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An ultrasonic study of acrylates with dodecane-1-ol at 313.15 K

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ABSTRACT

Ultrasonic velocities of binary liquid mixtures of methyl acrylate, ethyl acrylate, butyl acrylate and methyl methacrylate with dodecane-1-ol have been measured at 313.15 K and at atmospheric pressure. Deviations in isentropic compressibility were calculated and have been fitted to Redlich-Kister polynomial equation. Ultrasonic velocities calculated theoretically using Nomoto, Van Dael, free length theory and collision factor theory. Different derived thermodynamic parameters like relative association, molecular association, Rao's constant (molar sound velocity), excess specific acoustic impendence, excess intermolecular free length, excess available volume and excess intrinsic pressure were also calculated. Graphical representations of these parameters used to explain type and extent of intermolecular interactions in these binary systems.

Keywords Nomoto Theory, Rao's Constant, Van Dael, Redlich-Kister Equation, Molecular Interactions.

INTRODUCTION

In the recent years, much importance has been given to behavior of mixed solvents rather than a single solvent because of their wide range of applications in many chemical, industrial and biological processes. The composition and temperature dependence of volumetric, acoustic, transport and surface properties of associated liquid system provides substantial information of molecular influence on intensity of intermolecular interactions among component molecules and can be used as a powerful tool for studying intermolecular interactions in liquid systems. Ultrasonic velocity measurement of liquid mixtures of non electrolytes provides an excellent tool to investigate inter and intramolecular interactions between unlike and like molecules. Alkanols exist in form of aggregates. When they are mixed with other non electrolyte molecules, aggregates dissociate and form intermolecular complexes with unlike molecules.

The velocity of sound is very important for liquids to study molecular interactions and to elucidate internal structure of liquid mixture. The knowledge of sound velocity in liquids has been found very helpful in study of structural isomerization and molecular motions of liquid n-alkanes [1], high velocity interpartical collisions [2], ultra spectrometry for liquids [3], in multiphase flows [4], crystal growth from solutions [5], aqueous fluids [6], convective flow electrochemistry [7], desorption of metal ions from activated carbon [8], gas phase RTD measurements in gas and gas-solid reactors [9], acoustical absorption spectrometry study [10], sonochemical removal of nitric oxide from flue gases [11], shear impendence spectrometry [12]. Density and ultrasonic velocity are important basic data used in process simulation, equipment
design, solution theory and molecular dynamics [2, 3].

Literature survey reveals that, molecular interactions of present binary liquid mixtures of acrylic esters with dodecane-1-ol have not much studied, therefore, we have planned to study exhaustively kind of molecular interactions in these binary systems.

MATERIALS AND METHODS

All chemicals 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

Ultrasonic velocities were measured [13] 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 %. The experimental ultrasonic velocities of dodecane-1-ol, methyl acrylate (MA), ethyl acrylate (EA), butyl acrylate (BA) and methyl methacrylate (MMA) at 313.15 K were observed as 1350, 1118, 1123, 1157 and 1139 $m.s^{-1}$ respectively.

Computational Part

Deviation in isentropic compressibility were calculated using,

$$\Delta\kappa_s = \kappa_s - \kappa_s^{id} \quad (1)$$

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

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

κ_s^{id} was calculated from relation,

$$\kappa_s^{id} = \sum \phi i[\kappa_{s,i} + TV^o_i(\alpha^{o\,2}_i)/C_{p,i}] - [T(\sum x_iV^o_i)(\sum \phi_i \alpha^o_i)^2 / \sum x_iC_{p,i}] \quad (3)$$

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

$$\phi_i = x_iV^o_i / (\sum x_iV^o_i) \quad (4)$$

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,

$$\alpha = [(\rho_1/ \rho_2)-1]/ (T_2-T_1) \quad (5)$$

From ultrasonic velocity different thermodynamic parameters like relative association (R_A), molecular association (M_A), Rao's constant or molar sound velocity (R), 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,

$$R_A = (\rho_{mix} / \rho)(u/u_{mix})^{1/3} \quad (6)$$

$$M_A = [(u/\Sigma x_1u_1)^2-1] \quad (7)$$

$$R = (M/ \rho)\, u^{1/3} \quad (8)$$

$$Z = u\rho \quad (9)$$

$$L_f = K(\kappa_s)^{1/2} \quad (10)$$

$$V_a = V_m\,[1-(u_{expt}/u_\infty)] \quad (11)$$

Where M is average molecular weight, K is temperature dependent constant whose value is 2.030×10^{-6} at 313.15 K, u_∞ = 1600 m/s.

For binary liquid mixtures intrinsic pressure can be given as,

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

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,

$$Y^E = Y - Y^{id} \quad (13)$$

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 1.

Table 1. Ultrasonic Velocities (u), Isentropic Compressibility Deviation ($\Delta\kappa_s$), Relative association (R_A), Molecular association (M_A), Rao's constant (R), Excess specific acoustic impendence (Z^E), Excess intermolecular free length (L_f^E), Excess available volume (Va^E), Excess intrinsic pressure (π_i^E) for Acrylates (1) + Dodecane-1-ol (2).

X_1	u ($m.s^{-1}$)	$\Delta\kappa_s$ (TPa^{-1})	R_A	M_A	R	Z^E ($Kg.m^{-2}.s^{-1}$)	L_f^E (m)	Va^E ($m^3.mol^{-1}$)	π_i^E (atm)
MA (1) + Dodecane-1-ol (2)									
0	1350	0	1	0	2.512	0	0	0	0
0.0554	1336	7.92	0.002	-0.002	2.423	-4.98	0.001	1.201	-324.57
0.1000	1325	13.77	0.003	-0.003	2.350	-8.32	0.002	2.028	-381.23
0.1555	1311	21.35	0.005	-0.004	2.261	-12.75	0.002	2.987	-515.40
0.1998	1300	27.10	0.006	-0.006	2.190	-15.99	0.003	3.638	-546.12
0.2554	1287	33.16	0.007	-0.006	2.102	-19.12	0.004	4.238	-651.54
0.2999	1276	38.44	0.008	-0.007	2.032	-21.91	0.004	4.700	-659.40
0.3554	1262	45.00	0.010	-0.009	1.944	-25.35	0.006	5.191	-732.84
0.3999	1252	48.43	0.010	-0.008	1.874	-26.81	0.006	5.353	-722.16
0.4553	1239	52.78	0.011	-0.009	1.788	-28.73	0.006	5.509	-770.16
0.5000	1229	55.14	0.012	-0.008	1.719	-29.56	0.007	5.496	-740.63
0.5557	1216	57.88	0.012	-0.008	1.633	-30.55	0.007	5.422	-764.86
0.5999	1206	58.86	0.012	-0.008	1.565	-30.66	0.007	5.246	-713.38
0.6546	1193	59.73	0.013	-0.009	1.481	-30.73	0.007	4.976	-713.61
0.6999	1183	58.23	0.012	-0.008	1.412	-29.55	0.007	4.595	-648.41
0.7553	1171	54.26	0.011	-0.006	1.327	-27.09	0.007	3.998	-625.58
0.7999	1161	49.95	0.011	-0.006	1.260	-24.66	0.006	3.467	-536.80
0.8555	1149	41.35	0.009	-0.004	1.177	-20.12	0.005	2.662	-495.77
0.8999	1139	32.56	0.007	-0.004	1.110	-15.74	0.004	1.957	-384.26
0.9555	1127	17.10	0.004	-0.002	1.027	-8.24	0.002	0.939	-320.20
1	1118	0	0	0	0.962	0	0	0	0
EA (1) + Dodecane-1-ol (2)									
0	1350	0	1	0	2.514	0	0	0	0
0.0554	1339	6.11	0.001	-0.002	2.435	-3.40	0.000	1.047	-305.01
0.1000	1329	10.79	0.002	-0.003	2.373	-5.93	0.001	1.780	-361.68
0.1555	1318	16.68	0.003	-0.004	2.295	-9.07	0.001	2.623	-489.22
0.1998	1309	21.10	0.003	-0.006	2.233	-11.33	0.002	3.197	-518.52
0.2554	1298	25.54	0.004	-0.006	2.156	-13.27	0.002	3.712	-614.09
0.2999	1289	29.56	0.004	-0.007	2.094	-15.23	0.002	4.125	-620.49
0.3554	1278	33.37	0.005	-0.007	2.017	-16.76	0.003	4.447	-685.06
0.3999	1269	36.84	0.006	-0.008	1.956	-18.36	0.003	4.701	-670.49
0.4553	1259	39.83	0.006	-0.008	1.880	-19.45	0.003	4.834	-707.07
0.5000	1250	41.31	0.006	-0.008	1.820	-19.80	0.003	4.821	-674.95
0.5557	1239	43.08	0.007	-0.008	1.745	-20.28	0.004	4.763	-686.64
0.5999	1231	43.37	0.007	-0.008	1.685	-20.07	0.004	4.597	-638.05
0.6546	1220	43.65	0.007	-0.008	1.610	-19.95	0.004	4.360	-626.24
0.6999	1212	42.27	0.007	-0.008	1.550	-19.00	0.004	4.033	-561.44
0.7553	1202	38.84	0.006	-0.006	1.477	-17.05	0.003	3.506	-531.84
0.7999	1193	35.44	0.006	-0.006	1.418	-15.36	0.003	3.041	-449.86
0.8555	1183	28.87	0.004	-0.004	1.345	-12.24	0.003	2.332	-400.17
0.8999	1175	22.57	0.004	-0.004	1.286	-9.51	0.002	1.719	-303.38
0.9555	1165	11.56	0.002	-0.002	1.213	-4.69	0.001	0.821	-234.06
1	1123	0	0	0	1.156	0	0	0	0
BA (1) + Dodecane-1-ol (2)									
0	1350	0	1	0	2.512	0	0	0	0
0.0554	1339	2.94	0.000	0.000	2.456	-1.52	0.000	0.569	-211.64
0.1000	1329	6.40	0.001	-0.003	2.410	-3.59	0.001	1.142	-255.54
0.1555	1318	9.03	0.001	-0.003	2.354	-4.84	0.001	1.588	-348.67
0.1998	1309	11.28	0.001	-0.004	2.309	-5.96	0.001	1.929	-374.79

0.2554	1298	13.61	0.002	-0.004	2.253	-7.02	0.001	2.261	-441.32
0.2999	1289	15.59	0.002	-0.005	2.208	-7.98	0.001	2.510	-449.43
0.3554	1278	17.56	0.002	-0.005	2.153	-8.84	0.001	2.731	-492.01
0.3999	1269	19.21	0.003	-0.006	2.109	-9.62	0.001	2.887	-484.05
0.4553	1258	20.67	0.003	-0.006	2.053	-10.22	0.002	2.990	-505.52
0.5000	1250	20.65	0.002	-0.006	2.010	-9.90	0.001	2.934	-484.28
0.5557	1239	21.52	0.003	-0.006	1.955	-10.25	0.002	2.927	-486.22
0.5999	1231	20.87	0.002	-0.005	1.912	-9.69	0.001	2.783	-452.90
0.6546	1220	20.98	0.003	-0.006	1.857	-9.72	0.002	2.665	-436.75
0.6999	1212	19.63	0.002	-0.005	1.814	-8.90	0.001	2.435	-390.64
0.7553	1201	18.77	0.003	-0.005	1.760	-8.56	0.002	2.202	-358.49
0.7999	1193	16.52	0.002	-0.004	1.717	-7.38	0.001	1.886	-303.37
0.8555	1183	13.11	0.002	-0.003	1.664	-5.76	0.001	1.442	-259.15
0.8999	1175	9.76	0.001	-0.002	1.621	-4.23	0.001	1.041	-192.19
0.9555	1165	4.88	0.001	-0.001	1.569	-2.17	0.000	0.494	-134.07
1	1157	0	0	0	1.526	0	0	0	0
MMA (1) + Dodecane-1-ol (2)									
0	1350	0	1	0	2.512	0	0	0	0
0.0554	1337	6.47	0.002	-0.002	2.432	-4.18	0.001	1.012	-275.74
0.1000	1327	11.16	0.003	-0.003	2.369	-7.07	0.001	1.692	-320.45
0.1555	1315	16.29	0.004	-0.003	2.291	-10.05	0.002	2.378	-435.20
0.1998	1305	20.70	0.005	-0.004	2.228	-12.65	0.003	2.912	-458.00
0.2554	1293	25.36	0.006	-0.005	2.150	-15.23	0.003	3.417	-544.59
0.2999	1283	29.33	0.007	-0.006	2.088	-17.45	0.004	3.800	-548.59
0.3554	1271	33.34	0.007	-0.006	2.010	-19.52	0.004	4.123	-609.55
0.3999	1261	36.73	0.008	-0.007	1.948	-21.33	0.005	4.357	-595.41
0.4553	1249	39.89	0.009	-0.008	1.871	-22.84	0.005	4.500	-632.74
0.5000	1240	41.22	0.009	-0.007	1.810	-23.26	0.005	4.478	-604.12
0.5557	1228	43.18	0.010	-0.008	1.734	-24.08	0.005	4.443	-620.48
0.5999	1219	43.33	0.010	-0.007	1.673	-23.85	0.005	4.279	-575.72
0.6546	1208	42.43	0.009	-0.006	1.598	-22.98	0.005	3.980	-573.44
0.6999	1199	40.89	0.009	-0.006	1.537	-21.87	0.005	3.672	-514.69
0.7553	1187	38.94	0.009	-0.006	1.462	-20.67	0.005	3.280	-492.60
0.7999	1178	35.39	0.008	-0.005	1.402	-18.61	0.005	2.840	-417.80
0.8555	1167	29.00	0.006	-0.004	1.328	-15.07	0.004	2.187	-381.30
0.8999	1158	22.57	0.005	-0.004	1.269	-11.67	0.003	1.610	-289.74
0.9555	1148	10.57	0.002	-0.001	1.195	-5.39	0.001	0.718	-236.92
1	1139	0	0	0	1.136	0	0	0	0

Nomoto [14] 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,

$$R = x_1R_1 + x_2R_2 \quad (14)$$

where R_1 and R_2 are molar sound velocities, x_1 and x_2 are mole fractions respectively. The molar sound velocity (R) also known as Rao's constant, is related to sound velocity (u) and density (ρ) by relation,

$$R = (M / \rho)\, U^{1/3} \quad (15)$$

Hence, speed of sound is given by,

$$u = (R/V)^3 = [(x_1R_1 + x_2 R_2)/ (x_1V_1 + x_2V_2)]^3 \quad (16)$$

According to Van Dael and Vangeel [15] assumption adiabatic compressibility (βs) of mixture given by,

$$\beta s_{(im)} = \phi_1 v_1 \beta s_{(1)} / v_{im} + \phi_2 v_2 \beta s_{(2)} / v_{im} \quad (17)$$

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

Schaffs [16, 17] on basis of collision factor theory gave relation for sound velocity in liquids,

$$u = u_\infty Srf = u_\infty SB/V \quad (18)$$

Where u_∞ = 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 [18, 19] free length theory is,

$$u_{mix} = K/ (L_{f(mix)}\rho_{(mix)}^{1/2}) \quad (19)$$

Where K is a temperature dependent constant.

Ultrasonic velocities from these theories with percentage error are given in Table 2.

Table 2. Comparison of experimental ultrasonic velocity from various theories with % errors for Acrylates (1) + Dodecane-1-ol (2).

X_1	Ultrasonic Velocity					% Errors for Ultrasonic Velocity			
	Expt.	NOM	VAN	CFT	FLT	NOM	VAN	CFT	FLT
MA (1) + Dodecane-1-ol (2)									
0	1350	1350	1350	1350	1343	9.57	63.21	4.55	0.71
0.0554	1336	1344	1295	1341	1330				
0.1000	1325	1339	1259	1335	1322				
0.1555	1311	1333	1220	1326	1310				
0.1998	1300	1327	1195	1319	1300				
0.2554	1287	1320	1167	1309	1288				
0.2999	1276	1314	1149	1302	1278				
0.3554	1262	1305	1130	1292	1265				
0.3999	1252	1298	1117	1284	1255				
0.4553	1239	1288	1104	1273	1242				
0.5000	1229	1280	1095	1264	1231				
0.5557	1216	1268	1088	1252	1218				
0.5999	1206	1259	1083	1242	1207				
0.6546	1193	1245	1080	1229	1193				
0.6999	1183	1233	1079	1218	1181				
0.7553	1171	1217	1081	1203	1165				
0.7999	1161	1203	1084	1190	1153				
0.8555	1149	1183	1090	1173	1137				
0.8999	1139	1165	1096	1158	1123				
0.9555	1127	1140	1107	1137	1105				
1	1118	1118	1118	1118	1090				
EA (1) + Dodecane-1-ol (2)									
0	1350	1350	1350	1350	1343	1.59	49.48	0.61	4.91
0.0554	1339	1343	1308	1341	1331				
0.1000	1329	1338	1279	1333	1321				
0.1555	1318	1330	1247	1323	1309				
0.1998	1309	1324	1225	1315	1299				
0.2554	1298	1316	1202	1305	1287				
0.2999	1289	1309	1185	1297	1277				
0.3554	1278	1299	1167	1286	1264				
0.3999	1269	1291	1155	1277	1254				
0.4553	1259	1281	1142	1266	1241				
0.5000	1250	1272	1134	1256	1230				
0.5557	1239	1260	1125	1244	1217				
0.5999	1231	1250	1119	1234	1206				
0.6546	1220	1237	1114	1222	1193				
0.6999	1212	1225	1111	1211	1181				
0.7553	1202	1210	1109	1196	1167				
0.7999	1193	1196	1109	1185	1155				
0.8555	1183	1178	1111	1169	1140				
0.8999	1175	1163	1113	1156	1128				
0.9555	1165	1142	1118	1138	1112				
1	1123	1123	1123	1123	1098				
BA (1) + Dodecane-1-ol (2)									
0	1350	1350	1350	1350	1343	1.70	6.94	0.72	36.50
0.0554	1339	1343	1326	1341	1339				
0.1000	1329	1337	1309	1334	1336				
0.1555	1318	1329	1289	1325	1332				
0.1998	1309	1322	1275	1318	1329				
0.2554	1298	1314	1259	1308	1325				
0.2999	1289	1307	1247	1301	1322				
0.3554	1278	1298	1233	1291	1318				
0.3999	1269	1290	1223	1283	1316				
0.4553	1258	1280	1212	1273	1312				
0.5000	1250	1272	1204	1264	1310				
0.5557	1239	1262	1195	1254	1306				
0.5999	1231	1253	1188	1245	1304				
0.6546	1220	1242	1181	1234	1300				
0.6999	1212	1232	1176	1225	1298				
0.7553	1201	1220	1171	1213	1295				

0.7999	1193	1209	1167	1204	1293				
0.8555	1183	1196	1163	1191	1290				
0.8999	1175	1184	1161	1181	1288				
0.9555	1165	1169	1158	1168	1284				
1	1157	1157	1157	1157	1284				
				MMA (1) + Dodecane-1-ol (2)					
0	1350	1350	1350	1350	1343	5.36	30.72	2.21	0.15
0.0554	1337	1344	1310	1342	1333				
0.1000	1327	1339	1283	1335	1324				
0.1555	1315	1332	1253	1326	1314				
0.1998	1305	1326	1232	1319	1305				
0.2554	1293	1319	1210	1309	1294				
0.2999	1283	1312	1194	1302	1286				
0.3554	1271	1304	1177	1292	1275				
0.3999	1261	1297	1166	1284	1266				
0.4553	1249	1287	1154	1274	1255				
0.5000	1240	1279	1145	1265	1246				
0.5557	1228	1268	1137	1254	1235				
0.5999	1219	1259	1132	1245	1226				
0.6546	1208	1247	1127	1233	1214				
0.6999	1199	1236	1125	1222	1205				
0.7553	1187	1221	1124	1209	1193				
0.7999	1178	1209	1124	1198	1183				
0.8555	1167	1192	1126	1183	1170				
0.8999	1158	1177	1128	1170	1159				
0.9555	1148	1157	1133	1153	1145				
1	1139	1139	1139	1139	1135				

Deviation in isentropic compressibility were fitted to Redlich-Kister [20] equation of type,

$$Y = x_1x_2 \sum_{i}^{n} a_i (x_1 - x_2)^i \qquad (20)$$

Where Y is $\Delta\kappa_s$ and n is degree of polynomial. Coefficient a_i was obtained by fitting Eq (20) 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,

$$\sigma(Y) = \left[\frac{\sum (Y_{\exp t} - Y_{calc})^2}{N - n} \right]^{1/2} \qquad (21)$$

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 3.

Table 3. Adjustable parameters of Eq (20) and (21) for deviation in isentropic compressibility for Acrylates (1) + Dodecane-1-ol (2).

a_0	a_1	a_2	a_3	a_4	σ
		MA (1) + Dodecane-1-ol (2)			
61.5299	40.1742	5.0251	20.7947	29.5254	0.40274
		EA (1) + Dodecane-1-ol (2)			
27.5067	25.2496	7.8912	3.2143	4.5368	0.30337
		BA (1) + Dodecane-1-ol (2)			
4.9431	6.3279	12.1135	6.7849	-14.9327	0.34535
		MMA (1) + Dodecane-1-ol (2)			
45.8629	35.0981	16.9710	-10.3237	-6.3066	0.53175

RESULTS AND DISCUSSION

Figure 1 represents graphical variation of deviation in isentropic compressibility for acrylates with dodecane-1-ol, which 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 [21] interactions, interstitial accommodation and orientational ordering lead to a more compact structure, making $\Delta\kappa_s$ negative and breakup of the alkanols structures tend to make $\Delta\kappa_s$ positive. Positive values of $\Delta\kappa_s$ observed when H-bonded aggregates of dodecane-1-ol break up progressively with addition of acrylate. De-clustering of dodecane-1-ol in presence of acrylates may also lead to positive $\Delta\kappa_s$ values. There is high tendency of 1-alkanols to undergo self association via intermolecular hydrogen bonding.

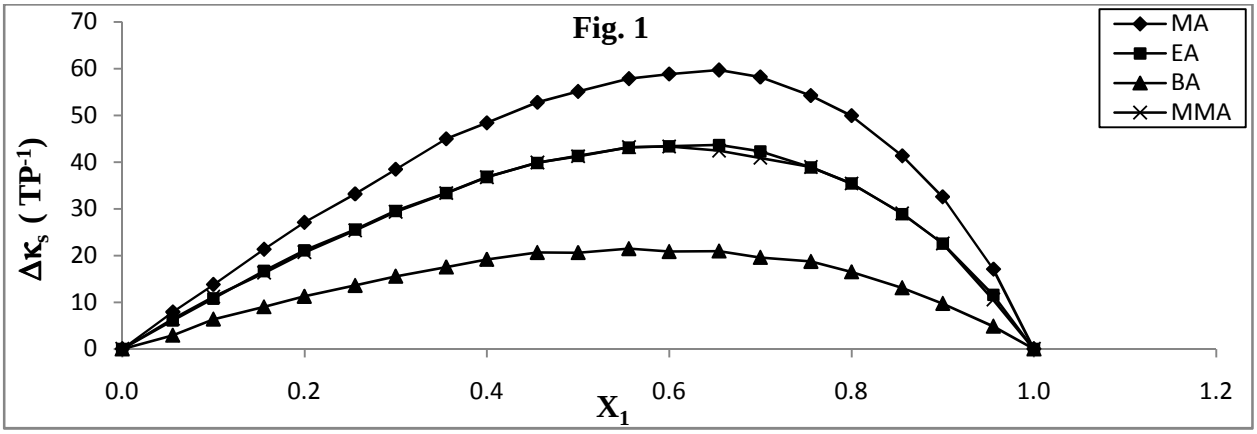

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Figure 1. Variation of deviation in isentropic compressibility for acrylic esters (1) + dodecane-1-ol (2).

It is well known that 1-alkanols form a variety of species with different degrees of association in pure state; polymeric linear associates are expected to be predominant in pure state. Addition of acrylate to dodecane-1-ol may results in following effects:

(i) Rupturing or disruption of associate structures in alkanols.
(ii) Formation of new species because of weak interactions between ester and alkanols.
(iii) Free volume changes upon mixing of components of different sizes.

The first effect contributes positively to deviation in isentropic compressibilities and negatively to deviation in viscosities. However, contributions due to effects (ii) and (iii) are in opposite directions [22].

Nikam [23] have shown that, R_A is influenced by two factors, (i) breaking of solvent molecules on mixing and (ii) specific interactions leading to complex formation between molecules of system. The former resulting in decrease and latter in an increase of relative association. Hence by considering second factor, it can be concluded that, specific intermolecular interactions are present and which are responsible for formation of complexes between the component molecules.

Molecular association (M_A) is a measure of non-ideality of system [24]. Generally, these values become negative as strength of interaction between component molecules increases.

Rao's constant or molar sound velocity (R) gives information on formation of a complex [25, 26] and on association of components. The values of R are sensitive to structure of molecules [27]. These values are not greatly influenced by temperature. This is in accordance with the theoretical expectation that R is independent of temperature [28, 29].

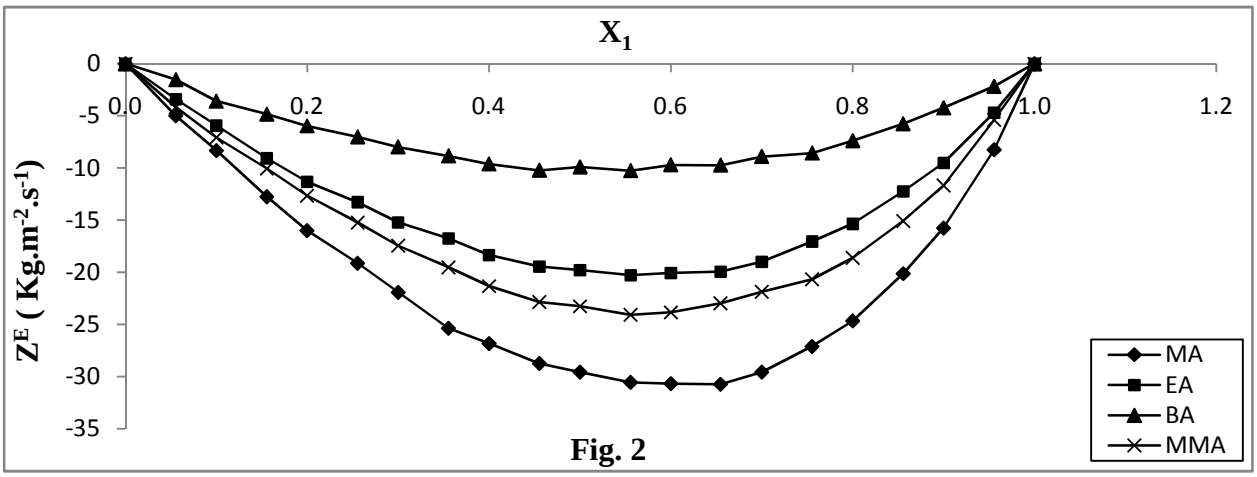

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Figure 2. Variation of excess specific acoustic impedance for acrylic esters (1) + dodecane-1-ol (2).

Figure 2 represents graphical variation of Z^E for acrylates with dodecane-1-ol. The curves exhibit negative values as chain length and branching of acrylates decreases which also show weak interactions between the component molecules. Z^E are more negative for mixtures containing branched acrylates due to more steric hindrance towards heteromolecular interactions. Similar behaviour was also reported for DMSO + toluene [30] and toluene + iso-butyl methyl ketone [31] binary mixtures.

Table 1 shows values of excess intermolecular free length to be positive for all systems. The trends are symmetric in all systems and follow same order as in case of deviation in isentropic compressibility. In pure alkanols such as, dodecane-1-ol molecules are self associated through hydrogen bond, mixing of acrylates will induce rupture of hydrogen bonds in liquids with subsequent increase in L_f^E values. Similar results were reported earlier by Ali [32].

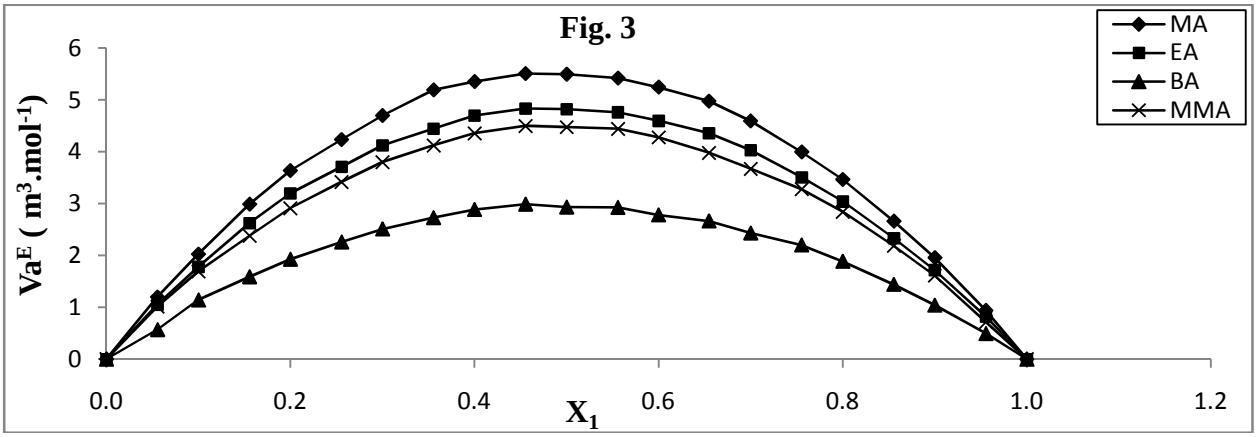

Figure 3. Variation of excess available volume for acrylic esters (1) + dodecane-1-ol (2).

Figure 3 represents graphical variation of V_a^E for acrylates with dodecane-1-ol. These positive values may be attributed to strong interactions between acrylates and dodecane-1-ol. Negative values suggest 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.

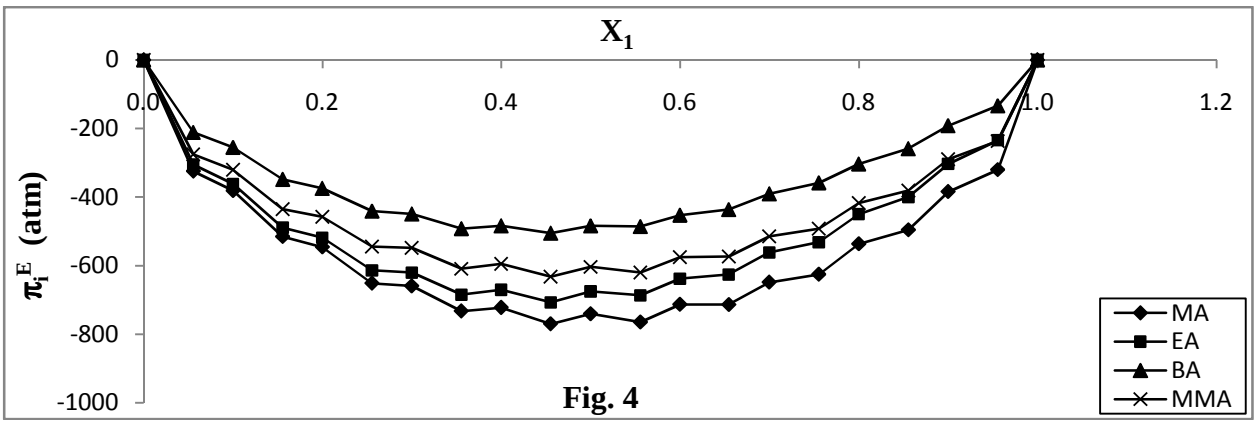

Figure 4. Variation of excess intrinsic pressure for acrylic esters (1) + dodecane-1-ol (2).

The variations of excess internal pressure (π_i^E) are represented in Figure 4. Excess internal pressure π_i^E has been used [33] to study the intermolecular interactions in binary liquid mixtures. The values of π_i^E are found to be negative in all binary mixtures of dodecane-1-ol with acrylates suggesting weak interactions.

Ultrasonic velocities for all binary mixtures have also been calculated theoretically using Nomoto, Van Dael, Jacobson's free length theory (FLT) and collision factor theory (CFT). Calculated ultrasonic velocities along with average percentage error are summarized in Table 2. A close scrutiny of result indicates that CFT does succeed in computing the ultrasonic velocity value for all mixtures studied in the present investigation to a greater degree of accuracy as compared with Nomoto, Van Dael and FLT. Naturally FLT is not applicable to systems having self associated components and hence shows error range much larger for all binary mixtures.

Evaluated values of deviation isentropic compressibility ($\Delta\kappa_s$) were fitted to Redlich-Kister polynomial equation represented in Table 3 with standard percentage deviation. It is a powerful and versatile correlating tool for various excess thermodynamic properties. 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 [34]. Redlich-Kister regressor is very powerful and frequently used to correlate vapor-liquid equilibrium data [35].

CONCLUSION

In the present paper, an attempt is made to measure density, viscosity and speed of sound of methyl acrylate, ethyl acrylate, butyl acrylate and methyl methacrylate with dodecane-1-ol at 313.15 K. Positive values of deviation in isentropic compressibility ($\Delta\kappa_s$) signify decreasing dipole-dipole interactions due to decreasing proton donating abilities. The increase in molar sound velocity (R) with mole fraction indicates specific interactions while decrease in these values suggests the presence of dispersive forces between the components of the binary liquid mixtures. Negative values of excess specific acoustic impedance (Z^E) suggest that, dispersive forces are dominant over specific interaction and positive values indicate the presence of strong specific interactions. Excess intermolecular free length (L_f^E) values decreases with increase of chain length and branching of acrylates. Positive values of excess available volume (V_a^E) indicate presence of strong specific interaction. Values of excess intrinsic pressure (π_i^E) are found to be negative suggesting weak interactions. It may be concluded that, Schaff''s collision factor theory (CFT) is most suitable for the present binary liquid systems.

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