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Studies of excess thermodynamic parameters of binary liquid mixtures of methyl methacrylate with higher branched alkane-2-ols at 303.15 K

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ABSTRACT

New experimental thermodynamic data involving density, viscosity and ultrasonic velocity of the binary liquid mixture of methyl methacrylate with heptane-2-ol, octane-2-ol and decane-2-ol at 303.15 K temperature 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 several semi empirical approaches like Hind, Choudhary-Katti, Grunberg-Nissan, Tamura and 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 the binary liquid mixtures at both temperatures. The results were discussed in terms of molecular interactions prevailing in the mixtures.

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KEYWORDS

Acrylic ester + decane-2-ol;
Density;
Jouyban acree model;
Redlich-Kister equation;
Semi-empirical equations;
McAllister model.

INTRODUCTION

Thermodynamic 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. Such type of derived thermodynamic parameters helpful to understand the strength of molecular interactions, hydrogen bonding phenomenon which based on polarity and size of molecules of two liquids in a solution in definite composition and over a fixed temperature range. Properties of liquid-liquid binary mixtures are very important qualitatively and quantitatively as a part of studies of thermodynamic, acoustic and transport aspects. Compositional dependence of thermodynamic properties has proved to be a very useful tool in understanding nature and extent of pattern of molecular aggregation resulting from interactions. This study is a powerful means of characterizing various aspects of physicochemical behaviors of liquid mixtures and molecular interactions.

Mixing volume effects are also important from theoretical as well as practical point of view. These properties found many applications in paints, varnishes, cleaning products, antioxidant agents, inks, adhesives, dispersion for textiles, papers, polystyrene, etc. where volume effects are also involve in conversion of formulation from gravimetric to volumetric analysis. Properties like molar volume and their deviations from ideality and variation with temperature and composition of binary mixtures are useful to design engineering processes in chemical and biological industries. Also, volumetric and ultrasonic properties have practical importance in understanding interactions and physicochemical behavior. The mixing of different compounds gives rise to solutions that generally don't behave ideally. Deviation from ideality may be expressed by many thermodynamic variables, particularly by excess properties. Excess properties of mixtures correspond to difference between actual and properties if system behaves ideally and thus are useful in study of molecular interactions and arrangements. In particular, they reflect interactions that take place between solute-solute, solute-solvent and solvent-solvent species.

Thus keeping both industrial and scientific interests in mind, here we report the measured densities, ρ, viscosities, η and ultrasonic velocities, u, of binary liquid mixtures of methyl methacrylate (MMA) with heptane-2-ol, octane-2-ol and decane-2-ol at 303.15 K temperature. The derived parameters excess molar volume, V^E, deviation in viscosity, $\Delta\eta$ and deviation in isentropic compressibility have been used to gain a better understanding of the intermolecular interactions between the component molecules of the liquid mixtures.

EXPERIMENTAL

Chemicals used in the present study were of analytical grade. The masses were recorded on a Mettlar one pan balance, which can read up to fifth place of decimal, with an accuracy of ± 0.01 mg. The estimated uncertainty in mole fraction was $<1\times10^{-4}$. The densities of the solutions were measured using a single capillary pycnometer made up of borosil glass with a bulb of 8cm³ and capillary with internal diameter of 0.1cm was chosen for present work. The reproducibility of density measurement was $\pm 5\text{x}10^{-5}$ g/cm³. The dynamic viscosities were measured using an Ubbelohde suspended level viscometer calibrated with conductivity water. The uncertainty in dynamic viscosities is ± 0.003 mPa.s. The ultrasonic velocities were measured[1] at a frequency of 2 MHz in these solutions by a single crystal ultrasonic interferometer (Mittal's F-81 model). The error 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, Viscosities, η, Ultrasonic velocities, u, for pure components at 303.15 K.

Liquid	ρ/ (g.cm^{-3})		η/(mPa.s)		u / (m.s^{-1})	
	Expt.	Lit.	Expt.	Lit.	Expt.	Lit.
Methyl Methacrylate	0.93172	0.93174[2]	0.549	---	1168	---
Heptane-2-ol	0.80932	0.80931[3]	4.38	4.385[3]	1293	1294[3]
Octane-2-ol	0.8135	0.81352[3]	5.392	5.397[3]	1365	1366[3]
Decane-2-ol	0.81779	---	8.593	---	1401	---

The excess molar volumes, V^E, of the solutions of molar compositions x were calculated from the densities of the pure liquids and their mixtures according to the following equation,

$$V^E/\,\mathrm{cm^3mol^{-1}} = [x_1M_1+x_2M_2]/\rho_{12} - [(x_1M_1/\rho_1)+(x_2M_2/\rho_2)] \quad (1)$$

where ρ_{12} is the density of the mixture and $x_{1,}M_1, \rho_1$, and $x_{2,}M_2, \rho_2$ are the mole fraction, the molecular weight, and the density of pure components 1and 2, respectively. The viscosity deviations ($\Delta\eta$) were calculated using equation,

$$\Delta\eta\,/\mathrm{mPa.s} = \eta_{12} - x_1\eta_1 - x_2\eta_2 \quad (2)$$

where η_{12} is the viscosity of the mixture and x_1, x_2 and η_1, η_2 are the mole fraction and the viscosity of pure components 1and 2 respectively[4].

The excess isentropic compressibility (κ_s^E) was obtained using the relation,

$$\kappa_s^E\,/\,(\mathrm{TPa^{-1}}) = \kappa_s - \kappa_s^{id} \quad (3)$$

where κ_s is the isentropic compressibility and was calculated using the Laplace relation, that is, $\kappa_s = (1/u^2\rho)$ and κ_s^{id} was calculated from the relation[4].

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

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

$$\phi_{i} = x_iV^o_i / (\Sigma x_iV^o_i) \qquad (5)$$

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

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

The other required values were taken from literature[4,5].

The densities (ρ), viscosities (η), ultrasonic velocities (*u*), excess molar volumes (V^E), deviations in viscosity (Δ*η*) and deviation in isentropic compressibility ($\Delta\kappa_s^E$) of three binary liquid mixtures at 303.15 K are listed as a function of mole fraction in TABLE 2.

The excess molar volume, deviations in viscosity and deviation in isentropic compressibility were fitted to Redlich Kister[4] equation of the type,

TABLE 2 : Densities, *ρ*, Viscosities, *η*, Ultrasonic velocities, *u*, Excess molar volumes, V^E, Viscosity deviation, Δ*η*, and deviation in isentropic compressibilities, $\Delta\kappa_s$, for MMA (1) + Alkane-2-ols (2) at 303.15 K.

X_1	ρ ($g.cm^{-3}$)	V^E (cm^3mol^{-1})	η (mPa.s)	Δη (mPa.s)	u ($m.s^{-1}$)	Δκs (TPa^{-1})
MMA (1) + Heptane-2-ol (2)						
0	0.80932	0	4.380	0	1293	0
0.0551	0.81401	0.081	3.903	-0.264	1286	1.754
0.0998	0.81940	0.130	3.560	-0.438	1280	3.488
0.1555	0.82300	0.190	3.172	-0.613	1273	4.963
0.1998	0.82722	0.229	2.891	-0.723	1267	6.476
0.2555	0.83265	0.271	2.576	-0.825	1260	7.672
0.2999	0.83714	0.301	2.349	-0.882	1254	9.000
0.3555	0.84298	0.327	2.093	-0.925	1247	9.872
0.3999	0.84781	0.342	1.908	-0.940	1241	10.944
0.4555	0.85406	0.354	1.701	-0.934	1234	11.504
0.4999	0.85928	0.355	1.550	-0.915	1229	11.011
0.5556	0.86597	0.352	1.382	-0.871	1222	11.222
0.5999	0.87157	0.345	1.260	-0.822	1216	11.676
0.6554	0.87879	0.323	1.124	-0.747	1210	10.176
0.6995	0.88489	0.302	1.023	-0.675	1204	10.198
0.7554	0.89265	0.267	0.913	-0.575	1197	9.546
0.7999	0.89923	0.233	0.832	-0.484	1192	7.872
0.8555	0.90765	0.182	0.742	-0.362	1185	6.662
0.8999	0.91476	0.135	0.676	-0.257	1180	4.542
0.9555	0.92387	0.081	0.602	-0.117	1173	2.725
1	0.93172	0	0.549	0	1168	0
MMA (1) + Octane-2-ol (2)						
0	0.81350	0	5.392	0	1365	0
0.0551	0.81753	0.087	4.750	-0.373	1353	3.132
0.0998	0.82094	0.142	4.292	-0.616	1344	5.909
0.1555	0.82538	0.207	3.780	-0.859	1332	8.763
0.1998	0.82907	0.252	3.416	-1.009	1323	11.362
0.2555	0.83394	0.299	3.007	-1.147	1312	13.875
0.2999	0.83797	0.330	2.718	-1.222	1303	15.209
0.3555	0.84325	0.361	2.396	-1.276	1291	17.421
0.3999	0.84774	0.378	2.162	-1.293	1282	18.251
0.4555	0.85352	0.390	1.906	-1.282	1272	18.926
0.4999	0.85845	0.390	1.721	-1.251	1263	20.422
0.5556	0.86486	0.389	1.515	-1.187	1252	20.362
0.5999	0.87023	0.378	1.369	-1.118	1243	20.308
0.6554	0.87724	0.358	1.207	-1.013	1232	19.618
0.6995	0.88326	0.333	1.089	-0.913	1224	18.747
0.7554	0.89109	0.294	0.959	-0.774	1213	17.045
0.7999	0.89766	0.257	0.867	-0.651	1205	15.561
0.8555	0.90637	0.200	0.764	-0.485	1195	11.533
0.8999	0.91371	0.150	0.690	-0.343	1186	9.043
0.9555	0.92324	0.086	0.608	-0.159	1176	5.211
1	0.93172	0	0.549	0	1168	0
MMA (1) + Decane-2-ol (2)						
0	0.81779	0	8.593	0	1401	0
0.0551	0.82099	0.091	7.377	-0.770	1387	4.995
0.0998	0.82368	0.164	6.528	-1.261	1376	8.712
0.1555	0.82725	0.238	5.605	-1.739	1362	13.481
0.1998	0.83029	0.294	4.959	-2.025	1351	16.925
0.2555	0.83434	0.347	4.254	-2.283	1337	21.290
0.2999	0.83776	0.385	3.766	-2.415	1327	23.404
0.3555	0.84232	0.421	3.232	-2.502	1313	27.270
0.3999	0.84623	0.439	2.859	-2.517	1303	28.798
0.4555	0.85141	0.455	2.455	-2.474	1290	30.884
0.4999	0.85585	0.458	2.172	-2.399	1279	32.830
0.5556	0.86176	0.457	1.865	-2.259	1266	33.941
0.5999	0.86685	0.442	1.650	-2.117	1256	33.885
0.6554	0.87367	0.417	1.416	-1.904	1244	32.507
0.6995	0.87951	0.390	1.253	-1.709	1234	31.270
0.7554	0.88741	0.338	1.075	-1.442	1221	29.463
0.7999	0.89420	0.299	0.952	-1.206	1211	26.671
0.8555	0.90340	0.231	0.817	-0.895	1199	21.453
0.8999	0.91136	0.171	0.723	-0.631	1189	16.754
0.9555	0.92216	0.089	0.620	-0.287	1177	8.724
1	0.93172	0	0.549	0	1168	0

$$\mathbf{Y = x_1 x_2 \sum_{i}^{n} a_i (x_1 - x_2)^i} \qquad (7)$$

Where *Y* is either V^E or $\Delta\eta$ or κ_s^E and *n* is the degree of polynomial. Coefficient a_i was obtained by fitting Eq (7) to experimental results using a least-squares regression method. In each case, the optimum number of coefficients is ascertained from an examination of the variation in standard deviation (σ).

σ was calculated using the relation,

$$\sigma(Y) = \left[\frac{\sum (Y_{expt} - Y_{cacl})^2}{N - n}\right]^{1/2} \qquad (8)$$

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

TABLE 3 : Adjustable parameters of Eq 7 and 8 for the mathematical representation of deviation and excess functions for MMA (1) + Alkane-2-ols (2) at 303.15 K.

	a_0	a_1	a_2	a_3	a_4	σ
			MMA (1) + Heptane-2-ol (2)			
$V^E/(\mathrm{cm^3 mol^{-1}})$	2.1452	-0.0335	-4.0486	0.1587	4.5504	0.21942
$\Delta\eta/(\mathrm{mPa.s})$	-3.6576	1.2238	-0.3045	0.0626	-0.0182	0.00029
$\kappa_s^E\ /(\mathrm{TPa^{-1}})$	36.5064	2.2444	-30.2232	12.1241	34.8877	1.25853
			MMA (1) + Octane-2-ol (2)			
$V^E/(\mathrm{cm^3 mol^{-1}})$	1.5897	-0.0532	-0.2913	0.2265	0.6678	0.00467
$\Delta\eta/(\mathrm{mPa.s})$	-5.0030	1.8242	-0.4941	0.1156	-0.0454	0.00037
$\kappa_s^E\ /(\mathrm{TPa^{-1}})$	48.3278	14.1273	-33.6608	-88.1632	139.3858	0.97441
			MMA (1) + Decane-2-ol (2)			
$V^E/(\mathrm{cm^3 mol^{-1}})$	1.8444	-0.0604	-0.1045	0.2568	0.2205	0.00409
$\Delta\eta/(\mathrm{mPa.s})$	-9.5985	4.1354	-1.3503	0.3866	-0.1303	0.00085
$\kappa_s^E\ /(\mathrm{TPa^{-1}})$	36.8787	15.7813	-2.5759	18.2536	20.5177	0.36790

Several semi empirical relations have been proposed to evaluate the dynamic viscosity *η* and to check the suitability of the equation for experimental data fits by taking into account the number of empirical adjustable coefficients. The equations of Hind, Choudhary-Katti, Grunberg-Nissan and Tamura-Kurata have one adjustable parameter.

The expression for Hind[6] equation is,

$$\eta_{12} = x_1^2 \eta_1 + x_2^2 \eta_2 + 2x_1 x_2 H_{12} \qquad (9)$$

where H_{12} is the interaction parameter.

The expression for Choudhary-Katti[7] equation is,

$$\ln(\eta_n V_m) = x_1 \ln(\eta_1 V_1) + x_2 \ln(\eta_2 V_2) + x_1 x_2 [Wvis/(_{RT})] \qquad (10)$$

where *Wvis* is the interaction energy for activation of viscous flow.

The expression for Grunberg-Nissan[8] equation is,

$$\ln \eta_{12=} x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1 x_2 G_{12} \qquad (11)$$

where G_{12} is a parameter proportional to the interchange energy.

Tamura and Kurata[9] developed expression for viscosity of binary mixtures as,

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

where T_{12} is the interaction parameter, ϕ_1 and ϕ_2 are the volume fractions. The calculated values of adjustable parameters H_{12}, *Wvis*, G_{12} and T_{12} with their standard deviations (σ) calculated using equation (15) are given in TABLE 4.

TABLE 4 : Adjustable parameters of Eq 9, 10, 11, 12 and 15 for MMA (1) + Alkane-2-ols (2) at 303.15 K.

η_{12}	σ	Wvis	σ	G_{12}	σ	T_{12}	σ
			MMA (1) + Heptane-2-ol (2)				
0.605	7.317	0.055	0.161	-0.001	0.021	0.340	10.734
			MMA (1) + Octane-2-ol (2)				
0.418	10.338	0.090	0.083	-0.001	0.028	0.039	16.558
			MMA (1) + Decane-2-ol (2)				
-0.367	20.913	0.184	0.260	-0.001	0.035	-1.498	37.337

McAllister's multibody interaction model[10] was widely used to correlate kinematic viscosity, υ, data. The 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 the relation,

$$\ln \nu = x_1^3 \ln \nu_1 + x_2^3 \ln \nu_2 + 3 x_1^2 x_2 \ln Z_{12} + 3 x_1 x_2^2 \ln Z_{21} - \ln [x_1 + (x_2 M_2/M_1)] + 3 x_1^2 x_2 \ln[(2/3)+(M_2/3M_1)] + 3 x_1 x_2^2 \ln[(1/3)+(2M_2/3M_1)] + x_2^3 \ln(M_2/M_1) \quad (13)$$

Similarly, the four body model was defined by the relation,

$$\ln \nu = x_1^4 \ln \nu_1 + 4 x_1^3 x_2 \ln Z_{1112} + 6 x_1^2 x_2^2 \ln Z_{1122} + 4 x_1 x_2^3 \ln Z_{2221} + x_2^4 \ln \nu_2 - \ln [x_1 + x_2 (M_2/M_1)] + 4 x_1^3 x_2 \ln [(3+M_2/M_1)/4] + 6 x_1^2 2 x_2^2 \ln[1+M_2/M_1)/2] + 4 x_1 x_2^3 \ln [(1+ 3M_2/M_1)/4] + x_2^4 \ln (M_2/M_1) \quad (14)$$

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

To perform a numerical comparison of the correlating capability of above Eq (9 to 14) we have calculated the standard percentage deviation (σ %) using the relation,

$$\sigma \% = [1/ (\eta_{expt} - k) \times \Sigma(100 (\eta_{expt} - \eta_{cal}) / \eta_{expt})^2]^{1/2} \quad (15)$$

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

The interaction parameters H_{12}, *Wvis*, G_{12}, T_{12}, Z_{12}, Z_{21}, Z_{1112}, Z_{1122} and Z_{2221} in the above Eq (9 to 14) have been considered as adjustable parameters, estimated by a non-linear regression analysis based on a least-squares method. The parameters Z_{12}, Z_{21}, Z_{1112}, Z_{1122} and Z_{2221} are presented with their standard percentage deviation (σ %) in TABLE 5.

Recently Jouyban and Acree[11,12] proposed a model for correlating the density and viscosity of liquid mixtures at wide range of temperatures. This model could be used in data modeling (Jouyban & Khoubnasabjafari, 2005 a, b). The proposed equation is,

$$\ln y_{mT} = f_1 \ln y_{1T} + f_2 \ln y_{2T} + f_1 f_2 \Sigma [A_j (f_1 - f_2)^j / T] \quad (16)$$

where y_{mT}, y_{1T} and y_{2T} is density or viscosity of the mixture and solvents 1 and 2 at temperature *T*, respectively, f_1 and f_2 are the volume fractions of solvents in case of density, and mole fraction in case of viscosity, 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 and viscosity as,

$$APD = (100/N) \Sigma [(| y_{expt} - y_{cal} |)/ y_{expt})] \quad (17)$$

Where *N* is the number of data points in each set. The optimum numbers of constants *Aj*, in each case, were determined from the examination of the average percentage deviation value. The constants *Aj* calculated from the least square analysis along with the average percentage deviation (APD) are presented in TABLE 6. The proposed model provides reasonably accurate calculations for the density and viscosity of binary liquid mixtures at various temperatures.

TABLE 5 : Adjustable parameters of Eq 13, 14 and 15 for MMA (1) + Alkane-2-ols (2) at 303.15 K.

Z_{12}	Z_{21}	σ	Z_{1112}	Z_{1122}	Z_{2221}	Σ
MMA (1) + Heptane-2-ol (2)						
1.256	2.620	0.155	1.039	1.681	3.138	1.033
MMA (1) + Octane-2-ol (2)						
1.354	3.015	0.026	1.099	1.756	3.668	1.671
MMA (1) + Decane-2-ol (2)						
1.616	4.136	0.043	1.253	1.996	5.215	6.277

TABLE 6 : Adjustable parameters of Eq 16 and 17 for MMA (1) + Alkane-2-ols (2).

	a_0	a_1	a_2	a_3	a_4	σ	*APD*
MMA (1) + Heptane-2-ol (2)							
ρ/ (g.cm$^{-3)}$	-13.1455	-1.3160	3.1122	-0.8080	-4.6324	3.3534	0.0284
η/(mPa.s)	-0.1286	-1.1918	-2.5290	2.3414	4.0122	2.0253	0.0195
u / (m.s^{-1})	0.0113	-0.4540	-0.4793	0.9442	0.3768	1263.4309	0.0184
MMA (1) + Octane-2-ol (2)							
ρ/ (g.cm$^{-3)}$	-16.9505	-2.7076	0.3434	-0.8721	-1.9710	4.1461	0.0192
η/(mPa.s)	-0.2333	-0.6186	-0.4581	0.7979	0.7709	2.3693	0.0189
u / (m.s^{-1})	-0.0781	0.1045	1.3999	-0.4475	-2.9440	1301.2777	0.0204
MMA (1) + Decane-2-ol (2)							
ρ/ (g.cm$^{-3)}$	-24.0460	-6.1348	-1.3152	-0.9964	-0.8606	5.5675	0.0138
η/(mPa.s)	-0.1447	-0.4685	-0.0426	0.0230	-0.0949	3.4120	0.0241
u / (m.s^{-1})	0.0404	0.1906	-0.6552	-0.5028	1.0571	1318.5762	0.0205

RESULTS AND DISCUSSION

A graphical comparison of the dependence of excess molar volume, V^E, at 303.15 K for the binary mixtures of each alkane-2-ols with methyl methacrylate is given in Figure 1.

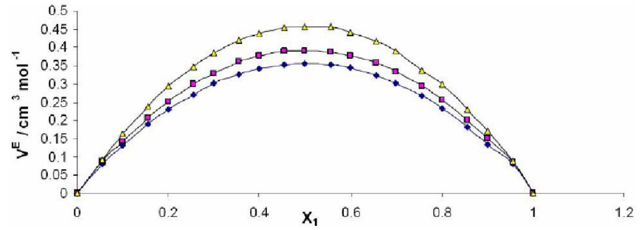

Figure 1 : Variation of excess molar volumes with MMA mole fraction for binary mixtures of MMA + alkane-2-ols at 303.15 K, ♦, heptane-2-ol, ■, octane-2-ol, ▲, decane-2-ol.

A systematic increase in V^E is noted with the rise in the carbon chain length of heptane-2-ol to decane-2-ol for all the binary mixtures. As far as we are aware, there are no literature data on any of properties for the binary mixtures of MMA + heptane-2-ol, octane-2-ol and decane-2-ol with which we can compare our results. The observed positive excess molar volumes in the present investigation may be discussed in terms of several effects. Excess molar volumes can be considered as arising from three types of interactions between the component molecules :-(a) Physical interaction consisting mainly of dispersion forces or weak dipole interaction and making a positive contribution, (b) Chemical or specific interactions which include charge transfer forming hydrogen bonds and other complex forming interactions resulting in a negative contribution, (c) Negative contribution is also possible due to difference in size and shapes of component molecules of mixtures. Positive excess molar volume explains systematic variations of methyl methacrylate with alkane-2-ols species suggest the dominance of non-specific interactions. As the carbon chain length of alkane-2-ols increases, the steric factors prevent geometrical fitting and thus the excess molar volumes are found to be positive. Positive values of excess molar volumes can be visualized as being due to a closer approach of unlike molecules having significantly different molecular size. Due to presence of nonpolar molecule like acrylic esters, H-bonding in alcohol molecule breaks and system shows weak intermolecular interactions. Positive values of excess molar volumes shows volume expansion is taking place causing rupture of H-bonds in self associated alcohols.

The observed large negative values of viscosity deviation, $\Delta\eta$, in general indicate a high dilution of alkane-2-ol viscosities in the presence of methyl methacrylate species in Figure 2.

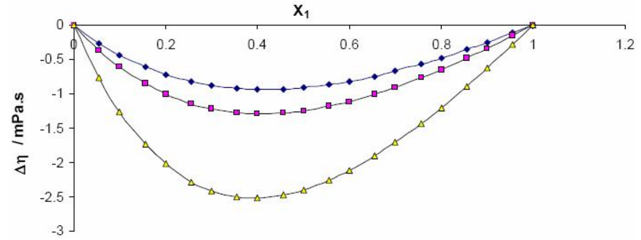

Figure 2 : Variation of deviation in viscosities with MMA mole fraction for binary mixtures of MMA + alkane-2-ols at 303.15 K, ♦, heptane-2-ol, ■, octane-2-ol, ▲, decane-2-ol.

The decrease in viscosity values can be ascribed to the structure breaking-up of these alkanols associates by unlike ester species. This result is also attributed to rupture of hydrogen bonds between alkane-2-ols molecules by methyl methacrylate to be based on negative excess viscosities. This type of interaction seems to be dominant when the share of ester in the mixture is small. 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. 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 methyl methacrylate with the branched alcohol.

Figure 3 indicates that deviation the isentropic compressibilities, $\Delta\kappa_s$, for all the binary mixtures are positive. This type nature was found due to, (i) hydrogen bonded aggregates of alkane-2-ols breaks up progressively with the addition of another combining component in the mixture and (ii) weak interactions between unlike molecules. These two factors contribute to negative deviation in ultrasonic velocity and positive deviation in excess isentropic compressibility. Positive values are ascribed to expansion in volume due to dissociation, depolymerisation of hydrogen bonded alkanols molecular aggregates and is also due to dipole-dipole interactions between the two combining species.

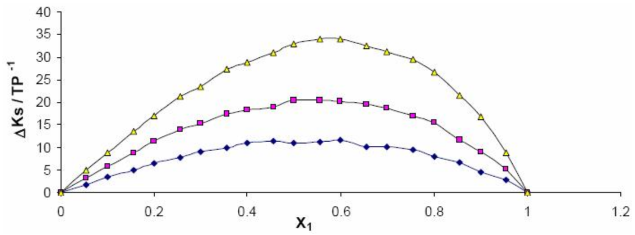

Figure 3 : Variation of deviation in isentropic compressibility with MMA mole fraction for binary mixtures of MMA + alkane-2-ols at 303.15 K, ♦, heptane-2-ol, ■, octane-2 ol, ▲, decane-2-ol.

Grunberg-Nissan models used to correlate mixture viscosity shows least negative values of G_{12} parameters supporting weak molecular interactions. Hind, Choudhary-Katti and Tamura and Kurata model shows slightly positive values of their H_{12}, *Wvis* and T_{12} adjustable parameters respectively, supporting existing of weak interactions for all binary liquid mixtures at both temperatures. In the similar way, among McAllister three and four body models shows the values of Z_{12}, Z_{21}, Z_{1112}, Z_{1122} and Z_{2221} adjustable parameters positive, supporting weak type of molecular interactions for all the four binary liquid mixtures. Lowest values of the standard deviations for the McAllister there body model suggests that it is most suitable than the other one.

CONCLUSIONS

The overall positive magnitude of excess molar volumes for the systems of methyl methacrylate with the alkane-2-ols is the result of the breaking and dislocation of the ester's dipole-dipole association. The free volume difference and interstitial accommodation of smaller molecules are chief factors for negative excess molar volumes. In higher alcohols, geometrical fitting of one into other is negligibly small; therefore association decreases with increase in chain length of alcohols. Positive values of excess isentropic compressibilities are ascribed to expansion in volume due to dissociation, depolymerisation of hydrogen bonded alkanols molecular aggregates and is also due to dipole-dipole interactions between the two combining species.

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