Ultrasonic Velocities of Acrylates with 2-Hexanol

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Abstract
Ultrasonic velocities of binary liquid mixtures of methyl acrylate, ethyl acrylate and butyl acrylate with hexane-2-ol have been measured at 313.15 K and at atmospheric pressure. Deviations in isentropic compressibility were calculated using ultrasonic velocity and have been fitted to Redlich-Kister polynomial equation. Ultrasonic velocities were calculated theoretically using Nomoto, Van Dael, free length theory and collision factor theory. Graphical representation of excess thermodynamic parameter such as deviation in isentropic compressibility used to explain type and extent of intermolecular interactions in present binary liquid systems.

Keywords Ultrasonic Velocity, Van Dael, Free Length Theory, Redlich Kister Equation.
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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 physico-chemical data are often required in many industrial processes (flow, mass transfer or heat transfer calculation, polymerization, solvolysis, etc.) and also leads to formulations of a large number of methods for correlating or predicting physical properties. Therefore in view of practical importance of mixed solvents, a deeper knowledge of their solution structure and intermolecular interactions between component molecules at molecular level thus becomes essential. Recently, researchers in this field have been focusing their interest more sharply on molecular structure along with some representative macroscopic property that serves to characterize it. 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 these 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.

Experimental

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 one pan balance, with an accuracy of ± 0.01 mg. Ultrasonic velocities were measured [1] at frequency of 2 MHz by single crystal ultrasonic interferometer (F-81 Mittal Enterprises, New Delhi, India). Accuracy in velocity measurements is ± 0.1 %.

The experimental ultrasonic velocities of methyl acrylate (MA), ethyl acrylate (EA), butyl acrylate (BA) and hexane-2-ol at 313.15 K observed as 1118 $m.s^{-1}$, 1123 $m.s^{-1}$, 1157 $m.s^{-1}$ and 1243 $m.s^{-1}$ (1242 $m.s^{-1}$) [2] respectively. Value in parenthesis is from literature.

Deviation in isentropic compressibility were calculated using relation as follows,

$$\Delta\kappa_s / TPa^{-1} = \kappa_s - \kappa_s^{id} \qquad (1)$$

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

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

κ_s^{id} was calculated from relation,

$$\kappa_s^{id} = \sum \phi i[\kappa_{s,i} + TV^o_i(\alpha^o_i{}^2)/C_{p,i}] - [T(\sum x_i V^o_i)(\sum \phi_i \alpha^o_i)^2 / \sum x_i C_{p,i}] \qquad (3)$$

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

$$\phi_i = x_i V^o_i / (\sum x_i V^o_i) \qquad (4)$$

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,

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

Nomoto [3] 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,

$$R = x_1R_1 + x_2R_2 \qquad (6)$$

where R_1 and R_2 are molar sound velocities, x_1 and x_2 are mole fractions respectively.

According to Vangeel [4] assumption adiabatic compressibility (βs) of mixture is,

$$\beta s_{(im)} = \phi_1 v_1 \beta s_{(1)} /v_{im} + \phi_2 v_2 \beta s_{(2)} /v_{im} \qquad (7)$$

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

Schaffs [5, 6] on basis of collision factor theory gave relation for velocity in liquids,

$$u = u_\infty Srf = u_\infty SB/V$$

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.

Sound velocity in mixtures evaluated from Jacobson's [7, 8] free length theory is,

$$u_{mix} = K/ (L_{f(mix)}\rho_{(mix)}^{1/2}) \qquad (9)$$

Where K is a temperature dependent constant.

Ultrasonic velocities, deviation in isentropic compressibilities and ultrasonic velocities derived from various theories with percentage error represented in Table 1.

Deviation in isentropic compressibility were fitted to Redlich-Kister [9] equation,

$$Y = x_1 x_2 \sum_{i}^{n} a_i (x_1 - x_2)^i \qquad (10)$$

Where Y is $\Delta\kappa_s$ and n is degree of polynomial. Coefficient a_i was obtained by fitting Eq (10) to experimental results using a least-squares regression method. Optimum number of coefficients is ascertained from examination of variation in standard deviation (σ) calculated using relation,

$$\sigma\,(Y) = \left[\frac{\sum (Y_{\exp t} - Y_{calc})^2}{N - n} \right]^{1/2} \qquad (11)$$

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 2.

Results and Discussion

Figure 1 represents graphical variation of deviation in isentropic compressibility for acrylates with hexane-2-ol at 313.15 K. Variations in ultrasonic velocity and compressibilities 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 the alkanols structures tend to make $\Delta\kappa_s$ positive.

Sign of $\Delta\kappa_s$ decides compactness due to molecular rearrangement. The magnitude of various contributions depends mainly on relative molecular size of components. The positive values of $\Delta\kappa_s$ signify decreasing dipole-dipole interactions due to decreasing proton donating abilities. De-clustering of hexane-2-ol in presence of acrylates may also lead to positive $\Delta\kappa_s$ values. There is high tendency of 2-alkanols to undergo self association via intermolecular hydrogen bonding.

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 1. 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. Free length theory is naturally not applicable to systems having self associated components. The error range in the case of FLT is much larger for all the binary mixtures.

Evaluated values of deviation isentropic compressibility ($\Delta\kappa_s$) were fitted to Redlich-Kister polynomial equation represented in Table 2 with standard percentage deviation. Redlich- Kister equation 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 that its use has been extended to other properties such as deviation isentropic compressibility.

Acknowledgement

Tables:

Table 1. Ultrasonic velocities (u), deviation in isentropic compressibilities ($\Delta\kappa_s$), ultrasonic velocities derived from Nomato, Van Deal, CFT and FLT theories with % errors for Acrylates (1) + Hexane-2-ol (2) at 313.15 K.

X_1	u (m.s^{-1})	$\Delta\kappa_s$ (TPa^{-1})	Ultrasonic Velocity				% Errors for Ultrasonic Velocity			
			NOM	VAN	CFT	FLT	NOM	VAN	CFT	FLT
Methyl Acrylate + Hexane-2-ol										
0	1243	0	1243	1243	1243	1219	0	0	0	3.606
0.055	1236	2.26	1238	1233	1236	1210	0.021	0.073	0	4.341
0.100	1230	4.26	1233	1225	1230	1204	0.077	0.191	0.001	4.573
0.155	1223	6.10	1228	1215	1223	1195	0.159	0.411	0.001	5.102
0.200	1217	7.98	1223	1208	1218	1189	0.269	0.557	0.004	5.359
0.255	1210	9.45	1217	1199	1211	1181	0.38	0.789	0.005	5.823
0.300	1204	11.04	1213	1193	1205	1174	0.516	0.892	0.011	6.005
0.355	1197	12.16	1206	1185	1198	1167	0.627	1.049	0.012	6.38
0.400	1191	13.44	1201	1179	1193	1161	0.761	1.067	0.022	6.464
0.455	1184	14.14	1195	1172	1186	1153	0.842	1.114	0.024	6.74
0.500	1179	13.61	1189	1166	1180	1148	0.792	1.215	0.012	7.096
0.555	1172	13.85	1183	1159	1173	1140	0.816	1.146	0.014	7.29
0.600	1166	14.38	1177	1154	1168	1135	0.871	0.983	0.024	7.202
0.655	1160	12.66	1170	1149	1161	1128	0.686	0.979	0.006	7.654
0.700	1154	12.66	1164	1144	1155	1122	0.678	0.762	0.013	7.458
0.755	1147	11.82	1156	1139	1148	1116	0.586	0.542	0.016	7.291
0.800	1142	9.83	1149	1134	1143	1111	0.409	0.443	0.006	7.431
0.856	1135	8.18	1141	1129	1136	1105	0.28	0.236	0.007	7.169
0.900	1130	5.68	1134	1126	1130	1100	0.136	0.14	0.001	7.18
0.955	1123	3.41	1125	1121	1123	1093	0.043	0.021	0.001	7.036
1	1118	0	1118	1118	1118	1090	0	0	0	6.438
Ethyl Acrylate + Hexane-2-ol										
0	1243	0	1243	1243	1243	1219	0	0	0	3.606
0.055	1236	1.01	1237	1235	1236	1212	0.007	0.004	0	3.913
0.100	1230	2.26	1232	1229	1231	1205	0.029	0.007	0.002	4.126
0.155	1224	1.81	1226	1221	1224	1197	0.025	0.045	0.001	4.816
0.200	1218	3.03	1221	1215	1218	1191	0.06	0.043	0	4.891

0.255	1211	3.84	1215	1208	1211	1184	0.092	0.054	0.001	5.148
0.300	1206	3.63	1210	1202	1206	1178	0.089	0.086	0	5.534
0.355	1199	4.33	1203	1195	1199	1170	0.122	0.089	0	5.683
0.400	1194	4.03	1198	1190	1194	1165	0.112	0.118	0.001	6.011
0.455	1187	4.62	1191	1183	1187	1158	0.14	0.107	0	6.035
0.500	1182	4.24	1186	1178	1182	1152	0.124	0.127	0.001	6.334
0.556	1175	4.67	1179	1171	1175	1146	0.143	0.104	0	6.21
0.600	1170	4.18	1174	1166	1170	1141	0.12	0.112	0.001	6.342
0.655	1163	4.56	1167	1160	1163	1134	0.132	0.077	0	6.144
0.700	1158	3.98	1162	1155	1158	1129	0.105	0.075	0	6.169
0.755	1151	4.18	1155	1149	1151	1123	0.105	0.041	0.001	5.891
0.800	1146	3.40	1149	1144	1146	1118	0.073	0.035	0	5.847
0.856	1140	1.94	1142	1138	1140	1112	0.029	0.034	0.001	5.831
0.900	1135	1.07	1136	1133	1135	1108	0.011	0.023	0.001	5.703
0.955	1128	0.90	1129	1128	1128	1103	0.006	0.002	0.001	4.993
1	1123	0	1123	1123	1123	1098	0	0	0	5.118
Butyl Acrylate + Hexane-2-ol										
0	1243	0	1243	1243	1243	1219	0	0	0	3.606
0.055	1238	-0.93	1238	1237	1238	1222	0.002	0.006	0	1.667
0.100	1234	-1.55	1233	1232	1234	1224	0.004	0.016	0	0.64
0.155	1229	-2.21	1228	1227	1229	1227	0.009	0.033	0	0.026
0.200	1225	-2.61	1224	1222	1225	1229	0.012	0.047	0	0.125
0.255	1220	-2.97	1219	1217	1220	1232	0.015	0.062	0.001	1.027
0.300	1217	-4.52	1214	1213	1216	1235	0.045	0.122	0.002	2.158
0.356	1212	-4.63	1209	1208	1212	1238	0.045	0.131	0.001	4.656
0.400	1208	-4.60	1205	1204	1208	1241	0.044	0.132	0.001	7.384
0.455	1203	-4.41	1201	1199	1203	1244	0.039	0.126	0	11.693
0.500	1199	-4.21	1197	1195	1199	1247	0.034	0.118	0	16.069
0.556	1194	-3.81	1192	1190	1194	1251	0.026	0.101	0.001	22.543
0.600	1191	-4.75	1188	1187	1191	1254	0.049	0.138	0.001	27.694
0.655	1186	-4.09	1184	1182	1186	1257	0.034	0.106	0	36.312
0.700	1182	-3.48	1180	1179	1182	1261	0.023	0.08	0	44.299
0.755	1177	-2.57	1176	1174	1177	1265	0.011	0.048	0.001	55.478
0.800	1174	-3.20	1172	1171	1174	1268	0.023	0.062	0.001	64.074
0.855	1169	-2.06	1168	1167	1169	1272	0.008	0.028	0	77.975
0.900	1165	-1.07	1165	1164	1165	1276	0.002	0.009	0.001	90.254
0.956	1161	-1.16	1160	1160	1161	1280	0.003	0.007	0.001	105.19
1	1157	0	1157	1157	1157	1284	0	0	0	120.08

Table 2. Parameters of Redlich-Kister polynomial equation for deviation in isentropic compressibilities for Acrylates (1) + Hexane-2-ol (2) at 313.15 K.

Property	a_0	a_1	a_2	a_3	a_4	σ
	Methyl Acrylate + Hexane-2-ol					
κ_s^E /(TPa^{-1})	41.0059	3.5098	-11.1253	13.8390	18.4998	0.39048
	Ethyl Acrylate + Hexane-2-ol					
κ_s^E /(TPa^{-1})	8.6617	1.9202	-1.9092	-6.2032	3.7622	0.42123
	Butyl Acrylate + Hexane-2-ol					
κ_s^E /(TPa^{-1})	-14.4691	4.1375	15.1145	-8.8856	-21.2241	0.46749

Figure:
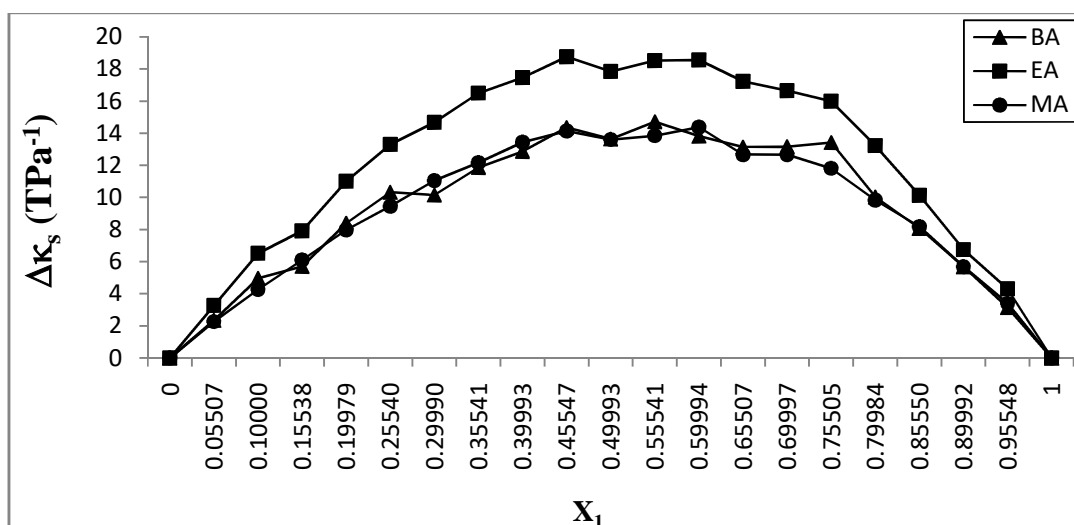
Figure 1: Plot of deviation in isentropic compressibility ($\Delta\kappa_s$) against mole fraction for

Acrylates (1) + Hexane-2-ol (2) at 313.15

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