.1134/S0036024412130195
33. Murali Krishna Patwari, Ranjith Kumar Bachu, Sathyanarayana Boodida, and Satyanarayana Nallani. Densities, Viscosities, and Speeds of Sound of Binary Liquid Mixtures of Sulfolane with Ethyl Acetate, n-Propyl Acetate, and n-Butyl Acetate at Temperature of (303.15, 308.15, and 313.15) K. J. Chem. Eng. Data 2009, 54, 3, 1069–1072. https://doi.org/10.1021/je800653d

34. Arthur I. Vogel. Physical properties and chemical constitution. Part XIII. Aliphatic carboxylic esters. J. Chem. Soc., 1948, 624-644. https://doi-org.sndl1.arn.dz/10.1039/JR9480000624
35. Akl M. Awwad and Amar H. Al-Dujaili. Density, Refractive Index, Permittivity, and Related Properties for N-Formylmorpholine + Ethyl Acetate and + Butanone at 298.15 K. Journal of Chemical & Engineering Data 2001 46 (6), 1349-1350 https://doi.org/10.1021/je000332j
36. Jhoany Acosta, Alberto Arce, Eva Rodil, and Ana Soto. Densities, Speeds of Sound, Refractive Indices, and the Corresponding Changes of Mixing at 25 °C and Atmospheric Pressure for Systems Composed by Ethyl Acetate, Hexane, and Acetone. Journal of Chemical & Engineering Data 2001 46 (5), 1176-1180 https://doi.org/10.1021/je0100490
37. S.LOswal, P. Oswal, P.S Modi, J.P Dave, R.LGardas. Acoustic, volumetric, compressibility and refractivity properties and Flory's reduction parameters of some homologous series of alkyl alkanoates from 298.15 to 333.15 K. Thermochimica Acta Volume 410, Issues 1–2, 9 February 2004, Pages 1-14. https://doi-org.sndl1.arn.dz/10.1016/S0040-6031(03)00368-X
38. Shantilal Oswal and Manapragada V. Rathnam. Viscosity data of binary mixtures: ethyl acetate + cyclohexane, + benzene, + toluene, + ethylbenzene + carbon tetrachloride, and + chloroform at 303.15 K. Canadian Journal of Chemistry. Volume 62, Number 12 December 1984. https://doi.org/10.1139/v84-482
39. Tejraj M. Aminabhavi and Kamalika Banerjee. Density, Viscosity, Refractive Index, and Speed of Sound in Binary Mixtures of Acrylonitrile with Methyl Acetate, Ethyl Acetate, n-Propyl Acetate, n-Butyl Acetate, and 3-Methylbutyl-2-acetate in the Temperature Interval (298.15–308.15) K. Journal of Chemical & Engineering Data 1998 43 (4), 514-518 https://doi.org/10.1021/je9800454
40. 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. https://doi.org/10.1016/j.cdc.2019.100299
41. Sk. Md Nayeem, M. Kondaiah, K. Sreekanth, D. Krishna Rao. Acoustic and volumetric investigations in aromatic, cyclic and aliphatic ketones with dimethyl sulphoxide at 308.15 K. Arab. J. Chem. (2015) http://dx.doi.org/10.1016/j.arabjc.2015.08.005
42. K. Rajagopal, S. Chenthilnath, Excess thermodynamic studies of binary liquid mixtures of 2-methyl-2-propanol with ketones. Indian J. Pure Appl. Phys. 48 (2010) 326–333.
43. Benson, G.C., Kiyohara, O.: Evaluation of excess isentropic compressibilities and isochoric heat capacities. J. Chem. Thermodyn. **11**, 1061–1064 (1979).
44. Herbert VogeL and Alarich Weiss. Transport Properties of Liquids, 111. Viscosity of Athermal Liquid Mixtures. *Berichte der Bunsengesellschaft für physikalische Chemie*. 86-3 (1982). 193–198. https://doi.org/10.1002/bbpc.19820860304

45. R. J. Fort and W. R. Moore. Viscosities of binary liquid mixtures. *Trans. Faraday Soc.* 1966, 62, 1112-1119. https://doi.org/10.1039/TF9666201112

46. T.M. Reed, T.E. Taylor. Viscosities of Liquid Mixtures. J. Phys. Chem. 63 (1959) 58–67. https://doi.org/10.1021/j150571a016

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