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Thermodynamic study of binary mixtures of methyl acrylate and ethyl acrylate with octane-1-ol

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ABSTRACT

Thermodynamic properties involving density and ultrasonic velocities of binary liquid mixtures of methyl acrylate and ethyl acrylate with octane-1-ol measured at 298.15 and 308.15 K temperatures and at atmospheric pressure. These fundamental properties have been fitted to recently proposed Jouyban-Acree model. Excess molar volume and deviations in isentropic compressibility were calculated from density and ultrasonic velocity respectively, and have been fitted to Redlich-Kister polynomial equation. The experimental values of ultrasonic velocity were used to calculate different derived thermodynamic parameters like excess specific acoustic impendence, excess intermolecular free length, excess available volume and excess intrinsic pressure. Graphical representations of all excess thermodynamic parameters used to explain type and extent of intermolecular interactions. Graphical variation for all these parameters shows positive deviation for excess molar volume, deviation in isentropic compressibility, excess intermolecular free length, excess available volume and negative deviation for excess specific acoustic impendence, excess intrinsic pressure.

Keywords: Redlich-Kister Equation, Molecular Interactions, Jouyban-Acree Model, Excess Specific Acoustic Impendence, Excess Intrinsic Pressure.

INTRODUCTION

The knowledge of thermodynamic and physical properties of liquid-liquid systems is of considerable importance due to their wide range of applicability as solvent media in various physicochemical studies, in processing and product formation in many industrial applications. Measurements of some of the bulk properties like density, viscosity and ultrasonic velocity of liquids provide an insight into the investigation of the intermolecular arrangement of liquids and help to understand the thermodynamic and acoustic properties of the liquid mixtures.

Volume properties and evaluation of thermodynamic properties gives the better knowledge of the processes that occur in the mixture. Better understanding of these kinds of properties of fluids is essential in designing processes involving heat transfer, mass transfer and fluid flow. The more information of magnitudes such as excess molar volume of a given component of a mixture, the more efficient the design of engineering processes in which these magnitudes are involved. Binary liquid mixtures rather than single component liquid system are widely used in processing and product formulations in many industrial applications. Among the various properties considered in process and product design and optimization excess molar volumes is most important. Ultrasonic velocity measurement of liquid mixtures of non electrolytes provides an excellent tool to investigate inter and intramolecular interactions between unlike and like molecules. Alcohols exist in form of aggregates. When they are mixed with non electrolyte molecules, aggregates of alcohol dissociate and form intermolecular complexes with unlike molecules.

Literature survey reveals that, molecular interactions of present binary liquid mixtures containing methyl acrylate and ethyl acrylate with octane-1-ol at temperatures 298.15 and 308.15 K have not much studied. Attempts have been made to probe liquid structure through evaluation of density and ultrasonic velocity. We have thus undertaken thermodynamic study of binary liquid systems containing many polar and non-polar liquids to investigate molecular interactions.

MATERIALS AND METHODS

Methyl acrylate (MA), ethyl acrylate (EA) and octane-1-ol used of mass fraction purities > 0.998 (E-Merck) were double distilled; middle fraction collected of all liquids was stored over 0.4 nm molecular sieves. Masses were recorded on a Mettlar balance, with an accuracy of ± 0.01 mg. The temperature was controlled using a constant temperature controlled water bath (Gemini Scientific Instruments, Chennai, India) having accuracy ± 0.02^0 C.

Experimental Part

Densities were measured [1] using a single capillary pycnometer made up of borosil glass with a bulb of 8 cm^3 and capillary with internal diameter of 0.1 cm. The accuracy in density measurement was $\pm 5\times10^{-5}$ g/cm^3. Ultrasonic velocities were measured [2] at frequency of 2 MHz by single crystal ultrasonic interferometer (Model F-81, Mittal Enterprises, New Delhi, India). Accuracy in velocity measurements is ± 0.1 %. A comparison of measured values of pure components with the literature values as presented in Table 1 shows a good agreement.

Table 1. Densities (ρ) and ultrasonic velocities (u) for pure components at T = 298.15 and 308.15 K.

Property	T = 298.15 K		T = 308.15 K	
	Expt.	Lit.	Expt.	Lit.
		Octane-1-ol		
ρ ($g.cm^{-3}$)	0.82160	0.82150 [3]	0.81453	0.81467 [4]
u ($m.s^{-1}$)	1351	1347 [3]	1319	1314 [5]
		Methyl Acrylate		
ρ ($g.cm^{-3}$)	0.94751	0.94750 [6]	0.93561	0.93560 [6]
u ($m.s^{-1}$)	1185	---	1140	---
		Ethyl Acrylate		
ρ ($g.cm^{-3}$)	0.91632	0.91630 [6]	0.90400	0.90460 [6]
u ($m.s^{-1}$)	1167	---	1137	---

Computational Part

Excess molar volumes of solutions were calculated from densities of pure liquids and their mixtures according to equation,

$$V^E = [x_1M_1+x_2M_2]/\rho_{12} - [(x_1M_1/\rho_1)+(x_2M_2/\rho_2)] \qquad (1)$$

where ρ_{12} is density of mixture and x_1, M_1, ρ_1 and x_2, M_2, ρ_2 are mole fractions, molecular weights and densities of pure components 1 and 2, respectively.

Deviation in isentropic compressibility were calculated using,

$$\Delta\kappa_s = \kappa_s - \kappa_s^{id} \qquad (2)$$

where κ_s is isentropic compressibility and was calculated using Laplace relation,

$$\kappa_s = (1/u^2\rho) \qquad (3)$$

κ_s^{id} was calculated from relation,

$$\kappa_s^{id} = \sum \phi i[\kappa_{s,i} + TV^o_i(\alpha^{o\,2}_i)/C_{p,i}] - [T(\sum x_iV^o_i)(\sum \phi_i \alpha^o_i)^2 / \sum x_iC_{p,i}] \qquad (4)$$

where ϕ_i is ideal state volume fraction of component i in mixture stated and is defined by,

$$\phi_i = x_iV^o_i / (\sum x_iV^o_i) \qquad (5)$$

T is temperature and $\kappa_{s,i}$, $V^o_{i,}$ α^o_i, and $C_{p,i}$ are isentropic compressibility, molar volume, coefficient of isobaric thermal expansion and molar heat capacity respectively for pure component i. α^o_i is calculated from measured densities by relation,

$$\alpha = [(\rho_1/\rho_2)-1]/(T_2-T_1) \qquad (6)$$

Densities, ultrasonic velocities, excess molar volumes and deviation in isentropic compressibilities of binary liquid mixtures are summarized in Table 2.

Table 2. Densities (ρ), ultrasonic velocities (u), excess molar volumes (V^E) and deviation in isentropic compressibilities ($\Delta\kappa_s$) of Acrylates (1) + Octane-1-ol (2) at T = 298.15 and 308.15 K.

X_1	T = 298.15 K				T = 308.15 K			
	ρ ($g.cm^{-3}$)	V^E (cm^3mol^{-1})	u ($m.s^{-1}$)	$\Delta\kappa_s$ (TPa^{-1})	P ($g.cm^{-3}$)	V^E (cm^3mol^{-1})	u ($m.s^{-1}$)	$\Delta\kappa_s$ (TPa^{-1})
MA (1) + Octane-1-ol (2)								
0	0.82160	0	1351	0	0.81453	0	1319	0
0.0552	0.82482	0.162	1341	4.59	0.81785	0.118	1308	5.21
0.0997	0.82782	0.237	1333	7.93	0.82076	0.191	1300	8.27
0.1553	0.83170	0.339	1324	10.96	0.82460	0.275	1289	13.03
0.1997	0.83499	0.415	1316	14.05	0.82785	0.337	1281	15.77
0.2554	0.83941	0.484	1307	16.62	0.83218	0.395	1271	18.94
0.2991	0.84310	0.532	1299	19.41	0.83579	0.436	1263	21.37
0.3550	0.84815	0.579	1290	21.34	0.84072	0.475	1252	25.06
0.3999	0.85248	0.605	1282	23.47	0.84493	0.497	1244	26.75
0.4554	0.85821	0.625	1273	24.72	0.85049	0.515	1234	28.53
0.4998	0.86313	0.625	1265	26.30	0.85524	0.515	1226	29.61
0.5555	0.86971	0.618	1256	26.64	0.86159	0.51	1216	30.41
0.5999	0.87334	0.601	1249	26.30	0.86702	0.494	1208	30.63
0.6554	0.88292	0.563	1240	25.56	0.87429	0.464	1199	28.94
0.6999	0.88946	0.522	1233	24.19	0.88054	0.431	1191	28.04
0.7556	0.89825	0.458	1224	22.07	0.88894	0.378	1181	26.14
0.7998	0.90582	0.395	1217	19.54	0.89614	0.327	1174	22.59
0.8554	0.91608	0.303	1208	15.76	0.90589	0.251	1164	18.82
0.8999	0.92499	0.218	1201	11.69	0.91433	0.181	1157	13.50
0.9555	0.93717	0.088	1192	5.76	0.92582	0.075	1147	7.32
1	0.94751	0	1185	0	0.93561	0	1140	0
EA (1) + Octane-1-ol (2)								
0	0.82160	0	1351	0	0.81453	0	1319	0
0.0555	0.82479	0.094	1340	3.14	0.81770	0.063	1308	3.27
0.0999	0.82750	0.154	1331	5.74	0.82029	0.118	1300	4.97
0.1555	0.83104	0.223	1321	7.56	0.82370	0.176	1289	8.04
0.1998	0.83398	0.272	1312	10.00	0.82654	0.214	1280	10.66
0.2556	0.83788	0.321	1301	12.54	0.83028	0.255	1270	12.25
0.2997	0.84111	0.354	1293	13.64	0.83337	0.282	1262	13.45
0.3551	0.84534	0.387	1283	14.80	0.83743	0.306	1251	15.93
0.3999	0.84895	0.404	1274	16.55	0.84086	0.322	1243	16.67
0.4551	0.85360	0.416	1264	17.27	0.84528	0.332	1233	17.52
0.4998	0.85754	0.420	1256	17.52	0.84900	0.338	1225	17.89
0.5555	0.86272	0.413	1245	18.72	0.85392	0.331	1215	18.00
0.5998	0.86704	0.401	1237	18.55	0.85799	0.322	1207	17.94
0.6550	0.87268	0.378	1227	18.05	0.86332	0.300	1197	17.55
0.6999	0.87752	0.350	1219	17.13	0.86787	0.278	1189	16.71
0.7555	0.88383	0.306	1210	14.42	0.87378	0.244	1179	15.40
0.7998	0.88912	0.264	1202	12.94	0.87872	0.210	1171	14.05
0.8554	0.89611	0.203	1192	10.54	0.88525	0.160	1162	10.35
0.8999	0.90201	0.147	1184	8.17	0.89075	0.114	1154	8.07
0.9550	0.90980	0.056	1175	3.40	0.89802	0.035	1145	3.27
1	0.91632	0	1167	0	0.90400	0	1137	0

From ultrasonic velocity different thermodynamic parameters like specific acoustic impendence (Z), intermolecular free length (L_f), available volume (V_a) and intrinsic pressure (π_i) can be calculated, which provides better insight in understanding of molecular interactions in pure and binary liquids, which are given by relations,

$$Z = u\rho \qquad (7)$$

$$L_f = K(\kappa_s)^{1/2} \qquad (8)$$

$$V_a = V_m[1-(u_{expt}/u_\infty)] \qquad (9)$$

Where M is average molecular weight, K is temperature dependent constant whose value is 1.976×10^{-6} and 2.008×10^{-6} at 298.15 and 308.15 K respectively, $u_\infty = 1600$ m/s.

For binary liquid mixtures intrinsic pressure can be given as,

$$\pi_i = bRT\,(K\eta_{12}/u_{12})^{1/2}(\rho_{12}^{2/3}/M_{12}^{7/6}) \qquad (10)$$

Where b is packing factor, K is a constant temperature independent having value of 4.28×10^9, R is gas constant and η_{12}, u_{12}, ρ_{12} are mixture's viscosity, ultrasonic velocity and density.

The excess functions are important to understand molecular interactions between components of liquid mixtures. Excess function Y^E represents excess of a given quantity Y of a real mixture over its value for an ideal mixture Y^{id} at the same conditions of temperature, pressure and composition. It is expressed by following relation,

$$Y^E = Y - Y^{id} \qquad (11)$$

where Y denotes Z, L_f, Va, π_i and Y^E represents corresponding excess thermodynamic properties such as excess specific acoustic impedance (Z^E), excess intermolecular free length (L_f^E), excess available volume (V_a^E) and excess intrinsic pressure (π_i^E).

These excess thermodynamic parameters are represented in Table 3.

Deviation in isentropic compressibility were fitted to Redlich-Kister [7] equation of type,

$$Y = x_1x_2 \sum_i^n a_i(x_1 - x_2)^i \qquad (12)$$

Where Y is V^E or $\Delta\kappa_s$ and n is degree of polynomial. Coefficient a_i was obtained by fitting Eq (12) to experimental results using a least-squares regression method. Optimum number of coefficients is ascertained from an examination of variation in standard deviation (σ) calculated using relation,

$$\sigma(Y) = \left[\frac{\sum (Y_{expt} - Y_{calc})^2}{N-n}\right]^{1/2} \qquad (13)$$

Where *N* is number of data points and *n* is number of coefficients. Calculated values of coefficients a_i along with standard deviations are given in Table 4.

Table 3. Excess specific acoustic impendence (Z^E), excess intermolecular free length (L_f^E), excess available volume (Va^E) and excess intrinsic pressure (π_{int}^E) for Acrylates (1) + Octane-1-ol (2) at T = 298.15 and 308.15 K.

X_1	T = 298.15 K				T = 308.15 K			
	Z^E (Kg.m^{-2}.s^{-1})	L_f^E (m)	Va^E (m^3.mol^{-1})	π_{int}^E (atm)	Z^E (Kg.m^{-2}.s^{-1})	L_f^E (m)	Va^E (m^3.mol^{-1})	π_{int}^E (atm)
				MA (1) + Octane-1-ol (2)				
0	0	0	0	0	0	0	0	0
0.0552	-4.61	0.001	0.473	-277.02	-4.19	0.001	0.527	-235.53
0.0997	-7.78	0.002	0.807	-334.78	-6.60	0.002	0.828	-280.72
0.1553	-10.80	0.002	1.092	-456.74	-10.25	0.002	1.255	-378.68
0.1997	-13.70	0.003	1.360	-487.25	-12.34	0.003	1.484	-402.06
0.2554	-16.15	0.004	1.565	-575.74	-14.68	0.003	1.729	-475.85
0.2991	-18.63	0.004	1.775	-583.36	-16.44	0.004	1.899	-480.38
0.3550	-20.42	0.005	1.893	-644.06	-19.03	0.005	2.135	-531.96
0.3999	-22.23	0.005	2.020	-633.61	-20.17	0.005	2.216	-521.47
0.4554	-23.32	0.005	2.059	-662.74	-21.32	0.005	2.280	-548.86
0.4998	-24.53	0.006	2.122	-632.39	-21.96	0.005	2.297	-523.10
0.5555	-24.75	0.006	2.076	-639.90	-22.36	0.006	2.269	-533.19
0.5999	-24.37	0.006	1.994	-593.33	-22.34	0.006	2.213	-492.49
0.6554	-23.56	0.005	1.869	-577.76	-21.00	0.005	2.025	-484.67
0.6999	-22.25	0.005	1.720	-517.41	-20.20	0.005	1.895	-432.09
0.7556	-20.21	0.005	1.510	-481.50	-18.66	0.005	1.689	-407.23
0.7998	-17.85	0.004	1.298	-404.36	-16.08	0.004	1.423	-342.44
0.8554	-14.32	0.003	1.005	-349.09	-13.26	0.003	1.127	-301.51
0.8999	-10.60	0.002	0.724	-260.72	-9.49	0.002	0.790	-227.92
0.9555	-5.12	0.001	0.343	-189.46	-5.03	0.001	0.401	-169.06
1	0	0	0	0	0	0	0	0
				EA (1) + Octane-1-ol (2)				
0	0	0	0	0	0	0	0	0
0.0555	-2.51	0.000	0.389	-229.11	-2.23	0.000	0.393	-190.97
0.0999	-4.52	0.001	0.691	-294.92	-3.34	0.001	0.604	-242.28
0.1555	-5.86	0.001	0.914	-406.18	-5.38	0.001	0.930	-330.03
0.1998	-7.68	0.001	1.163	-445.48	-7.10	0.001	1.184	-358.99
0.2556	-9.52	0.002	1.409	-521.73	-8.02	0.002	1.345	-424.08
0.2997	-10.25	0.002	1.512	-540.20	-8.71	0.002	1.455	-435.87
0.3551	-10.98	0.002	1.608	-587.98	-10.22	0.002	1.647	-474.29
0.3999	-12.17	0.002	1.737	-585.57	-10.57	0.002	1.694	-472.30
0.4551	-12.54	0.002	1.769	-604.26	-10.97	0.002	1.735	-490.62
0.4998	-12.60	0.002	1.761	-584.88	-11.09	0.002	1.734	-473.62
0.5555	-13.32	0.003	1.800	-579.59	-11.01	0.002	1.699	-472.97
0.5998	-13.08	0.003	1.743	-542.12	-10.87	0.002	1.651	-440.52
0.6550	-12.59	0.003	1.643	-516.68	-10.50	0.002	1.562	-422.57
0.6999	-11.84	0.003	1.522	-465.86	-9.91	0.002	1.450	-381.06
0.7555	-9.85	0.002	1.271	-420.50	-9.03	0.002	1.288	-345.10
0.7998	-8.76	0.002	1.109	-354.55	-8.18	0.002	1.135	-290.93
0.8554	-7.06	0.002	0.868	-291.85	-5.91	0.001	0.831	-243.35
0.8999	-5.43	0.001	0.648	-213.94	-4.58	0.001	0.622	-179.08
0.9550	-2.16	0.000	0.278	-134.31	-1.71	0.000	0.264	-118.46
1	0	0	0	0	0	0	0	0

Table 4. Adjustable parameters of Eq (12) and (13) for excess molar volume (V^E) and deviation in isentropic compressibility ($\Delta\kappa_s$) for Acrylates (1) + Octane-1-ol (2) at T = 298.15 and 308.15 K.

Property	T (K)	a_0	a_1	a_2	a_3	a_4	σ
			MA (1) + Octane-1-ol (2)				
V^E (cm^{3}mol^{-1})	298.15	2.5102	0.1624	-0.0208	-0.7417	0.1396	0.00922
	308.15	2.0596	0.0804	0.1094	-0.3670	-0.1856	0.00475
$\Delta\kappa_s$ (TPa^{-1})	298.15	57.8060	20.3385	-8.1963	-9.7369	18.2221	0.22979
	308.15	56.3974	19.8298	-15.8468	0.4727	34.9854	0.38183
			EA (1) + Octane-1-ol (2)				
V^E (cm^{3}mol^{-1})	298.15	1.6647	0.0812	0.2133	-0.3439	-0.4121	0.00522
	308.15	1.3155	0.0687	0.4354	-0.2615	-0.9328	0.00678
$\Delta\kappa_s$ (TPa^{-1})	298.15	22.3283	12.6033	4.8396	-11.6714	-8.4208	0.42764
	308.15	16.8106	11.7003	17.1934	-11.6787	-27.1023	0.41004

Jouyban-Acree [8-9] recently proposed model for correlating density of liquid mixtures at various temperatures. The proposed equation is,

$$\ln y_{mT} = f_1 \ln y_{1T} + f_2 \ln y_{2T} + f_1 f_2 \sum [A_j (f_1 - f_2)^{j}/T] \qquad (14)$$

where y_{mT}, y_{1T} and y_{2T} is density of mixture and solvents 1 and 2 at temperature T, respectively, f_1 and f_2 are volume fractions of solvents in case of density and Aj are the model constants. The correlating ability of the Jouyban-Acree model was tested by calculating the average percentage deviation (APD) between the experimental and calculated density as,

$$APD = (100/N) \sum [(| y_{expt} - y_{cal} |)/ y_{expt})] \qquad (15)$$

where N is the number of data points in each set. The optimum numbers of constants Aj, in each case, are determined from the examination of the average percentage deviation value. Jouyban–Acree model was not previously applied to ultrasonic velocity measurements, we extend Jouyban–Acree model to ultrasonic velocity Eqn. (14) of liquid mixtures with f as mole fraction and apply Eqn. (15) for correlating ability of model. The constants (Aj) calculated from least square analysis along with average percentage deviation (APD) are presented in Table 5.

Table 5. Parameters of Eq (14) and (15) for Acrylates (1) + Octane-1-ol (2)

Property	a_0	a_1	a_2	a_3	a_4	σ	APD
			MA (1) + Octane-1-ol (2)				
ρ ($g.cm^{-3}$)	-25.3934	-6.5289	-2.0030	0.9314	0.7739	5.8324	0.0277
u ($m.s^{-1}$)	-0.0601	-0.1279	1.0583	0.5760	-1.9151	1280.4161	0.0187
			EA (1) + Octane-1-ol (2)				
ρ ($g.cm^{-3}$)	-13.1672	-2.3792	-1.2754	0.7580	1.9006	3.4139	0.0256
u ($m.s^{-1}$)	0.0034	-1.0261	-1.0136	2.5006	2.1942	1276.7302	0.0211

RESULTS AND DISCUSSION

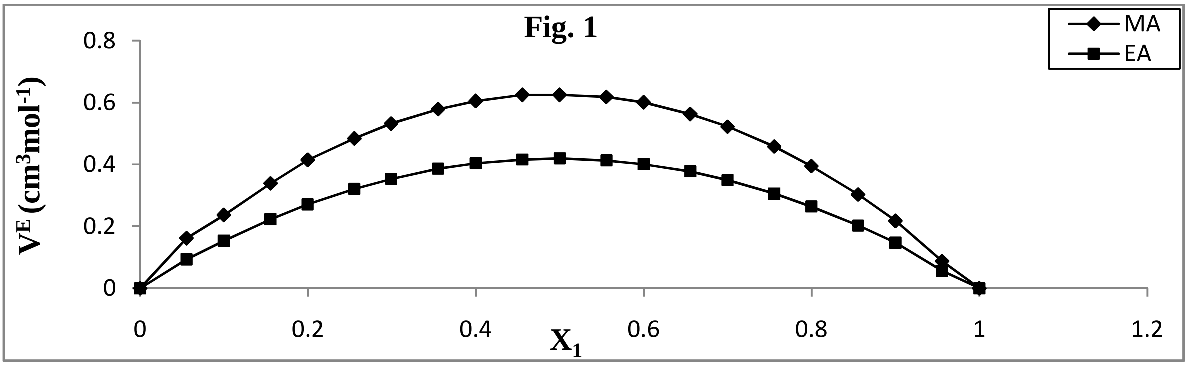

Fig 1. Variation of excess molar volumes for acrylates (1) + octane-1-ol (2) at 298.15 K

Excess molar volumes found to be positive for all the systems, where dispersion, induction and dipolar forces are operating, whereas existence of specific interactions between the mixing components of the various binary systems tends to make excess molar volumes negative [10]. Since, normally dispersive interaction between unlike molecules is weaker than those between like molecules, it is reasonable that they contribute positively [11-12] to excess molar volumes.

Changes in excess molar volume takes place during mixing which is the result of several effects that operate in the same or opposite directions. The most important ones are:-

1. A positive effect caused by the break-up of the structure of one or both components originating from nonchemical or chemical interactions, such as, hydrogen bonding or complex formatting interactions; such as, self-association.
2. A negative one, due to physical interactions (heteroassociation) or geometric fitting of on component into the second, leading to a more compact packing (interstitial accommodation). The second contribution becomes more important with increasing sphericicity of the solute molecule and higher molar volume of the solvent [13].

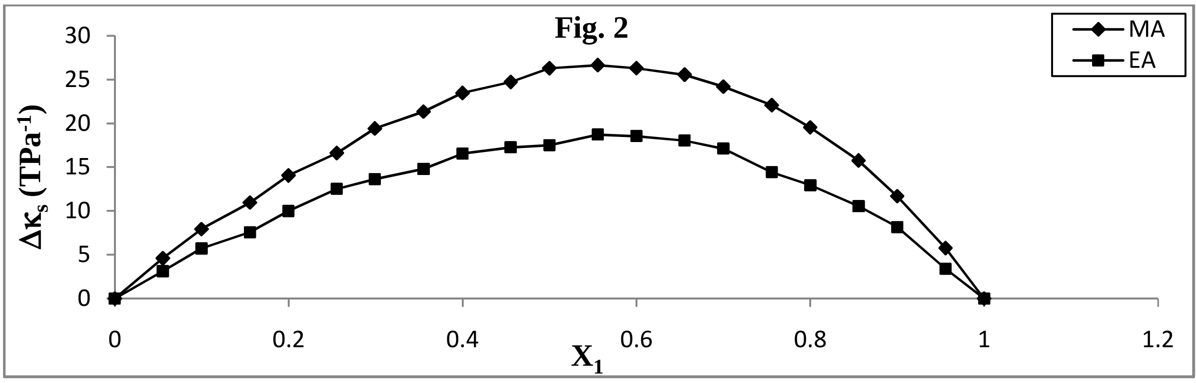

Fig 2. Variation of deviation in isentropic compressibility for acrylates (1) + octane-1-ol (2) at 298.15 K

A strong molecular interaction through charge transfer, dipole-induced dipole, dipole-dipole [14] interactions, interstitial accommodation and orientational ordering lead to a more compact structure, making $\Delta\kappa_s$ negative and breakup of alkanols structures tend to make $\Delta\kappa_s$ positive. Sign of $\Delta\kappa_s$ and V^E decides compactness due to molecular rearrangement. Magnitude of various contributions depends mainly on relative molecular size of components. De-clustering of octane-1-ol in presence of acrylates lead to positive $\Delta\kappa_s$ values.

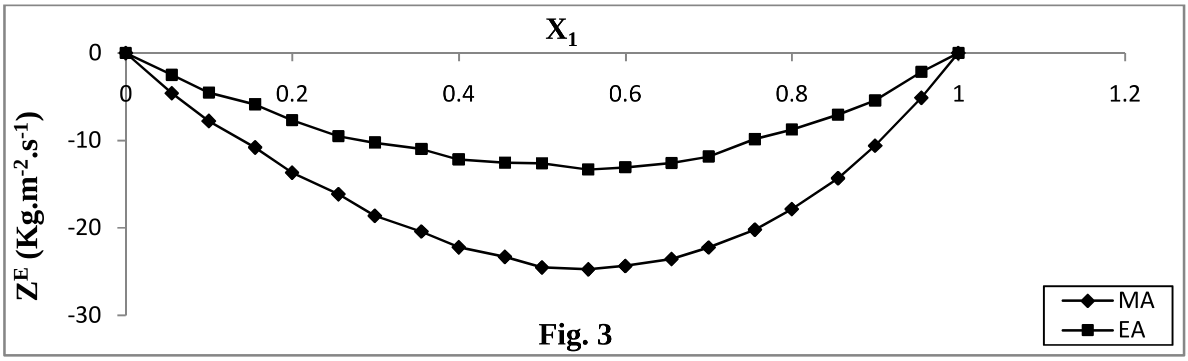

Fig 3. Variation of excess specific acoustic impedance for acrylates (1) + octane-1-ol (2) at 298.15 K

The positive values indicate the presence of strong specific interactions and negative values corresponds mainly to the existence of dispersive forces. Thus from above discussion reinforces our views that in the present systems dispersion forces are dominant and the geometrical fitting is also observed.

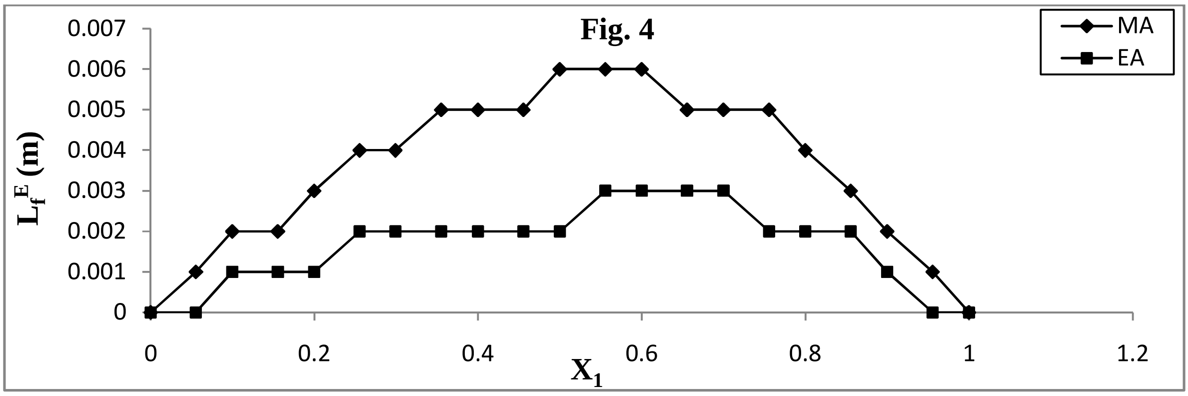

Fig 4. Variation of excess intermolecular free length for acrylates (1) + octane-1-ol (2) at 298.15 K

Excess intermolecular free lengths are found to be positive for both systems. The trends are symmetric. L_f^E values increase with increase of chain length acrylates. This may be due to fewer protons donating ability of 1-octanol. In pure alkanols, molecules are self associated through hydrogen bond, mixing of acrylates with 1-octanol will induce rupture of hydrogen bonds in liquids with subsequent increase in L_f^E values. Deviation in compressibility and excess free length become increasingly negative with increasing strength of interaction between component molecules.

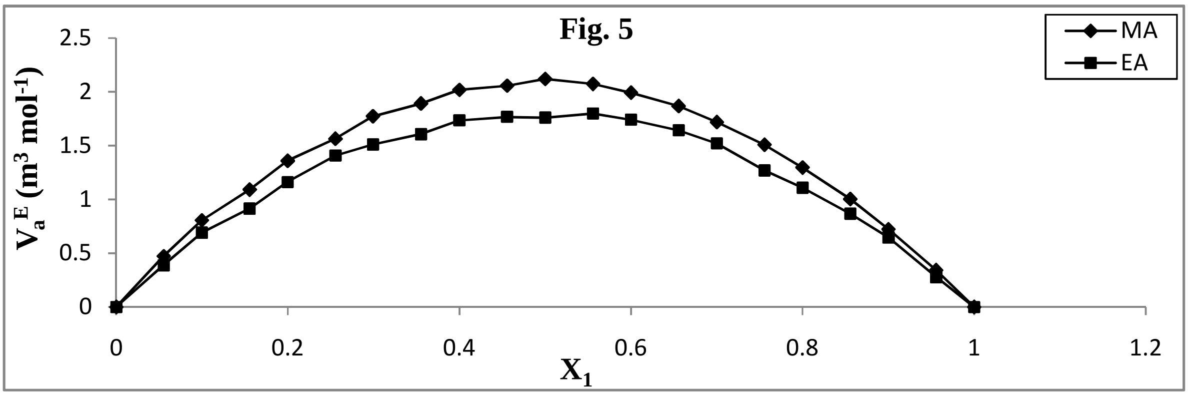

Fig 5. Variation of excess available volume for acrylates (1) + octane-1-ol (2) at 298.15 K

Positive values of Va^E indicate presence of strong specific interaction. This nature may be attributed to strong interactions between acrylate and alkanols. On the other hand, negative values of it means weak interactions due to, possible accommodation, large difference in molar volume, dipole-dipole interactions, dipole-induced dipole interactions and van der Waal's forces of attraction.

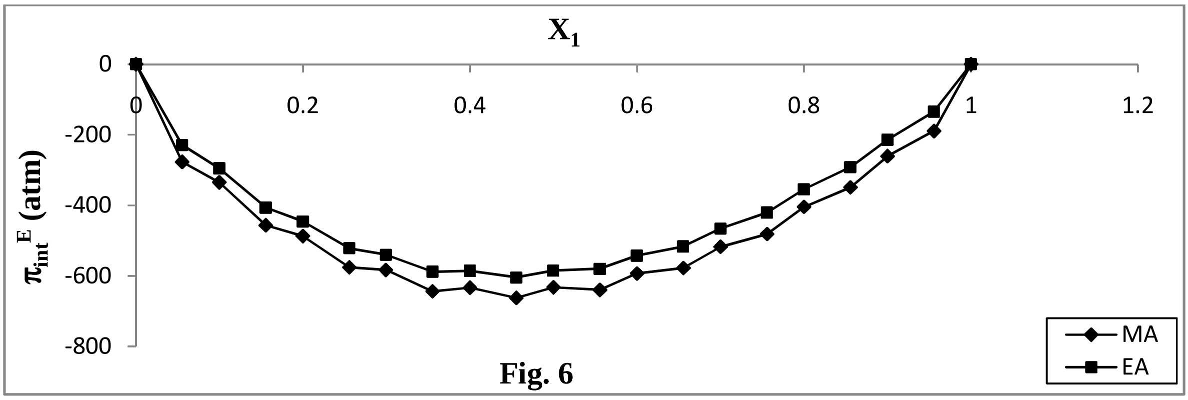

Fig 6. Variation of excess intrinsic pressure for acrylates (1) + octane-1-ol (2) at 298.15 K

Excess internal pressure π_i^E has been used [15-20] to study the intermolecular interactions in binary liquid mixtures. The values of π_i^E are found to be negative throughout the mole fraction in all binary mixtures of alkanols with acrylate suggesting weak interactions.

Evaluated values of excess thermodynamic parameters such as excess molar volume (V^E) and deviation isentropic compressibility ($\Delta\kappa_s$) were fitted to Redlich-Kister polynomial equation at both temperatures and are represented as in Table 4 with their standard percentage deviation. Redlich-Kister equation was originally developed to correlate the excess Gibb's energy function and calculate the values of the activity coefficients. It turned out to be such a powerful and versatile correlating tool that its use has been extended to other properties, particularly excess molar volumes and excess enthalpies of mixing. It suffers from important drawback that values of adjustable parameters change as number in series is increased, so that no physical interpretation can be attached to them [21-22].

The constants (Aj) calculated from least square analysis along with average percentage deviation (APD) are presented in Table 5. Experimentally measured fundamental thermodynamic properties such as density and ultrasonic velocity were correlated using recently proposed Jouyban-Acree model.

CONCLUSION

Positive values of excess molar volumes shows volume expansion is taking place causing rupture of H-bonds in self associated alcohols. Positive values of $\Delta\kappa_s$ observed when H-bonded aggregates of alkanols break up progressively with addition of acrylates. For mixture containing alkanols, the negative values of Z^E suggests that, dispersive forces are dominant over the specific interaction. Rupturing of hydrogen bonding in liquids leads to increase in L_f^E values. Positive values of Va^E indicate presence of strong specific interaction. The values of π_i^E are found to be negative suggesting weak interactions. Redlich-Kister regressor is very powerful and frequently used to correlate vapour-liquid equilibrium data and excess properties. The proposed model provides reasonably accurate calculations for these fundamental thermodynamic parameters of binary liquid mixtures.

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