Excess parameters of binary liquid mixtures of ethyl benzoate with o-xylene, p-xylene and o-chlorotoulene at different temperatures

G. Lakshmana Rao, P. B. Sandhya Sri, G. R. Satyanarayana, K. A. K. Raj Kumar and C. Rambabu[*]

Department of Chemistry, Acharya Nagarjuna University, Guntur, Andhra Pradesh, India

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ABSTRACT

Densities, ultrasonic velocities and viscosities of binary liquid mixtures of ethyl benzoate with o-xylene(OX), p-xylene(PX) and o-chlorotoulene(OCT) have been measured at 303.15K, 308.15K, 313.15K and 318.15K temperatures over the entire composition range of mole fractions. These components are selected to study the effect of substituent and effect of certain positions on different thermodynamic parameters of the mixtures. Using these experimental values, excess molar volume (V^E), deviation in adiabatic compressibility ($\Delta\beta_{ad}$), excess free length(L_f^E) and deviation in viscosities($\Delta\eta$) are calculated. These excess parameters are fitted to Redlich-Kister type polynomial equation. The values of parameters obtained are calculated along with the standard deviation (σ).

Key words: Densities, ultrasonic velocities, viscosities, excess molar volume, deviation in adiabatic compressibility, excess free length and deviation in viscosity and molecular interaction.
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INTRODUCTION

The knowledge of physical and chemical properties of non-aqueous binary liquid mixtures has relevance in theoretical and applied areas of research. The binary mixtures of aromatic hydrocarbons are very useful because they find many applications in the studies of preferential interaction of polymers and polymer phase diagrams and in mixed solvents [1, 2]. Esters are one of the special kinds of chemicals with sweet odor and less toxic nature. They have many industrial applications in perfumes, cosmetics etc. Aromatic hydrocarbons like xylenes are frequently used as octane enhancers in vehicle fuels. Hence it is very interesting to study the effect of xylenes on the physical and chemical properties of ethyl benzoate by mixing them in different proportions at different temperatures.

The excess properties of binary liquid mixtures have proved to be very useful indicator of the existence of significant effects resulting from intermolecular interactions [3, 4]. The advantage of in-depth and wide study of this inter-relationship is twofold: first, it provides experimental background to develop, test and improve thermo dynamical models for calculating and predicting fluid phase equilibria; second, it offers a wide range of possibilities for continuous adjustment of physical properties of a given solvent [5].

The detailed survey of literature indicated that some work regarding determination of excess parameters of xylenes has been done with different combinations at different temperatures. But with ethyl benzoate combination, this type of work has been done at only 303.15 and 313.15K temperatures and also not found with ultrasonic studies. With a view to understand the nature of interactions between ethylbonzoate and xylenes by taking the ultrasonic velocities

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into consideration and its related parameters, We selected this sytem for our study. As mentioned earlier, ethyl benzoate has several industrial applications and xylenes are also aromatic compounds. o-chlorotoulene is similar compound but with a difference in one substitute. Because of these aspects, We chose two xylenes and o-chlorotoulene for comparative study of molecular interactions with ethyl benzoate.

Experimental techniques and materials used
Ethyl benzoate, o-cresol, p-cresol and o-chlorotoulene obtained from Merck were purified as described in the literature [6, 7]. The purity of the samples was checked by comparing the measured densities with those reported in the literature [8-11] and these are given in Table 1.

The density was measured with a pycnometer having a bulb volume of about 25 cm^3 and an internal capillary diameter of about 1 mm. The density was then determined from the mass of the sample and the volume of pycnometer is used to determine the density. Uncertainties in density measurements were estimated to be within $\pm$ 0.0001 g cm^{-3}. The viscosity was measured using a commercial Ubbelohde capillary viscometer of 0.55 mm diameter calibrated with double distilled water at temperatures of 303.15, 308.15, 313.15 and 318.15K.

Table-1: Comparison of experimental densities (ρ), viscosities (η) and velocities (U) with literature values at 303.15K, 308.15K, 313.15K and 318.15K

Liquid		Density10^{-3}(kgm^{-3})		Viscosity (mPa s)		Velocity (m s^{-1})	
		Exp.	Lit.	Exp.	Lit.	Exp.	Lit.
Ethyl benzoate (EB)	303.15 K	1.0392	1.042[a]	1.7512	1.7495[a]	1346.2	1345.4[a]
o-xylene (OXL)	303.15 K	0.8705	0.8707[b]	0.728	0.705[c]	1336.2	1138.75[b]
p-xylene (PXL)	303.15 K	0.8528	0.8528[b]	0.579	0.5782[c]	1286.3	1288.43[b]
o-chlorotoluene (OCT)	303.15 K	1.0728	1.0725[d]	0.870	0.885[d]	1283.8	1283.8[d]

[a]Ref [8], [b]Ref [9], [c] Ref [10], [d] Ref [11]

Theoretical Considerations:
Assuming that ultrasonic absorption is negligible, adiabatic compressibilities can be obtained from the densities and ultrasonic sound velocities using the relation

$$\beta_{ad} = (\rho u^2)^{-1} \qquad\qquad\qquad ……….. \ (2)$$

The molar volumes of the binary mixtures were calculated using the equation
$$V = (X_1M_1+X_2M_2)/\rho \qquad\qquad ……….. \ (3)$$

Intermolecular free length (L$_f$) has been evaluated by Jacobson's formula
$$L_f = K/u\rho^{1/2} \qquad\qquad\qquad …………\ (4)$$

where K is the temperature dependent Jacobson constant and T is the absolute temperature.
The strength of interaction between the component molecules of binary mixtures is well reflected in the deviation of the excess functions from ideality. Thermodynamic excess functions are found to be very sensitive towards mutual interactions between component molecules of liquid mixtures. The sign and extent of deviation of these functions from ideality depends on the strength of interaction between unlike molecules.

The excess properties such as $\Delta\beta_{ad}$, V^E, $\Delta\eta$ and L_f^E have been calculated using the equation
$$Y^E = Y_{mix} - (X_1Y_1+X_2Y_2) \qquad\qquad ……….\ (5)$$

where Y^E is $\Delta\beta_{ad}$ or V^E or $\Delta\eta$ or L_f^E, and X represent mole fraction of the component and subscripts 1 and 2 stand for the components 1and 2. These excess functions were fitted to Redlich - Kister type polynomial equation [12].

$$Y_{cal}^E = X_1 X_2 \Sigma a_{j-1} (X_2-X_1)^{j-1} \qquad\qquad …..\ (6)$$

The values of coefficient a_{j-1} evaluated by the method of least squares with all points weighed equally with the standard deviations are listed in Table 3 and are calculated as
$$\sigma(Y^E) = (Y_{ob}^E - Y_{cal}^E)/(m-n))^{1/2} \qquad\qquad …..\ (7)$$

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where m is the number of experimental data points and n is the number of coefficients considered (n = 5 in the present calculation.)

RESULTS AND DISCUSSION

Computed values of V^E, $\Delta\beta_{ad}$, L_f^E, and $\Delta\eta$ along with the experimental values of U, ρ and η are presented in the Tables 2-4. Variations of excess parameters with the mole fraction of EB are represented in the figures 1(a) – 3(d). The sign of V^E of a system depends upon the relative magnitude of expansion and contraction of the two liquids due to mixing [12]. The factors that are responsible for expansion of volume on mixing of the components are: (1) Steric hindrance due to branching of chains (2) Formation of weaker solute-solvent bond than solute-solute and solvent-solvent bonds and (3)Dissociation of one component or all components.

The factors that lead to contraction in volume on mixing are: (a) Strong specific interaction usually a kind of chemical interaction. (b)Strong physical interaction such as dipole-dipole or dipole-induced dipole interactions.(c) Occupation of void spaces of one component by the other may be due to when the molecular sizes of the components differ by a large magnitude.

The sign and magnitude of excess molar volume would depend on the relative magnitude of contractive and expansive effect which arises on mixing of liquid components. The negative deviations in excess molar volume (V^E) are observed for these three systems. These are caused by some strong interactions between unlike molecules.

In EB molecules two polar bonds viz. >C=O, C-O-C bonds are present. But there is no scope for either of the hydrogen bonding between EB molecules. There are two +I (methyl) groups on in xylenes and one +I (methyl) group and one weak –I (Cl) in o-chlorotoulene molecules. Due to presence of +I (methyl) groups, xylene molecules are induced with partial charges (Though para xylene dipole moment is zero). This facilitates for dipole – induced dipole interactions between EB molecules and xylene molecules. But in case of o- xylene molecules, the presence of two methyl groups on adjacent positions hinders the approachment (steric hindrance) of other molecules (EB) towards them. Hence weak interaction than in case of p-xylene molecules is possible. The same trend is observed in the present study. Also the same trend was reported by Anil Kumar Nain et.al [14] and Nandibatla V. Sasty et.al [13]. The observations are again supported by the trends observed for excess acoustic impedance (Z^E) and excess ultrasonic velocity (U^E).

The π-electron density in derivatives of benzene ring depends upon the group that is attached to it. There may be some n…….π interactions between the pair of electrons on carbonyl oxygen of ester and π electron clouds of benzene ring in p-xylene and ortho chlorotoulene molecules. This was supported by C.Yang, W.Xu, and P.Ma [15]. In case of ortho chlorotoulene molecules, one strong +I (methyl) group and one weak –I (Cl) group are present on benzene ring at adjacent positions. Hence less polarization is observed. So weak interactions between orthochlorotoulene molecules and EB molecules are expected. The same is observed in the present study.

For this system a little deviation is observed in all parameters. This can be explained by the following aspects
• Almost similar sizes of EB and OCT molecules. According to Fort and Moore [16] molecules with equal size do not mix thoroughly.
• Due to the presence of one +I and one –I, there is a little possibility for OCT molecules to be polarised. Hence very weak associative forces may be present.

In general, the deviation [17] in adiabatic compressibility can be explained by taking into consideration of the following factors:2
(a) Loss of dipolar association and difference in size and shape of component molecules which lead to decrease in velocity and increase in compressibility.
(b) Dipole-Dipole interaction or hydrogen bonded complex formation between unlike molecules which lead to increase in sound velocity and decrease of compressibility.

TABLE-2
System-I : Ethylbenzoate(X₁) + o-xylene(X₂)
Ultrasonic velocities, Densities, Viscosities and related excess parameters

Mole	fraction	X_1	Velocity U m/s	Density ρ(kg/m³)	Viscosity	η cP	V^E	cm³ mol⁻¹	$\Delta\beta_{ad}\times10^{-12}$ m²N⁻¹	L_f^E (Å)	$\Delta\eta$ cP
					303.15K						
	0.0000		1336.2	870.5	0.728			0.0000	0.0000	0.0000	0.0000
	0.0857		1338.4	889.0	0.808			-0.2272	-0.0973	-0.0019	-0.0080
	0.1742		1340.3	907.4	0.892			-0.4384	-0.1780	-0.0036	-0.0140
	0.2656		1341.8	925.5	0.980			-0.6069	-0.2410	-0.0049	-0.0200
	0.3601		1343.0	943.3	1.072			-0.7336	-0.2838	-0.0058	-0.0240
	0.4577		1344.0	960.7	1.170			-0.8055	-0.3023	-0.0062	-0.0260
	0.5587		1344.8	977.6	1.275			-0.8093	-0.2951	-0.0061	-0.0250
	0.6632		1345.4	994.1	1.384			-0.7589	-0.2649	-0.0055	-0.0220
	0.7715		1345.8	1009.9	1.500			-0.6127	-0.2066	-0.0043	-0.0170
	0.8837		1346.1	1024.9	1.623			-0.3558	-0.1166	-0.0024	-0.0090
	1.0000		1346.2	1039.2	1.751			0.0000	0.0000	0.0000	0.0000
					308.15K						
	0.0000		1312.1	869.4	0.656			0.0000	0.0000	0.0000	0.0000
	0.0857		1314.6	887.9	0.726			-0.2677	-0.1106	-0.0023	-0.0110
	0.1742		1317.2	906.1	0.801			-0.4929	-0.1907	-0.0040	-0.0190
	0.2656		1319.5	924.0	0.881			-0.6767	-0.2530	-0.0053	-0.0250
	0.3601		1321.7	941.5	0.965			-0.8063	-0.2904	-0.0062	-0.0290
	0.4577		1323.6	958.6	1.055			-0.8824	-0.3093	-0.0066	-0.0310
	0.5587		1325.4	975.4	1.150			-0.9190	-0.3066	-0.0066	-0.0310
	0.6632		1327.2	991.5	1.252			-0.8613	-0.2730	-0.0059	-0.0270
	0.7715		1328.8	1006.9	1.360			-0.7086	-0.2146	-0.0047	-0.0210
	0.8837		1330.2	1021.2	1.475			-0.4039	-0.1254	-0.0027	-0.0120
	1.0000		1331.9	1034.8	1.596			0.0000	0.0000	0.0000	0.0000
					313.15K						
	0.0000		1293.2	867.7	0.620			0.0000	0.0000	0.0000	0.0000
	0.0857		1295.8	886.4	0.681			-0.3276	-0.1190	-0.0026	-0.0110
	0.1742		1298.3	904.6	0.746			-0.5852	-0.2099	-0.0045	-0.0190
	0.2656		1300.8	922.2	0.816			-0.7606	-0.2693	-0.0058	-0.0260
	0.3601		1303.2	939.7	0.891			-0.9241	-0.3114	-0.0068	-0.0300
	0.4577		1305.5	956.6	0.971			-1.0073	-0.3268	-0.0072	-0.0310
	0.5587		1307.7	973.0	1.056			-1.0244	-0.3187	-0.0070	-0.0310
	0.6632		1309.8	988.7	1.147			-0.9475	-0.2841	-0.0063	-0.0270
	0.7715		1311.8	1003.6	1.244			-0.7620	-0.2221	-0.0050	-0.0200
	0.8837		1313.8	1017.4	1.347			-0.4238	-0.1261	-0.0028	-0.0110
	1.0000		1316.0	1030.6	1.455			0.0000	0.0000	0.0000	0.0000
					318.15K						
	0.0000		1273.2	865.8	0.588			0.0000	0.0000	0.0000	0.0000
	0.0857		1275.7	884.5	0.641			-0.3627	-0.1286	-0.0028	-0.0120
	0.1742		1278.4	902.5	0.699			-0.6279	-0.2177	-0.0048	-0.0210
	0.2656		1281.0	920.1	0.762			-0.8396	-0.2837	-0.0063	-0.0270
	0.3601		1283.6	937.3	0.829			-0.9987	-0.3248	-0.0073	-0.0310
	0.4577		1286.2	954.0	0.901			-1.0921	-0.3402	-0.0076	-0.0330
	0.5587		1288.8	970.0	0.977			-1.0923	-0.3273	-0.0074	-0.0330
	0.6632		1291.3	985.4	1.059			-1.0128	-0.2915	-0.0066	-0.0300
	0.7715		1293.8	1000.1	1.147			-0.8387	-0.2291	-0.0052	-0.0230
	0.8837		1296.4	1013.6	1.241			-0.4979	-0.1302	-0.0030	-0.0140
	1.0000		1299.0	1026.0	1.343			0.0000	0.0000	0.0000	0.0000

The strength of the interaction between the components increases/decreases when excess values tend to become increasingly negative/decreasingly positive. This may be qualitatively explained in terms of closer approach of unlike molecules leading to reductions in compressibility and volume. The negative L_f^E values indicate that sound wave has to travel a shorter distance. It is due to dominant nature of interactions between unlike molecules. The $\Delta\beta_{ad}$ and L_f^E minima occur at the same concentrations further strengthens the occurrence of molecular associations.

The interdependence of intermolecular free length and ultrasonic velocity was evolved from a model for sound propagation proposed by Eyring & Kincaid [18]. The variation of ultrasonic velocity in a solution depends upon the increase or decrease of intermolecular free length after mixing the components. The ultrasonic velocity should decrease if the intermolecular free length increases or vice versa as a result of mixing of components. This fact is observed in the present investigation for **Ethyl benzoate (EB) + p-xylene   > Ethyl benzoate (EB) + o-xylene > Ethyl benzoate (EB) + o-chlorotoulene** systems. It is also observed that velocity decreases with increase in

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temperature at any concentration. The ultrasonic velocity values decrease with increase of temperature due to breaking of hetero and homo molecular clusters at high temperatures [19].

TABLE-3
System-II : Ethylbenzoate(X_1) + p-xylene(X_2)
Ultrasonic velocities, Densities, Viscosities and related excess parameters

Mole fraction X_1	Velocity U m/s	Density ρ (kg/m^3)	Viscosity η cP	V^E cm^3 mol^{-1}	$\Delta\beta_{ad}\times10^{-12}$ m^{2}N^{-1}	L_f^E (Å)	$\Delta\eta$ cP
			303.15K				
0.0000	1286.3	852.8	0.579	0.0000	0.0000	0.0000	0.0000
0.0874	1293.4	875.9	0.669	-0.6428	-0.1311	-0.0029	-0.0120
0.1772	1299.9	898.3	0.766	-1.1717	-0.2425	-0.0054	-0.0210
0.2697	1306.2	919.9	0.867	-1.5786	-0.3251	-0.0072	-0.0280
0.3648	1312.4	940.6	0.975	-1.8552	-0.3739	-0.0083	-0.0320
0.4628	1318.6	960.3	1.088	-1.9918	-0.3874	-0.0087	-0.0330
0.5638	1324.6	978.9	1.206	-1.9779	-0.3713	-0.0084	-0.0340
0.6678	1330.4	996.2	1.331	-1.7879	-0.3238	-0.0073	-0.0310
0.7751	1335.9	1012.2	1.464	-1.4219	-0.2492	-0.0057	-0.0230
0.8858	1341.2	1026.5	1.604	-0.8230	-0.1394	-0.0032	-0.0130
1.0000	1346.2	1039.2	1.751	0.0000	0.0000	0.0000	0.0000
			308.15K				
0.0000	1274.2	846.7	0.551	0.0000	0.0000	0.0000	0.0000
0.0874	1280.4	870.1	0.628	-0.6778	-0.1561	-0.0035	-0.0140
0.1772	1286.4	892.7	0.713	-1.2227	-0.2780	-0.0062	-0.0230
0.2697	1292.5	914.6	0.803	-1.6558	-0.3619	-0.0081	-0.0300
0.3648	1298.5	935.5	0.898	-1.9407	-0.4104	-0.0092	-0.0340
0.4628	1304.4	955.4	0.999	-2.0822	-0.4259	-0.0096	-0.0360
0.5638	1310.1	974.2	1.104	-2.0701	-0.4115	-0.0093	-0.0360
0.6678	1315.8	991.6	1.216	-1.8650	-0.3582	-0.0082	-0.0330
0.7751	1321.3	1007.7	1.335	-1.4810	-0.2752	-0.0063	-0.0260
0.8858	1326.7	1022.1	1.461	-0.8610	-0.1544	-0.0035	-0.0160
1.0000	1331.9	1034.8	1.596	0.0000	0.0000	0.0000	0.0000
			313.15K				
0.0000	1251.6	842.9	0.507	0.0000	0.0000	0.0000	0.0000
0.0874	1258.1	866.4	0.574	-0.7054	-0.1603	-0.0036	-0.0160
0.1772	1264.5	889.2	0.650	-1.2901	-0.2872	-0.0065	-0.0250
0.2697	1271.0	911.1	0.729	-1.7324	-0.3739	-0.0086	-0.0340
0.3648	1277.5	932.0	0.816	-2.0248	-0.4244	-0.0098	-0.0370
0.4628	1284.0	951.9	0.906	-2.1726	-0.4411	-0.0102	-0.0400
0.5638	1290.5	970.6	1.002	-2.1514	-0.4226	-0.0098	-0.0390
0.6678	1296.9	988.0	1.105	-1.9496	-0.3720	-0.0087	-0.0350
0.7751	1303.3	1003.9	1.214	-1.5396	-0.2848	-0.0067	-0.0280
0.8858	1309.7	1018.2	1.331	-0.9055	-0.1612	-0.0038	-0.0160
1.0000	1316.0	1030.6	1.455	0.0000	0.0000	0.0000	0.0000
			318.15K				
0.0000	1233.5	837.3	0.482	0.0000	0.0000	0.0000	0.0000
0.0874	1239.8	861.1	0.542	-0.7498	-0.1706	-0.0039	-0.0160
0.1772	1246.2	884.0	0.609	-1.3451	-0.2980	-0.0069	-0.0260
0.2697	1252.7	906.1	0.681	-1.8089	-0.3877	-0.0090	-0.0350
0.3648	1259.1	927.2	0.758	-2.1194	-0.4443	-0.0104	-0.0400
0.4628	1265.7	947.3	0.841	-2.2820	-0.4621	-0.0108	-0.0420
0.5638	1272.3	966.1	0.928	-2.2587	-0.4436	-0.0104	-0.0420
0.6678	1278.9	983.5	1.022	-2.0380	-0.3893	-0.0092	-0.0380
0.7751	1285.6	999.4	1.122	-1.6063	-0.2969	-0.0070	-0.0310
0.8858	1292.3	1013.7	1.229	-0.9476	-0.1688	-0.0040	-0.0200
1.0000	1299.0	1026.0	1.348	0.0000	0.0000	0.0000	0.0000

The viscosity deviations depend on strength of interactions between like and unlike molecules. The dependence of $\Delta\eta$ on composition for the mixtures under study may be explained in terms of physical and chemical factors [20,21]. The positive values of $\Delta\eta$ signify strong intermolecular interactions and negative $\Delta\eta$ values are represents weaker interaction between unlike molecules. Specific chemical interactions involving hydrogen bond formation and dipole-dipole interactions between various components of liquids mixtures making the structure more compact and result in positive viscosity deviations. The sign and magnitude of $\Delta\eta$ also varies with structural characteristics of liquid components arising from geometrical fitting of one component into the structure of other component due to difference in molecular size and

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shape of components. The negative values of $\Delta\eta$ for all the three systems can be explained by the molecular sizes, as explained in the previous discussion.

TABLE-4
System-III : Ethylbenzoate(X_1) + o-chlorotoulene(X_2)
Ultrasonic velocities, Densities, Viscosities and related excess parameters

Mole fraction X_1	Velocity U m/s	Density ρ gm/cm^3	Viscosity η cP	V^E cm^3 mol^{-1}	$\Delta\beta_{ad}\times10^{-12}$ m^{2}N^{-1}	L_f^E (Å)	$\Delta\eta$ cP
			303.15K				
0.0000	1283.8	1072.6	0.870	0.0000	0.0000	0.0000	0.0000
0.0832	1289.4	1070.3	0.939	-0.1168	-0.0048	0.0000	-0.0040
0.1695	1295.1	1067.9	1.009	-0.2271	-0.0109	0.0000	-0.0100
0.2592	1300.9	1065.2	1.083	-0.3071	-0.0157	-0.0001	-0.0150
0.3525	1306.9	1062.3	1.162	-0.3668	-0.0183	-0.0001	-0.0190
0.4495	1313.1	1059.2	1.245	-0.4047	-0.0191	-0.0001	-0.0210
0.5505	1319.4	1055.8	1.334	-0.4069	-0.0190	-0.0001	-0.0210
0.6558	1325.9	1052.2	1.430	-0.3834	-0.0174	-0.0001	-0.0180
0.7656	1332.6	1048.2	1.531	-0.3061	-0.0113	0.0000	-0.0130
0.8802	1339.4	1043.9	1.638	-0.1841	-0.0051	0.0000	-0.0070
1.0000	1346.2	1039.2	1.751	0.0000	0.0000	0.0000	0.0000
			308.15K				
0.0000	1265.7	1068.0	0.776	0.0000	0.0000	0.0000	0.0000
0.0832	1271.5	1065.8	0.836	-0.1268	-0.0092	-0.0001	-0.0080
0.1695	1277.4	1063.5	0.899	-0.2475	-0.0200	-0.0003	-0.0160
0.2592	1283.5	1060.9	0.967	-0.3380	-0.0274	-0.0003	-0.0220
0.3525	1289.8	1058.0	1.040	-0.3964	-0.0315	-0.0004	-0.0250
0.4495	1296.3	1055.0	1.118	-0.4451	-0.0353	-0.0004	-0.0270
0.5505	1303.0	1051.6	1.201	-0.4456	-0.0347	-0.0004	-0.0260
0.6558	1309.9	1048.0	1.290	-0.4203	-0.0328	-0.0004	-0.0240
0.7656	1317.1	1044.0	1.385	-0.3405	-0.0242	-0.0003	-0.0190
0.8802	1324.4	1039.5	1.487	-0.1884	-0.0125	-0.0001	-0.0110
1.0000	1331.9	1034.8	1.596	0.0000	0.0000	0.0000	0.0000
			313.15K				
0.0000	1244.5	1062.3	0.732	0.0000	0.0000	0.0000	0.0000
0.0832	1250.6	1060.4	0.783	-0.1449	-0.0154	-0.0002	-0.0090
0.1695	1256.9	1058.3	0.838	-0.2726	-0.0290	-0.0005	-0.0170
0.2592	1263.4	1055.9	0.897	-0.3701	-0.0394	-0.0006	-0.0220
0.3525	1270.2	1053.3	0.961	-0.4477	-0.0460	-0.0007	-0.0260
0.4495	1277.2	1050.5	1.029	-0.5040	-0.0513	-0.0008	-0.0280
0.5505	1284.4	1047.3	1.102	-0.5121	-0.0525	-0.0008	-0.0280
0.6558	1291.9	1043.7	1.181	-0.4686	-0.0473	-0.0007	-0.0250
0.7656	1299.7	1039.7	1.266	-0.3694	-0.0356	-0.0005	-0.0200
0.8802	1307.7	1035.3	1.357	-0.2101	-0.0201	-0.0003	-0.0110
1.0000	1316.0	1030.6	1.455	0.0000	0.0000	0.0000	0.0000
			318.15K				
0.0000	1228.1	1060.1	0.704	0.0000	0.0000	0.0000	0.0000
0.0832	1234.1	1058.1	0.748	-0.1624	-0.0181	-0.0003	-0.0090
0.1695	1240.3	1055.9	0.795	-0.3082	-0.0344	-0.0006	-0.0170
0.2592	1246.7	1053.4	0.846	-0.4244	-0.0478	-0.0008	-0.0240
0.3525	1253.4	1050.6	0.902	-0.5090	-0.0559	-0.0010	-0.0270
0.4495	1260.3	1047.5	0.962	-0.5598	-0.0614	-0.0011	-0.0290
0.5505	1267.5	1044.1	1.027	-0.5617	-0.0604	-0.0010	-0.0290
0.6558	1274.9	1040.2	1.097	-0.5242	-0.0570	-0.0010	-0.0260
0.7656	1282.6	1035.9	1.172	-0.4172	-0.0457	-0.0008	-0.0210
0.8802	1290.6	1031.0	1.254	-0.2212	-0.0249	-0.0004	-0.0120
1.0000	1299.0	1026.0	1.343	0.0000	0.0000	0.0000	0.0000

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TABLE-5
Values of coefficints and standard deviation (σ)

| Temp K	A_0	A_1	A_2	A_3	A_4	σ
**System-I : ethylbenzoate(X_1) + o-xylene(X_2)**					
	Excess Molar Volume(V^E)					
303.15K	-3.2755	0.3654	-0.0809	-0.0538	0.3407	0.0041
308.15K	-3.6035	0.6359	-0.7006	-0.5402	0.9545	0.0054
313.15K	-4.1082	0.5762	0.2468	-0.9313	-0.3993	0.0108
318.15K	-4.4308	0.3559	0.1408	-0.2413	-0.9561	0.0103
	Deviation in Adiabatic compressibility($\Delta\beta_{ad}$)					
303.15K	-1.2125	-0.0674	0.0416	-0.0033	0.0010	0.0010
308.15K	-1.2396	-0.0708	-0.0648	-0.0625	-0.0701	0.0017
313.15K	-1.3071	-0.1114	-0.0332	-0.0974	-0.0848	0.0017
318.15K	-1.3569	-0.1609	-0.0162	-0.0904	-0.1865	0.0022
	Deviation in Viscosity (Δη)					
303.15K	-0.1043	-0.0081	0.0316	-0.0014	-0.0253	0.0004
308.15K	-0.1243	-0.0077	0.0076	-0.0094	-0.0203	0.0003
313.15K	-0.1238	-0.0117	-0.0173	-0.0164	0.0305	0.0006
318.15K	-0.1328	0.0001	-0.0192	-0.0152	0.0032	0.0004
	Excess free length(L_f^E)					
303.15K	-0.0249	-0.0005	0.0011	-0.0001	0.0000	0.0000
308.15K	-0.0265	-0.0007	-0.0014	-0.0013	-0.0015	0.0000
313.15K	-0.0287	-0.0016	-0.0006	-0.0022	-0.0019	0.0000
318.15K	-0.0305	-0.0029	-0.0002	-0.0020	-0.0043	0.0001
	System-II : ethylbenzoate(X_1) + p-xylene(X_2)					
	Excess Molar Volume(V^E)					
303.15K	-8.0167	0.0812	-0.1586	-0.0491	0.0499	0.0045
308.15K	-8.3761	0.0272	-0.1974	-0.0174	-0.0070	0.0061
313.15K	-8.7378	0.0160	-0.3952	0.0847	0.2131	0.0031
318.15K	-9.1806	0.0199	0.0709	-0.0103	-0.6090	0.0030
	Deviation in Adiabatic compressibility($\Delta\beta_{ad}$)					
303.15K	-1.5384	-0.2632	-0.0545	0.1382	0.1524	0.0009
308.15K	-1.6927	-0.2684	-0.1177	-0.0018	0.0808	0.0014
313.15K	-1.7535	-0.2687	-0.1265	0.0121	0.0961	0.0007
318.15K	-1.8396	-0.2538	-0.0073	-0.0506	-0.1224	0.0008
	Deviation in Viscosity(Δη)					
303.15K	-0.1329	0.0074	-0.0599	-0.0368	0.0815	0.0009
308.15K	-0.1448	0.0028	-0.0327	-0.0187	-0.0006	0.0004
313.15K	-0.1599	-0.0120	-0.0231	-0.0200	-0.0085	0.0009
318.15K	-0.1684	-0.0046	-0.0332	0.0096	-0.0243	0.0006
	Excess free length(L_f^E)					
303.15K	-0.0345	-0.0052	-0.0009	0.0032	0.0034	0.0000
308.15K	-0.0383	-0.0052	-0.0024	0.0000	0.0019	0.0000
313.15K	-0.0406	-0.0054	-0.0026	0.0004	0.0023	0.0000
318.15K	-0.0431	-0.0051	0.0002	-0.0011	-0.0029	0.0000
	System-III : ethylbenzoate(X_1) +o-chorotoulene(X_2)					
	Excess Molar Volume (V^E)					
303.15K	-1.6481	0.1358	-0.1046	-0.0157	0.1761	0.0036
308.15K	-1.8130	0.1528	-0.1013	-0.1623	0.3877	0.0055
313.15K	-2.0579	0.1761	0.3453	-0.1880	-0.2487	0.0033
318.15K	-2.2806	0.1849	0.0002	-0.3872	0.4575	0.0042
	Deviation in Adiabatic compressibility($\Delta\beta_{ad}$)					
303.15K	-0.0764	-0.0026	-0.0314	-0.0211	0.1036	0.0007
308.15K	-0.1431	0.0058	-0.0213	-0.0230	0.0945	0.0008
313.15K	-0.2081	0.0081	0.0014	-0.0281	0.0306	0.0007
318.15K	-0.2488	0.0084	-0.0232	-0.0210	0.0688	0.0007
	Deviation in Viscosity(Δη)					
303.15K	-0.0845	-0.0073	0.0303	0.0200	0.0113	0.0003
308.15K	-0.1078	-0.0115	-0.0216	0.0140	0.0399	0.0003
313.15K	-0.1128	-0.0043	0.0050	-0.0069	-0.0024	0.0004
318.15K	-0.1157	-0.0114	-0.0327	0.0102	0.0497	0.0004
	Excess free length(L_f^E)					
303.15K	-0.0003	-0.0001	-0.0008	-0.0005	0.0026	0.0000
308.15K	-0.0018	0.0001	-0.0005	-0.0005	0.0024	0.0000
313.15K	-0.0032	0.0001	0.0000	-0.0007	0.0008	0.0000
318.15K	-0.0043	0.0001	-0.0006	-0.0005	0.0017	0.0000

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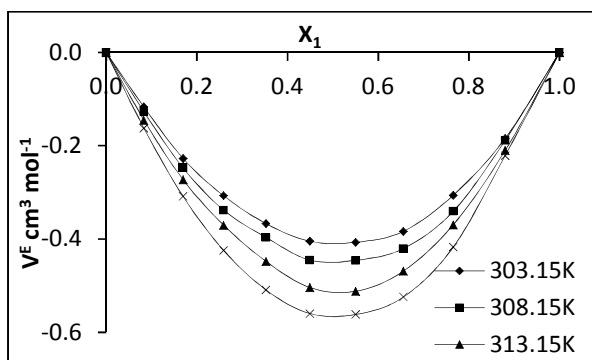
Fig1(a): Variation of excess molar volume with mole fraction of EB for the system EB + OX
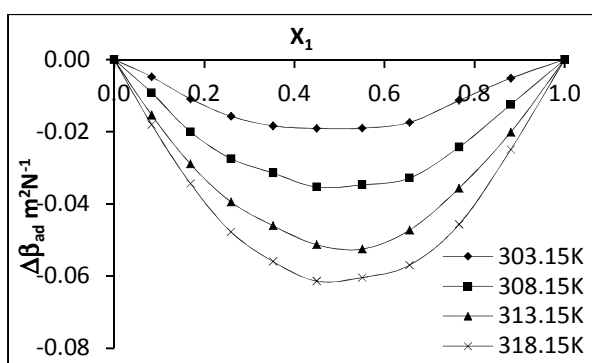

Fig1(b) Variation of deviation in adiabatic compressibility with mole fraction of EB for the system EB+OX
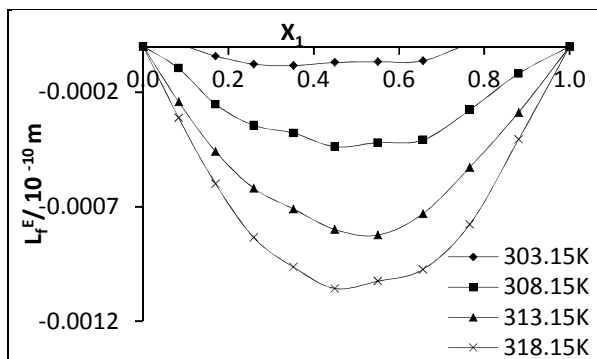

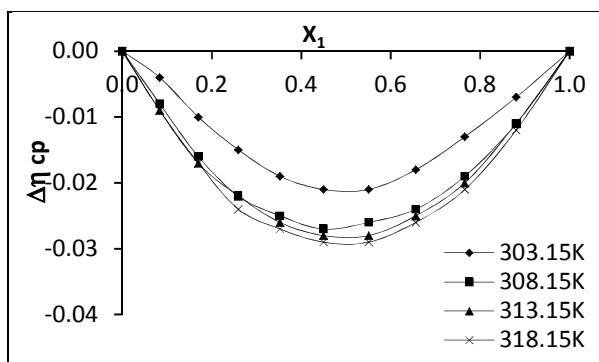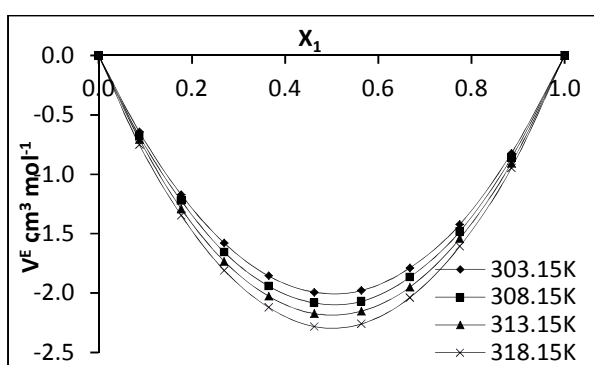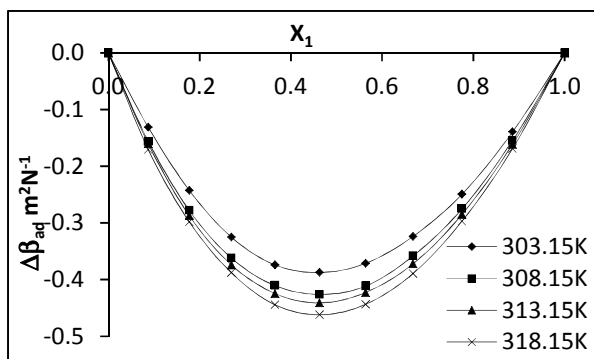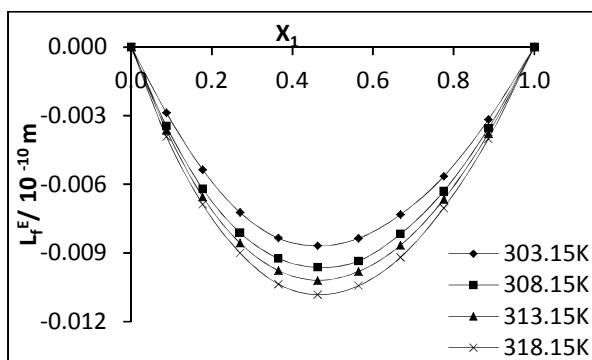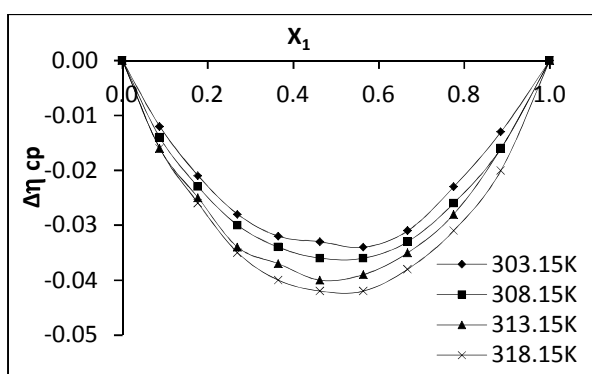**Fig1(c): Variation of excess free length with mole fraction of EB for the system EB+OX**

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Fig1(d): Variation of deviation in viscosity with mole fraction of EB for the system EB+OX

Fig2(a): Variation of excess molar volume with mole fraction of EB for the system EB + PX

Fig 2(b):Variation of deviation in adiabatic compressibility with mole fraction of EB for the system EB + PX

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Fig 2(c): Variation of excess free length with mole fraction of EB for the system EB + PX

Fig 2(d):Variation of excess viscosity with mole fraction of EB for the system EB + PX
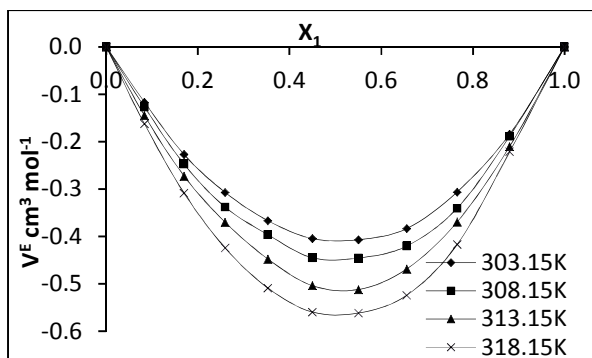

Fig3(a)Variation of excess molar volume with mole fraction of EB for the system EB +OCT
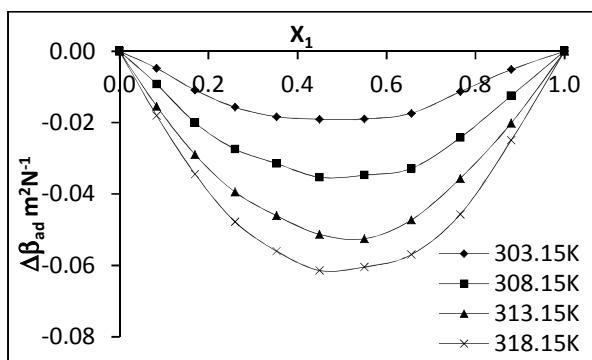
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Fig 3(b):Variation of deviation in adiabatic compressibility with mole fraction of EB for the system EB + OCT
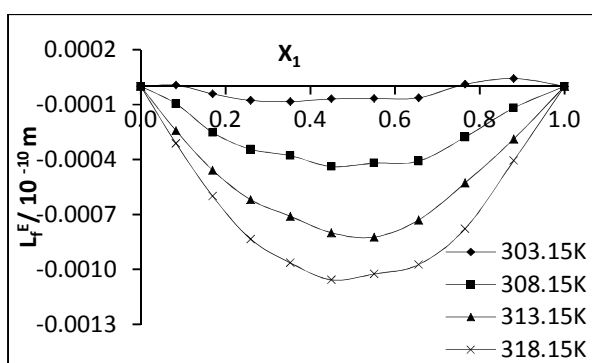

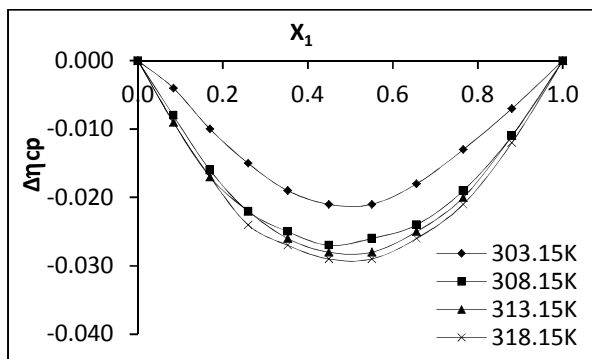**Fig 3(c):Variation of excess free length with mole fraction of EB for the system EB + OCT**

Fig 3(d): Variation of excess viscosity with mole fraction of EB for the system EB + OCT

CONCLUSION

Excess molar volumes (V^E), deviation in adiabatic compressibility ($\Delta\beta_{ad}$), excess intermolecular free length (L_f^E), deviation in viscosity ($\Delta\eta$), are observed in negative trends. The changes in values of all excess parameters are non linear and parabolic. There is little deviations observed for almost all parameters for **Ethyl benzoate (EB) + o-chlorotoulene** system.

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