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Ultrasonic Velocity of Acrylates with Decane-2-ol at 313.15 K

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Abstract
Thermodynamic data involving ultrasonic velocities of binary liquid mixtures of methyl acrylate, ethyl acrylate and butyl acrylate with decane-2-ol have been measured at 313.15 K and at atmospheric pressure. Study of thermodynamic properties involves challenges of interpreting the excess quantities as a means of understanding the nature of intermolecular interactions among the mixed components. Experimental values of ultrasonic velocities were correlated with recently proposed Jouyban-Acree model. Deviations in isentropic compressibility were calculated and have been fitted to Redlich-Kister polynomial equation. Excess parameters like specific acoustic impendence, intermolecular free length, available volume, intrinsic pressure, molecular association and molar sound velocity were also calculated. Graphical representations of excess derived thermodynamic parameters used to explain the type and extent of intermolecular interactions.
Keywords: *Intramolecular interactions, isentropic compressibility, specific acoustic impendence, available volume, Jouyban Acree model.*

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I. Introduction

Thermodynamic properties are essential in designing industrial equipments. There has been an increasing interest in the study of molecular interactions and a number of experimental techniques have been used to investigate the interactions between the components of binary liquid mixtures. The knowledge of thermodynamic properties of liquid-liquid systems is of considerable importance due to their wide range of applicability as solvent media in various physicochemical studies, in processing and product formation. Study of thermodynamic properties involves challenges of interpreting the excess quantities as a means of understanding the nature of intermolecular interactions among the mixed components. The knowledge of sound velocity in liquids has been found very helpful in the study of ultra-spectrometry for liquids[1], in multiphase flows[2], crystal growth from solutions[3], structural isomerization and molecular motions of liquid n-alkanes[4], sonochemical removal of nitric oxide from flue gases[5], shear impendence spectrometry[6], ultrasonic spectrometry of polystyrene latex suspensions[7]. Density and ultrasonic velocity are important basic data used in process simulation, equipment design, solution theory and molecular dynamics[8].

II. Materials And Methods

Chemicals used in present study were of analytical grade and supplied by S. D. Fine Chemicals Pvt., Mumbai (India) with quoted mass fraction purities: decane-2-ol (> 0.998), methyl acrylate, MA, (> 0.997), ethyl acrylate, EA, (> 0.998) and butyl acrylate, BA, (> 0.995).

Experimental Part

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. Ultrasonic velocities were measured at frequency of 2 MHz by a single crystal ultrasonic interferometer (Model F-81, Mittal Enterprises, New Delhi, India) [9]. Temperature was controlled using water bath (Gemini Scientific Instruments, Chennai, India) having accuracy ± 0.02 ^{0}C.

Ultrasonic velocities of decane-2-ol, methyl acrylate, ethyl acrylate and butyl acrylate at 313.15 K were observed as 1362, 1118, 1123 and 1157 m.s^{-1} respectively.

Computational Part

Deviation in isentropic compressibility were calculated using relation,

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

Where κ_S is isentropic compressibility and was calculated using Laplace relation,

$$\kappa_S = (1/ u2\rho) \quad (2)$$

κs^{id} was calculated from relation,

$$\kappa s^{id} = \Sigma \phi i[\kappa s,i + TVoi(\alpha oi2) / Cp,i] - [T(\Sigma xiVoi) (\Sigma \phi i\alpha oi)2 / \Sigma xiCp,i] \quad (3)$$

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

$$\phi i = xiVoi / (\Sigma xiVoi) \quad (4)$$

T is temperature and $\kappa s,i$, Voi, αoi, and Cp,i are isentropic compressibility, molar volume, coefficient of isobaric thermal expansion and molar heat capacity respectively, for pure component i. αoi is calculated from measured densities by relation,

$$\alpha = [(\rho 1/ \rho 2)-1] / (T2-T1) \quad (5)$$

From ultrasonic velocity different thermodynamic parameters like specific acoustic impendence (Z), intermolecular free length (Lf), available volume (Va), intrinsic pressure (πint), can be calculated, which provides better insight in understanding of molecular interactions in pure and binary liquids mixtures, which are given by relations,

$$Z = u\rho \quad (6)$$

$$Lf = K(\kappa s)1/2 \quad (7)$$

$$Va = Vm [1-(uexpt /u\infty)] \quad (8)$$

Where K is the temperature dependent constant whose values are 1.976×10^{-6} at 313.15 K respectively, $u\infty$ = 1600 m/s.

For binary liquid mixtures intrinsic pressure can be given as,

$$\pi i = bRT (K\eta 12/u12)1/2(\rho 122/3/M127/6) \quad (9)$$

Where b is packing factor, K is a temperature independent constant having value of 4.28×10^9, R is gas constant and η_{12}, u_{12}, ρ_{12} are viscosity, ultrasonic velocity and density of mixture respectively.

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 same conditions of temperature, pressure and composition. It is expressed by following relation,

$$Y^E = Y- Y^{id} \quad (10)$$

Where Y denotes Z, Lf, Va, πint and Y^E represents corresponding excess thermodynamic properties such as excess specific acoustic impedance (Z^E), excess intermolecular free length (Lf^E), excess available volume (Va^E) and excess intrinsic pressure (πint^E).

Molecular association (M_A) and Rao's constant or molar sound velocity (R) for liquid mixtures can be calculated as,

$$M_A = [(u/\Sigma x1u1)2-1] \quad (11)$$

$$R = (M/ \rho) u1/3 \quad (12)$$

Where M is average molecular weight.

Table No. 1: Ultrasonic Velocities (u), Isentropic Compressibility Deviation ($\Delta\kappa s$), Excess specific acoustic impendence (Z^E), Excess intermolecular free length (L_f^E), Excess available volume (Va^E), Excess intrinsic pressure (πint^E), Molecular association (M_A) and Rao's constant (R) for Acrylates (1) + Decane-2-ol (2) at 313.15 K.

X_1	u	$\Delta\kappa s$	Z^E	L_f^E	Va^E	π_{int}^E	M_A	R
	($m.s^{-1}$)	(TPa^{-1})	($Kg.m^{-2}.s^{-1}$)	(m)	($m^3.mol^{-1}$)	(atm)		
	Methyl Acrylate + Decane-2-ol							
0	1362	0	0	0	0	0	0	2.171
0.0552	1347	7.36	-4.96	0.001	1.017	-224.10	-0.002	2.101
0.0997	1335	13.08	-8.59	0.002	1.751	-254.20	-0.004	2.045
0.1555	1321	19.04	-12.15	0.002	2.453	-346.15	-0.005	1.976
0.1999	1309	24.54	-15.50	0.003	3.033	-360.40	-0.006	1.920
0.2554	1295	30.09	-18.63	0.004	3.555	-431.51	-0.007	1.851
0.3000	1284	34.01	-20.72	0.004	3.875	-433.76	-0.007	1.796
0.3555	1270	38.85	-23.26	0.005	4.213	-487.36	-0.008	1.728
0.3999	1259	42.17	-24.90	0.005	4.393	-474.87	-0.009	1.674
0.4538	1245	46.47	-27.09	0.006	4.585	-507.88	-0.010	1.608
0.4999	1234	48.37	-27.77	0.006	4.578	-492.04	-0.010	1.552
0.5554	1221	49.66	-28.00	0.006	4.465	-510.55	-0.009	1.485
0.5999	1210	50.69	-28.26	0.006	4.351	-473.90	-0.009	1.432
0.6550	1197	50.18	-27.51	0.006	4.074	-480.36	-0.009	1.366
0.6999	1186	49.30	-26.75	0.006	3.806	-432.72	-0.009	1.312
0.7555	1173	45.94	-24.56	0.006	3.337	-423.18	-0.008	1.247
0.7999	1163	41.39	-21.85	0.005	2.867	-361.27	-0.007	1.194
0.8555	1150	34.41	-17.96	0.005	2.228	-338.55	-0.006	1.129

0.8999	1140	26.41	-13.64	0.003	1.620	-262.39	-0.004	1.077
0.9555	1128	12.84	-6.51	0.002	0.743	-227.48	-0.002	1.013
1	1118	0	0	0	0	0	0	0.962
	Ethyl Acrylate + Decane-2-ol							
0	1362	0	0	0	0	0	0	2.171
0.0554	1348	4.69	-2.58	0.000	0.757	-186.63	-0.001	2.112
0.0999	1336	9.18	-5.23	0.001	1.396	-212.21	-0.003	2.065
0.1553	1322	13.69	-7.61	0.001	2.007	-285.62	-0.004	2.008
0.1998	1310	17.98	-10.00	0.002	2.519	-297.64	-0.006	1.961
0.2556	1296	22.10	-12.03	0.002	2.974	-354.19	-0.008	1.903
0.2999	1285	25.02	-13.39	0.002	3.259	-354.28	-0.008	1.857
0.3554	1272	27.51	-14.28	0.002	3.463	-396.13	-0.008	1.800
0.4000	1261	29.89	-15.30	0.002	3.629	-385.91	-0.009	1.755
0.4555	1247	32.85	-16.62	0.003	3.791	-410.01	-0.010	1.698
0.4999	1237	33.38	-16.50	0.003	3.744	-390.27	-0.009	1.653
0.5554	1224	34.10	-16.48	0.003	3.664	-401.23	-0.008	1.597
0.5999	1213	34.99	-16.76	0.003	3.599	-370.37	-0.009	1.553
0.6555	1200	34.44	-16.20	0.003	3.376	-369.14	-0.009	1.497
0.6999	1190	32.84	-15.16	0.003	3.108	-328.58	-0.008	1.453
0.7556	1177	30.62	-13.93	0.003	2.747	-315.53	-0.007	1.398
0.7999	1167	27.48	-12.30	0.003	2.369	-265.32	-0.006	1.354
0.8555	1155	21.64	-9.41	0.002	1.792	-242.86	-0.004	1.300
0.8999	1145	16.49	-7.07	0.001	1.307	-184.21	-0.003	1.257
0.9555	1133	7.58	-2.99	0.001	0.588	-150.75	-0.001	1.203
1	1123	0	0	0	0	0	0	1.160
	Butyl Acrylate + Decane-2-ol							
0	1362	0	0	0	0	0	0	2.171
0.0555	1350	1.91	-1.24	0.000	0.419	-119.45	-0.001	2.134
0.0998	1340	3.89	-2.63	0.000	0.775	-148.09	-0.002	2.104
0.1556	1328	5.70	-3.78	0.000	1.115	-202.81	-0.003	2.068
0.1998	1318	7.59	-5.05	0.001	1.409	-219.09	-0.005	2.038
0.2554	1306	9.30	-6.08	0.001	1.674	-258.69	-0.006	2.001
0.3000	1297	9.92	-6.35	0.001	1.787	-266.65	-0.005	1.973
0.3556	1285	11.44	-7.24	0.001	1.976	-291.97	-0.006	1.936
0.3998	1276	11.93	-7.42	0.001	2.035	-289.17	-0.006	1.907
0.4555	1264	13.21	-8.13	0.001	2.147	-302.27	-0.007	1.871
0.5000	1255	13.42	-8.15	0.001	2.142	-290.51	-0.007	1.843
0.5555	1244	13.19	-7.83	0.001	2.074	-292.80	-0.007	1.807
0.5999	1235	13.12	-7.69	0.001	2.013	-272.16	-0.006	1.778
0.6555	1224	12.50	-7.18	0.001	1.873	-263.36	-0.006	1.743
0.6999	1215	12.09	-6.88	0.001	1.754	-236.42	-0.006	1.715
0.7554	1204	10.98	-6.15	0.001	1.541	-217.39	-0.005	1.679
0.7999	1195	10.13	-5.63	0.001	1.361	-182.66	-0.005	1.651
0.8545	1185	7.38	-3.98	0.000	1.006	-154.27	-0.003	1.617
0.8999	1176	5.75	-3.08	0.000	0.745	-114.21	-0.003	1.588
0.9550	1166	2.07	-1.01	0.000	0.307	-78.53	0.000	1.554
1	1157	0	0	0	0	0	0	1.526

Deviation in isentropic compressibility were fitted to Redlich-Kister equation[10],

$$Y = x_1 x_2 \sum_{i}^{n} a_i (x_1 - x_2)^i \qquad (13)$$

Where Y is $\Delta\kappa_s$ and n is degree of polynomial. Coefficient a_i was obtained by fitting Eq (13) 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,

$$\sigma(Y) = \left[\frac{\sum (Y_{\exp t} - Y_{calc})^2}{N - n} \right]^{1/2} \qquad (14)$$

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.

Table No. 2: Parameters of Redlich - Kister Polynomial Equation for deviation in isentropic compressibility for Acrylates (1) + Decane-2-ol (2) at 313.15 K.

Property	a_0	a_1	a_2	a_3	a_4	σ
Δk_s /(TPa^{-1})	Methyl Acrylate + Decane-2-ol					
	53.2667	40.2340	26.3259	-5.7219	-11.7939	0.36265
	Ethyl Acrylate + Decane-2-ol					
	14.6449	16.7048	29.8820	-1.1945	-46.9233	0.33076
	Butyl Acrylate + Decane-2-ol					
	-1.5641	5.8635	19.6866	-5.8184	-37.5566	0.35663

Jouyban Acree recently proposed model for correlating ultrasonic velocities of liquid mixtures at various temperatures[11, 12]. The proposed equation is,

$$\ln ymT = f1 \ln y1T + f2 \ln y2T + f1f2\ \Sigma\ [Aj\ (f1-f2)\ j/T] \quad (15)$$

Where ymT, y1T and y2T is ultrasonic velocities of mixture, solvents 1 and 2 at temperature T, respectively, f1 and f2 are mole fraction and Aj are model constants. The correlating ability of model was tested by calculating the average percentage deviation (APD) between the experimental and calculated values of ultrasonic velocities as,

$$APD = (100/N)\ \Sigma\ [(|\ yexpt - ycal\ |)/\ yexpt)] \quad (16)$$

Where N is number of data points in each set. Jouyban Acree model provides reasonably accurate calculations for ultrasonic velocity of binary liquid mixtures and could be used in data modeling. The optimum numbers of constants Aj, in each case, are determined from the examination of the average percentage deviation value which is represented in Table 3.

Table 3: Parameters of Jouyban-Acree Model for ultrasonic velocity for Acrylates (1) + Decane-2-ol (2).

Property	a_0	a_1	a_2	a_3	a_4	σ	APD
u ($m.s^{-1}$)	Methyl Acrylate + Decane-2-ol						
	0.0818	-0.2291	-1.8521	0.5625	3.2343	1313.8158	0.0178
	Ethyl Acrylate + Decane-2-ol						
	0.0988	0.0216	-1.0346	-0.4437	1.2038	1310.0579	0.0201
	Butyl Acrylate + Decane-2-ol						
	-0.0444	-0.2932	-0.9405	0.7343	1.9723	1329.7640	0.0197

III. Results And Discussion

Table 1 represents variation of excess intermolecular free length (Lf^E) for acrylates with decane-2-ol. Values of Lf^E are found to be positive for all systems which suggests that, rupture of hydrogen bonded chain of decane-2-ol and resulting loosening exceeds the interaction i. e. hydrogen bonding and dipole-dipole between unlike molecules. The degree of intermolecular hydrogen bond also decreases as the intermolecular chain length is increased. Positive values of Va^E over entire range of composition mean strong molecular interactions. Values of πint^E are found to be negative in all binary liquid mixtures. Less magnitude of πint^E suggests that, weak types of intermolecular interactions are present with some dispersion due to dissociation of decane-2-ols aggregates with addition of solute (acrylates) in the binary liquid mixtures. Excess internal pressure is used to study intermolecular interactions in liquid mixtures.

Evaluated values of derived thermodynamic parameter such as deviation isentropic compressibility (Δκs) were fitted to Redlich-Kister polynomial equation at 313.15 K and are represented as in Table 2 with their standard percentage deviation. The Redlich - Kister equation was originally developed to correlate the excess Gibb's energy function and calculate the values of the activity coefficients. Experimentally measured fundamental values of ultrasonic velocity were correlated using recently proposed Jouyban-Acree model. Constants (Aj) calculated from least square analysis along with average percentage deviation (APD) are presented in Table 3.

Figure 1 shows graphical variation of deviation in isentropic compressibility (Δκs) of acrylates with decane-2-ol at 313.15 K. In present study of binary liquid mixtures, values of Δκs are found to be positive for all mixtures. Δκs attributed to relative strength of effects which influenced free space, according to which positive Δκs arises due to breaking of hydrogen bonds in self-associated decane-2-ol and physical dipole-dipole interactions between decane-2-ol monomers and multimers contribute to increase in free space, decrease in sound velocity and positive deviation in Δκs.

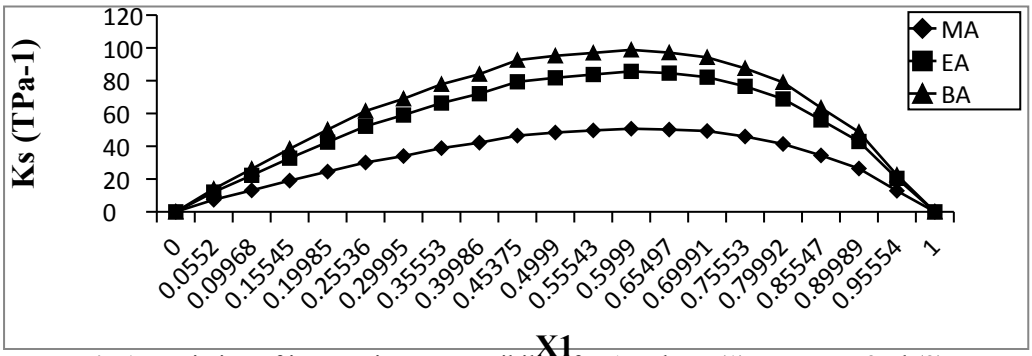

Fig.1: Variation of isentropic compressibility for Acrylates (1) + Decane-2-ol (2).

Figure 2 shows graphical variation of excess specific acoustic impendence (Z^E) with mole fraction acrylates with decane-2-ol at 313.15 K, which clearly indicates exactly reverse graphical variation of Δκs. Deviations in Z^E more negative, as length of carbon chain in acrylates increases. Negative values of Z^E in curves and opposite behavior in Δκs curves reinforce that, structure breaking effect and weak interactions between unlike molecules dominates.

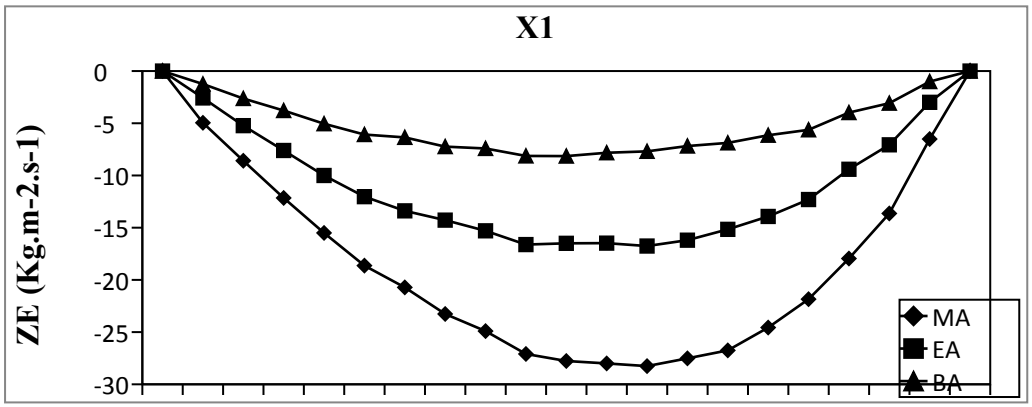

Fig.2: Variation of excess specific acoustic impedance for Acrylates (1) + Decane-2-ol (2).

IV. Conclusion

Positive values of Δκs decide compactness due to molecular arrangement. Negative values of Z^E represent the weak interactions are dominant over dispersion forces. Lf^E values increase with increase of chain length in acrylates. Positive values of Va^E mean strong molecular interactions. Negative values of πint^E suggest weak types of intermolecular interactions in liquid mixtures.

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References

[1] Hagen R, Behrends R and Kaatze V, Acoustical Properties of Aqueous Solutions of Urea: Reference Data for the Ultrasonic Spectrometry of Liquids, *J. Chem. Eng. Data*, 2004, 49 (4), 988.
[2] Vatanakul M, Zheng Y and Couturier M, Application of Ultrasonic Technique in Multiphase Flows, *Ind. Eng. Chem. Res.*, 2004, 43 (18), 5681.
[3] Kozhemyakin G N, Zolkina L V and Inatomi Y, Influence of Ultrasound on Crystal Growth from Solution and Related Flow Visualization, *Cryst. Growth Des.*, 2006, 6 (10), 2412.
[4] Behrends R and Kaatze U, Structural Isomerization and Molecular Motions of Liquid *n*-Alkanes. Ultrasonic and High-Frequency Shear Viscosity Relaxation, *J. Phys. Chem. A*, 2000, 104 (15), 3269.
[5] Owusu S O and Adewuyi Y G, Sonochemical Removal of Nitric Oxide from Flue Gases, *Ind. Eng. Chem. Res.*, 2006, 45 (13), 4475.
[6] Behrends R and Kaatze U, Hydrogen Bonding and Chain Conformational Isomerization of Alcohols Probed by Ultrasonic Absorption and Shear Impedance Spectrometry, *J. Phys. Chem. A*, 2001, 105 (24), 5829.
[7] Stieler T, Scholle F D, Weiss A, Ballauff M and Kaatze U, Ultrasonic Spectrometry of Polystyrene Latex Suspensions. Scattering and Configurational Elasticity of Polymer Chains, *Langmuir*, 2001, 17 (5), 1743.
[8] Protozov T, Protozov R and Suslick K S, *J. Ame. Chem. Soc.*, 2004, 126 (43), 1389.
[9] Mahajan A R, Mirgane S R and Deshmukh S B, Speed of ultrasound and thermodynamic properties of n-tetradecane in binary liquid mixtures at 298.15 K, International Journal of Research in Physical Chemistry, 2007, 4, 345.

[10] O. Redlich and A. T. Kister, Algebraic Representation of Thermodynamic Properties and the Classification of Solutions Ind. Eng.Chem., 1948, 40, 345.
[11] A. Jouyban, M. Khoubnasabjafari, Z. Fekari and Jr. W. E. Acree, Calculation of the viscosity of binary liquids at various temperatures using Jouyban Acre Model, Journal of Chemical and Pharmaceutical Bulletin, 2005, 53, 519.
[12] A. Jouyban, A. Fathi–Azarbayjani, M. Khoubnasabjafari and Jr. W. E. Acree, Mathematical representation of the density of liquid mixtures at various temperatures using Jouyban Acre Model, Indian Journal of Chemistry, 2005, 44, 1553.