

Molecular interactions in binary mixtures of acrylates with heptane-2-ol

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ABSTRACT

Viscosities and ultrasonic velocities of binary mixtures of methyl acrylate, ethyl acrylate and butyl acrylate with heptane-2-ol have been measured at 303.15 and 313.15 K and at atmospheric pressure. Deviations in viscosity and deviations in isentropic compressibility were calculated and have been fitted to Redlich-Kister equation. Ultrasonic velocities calculated theoretically to predict using Nomoto, Van Dael, free length theory and collision factor theory. Experimental viscosities were correlated by semi-empirical equations such as Heric-Brewer and McAllister three and four body model equations. Jouyban-Acree model used to correlate viscosity and ultrasonic velocity.

Keywords: Acrylates, Heptane-2-ol, Ultrasonic Velocity, Van Dael, Redlich-Kister Polynomial Equation, Jouyban Acree Model.

INTRODUCTION

Thermodynamic properties are also important in designing industrial equipments with better precision. There has been an increasing interest in study of molecular interactions and a number of experimental techniques have been used to investigate interactions between components of binary liquid mixtures. 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.

In literature, data exists for binary systems of ethyl ethanoate with ethyl acrylate, butyl acrylate, methyl methacrylate and styrene at 298.15 K [1], for volumetric behavior of acrylic esters with alkane-1-ols at 298.15 and 308.15 K [2], density and excess molar volume of binary systems of dimethyl sulfoxide + ethyl acrylate, butyl acrylate, methyl methacrylate and styrene at 298.15 K [3], volumetric properties of dimethyl sulfoxide with Methacrylic acid, vinyl acetate, butyl methacrylate and allyl methacrylate at 298.15 K [4].

Literature survey reveals that, molecular interactions of present binary liquid mixtures of acrylic esters with heptane-2-ol at 303.15 and 313.15 K have not much studied, therefore, we have planned to study exhaustively kind of molecular interactions in these binary systems.

MATERIALS AND METHODS

Chemicals used in present study were of analytical grade and supplied by S. D. Fine Chem. Pvt. Ltd. Mumbai with quoted mass fraction purities: methyl acrylate, MA, (> 0.997), ethyl acrylate, EA, (> 0.998), butyl acrylate, BA, (> 0.995) and heptane-2-ol, (> 0.999). Prior to use all liquids were stored over 0.4 nm molecular sieves to reduce water content. Masses were recorded on a Mettler balance, with an accuracy of ± 0.01 mg. The estimated uncertainty in mole fraction was $< 1 \times 10^{-4}$. Temperature was controlled using a constant temperature controlled water bath (Gemini Scientific Instruments, Chennai, India) having accuracy $\pm 0.02^\circ\text{C}$.

Experimental Part

Viscosities were measured [5] using an Ubbelohde viscometer. The accuracy in viscosities is ± 0.003 mPa.s. The ultrasonic velocities were measured at frequency of 2 MHz by single crystal ultrasonic interferometer (Model F-81, Mittal Enterprises, New Delhi, India) [5]. The accuracy in velocity measurements is $\pm 0.1\%$. Comparison of measured values of pure components with literature values are presented in Table 1.

Table 1. Viscosities (η) and ultrasonic velocities (u) for pure components.

Property	T = 303.15 K		T = 313.15 K	
	Expt.	Lit.	Expt	Lit.
Heptane-2-ol				
η (mPa.s)	4.380	4.385 [6]	2.980	2.981 [6]
u (m.s ⁻¹)	1293	1294 [6]	1254	1254 [6]
Methyl Acrylate				
η (mPa.s)	0.420	---	0.361	---
u (m.s ⁻¹)	1163	---	1118	---
Ethyl Acrylate				
η (mPa.s)	0.487	---	0.425	---
u (m.s ⁻¹)	1152	---	1123	---
Butyl Acrylate				
η (mPa.s)	0.737	---	0.636	---
u (m.s ⁻¹)	1190	---	1157	---

Computational Part

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

$$\Delta\eta = \eta_{12} - x_1\eta_1 - x_2\eta_2 \quad (1)$$

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.

Deviation in isentropic compressibility were calculated using,

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

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

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

κ_s^{id} was calculated from relation,

$$\kappa_s^{\text{id}} = \sum \phi_i [\kappa_{s,i} + TV_i^0(\alpha_i^0)^2/C_{p,i}] - [T(\sum x_i V_i^0) (\sum \phi_i \alpha_i^0)^2 / \sum x_i C_{p,i}] \quad (4)$$

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

$$\phi_i = x_i V_i^0 / (\sum x_i V_i^0) \quad (5)$$

Table 2. Viscosities (η), ultrasonic velocities (u), viscosity deviation ($\Delta\eta$) and deviation in isentropic compressibilities ($\Delta\kappa_s$) of acrylates (1) + heptane-2-ol (2) at T = (303.15 and 313.15) K.

X_1	T = 303.15 K				T = 313.15 K			
	η (mPa.s)	u (m.s ⁻¹)	$\Delta\eta$ (mPa.s)	$\Delta\kappa_s$ (TPa ⁻¹)	η (mPa.s)	u (m.s ⁻¹)	$\Delta\eta$ (mPa.s)	$\Delta\kappa_s$ (TPa ⁻¹)
	MA (1) + Heptane-2-ol (2)							
0	4.380	1293	0	0	2.980	1254	0	0
0.0553	3.847	1285	-0.314	3.86	2.651	1246	-0.184	3.73
0.0999	3.465	1279	-0.519	6.07	2.413	1240	-0.305	5.86
0.1555	3.042	1272	-0.722	8.21	2.146	1232	-0.427	9.08
0.1999	2.741	1266	-0.847	10.23	1.954	1226	-0.502	10.96
0.2554	2.407	1258	-0.962	13.16	1.738	1218	-0.573	13.77
0.2998	2.169	1253	-1.024	13.63	1.583	1212	-0.612	15.28
0.3554	1.904	1245	-1.069	16.07	1.407	1204	-0.642	17.55
0.4000	1.715	1239	-1.081	17.31	1.281	1198	-0.651	18.56
0.4551	1.507	1232	-1.071	18.04	1.140	1190	-0.648	20.33
0.4998	1.357	1226	-1.044	18.74	1.037	1184	-0.634	20.77
0.5555	1.190	1219	-0.990	18.73	0.922	1177	-0.603	20.29
0.5998	1.073	1213	-0.932	18.97	0.840	1171	-0.569	20.18
0.6555	0.942	1206	-0.842	18.17	0.747	1163	-0.516	20.27
0.6999	0.849	1201	-0.759	16.41	0.680	1157	-0.467	19.42
0.7550	0.746	1191	-0.644	18.75	0.605	1150	-0.398	17.16
0.7999	0.671	1188	-0.541	13.47	0.551	1144	-0.334	15.29
0.8552	0.590	1181	-0.403	10.77	0.490	1137	-0.250	11.81
0.8999	0.531	1175	-0.286	8.59	0.446	1131	-0.177	8.97
0.9555	0.466	1168	-0.130	4.59	0.396	1124	-0.082	3.97
1	0.420	1163	0	0	0.361	1118	0	0
	EA (1) + Heptane-2-ol (2)							
0	4.380	1293	0	0	2.980	1254	0	0
0.0553	3.877	1285	-0.287	1.72	2.675	1246	-0.163	2.45
0.0999	3.518	1278	-0.473	3.77	2.453	1240	-0.272	3.85
0.1555	3.113	1270	-0.662	5.30	2.202	1233	-0.381	4.81
0.1999	2.823	1263	-0.779	7.13	2.019	1227	-0.450	5.96
0.2554	2.499	1255	-0.886	8.43	1.812	1219	-0.515	7.99
0.2998	2.266	1249	-0.946	8.86	1.662	1213	-0.552	8.97
0.3554	2.006	1241	-0.990	9.85	1.491	1206	-0.581	9.35
0.4000	1.819	1235	-1.004	10.03	1.367	1200	-0.591	10.11
0.4551	1.610	1227	-0.997	10.73	1.227	1193	-0.589	10.18
0.4998	1.460	1220	-0.974	11.91	1.125	1187	-0.578	10.65
0.5555	1.293	1213	-0.926	10.97	1.010	1179	-0.551	11.82
0.5998	1.173	1206	-0.872	11.84	0.926	1174	-0.521	10.53
0.6555	1.039	1199	-0.791	10.49	0.832	1167	-0.475	9.89
0.6999	0.941	1193	-0.714	9.60	0.762	1161	-0.430	9.61
0.7550	0.834	1185	-0.607	9.17	0.685	1154	-0.366	8.55
0.7999	0.756	1179	-0.510	7.88	0.627	1148	-0.309	7.89
0.8552	0.669	1171	-0.382	6.90	0.563	1141	-0.232	6.29
0.8999	0.607	1165	-0.270	5.19	0.516	1135	-0.165	5.24
0.9555	0.537	1158	-0.123	2.04	0.463	1128	-0.076	2.87
1	0.487	1152	0	0	0.425	1123	0	0
	BA (1) + Heptane-2-ol (2)							
0	4.380	1293	0	0	2.980	1254	0	0
0.0553	3.968	1287	-0.210	-0.08	2.735	1248	-0.115	0.34
0.0999	3.666	1282	-0.350	0.13	2.554	1244	-0.192	-0.37
0.1555	3.320	1276	-0.494	0.11	2.344	1238	-0.272	0.05
0.1999	3.067	1272	-0.585	-0.78	2.188	1234	-0.324	-0.58
0.2554	2.779	1266	-0.672	3.91	2.009	1229	-0.373	-1.32
0.2998	2.570	1261	-0.721	-0.25	1.878	1224	-0.401	-0.51
0.3554	2.324	1255	-0.761	-0.16	1.721	1219	-0.426	-1.30
0.4000	2.147	1251	-0.776	-0.94	1.607	1214	-0.436	-0.47
0.4551	1.946	1245	-0.775	-0.66	1.475	1209	-0.437	-1.05
0.4998	1.797	1240	-0.762	-0.17	1.377	1205	-0.431	-1.50
0.5555	1.627	1235	-0.729	-1.04	1.263	1199	-0.415	-0.65
0.5998	1.503	1230	-0.692	-0.44	1.180	1195	-0.394	-1.00
0.6555	1.362	1225	-0.630	-1.21	1.083	1190	-0.360	-1.41
0.6999	1.258	1220	-0.573	-0.55	1.011	1185	-0.329	-0.30
0.7550	1.139	1214	-0.489	0.00	0.928	1180	-0.281	-0.65
0.7999	1.052	1210	-0.414	-2.32	0.866	1176	-0.239	-0.86
0.8552	0.953	1204	-0.310	0.14	0.795	1171	-0.180	-1.09

0.8999	0.881	1200	-0.221	-0.33	0.742	1166	-0.129	0.22
0.9555	0.798	1194	-0.101	0.45	0.681	1161	-0.059	0.08
1	0.737	1190	0	0	0.636	1157	0	0

T is temperature and $\kappa_{s,i}$, V_i^0 , α_i^0 , and $C_{p,i}$ are isentropic compressibility, molar volume, coefficient of isobaric thermal expansion and molar heat capacity respectively for pure component i. α_i^0 is calculated from measured densities by relation,

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

Values of viscosities, ultrasonic velocities, deviation in viscosity and deviation in isentropic compressibility of mixtures are listed in Table 2.

Nomoto [7] investigated additivity of molar volumes in those mixtures for which deviation from linearity of molecular sound velocity is small and it was revealed that a great part of these mixtures had also a good additivity relationship of molar volumes. The sound velocity based on assumption of linearity of molecular sound velocity,

$$R = x_1R_1 + x_2R_2 \quad (7)$$

where R_1 and R_2 are molar sound velocities and x_1 and x_2 are mole fractions respectively. The molar sound velocity (R) or Rao's constant related to sound velocity as,

$$u = (R/V)^3 = [(x_1R_1 + x_2R_2)/(x_1V_1 + x_2V_2)]^3 \quad (8)$$

According to Vangeel [8] assumption adiabatic compressibility (β_s) of mixture is given by,

$$\beta_{s(im)} = \phi_1 v_1 \beta_{s(1)} / v_{im} + \phi_2 v_2 \beta_{s(2)} / v_{im} \quad (9)$$

Where ϕ and v represent volume fraction and specific heat ratio, respectively.

Schaffs [9-10] on basis of collision factor theory gave relation for sound velocity in liquids,

$$u = u_\infty S r f = u_\infty S B / V \quad (10)$$

where $u_\infty = 1600$ m/s, S is collision factor and rf ($rf = B/V$) is space filling factor, B is actual volume of molecule per mole and V is molar volume.

The sound velocity in mixtures evaluated from Jacobson's free length theory [11-12] is,

$$u_{mix} = K / (L_{f(mix)} \rho_{(mix)}^{1/2}) \quad (11)$$

Where K is a temperature dependent constant.

Ultrasonic velocities derived from these theories with percentage error are given in Table 3.

Table 3. Comparison of experimental ultrasonic velocity with various theories with % errors for acrylates (1) + heptane-2-ol (2) at T = 303.15 K.

X ₁	Ultrasonic Velocity					% Errors for Ultrasonic Velocity			
	Expt.	NOM	VAN	CFT	FLT	NOM	VAN	CFT	FLT
MA (1) + Heptane-2-ol (2)									
0	1293	1293	1293	1293	1275	0.82	2.34	0.06	6.93
0.0553	1285	1288	1279	1286	1263				
0.0999	1279	1284	1268	1280	1256				
0.1555	1272	1279	1256	1274	1246				
0.1999	1266	1275	1247	1268	1239				
0.2554	1258	1269	1237	1261	1230				
0.2998	1253	1264	1229	1255	1223				
0.3554	1245	1258	1220	1248	1214				
0.4000	1239	1253	1213	1243	1207				
0.4551	1232	1247	1206	1236	1199				
0.4998	1226	1241	1200	1230	1192				
0.5555	1219	1234	1193	1223	1184				
0.5998	1213	1228	1189	1217	1178				
0.6555	1206	1221	1183	1210	1170				
0.6999	1201	1214	1180	1204	1164				
0.7550	1191	1206	1175	1197	1157				
0.7999	1188	1199	1172	1191	1151				
0.8552	1181	1190	1169	1183	1145				
0.8999	1175	1182	1167	1177	1139				
0.9555	1168	1172	1164	1169	1133				
1	1163	1163	1163	1163	1128				
EA (1) + Heptane-2-ol (2)									
0	1293	1293	1293	1293	1275	0.35	0.54	0.01	3.35
0.0553	1285	1287	1282	1285	1265				
0.0999	1278	1282	1273	1279	1257				
0.1555	1270	1275	1263	1271	1248				
0.1999	1263	1270	1255	1264	1241				
0.2554	1255	1263	1245	1256	1232				
0.2998	1249	1257	1238	1250	1225				
0.3554	1241	1250	1229	1242	1217				
0.4000	1235	1244	1222	1236	1210				
0.4551	1227	1237	1214	1228	1202				
0.4998	1220	1230	1208	1222	1196				
0.5555	1213	1223	1201	1214	1188				
0.5998	1206	1216	1195	1208	1182				
0.6555	1199	1208	1188	1200	1175				
0.6999	1193	1201	1183	1194	1169				
0.7550	1185	1193	1176	1186	1162				
0.7999	1179	1186	1172	1180	1157				
0.8552	1171	1177	1166	1172	1151				
0.8999	1165	1169	1161	1166	1145				
0.9555	1158	1160	1156	1158	1140				
1	1152	1152	1152	1152	1134				
BA (1) + Heptane-2-ol (2)									
0	1293	1293	1293	1293	1275	0.00	0.00	0.02	33.86
0.0553	1287	1287	1287	1287	1276				
0.0999	1282	1282	1282	1282	1276				
0.1555	1276	1277	1276	1276	1278				
0.1999	1272	1272	1271	1271	1279				
0.2554	1266	1266	1265	1258	1243				
0.2998	1261	1262	1260	1261	1282				
0.3554	1255	1256	1254	1255	1284				
0.4000	1251	1251	1250	1250	1286				
0.4551	1245	1245	1244	1244	1288				
0.4998	1240	1241	1239	1240	1290				
0.5555	1235	1235	1234	1234	1292				
0.5998	1230	1230	1229	1230	1295				
0.6555	1225	1225	1224	1224	1297				
0.6999	1220	1220	1219	1220	1300				
0.7550	1214	1215	1214	1214	1304				
0.7999	1210	1210	1209	1212	1322				
0.8552	1204	1204	1204	1204	1310				
0.8999	1200	1200	1200	1200	1313				
0.9555	1194	1194	1194	1194	1317				
1	1190	1190	1190	1190	1321				

Deviation in viscosity and deviation in isentropic compressibility were fitted to Redlich- Kister [13] equation of type,

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

where Y is either $\Delta\eta$ 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).

σ was calculated using relation,

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

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 for all binary liquid mixtures.

Table 4. Adjustable parameters of Eq (12) and (13) for excess functions for binary liquid mixture of acrylates (1) + heptane-2-ol (2) at T = (303.15 and 313.15) K.

Property	T (K)	a_0	a_1	a_2	a_3	a_4	σ
MA (1) + Heptane-2-ol (2)							
$\Delta\eta$ (mPa.s)	303.15	-4.1751	1.5597	-0.4430	0.1053	-0.0296	0.00026
	313.15	-2.5354	0.8609	-0.2036	0.0453	-0.0435	0.00030
$\Delta\kappa_s$ (TPa ⁻¹)	303.15	55.0523	16.8806	-11.4919	-5.3825	33.2059	0.92566
	313.15	55.0523	16.8806	-11.4919	-5.3825	33.2059	0.92566
EA (1) + Heptane-2-ol (2)							
$\Delta\eta$ (mPa.s)	303.15	-3.8937	1.3688	-0.3651	0.0851	-0.0180	0.00036
	313.15	-2.3098	0.7267	-0.1711	0.0258	-0.0129	0.00031
$\Delta\kappa_s$ (TPa ⁻¹)	303.15	20.1790	2.3508	20.8686	5.1101	-28.2534	0.48463
	313.15	20.7028	2.2310	-15.7638	6.8527	38.1490	0.39637
BA (1) + Heptane-2-ol (2)							
$\Delta\eta$ (mPa.s)	303.15	-3.0473	0.8813	-0.2115	0.0363	0.0223	0.00045
	313.15	-1.7253	0.4355	-0.0787	0.0144	-0.0164	0.00032
$\Delta\kappa_s$ (TPa ⁻¹)	303.15	-1.5512	-14.7492	-1.0719	23.7320	8.0086	1.20768
	313.15	-3.4737	0.3422	-11.4217	-2.6203	25.0093	0.45193

Heric-Brewer [14] proposed two parameter model of form,

$$\ln \eta = x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1 \ln M_1 + x_2 \ln M_2 - \ln(x_1 M_1 + x_2 M_2) + x_1 x_2 [\alpha_{12} + \alpha_{21}(x_1 - x_2)] \quad (14)$$

where α_{12} and α_{21} are interaction parameters.

McAllister's [15] multibody interaction model was widely used to correlate kinematic viscosity data having two parameters based on Eyring's theory of absolute reaction rates for interactions of both like and unlike molecules by a two dimensional three body model given as,

$$\ln v = x_1^3 \ln v_1 + x_2^3 \ln v_2 + 3 x_1^2 x_2 \ln Z_{12} + 3 x_1 x_2^2 \ln Z_{21} - \ln [x_1 + (x_2 M_2 / M_1)] + 3 x_1^2 x_2 \ln [(2/3) + (M_2 / 3 M_1)] + 3 x_1 x_2^2 \ln [(1/3) + (2 M_2 / 3 M_1)] + x_2^3 \ln (M_2 / M_1) \quad (15)$$

Similarly, four body model was defined by relation,

$$\ln v = x_1^4 \ln v_1 + 4 x_1^3 x_2 \ln Z_{1112} + 6 x_1^2 x_2^2 \ln Z_{1122} + 4 x_1 x_2^3 \ln Z_{2221} + x_2^4 \ln v_2 - \ln [x_1 + x_2 (M_2 / M_1)] + 4 x_1^3 x_2 \ln [(3 + M_2 / M_1) / 4] + 6 x_1^2 x_2^2 \ln [1 + (M_2 / M_1) / 2] + 4 x_1 x_2^3 \ln [(1 + 3 M_2 / M_1) / 4] + x_2^4 \ln (M_2 / M_1) \quad (16)$$

where α_{12} , α_{21} , Z_{12} , Z_{21} , Z_{1112} , Z_{1122} and Z_{2221} are model parameters and M_i and v_i are molecular mass and kinematic viscosity of pure component i .

To perform a numerical comparison of correlating capability of above Eq (14 to 16), we have calculated standard percentage deviation (σ %) using relation,

$$\sigma \% = [1/(\eta_{\text{expt}} - k) \times \sum (100 (\eta_{\text{expt}} - \eta_{\text{cal}}) / \eta_{\text{expt}})^2]^{1/2} \quad (17)$$

where k represents number of numerical coefficients in respective equations. All interaction parameters have been considered as adjustable parameters, estimated by a non-linear regression analysis based on a least-squares method. The parameters α_{12} , α_{21} , Z_{12} , Z_{21} , Z_{1112} , Z_{1122} and Z_{2221} are presented with their standard percentage deviation (σ %) in Table 5.

Table 5. Adjustable parameters of Eq (14), (15), (16) and (17) for binary liquid mixture of acrylates (1) + heptane-2-ol (2) at T = (303.15 and 313.15) K.

T (K)	α_{12}	α_{21}	σ	Z_{12}	Z_{21}	σ	Z_{1112}	Z_{1122}	Z_{2221}	σ
MA (1) + Heptane-2-ol (2)										
303.15	0.116	0.015	0.030	1.0680	2.412	0.030	0.853	1.359	2.950	0.554
313.15	0.110	0.012	0.057	0.851	1.794	0.057	0.697	1.054	2.148	2.705
EA (1) + Heptane-2-ol (2)										
303.15	0.044	0.004	0.027	1.174	2.531	0.027	0.964	1.594	3.060	0.718
313.15	0.038	-0.004	0.055	0.950	1.895	0.055	0.797	1.248	2.238	1.465
BA (1) + Heptane-2-ol (2)										
303.15	0.004	-0.004	0.142	1.547	2.899	0.142	1.323	2.220	3.390	1.605
313.15	0.002	-0.001	0.028	1.246	2.154	0.028	1.086	1.722	2.467	2.057

Recently Jouyban and Acree [16-17] proposed a model for correlating viscosity and ultrasonic velocity of liquid mixtures and could be used in data modelling. The equation is,

$$\ln y_{mT} = f_1 \ln y_{1T} + f_2 \ln y_{2T} + f_1 f_2 \sum [A_j (f_1 - f_2)^j / T] \quad (18)$$

where y_{mT} , y_{1T} and y_{2T} is viscosity or ultrasonic velocity of mixture and solvents 1 and 2 at temperature T, respectively, f_1 and f_2 are mole fraction in case of viscosity and A_j are model constants. Correlating ability was tested by calculating average percentage deviation between experimental and calculated properties as,

$$\text{APD} = (100/N) \sum [(|y_{\text{expt}} - y_{\text{cal}}|) / y_{\text{expt}}] \quad (19)$$

Where N is number of data points in each set. Optimum numbers of constants A_j were determined from examination of APD values which presented in Table 6.

Table 6. Adjustable parameters of Eq (18) and (19) for binary liquid mixture of acrylates (1) + heptane-2-ol (2).

Property	a_0	a_1	a_2	a_3	a_4	σ	APD
MA (1) + Heptane-2-ol (2)							
η (mPa.s)	-0.5137	1.4207	5.2344	-4.5237	-9.9763	1.8944	0.0262
u (m.s ⁻¹)	0.0731	-1.0396	-1.3523	1.8935	2.0855	1258.7529	0.0229
EA (1) + Heptane-2-ol (2)							
η (mPa.s)	-0.3056	0.6470	1.7390	-3.2838	-4.8876	1.9652	0.0226
u (m.s ⁻¹)	0.0595	-0.1540	0.3806	-0.0189	-1.3528	1255.1024	0.0194
BA (1) + Heptane-2-ol (2)							
η (mPa.s)	0.0478	-0.1256	-1.4952	-0.6498	0.5697	2.1714	0.0215
u (m.s ⁻¹)	-0.0309	-0.0079	1.0897	0.0043	-2.3064	1274.4707	0.0196

RESULTS AND DISCUSSION

A graphical comparison of deviation in viscosity at 303.15 K for acrylic esters with heptane-2-ol is shown in Fig. 1.

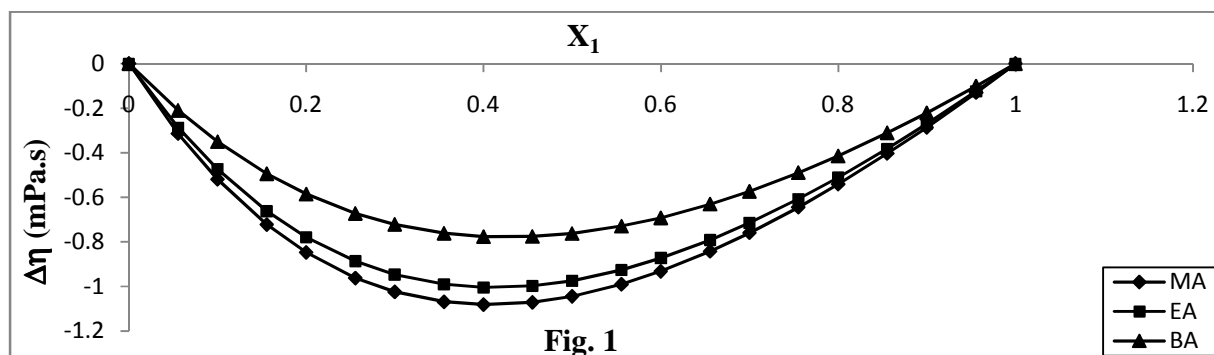


Figure 1. Variation of deviation in viscosity for binary mixtures of methyl acrylate (♦), ethyl acrylate (■), butyl acrylate (▲) (1) + heptane-2-ol (2) at 303.15 K.

Decrease in viscosity attributed to breaking of dipolar association of alkane-2-ol into small dipoles. Weak types of dipole-induced dipole type interactions are not sufficient to produce bulky or less mobile entities in system and hence decreased trend of viscosity. Strength of intermolecular electric donor-acceptor interaction is not only factor that influences viscosity deviation in liquid mixtures. Molecular size and shape of components and degree of association of mixture are equally important factors.

Breaking up of associated structures of heptane-2-ol on addition of acrylates, which is not compensated by combined effect due H-bonding between unlike molecules and interstitial fitting of smaller acrylate molecules into bigger branched decanol molecule.

A graphical comparison of deviation in isentropic compressibility at 303.15 K for acrylic esters with heptane-2-ol shown in Fig. 2.

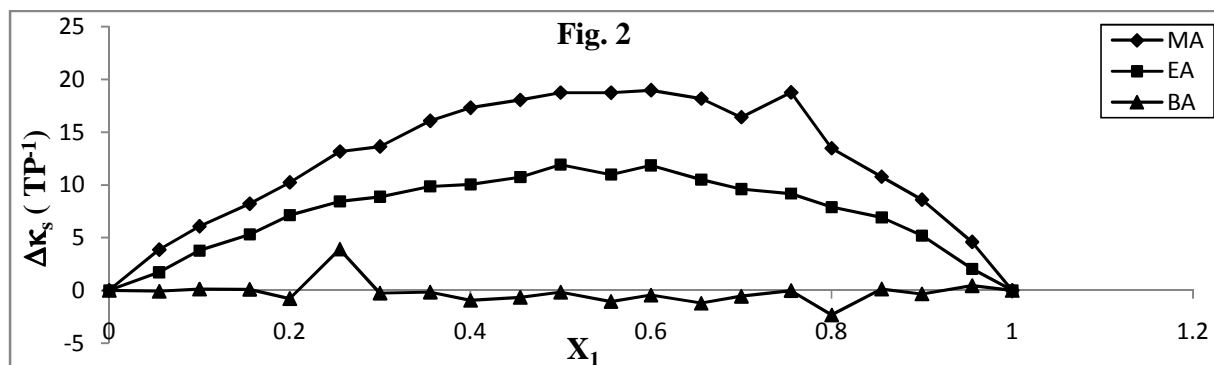


Figure 2. Variation of deviation in isentropic compressibility for binary mixtures of methyl acrylate (♦), ethyl acrylate (■), butyl acrylate (▲) (1) + heptane-2-ol (2) at 303.15 K.

Positive $\Delta\kappa_s$ values suggest that rupture of hydrogen bonded chains of dipolar interactions between acrylate molecules exceeds intermolecular interactions through dipole-dipole and hydrogen bonding between acrylate and alkanols molecules. Dipole-dipole interactions between these two component molecules decreases with increase of chain length and branching in alkanols, due to less proton donating ability in higher 2-alkanols and increased steric hindrance in branched alkanols.

The negative deviation for $\Delta\kappa_s$ values for binary liquid mixtures of butyl acrylate with 2-heptanol, indicates predominance of weak but specific structure making interactions of type $n\cdots\pi$ or $-\text{OH}\cdots\pi$ between acrylic ester's carbonyl lone pair of electrons and hydroxyl hydrogen of 2-alkanols or lone pair of electrons on oxygen of either

hydroxyl functional group of alkanols or carbonyl group of ester species and π electrons of the acrylic ester functional group.

Ultrasonic velocities with average percentage errors at 303.15 K are summarized in Table 3. A close scrutiny of result indicates that CFT does succeed in computing ultrasonic velocity value for all mixtures to a greater degree of accuracy as compared with Nomoto, Van Deal and FLT. Free length theory is naturally not applicable to systems having self associated components, hence shows large deviations from experimental values.

Table 4 shows standard deviations at 303.15 and 313.15 K for Redlich- Kister equation, which was originally developed to correlate excess Gibb's energy function and to calculate values of activity coefficients. It is a powerful and versatile correlating tool.

Similarly, parameters evaluated from equations proposed by Heric – Brewer (α_{12} , α_{21}), McAllister three body model (Z_{12} , Z_{21}) and McAllister four body model (Z_{1112} , Z_{1122} , Z_{2221}) are summarized with their standard percentage deviations in Table 5 shows values of standard errors of Heric – Brewer and McAllister three body model are exactly equal and higher than standard error of McAllister four body model in all binary liquid mixtures. Order of correlating ability of these models follows order, $(\alpha_{12}, \alpha_{21}) = (Z_{12}, Z_{21}) > (Z_{1112}, Z_{1122}, Z_{2221})$.

Experimentally measured viscosity and ultrasonic velocity were correlated using Jouyban-Acree model and constants (A_j) calculated from least square analysis with average percentage deviation (APD) are presented in Table 6.

CONCLUSION

The main effect in viscosity deviation of mixture is breaking of self interactions in compounds during mixing process. In heptane-2-ol molecule, due to decreased strength of hydrogen bonds positive values of excess isentropic compressibility are observed.

Acknowledgements

Author (SSP) acknowledge Department of Science and Technology, New Delhi, Government of India, for financial support by awarding Junior Research Fellowship. Authors are thankful to Prof. B. R. Arbad, Dr. B. A. M. University for their valuable suggestions.

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