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Thermodynamics of binary liquid mixtures of acrylates with dodecane-1-ol

Sujata S. Patil[a]* and Sunil R. Mirgane[b]

[a]*Dept. of Applied Science, Matsyodari Shikshan Sanstha's, College of Engineering and Technology, Jalna (M. S.), India*
[b]*P. G. Dept. of Chemistry, J. E. S. College, Jalna (M. S.), India*

ABSTRACT

Thermodynamic data involving density, viscosity and ultrasonic velocity of binary liquid mixture containing methyl acrylate, ethyl acrylate, butyl acrylate and methyl methacrylate with dodecane-1-ol at 303.15 K and at atmospheric pressure have been measured; these experimental values were correlated by Jouyban-Acree model. These basic parameters further used to evaluate excess molar volume, deviation in viscosity and deviation in isentropic compressibility of binary systems and these values were fitted to Redlich-Kister polynomial equation. The mixture viscosities were correlated by Grunberg-Nissan, Tamura-Kurata, McAllister three and four body model equations. The calculated excess molar volumes, deviation in isentropic compressibility were found to be positive and deviations in viscosity were found to be negative for all binary liquid mixtures.

Keywords: Binary Mixtures; Excess molar volume; Viscosity Deviation; Tamura-Kurata, Redlich-Kister polynomial equation.

INTRODUCTION

The equilibrium properties of a liquid mixture are strongly dependent on its local structure, often expressed in terms such as packing density, free volume or more exactly in terms of the radial distribution functions. This local structure depends on the forces between molecules and volumes of the molecules; in general it will change with the composition. This change in turn will be reflected in the thermodynamic properties of the mixtures. Contributions of this nature have either been ignored altogether, or correction to a state of null volume change on mixing has been adopted as a means of compensating for the effects referred. It will be apparent, however that, adjustment of one thermodynamic quantity (e. g. volume in this manner) will not in general, affect a simultaneous correction of others (e.g. the free energy of that part of it relating to the local structure) to their linearly interpolated values. The choice of volume as the property to be considered is arbitrary and there is assurance that nullity of volume change obviates consideration of other characteristic properties of the liquid [1]. Specifically, these properties correspond to determination of density, viscosity and ultrasonic velocity respectively. Further from these basic and fundamental thermodynamic properties we can derive number of parameters like excess molar volume, acoustic impendence, intermolecular free length, viscosity deviation, molecular association and many more. Properties of liquid-liquid binary mixtures are very important qualitatively and quantitatively as a part of studies of thermodynamic, acoustic and transport aspects.

In literature data exists for binary systems of ethyl ethanoate with ethyl acrylate, butyl acrylate, methyl methacrylate and styrene at 298.15 K [2], for volumetric behavior of acrylic esters with alkane-1-ols at 298.15 and 308.15 K [3], density and excess molar volume of the binary systems of dimethyl sulfoxide + ethyl acrylate, butyl acrylate, methyl methacrylate and styrene at 298.15 K [4], volumetric properties of binary systems of dimethyl sulfoxide with Methacrylic acid, vinyl acetate, butyl methacrylate and allyl methacrylate at 298.15 K [5], volumetric properties of toluene with ethyl acrylate, butyl acrylate, methyl methacrylate and styrene at 298.15 K [6], thermodynamic properties of methyl methacrylate with alkoxyethanols and 1-alcohols at 298.15 and 308.15 K [7], volumetric properties of ternary system 1,4-dioxane with butyl and ethyl acrylate and its binary at 298.15 K [8], volumetric properties of 3-methylbutyl ethanoate with ethyl acrylate, butyl acrylate, methyl methacrylate, styrene at 298.15 K [9].

To best of our knowledge no literature data are available for the excess molar volumes, viscosity deviation and deviation in isentropic compressibility of the binary liquid mixtures of dodecane-1-ol with methyl acrylate, ethyl acrylate, butyl acrylate and methyl methacrylate at 303.15 K. In view of these considerations, it was planned to study liquid-liquid binary systems containing polar and or hydrogen bonded or nonpolar liquids in association with industrially as well as biologically important solvent over the entire range of compositions.

MATERIALS AND METHODS

Chemicals used in present study were of analytical grade and supplied by S. D. Fine Chemicals Pvt. Ltd. Mumbai with quoted mass fraction purities: methyl acrylate, MA, (>0.997), ethyl acrylate, EA, (>0.998), butyl acrylate, BA, (>0.995) and methyl methacrylate, MMA, (>0.997). Dodecane-1-ol, (>0.999) was supplied by E-Merck. Prior to use all liquids were stored over 0.4 nm molecular sieves to reduce water content. The masses were recorded on a Mettlar balance, with an accuracy of ± 0.01 mg. The estimated uncertainty in mole fraction was $< 1\times10^{-4}$. Temperature was controlled using a constant temperature controlled water bath (Gemini Scientific Instruments, Chennai, India) having accuracy $\pm 0.02^0$ C.

Experimental Part

The densities of the solutions were measured [10] using a single capillary pycnometer made up of borosil glass with a bulb of $8 cm^3$ and capillary with internal diameter of 0.1cm. The reproducibility of density measurement was $\pm 5x10^{-5}$ g/cm^3. The dynamic viscosities were measured [10] using an Ubbelhode suspended level viscometer calibrated with conductivity water. The uncertainty in dynamic viscosities is ± 0.003 mPa.s. The ultrasonic velocities were measured [10] at a frequency of 2 MHz in these solutions by a single crystal variable path ultrasonic interferometer (Mittal's F-81 model, Mittal Enterprises, New Delhi, India). The error in velocity measurements is ± 0.1 %. A comparison of measured values of pure components with literature values presented in Table 1 shows a good agreement.

Table1. Densities (ρ), Viscosities (η) and Ultrasonic Velocities (u) for Pure Components at T = 303.15 K

Component	ρ / $g.m^{-3}$		η / mPa.s		u / $m.s^{-1}$	
	Expt.	Lit.	Expt.	Lit.	Expt.	Lit.
Dodecane-1-ol	0.82602	---	13.878	---	1399	---
Methyl Acrylate	0.94130	---	0.420	---	1163	---
Ethyl Acrylate	0.90950	---	0.487	---	1152	---
Butyl Acrylate	0.89000	---	0.737	---	1190	---
Methyl Methacrylate	0.93172	0.93174 [11]	0.549	---	1168	---

Computational Part

Excess molar volumes (V^E) were calculated from densities of pure liquids and their mixtures according to following equation,

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

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

Viscosity deviations ($\Delta\eta$) were calculated using equation,

$$\Delta\eta = \eta_{12} - x_1\eta_1 - x_2\eta_2 \tag{2}$$

where η_{12} is viscosity of mixture and x_1, x_2 and η_1, η_2 are mole fraction and viscosity of pure components 1 and 2, respectively [12].

Deviation in isentropic compressibility ($\Delta\kappa_s$) were obtained using relation,

$$\Delta\kappa_s = \kappa_s - \kappa_s^{id} \tag{3}$$

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

$$\kappa_s = (1/ u^2\rho) \qquad (4)$$

and κ_s^{id} was calculated from relation,

$$\kappa_s^{id} = \sum \phi i[\kappa_{s,i} + TV^o_i(\alpha^{o\,2}_i)/C_{p,i}] - [T(\sum x_iV^o_i)\,(\sum \phi_i\, \alpha^o_i)^2 / \sum x_iC_{p,i}] \qquad (5)$$

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

$$\phi_{i=}\ x_iV^o{}_i / (\sum x_iV^o{}_i) \qquad (6)$$

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

$$\alpha = [(\rho_1/ \rho_2)-1]/ (T_2-T_1) \qquad (7)$$

The other required values were taken from literature [13-14]. Experimental values of densities (ρ), viscosities (η), ultrasonic velocity (u), excess molar volume (V^E), deviation in viscosity (Δη) and deviation in isentropic compressibility ($\Delta\kappa_s$) of these mixtures at 303.15 K as a function of acrylic esters mole fraction are listed in Table 2.

Table 2. Densities (ρ), Viscosities (η), Ultrasonic Velocities (u), Excess Molar Volumes (V^E), Viscosity Deviations (Δη) and Deviation in Isentropic Compressibilities ($\Delta\kappa_s$) for Acrylates (1) + Dodecane-1-ol (2) at T = 303.15 K

X_1	ρ / $g.cm^{-3}$	η / mPa.s	u / $m.s^{-1}$	V^E / cm^3mol^{-1}	Δη / mPa.s	$\Delta\kappa_s$ / TPa^{-1}
			MA (1) + Dodecane-1-ol (2)			
0	0.82602	13.878	1399	0	0	0
0.0554	0.82791	11.431	1385	0.208	-1.701	7.25
0.0999	0.82998	9.783	1373	0.257	-2.750	13.39
0.1555	0.83257	8.055	1359	0.359	-3.730	20.19
0.1997	0.83481	6.900	1348	0.430	-4.290	25.34
0.2554	0.83789	5.679	1335	0.503	-4.762	30.73
0.2998	0.84058	4.861	1324	0.551	-4.981	35.41
0.3553	0.84425	4.003	1310	0.596	-5.092	41.18
0.3999	0.84747	3.426	1299	0.624	-5.069	45.23
0.4553	0.85189	2.822	1286	0.639	-4.928	49.01
0.4999	0.85585	2.414	1276	0.634	-4.735	50.94
0.5556	0.86120	1.987	1262	0.632	-4.413	54.39
0.5998	0.86594	1.702	1252	0.613	-4.103	55.08
0.6545	0.87246	1.406	1240	0.576	-3.663	54.38
0.6998	0.87847	1.200	1229	0.535	-3.259	54.00
0.7553	0.88674	0.988	1217	0.475	-2.722	50.05
0.7999	0.89425	0.845	1207	0.406	-2.267	45.82
0.8554	0.90483	0.696	1194	0.313	-1.669	38.88
0.8999	0.91451	0.596	1185	0.227	-1.171	29.19
0.9554	0.92842	0.491	1173	0.105	-0.528	14.58
1	0.94130	0.420	1163	0	0	0
			EA (1) + Dodecane-1-ol (2)			
0	0.82602	13.878	1399	0	0	0
0.0554	0.82793	11.524	1384	0.110	-1.611	6.17
0.0997	0.82957	9.935	1372	0.189	-2.607	11.06
0.1554	0.83180	8.244	1357	0.275	-3.552	17.01
0.1996	0.83371	7.109	1346	0.333	-4.095	20.72
0.2553	0.83630	5.899	1331	0.396	-4.559	26.32
0.2997	0.83853	5.084	1320	0.436	-4.780	29.61
0.3554	0.84155	4.218	1306	0.477	-4.900	33.61
0.3998	0.84415	3.636	1294	0.500	-4.888	37.42
0.4553	0.84769	3.018	1281	0.515	-4.762	39.50
0.4998	0.85075	2.600	1270	0.521	-4.584	41.39
0.5553	0.85493	2.159	1256	0.511	-4.282	43.41
0.5999	0.85858	1.860	1245	0.494	-3.984	44.15
0.6550	0.86350	1.546	1232	0.463	-3.560	43.46
0.6999	0.86788	1.330	1221	0.430	-3.175	42.56
0.7554	0.87383	1.105	1208	0.376	-2.657	39.46
0.7999	0.87908	0.951	1198	0.324	-2.215	35.24
0.8554	0.88631	0.790	1185	0.246	-1.632	28.98
0.8999	0.89274	0.681	1175	0.173	-1.146	21.78
0.9554	0.90180	0.565	1162	0.054	-0.518	11.05
1	0.90950	0.487	1152	0	0	0

BA (1) + Dodecane-1-ol (2)						
0	0.82602	13.878	1399	0	0	0
0.0554	0.82802	11.794	1387	0.083	-1.356	2.91
0.0997	0.82972	10.355	1377	0.138	-2.212	5.52
0.1554	0.83197	8.792	1364	0.199	-3.043	9.10
0.1998	0.83385	7.718	1354	0.243	-3.534	11.55
0.2555	0.83634	6.554	1342	0.289	-3.966	13.93
0.2999	0.83843	5.753	1333	0.319	-4.184	15.12
0.3554	0.84119	4.888	1321	0.348	-4.319	17.15
0.3997	0.84352	4.291	1311	0.363	-4.333	19.03
0.4554	0.84660	3.644	1300	0.376	-4.249	19.50
0.4998	0.84920	3.199	1290	0.379	-4.110	20.96
0.5554	0.85263	2.717	1279	0.376	-3.862	20.81
0.5999	0.85554	2.384	1270	0.367	-3.610	20.59
0.6554	0.85938	2.026	1258	0.346	-3.239	20.82
0.6999	0.86263	1.778	1249	0.326	-2.901	19.92
0.7553	0.86694	1.511	1238	0.291	-2.439	18.00
0.7999	0.87063	1.325	1229	0.251	-2.040	16.21
0.8554	0.87549	1.126	1218	0.199	-1.510	13.09
0.8999	0.87964	0.988	1209	0.151	-1.063	10.24
0.9555	0.88506	0.839	1199	0.099	-0.483	4.39
1	0.89000	0.737	1190	0	0	0
MMA (1) + Dodecane-1-ol (2)						
0	0.82602	13.878	1399	0	0	0
0.0554	0.82852	11.601	1385	0.100	-1.537	6.09
0.0997	0.83056	10.054	1374	0.196	-2.494	10.78
0.1554	0.83337	8.399	1360	0.291	-3.407	16.65
0.1996	0.83577	7.281	1349	0.357	-3.936	21.08
0.2553	0.83904	6.082	1336	0.425	-4.392	25.57
0.2997	0.84184	5.270	1325	0.471	-4.612	29.58
0.3554	0.84564	4.402	1312	0.515	-4.738	33.44
0.3998	0.84892	3.814	1302	0.539	-4.735	35.82
0.4553	0.85336	3.188	1289	0.557	-4.620	38.82
0.4998	0.85721	2.761	1278	0.564	-4.454	41.46
0.5553	0.86245	2.308	1266	0.556	-4.167	42.15
0.5999	0.86703	1.998	1255	0.541	-3.884	43.65
0.6550	0.87322	1.673	1243	0.509	-3.474	42.77
0.6999	0.87874	1.447	1233	0.473	-3.102	41.47
0.7554	0.88623	1.209	1221	0.418	-2.600	38.19
0.7999	0.89287	1.047	1211	0.362	-2.168	34.86
0.8554	0.90201	0.875	1199	0.281	-1.600	28.47
0.8999	0.91016	0.758	1189	0.205	-1.124	22.26
0.9554	0.92148	0.634	1177	0.101	-0.508	11.61
1	0.93172	0.549	1168	0	0	0

Excess molar volumes, deviations in viscosity and deviations in isentropic compressibility were fitted to Redlich-Kister equation of type,

$$Y = x_1x_2 \sum_{i}^{n} a_i (x_1 - x_2)^i \qquad (8)$$

Where Y is either V^E or $\Delta\eta$ or $\Delta\kappa_s$ and n is degree of polynomial. Coefficient a_i was obtained by fitting Eq (8) to experimental results using a least-squares regression method. Optimum number of coefficients is ascertained from an examination of variation in standard deviation (σ). σ was calculated using relation,

$$\sigma\,(Y) = \left[\frac{\sum (Y_{\exp t} - Y_{calc})^2}{N - n} \right]^{1/2} \qquad (9)$$

Where N is number of data points and n is number of coefficients [13]. The calculated values of the coefficients a_i along with standard deviations (σ) are given in Table 3.

Several relations have been proposed to evaluate viscosity (η) of liquid mixtures. Equations of Grunberg-Nissan, Tamura-Kurata have one adjustable parameter.

Table 3. Adjustable parameters of Eq (8) and (9) for Excess Functions for Acrylates (1) + Dodecane-1-ol (2) at T = 303.15 K

Property	a_0	a_1	a_2	a_3	a_4	σ
			MA (1) + Dodecane-1-ol (2)			
V^E / cm^3mol^{-1}	2.6059	0.2601	-0.6482	-1.1490	1.6156	0.01771
$\Delta\eta$ / mPa.s	-18.9403	10.0042	-4.1648	1.5308	-0.4306	0.00095
$\Delta\kappa_s$ / TPa^{-1}	63.9702	46.4952	31.1984	-4.3584	-20.5065	0.48994
			EA (1) + Dodecane-1-ol (2)			
V^E / cm^3mol^{-1}	2.0427	0.1422	0.4889	-0.5889	-1.0466	0.00996
$\Delta\eta$ / mPa.s	-18.3334	9.3523	-3.7423	1.2958	-0.3510	0.00042
$\Delta\kappa_s$ / TPa^{-1}	22.6215	23.8851	10.6619	-2.2682	-5.4251	0.30818
			BA (1) + Dodecane-1-ol (2)			
V^E / cm^3mol^{-1}	1.5505	-0.1220	-0.4864	0.5091	1.1142	0.00925
$\Delta\eta$ / mPa.s	-16.4402	7.5082	-2.6530	0.7831	-0.2069	0.00031
$\Delta\kappa_s$ / TPa^{-1}	3.7815	7.5504	27.3533	4.5778	-39.2832	0.37821
			MMA (1) + Dodecane-1-ol (2)			
V^E / cm^3mol^{-1}	2.2435	-0.0899	0.1383	0.3583	-0.3211	0.00476
$\Delta\eta$ / mPa.s	-17.8130	8.8159	-3.4360	1.1399	-0.2667	0.00047
$\Delta\kappa_s$ / TPa^{-1}	45.2921	23.2987	3.0290	16.8568	18.2497	0.41348

Grunberg-Nissan [15] proposed following empirical equation,

$$\ln \eta_{12} = x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1x_2G_{12} \tag{10}$$

where G_{12} is a parameter proportional to the interchange energy. The Eq (10) is particularly selected because characteristic constant parameter G_{12} allows for positive and negative deviations from additivity rule [14].

Tamura and Kurata [16] developed expression for viscosity of binary mixtures as,

$$\eta = x_1\phi_1 \eta_1 + x_2\phi_2 \eta_2 + 2(x_1x_2\phi_1\phi_2)^{1/2}T_{12} \tag{11}$$

where T_{12} is interaction parameter, ϕ_1 and ϕ_2 are volume fractions.

McAllister's multibody interaction model [17] was widely used to correlate kinematic viscosity data. Two parameter McAllister equation based on Eyring's theory of absolute reaction rates, taken into account interactions of both like and unlike molecules by a two dimensional three body model. The three body model was defined by relation,

$$\ln \nu = x_1^3 \ln \nu_1 + x_2^3 \ln \nu_2 + 3x_1^2 x_2 \ln Z_{12} + 3x_1 x_2^2 \ln Z_{21} - \ln[x_1+(x_2M_2/M_1)] + 3x_1^2 x_2 \ln[(2/3)+(M_2/3M_1)] + 3x_1x_2^2 \ln[(1/3)+(2M_2/3M_1)] + x_2^3 \ln(M_2/M_1) \tag{12}$$

Similarly, four body model was defined by relation,

$$\ln \nu = x_1^4 \ln \nu_1 + 4x_1^3x_2 \ln Z_{1112} + 6x_1^2x_2^2 \ln Z_{1122} + 4x_1x_2^3 \ln Z_{2221} + x_2^4 \ln \nu_2 - \ln[x_1+x_2(M_2/M_1)] + 4x_1^3x_2 \ln[(3+M_2/M_1)/4] + 6x_1^2 2x_2^2 \ln[1+M_2/M_1)/2] + 4x_1x_2^3 \ln[(1+3M_2/M_1)/4] + x_2^4 \ln(M_2/M_1) \tag{13}$$

Where Z_{12}, Z_{21}, Z_{1112}, Z_{1122} and Z_{2221} are model parameters, M_i and ν_i are molecular weight and kinematic viscosity of pure component i.

To perform a numerical comparison of the correlating capability of above Eq (10 to 13) we have calculated the standard percentage deviation (σ %) using the relation,

$$\sigma\% = [1/(\eta_{expt} - k) \times \sum (100(\eta_{expt} - \eta_{cal})/\eta_{expt})^2]^{1/2} \tag{14}$$

where k represents the number of numerical coefficients in the respective equations.

The terms G_{12}, T_{12}, Z_{12}, Z_{21}, Z_{1112}, Z_{1122} and Z_{2221} in above Eqs (10 to13) have been considered as adjustable parameters and were estimated by a non-linear regression analysis based on a least-squares method. These are presented with their standard percentage deviation (σ %) in Table 4.

Table 4. Adjustable parameters of Eq (10), (11), (12), (13) and (14) for Acrylates (1) + Dodecane-1-ol (2) at T = 303.15 K

G_{12}	σ	T_{12}	σ	Z_{12}	Z_{21}	σ	Z_{1112}	Z_{1122}	Z_{2221}	σ
MA (1) + Dodecane-1-ol (2)										
0.000	0.025	-5.774	16.022	1.675	5.210	0.200	1.202	1.813	7.018	13.367
EA (1) + Dodecane-1-ol (2)										
-0.001	0.025	4.732	86.453	1.801	5.484	0.065	1.325	2.175	7.251	14.763
BA (1) + Dodecane-1-ol (2)										
-0.001	0.030	-2.615	42.356	2.313	6.262	0.032	1.785	3.102	7.999	20.929
MMA (1) + Dodecane-1-ol (2)										
-0.001	0.023	-4.461	76.211	1.939	5.680	0.079	1.437	2.288	7.455	15.856

Recently Jouyban and Acree [18-19] proposed a model which provides reasonably accurate calculations for density and viscosity of binary liquid mixtures and could be used in data modeling. The equation is,

$$\ln y_{mT} = f_1 \ln y_{1T} + f_2 \ln y_{2T} + f_1 f_2 \sum [A_j (f_1 - f_2)^j / T] \quad (15)$$

where y_{mT}, y_{1T} and y_{2T} is density or viscosity of mixture, solvents 1 and 2 at temperature T, respectively, $f_1$and f_2 are volume fractions of solvents in case of density and mole fraction in case of viscosity. Aj are model constants.

Jouyban–Acree model was not previously applied to ultrasonic velocity measurements; we extend this model Eq (15) to ultrasonic velocity of liquid mixtures with f as mole fraction and again apply Eq (16) for correlating ability of model which was tested by calculating average percentage deviation (APD) between experimental and calculated density, viscosity and ultrasonic velocity given by following relation,

$$APD = (100/N) \sum [(| y_{expt} - y_{cal} |) / y_{expt})] \quad (16)$$

Where N is number of data points in each set. Optimum numbers of constants Aj were determined from average percentage deviation value. Constants Aj calculated from least square analysis along with average percentage deviation (APD) are represented in Table 5.

Table 5. Adjustable parameters of Eq (15) and (16) for Acrylates (1) + Dodecane-1-ol (2)

Property	a_0	a_1	a_2	a_3	a_4	σ	APD
MA (1) + Dodecane-1-ol (2)							
ρ / g.m^{-3}	-35.8822	-14.4987	-4.7883	-1.6088	-3.1256	8.0418	0.0355
η / mPa.s	-0.3910	1.2563	4.4627	-4.1517	-8.5936	4.7799	0.0249
u / m.s^{-1}	0.0182	0.0303	-0.3858	-0.2866	0.4190	1313.2180	0.0213
EA (1) + Dodecane-1-ol (2)							
ρ / g.m^{-3}	-22.1031	-7.5597	-3.6048	0.4497	2.3879	5.2287	0.0453
η / mPa.s	-0.1873	0.0605	-0.5018	-1.7158	-0.9880	4.9217	0.0158
u / m.s^{-1}	5.8684	-2.4528	-16.3339	30.0249	49.4370	1312.8065	0.5714
BA (1) + Dodecane-1-ol (2)							
ρ / g.m^{-3}	-11.4653	-2.1140	0.4519	-1.0777	-2.1107	3.0751	0.0216
η / mPa.s	-0.1818	0.2020	-0.0970	-1.2300	-0.9196	5.3158	0.0145
u / m.s^{-1}	0.0518	0.2541	-1.3768	-0.7142	2.2274	1329.1646	0.0184
MMA (1) + Dodecane-1-ol (2)							
ρ / g.m^{-3}	-27.6933	-9.0012	-2.8447	-1.8270	-0.8159	6.3393	0.0335
η / mPa.s	-0.2253	0.1431	0.4657	-1.4437	-1.9474	5.0259	0.0138
u / m.s^{-1}	0.0552	-0.2021	-1.5074	0.1069	1.8610	1317.9351	0.0202

RESULTS AND DISCUSSION

A graphical comparison of excess molar volume at 303.15 K for the binary mixtures of acrylates with dodecane-1-ol is given in Fig. 1.

A systematic decrease in V^E is noted with increase in carbon chain length of acrylates from methyl acrylate to butyl acrylate in all binary mixtures. Strength of interaction between component molecules of binary mixtures is well reflected in deviation of excess functions from ideality. Thermodynamic excess functions are found to be very sensitive towards mutual interactions between component molecules of liquid mixture. Sign and extent of deviations of these functions from ideality depends upon strength of interaction between unlike molecules. Excess molar volumes found to be positive and increases with increase in chain length of solute molecules. Disruption of hydrogen bonds in alkane-1-ol associates and dipole-dipole repulsive interactions between multimers and unimer alkane-1-ol species are mainly responsible for the observed positive values of V^E.

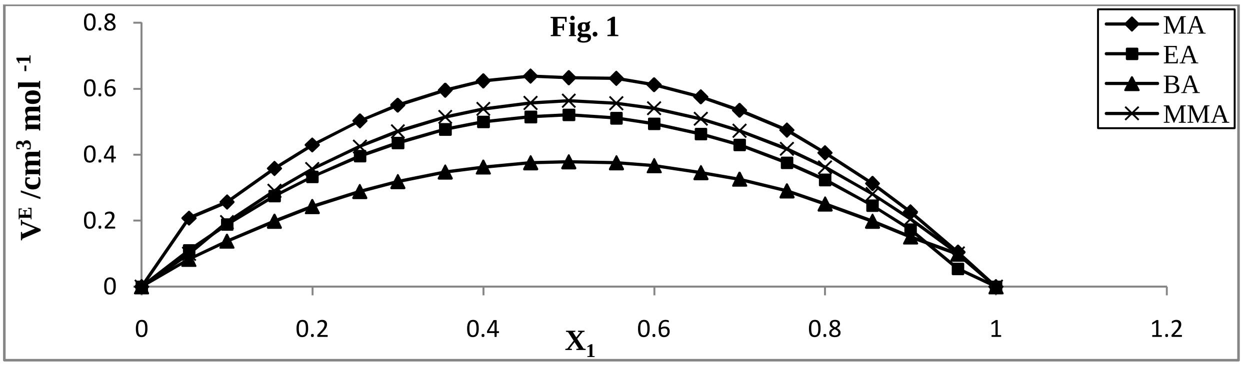

Fig. 1. Variation of excess molar volumes for Acrylates (1) + Dodecane-1-ol (2) at 303.15 K

A graphical comparison of deviation in viscosity at 303.15 K for binary mixtures of acrylates with dodecane-1-ol is given in Fig. 2.

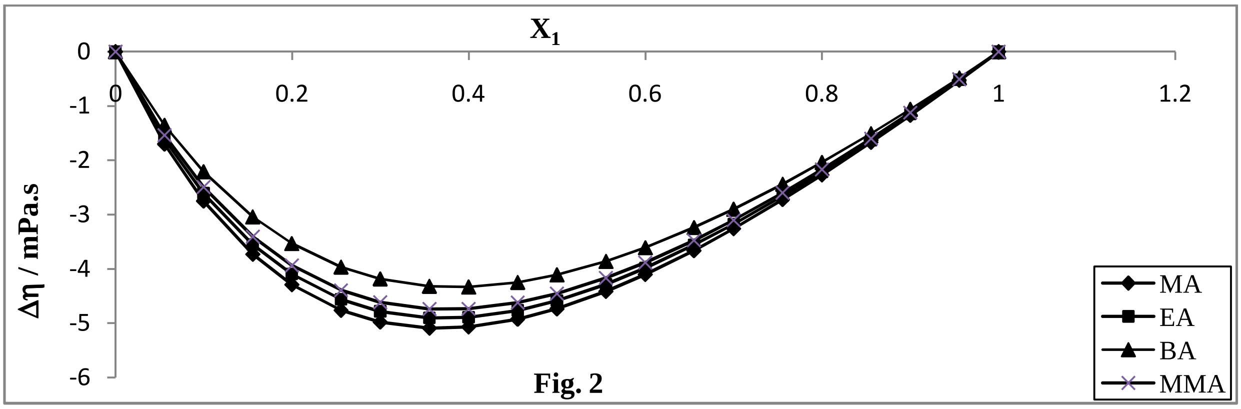

Fig. 2. Variation of deviation in viscosity for Acrylates (1) + Dodecane-1-ol (2) at 303.15 K

Weak types of dipole- induced dipole type of interactions are not sufficient to produce bulky or less mobile entities in system and hence decreased trend of viscosity is observed in the present binary liquid mixture of acrylics esters with the branched alcohol. Breaking of self association is important enough to overcome other effects that would increase viscosity. Negative values of $\Delta\eta$ over whole composition range suggests that, viscosities of associates formed between unlike molecules are relatively less than those of pure components, which is exhibited by decreased values of viscosity with mole fraction. This decrease in viscosity attributed to breaking of dipolar association of alcohol into small dipoles. Sign and magnitude of $\Delta\eta$ depends on the combined effect of factors like molecular size and shape of components. Values of viscosity deviation are found to be negative, whereas existence of specific interactions between mixing components tends to make intermolecular forces.

A graphical comparison of deviation in isentropic compressibility at 303.15 K for acrylates with dodecane-1-ol is given in Fig. 3. Variations in ultrasonic velocity and compressibilities in alkanols are mainly due to H-bonds, dispersion and interaction of hydrocarbon radicals of alkanols. A strong molecular interaction through charge transfer, dipole-induced dipole, dipole-dipole 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. $\Delta\kappa_s$ attributed to relative strength of effects which influenced free space, according to which positive $\Delta\kappa_s$ arise due to breaking of hydrogen bonds in self associated alkanols and physical dipole-dipole interactions between alkane-1-ol monomers and multimers contribute to increase in free space, decrease in sound velocity and positive deviation in isentropic compressibility this effect will be counteracted by changes of free volume in real mixtures.

Experimental viscosity data used to correlate with different semi-empirical equations like Grunberg-Nissan (G_{12}), Tamura and Kurata (T_{12}), McAllister three body model (Z_{12}, Z_{21}) and McAllister four body model (Z_{1112}, Z_{1122}, Z_{2221}). Their parameters with standard errors are summarized in Table 4. From different single parameter semi-empirical equations, least standard error is observed for Grunberg-Nissan equation parameter. Nigam [20] concluded from the study of binary liquid mixtures that, (i) If $\Delta\eta > 0$, $G_{12} > 0$ and magnitude of both are large, then strong specific interactions would be present. (ii) If $\Delta\eta < 0$, $G_{12} > 0$ then weak interactions would be present, and (iii) If $\Delta\eta < 0$, $G_{12} < 0$ and magnitude of both are large, then dispersion forces would be dominant. The order of correlating ability of these equations will be $G_{12} > (Z_{12}, Z_{21}) > (Z_{1112}, Z_{1122}, Z_{2221}) > T_{12}$. Interaction parameter of Tamura-Kurata equation shows highest values of standard errors in all binary liquid mixtures.

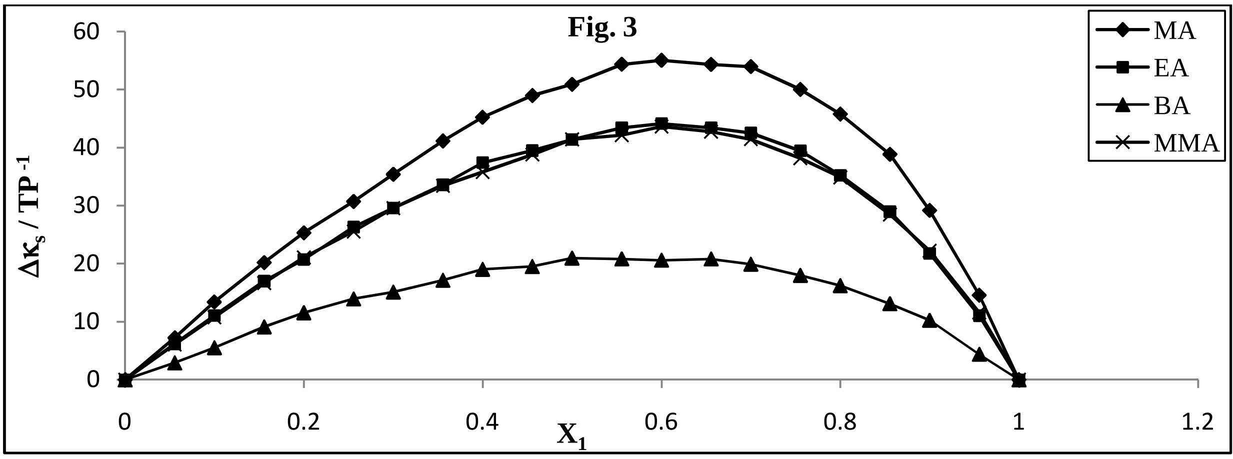

Fig. 3. Variation of deviation in isentropic compressibility for Acrylates (1) + Dodecane-1-ol (2) at 303.15 K

CONCLUSION

Positive values of excess molar volume (V^E) and deviation in isentropic compressibility ($\Delta\kappa_s$) over entire composition range are due to rupture of hydrogen bonded associates of alkanols dominate over hydrogen bonding between unlike molecules. Negative values of $\Delta\eta$ are observed due to breaking of hydrogen bonding of alkanols which makes mixture flow more easily. Positive values of $\Delta\kappa_s$ observed when H-bonded aggregates of alkanols break up progressively with addition of second component. From different semi-empirical equations, Grunberg-Nissan equation is most suitable for present binary mixtures due to lowest values of standard error as compared to other models.

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