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# Study of Ultrasonic Velocity of Acrylates with Decane-2-ol

***Sujata S. Patil[a] and Sunil R. Mirgane[b]**

*[a]Dept. of App. Sci., MSS's College of Engineering and Technology, Jalna – 431 203 (M. S.), India*
*[b]P. G. Dept. of Chemistry, J. E. S. College, Jalna - 431 203 (M. S.), India*

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**ABSTRACT**

*Thermodynamic data involving ultrasonic velocities of binary liquid mixtures of methyl acrylate, ethyl acrylate, butyl acrylate and methyl methacrylate with decane-2-ol have been measured at 298.15 K and at atmospheric pressure. Experimental values of ultrasonic velocities were correlated with Jouyban-Acree model. Deviations in isentropic compressibility were calculated and have been fitted to Redlich-Kister polynomial equation. Ultrasonic velocities were also calculated theoretically using various theories such as Nomoto, Van Dael, free length theory and collision factor theory. 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 these excess derived thermodynamic parameters used to explain type and extent of intermolecular interactions.*

**Keywords:** Free length theory, Intramolecular interactions, Jouyban Acree model, Isentropic compressibility, Specific acoustic impendence.

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## 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. This study is a powerful means of characterizing various aspects of physicochemical behaviors of liquid mixtures and molecular interactions.

Ultrasonic velocity measurement of liquid mixtures of non electrolytes provides an excellent tool to investigate inter and intramolecular interactions between unlike and like molecules in a binary liquid mixture. 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 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, 9].

Literature survey reveals that, molecular interactions of binary liquid mixtures of decane-2-ol with methyl acrylate, ethyl acrylate, butyl acrylate and methyl methacrylate have not much studied and explored over entire range of composition at 298.15 K temperature. Therefore, we have planned to study molecular interactions in present binary liquid systems.

## 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), butyl acrylate, BA, (> 0.995) and methyl methacrylate, MMA, (> 0.997). Prior to use, all liquids were stored over 0.4 nm molecular sieves to reduce water content. All acrylates were distilled before use.

### *Experimental Part*

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. Care was taken to avoid evaporation and contamination during mixing. The estimated uncertainty in mole fraction was < $1\times10^{-4}$. Ultrasonic velocities were measured [10] at frequency of 2 MHz by a single crystal ultrasonic interferometer (Model F-81, Mittal Enterprises, New Delhi, India). Accuracy in velocity measurements is ± 0.1 %. Temperature was controlled using a constant temperature controlled water bath (Gemini Scientific Instruments, Chennai, India) having accuracy ± 0.02 $^0$C. Ultrasonic velocities of decane-2-ol, methyl acrylate, ethyl acrylate, butyl acrylate and methyl methacrylate at 298.15 K were observed as 1423, 1185, 1167, 1207 and 1182 m.s$^{-1}$ respectively.

### *Computational Part*

There have been a number of studies on the measurements of ultrasonic velocities and isentropic compressibilities of liquid-liquid mixtures, as the deviations from the rectilinear dependence of velocities and compressibilities on the mole fractions throw much light on the physicochemical behaviour of liquid mixtures such as molecular association and dissociation as well as the strength of interactions between the components.

Deviation in isentropic compressibility were calculated using relation,

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

where $\kappa_s$ is isentropic compressibility and was calculated using Laplace relation,

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

$\kappa_s^{id}$ was calculated from relation,

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

where $\phi_i$ is ideal state volume fraction of component i in mixture and is defined by,

$$\phi_i = x_i V^o_i / (\Sigma x_i V^o_i) \quad (4)$$

T is temperature and $\kappa_{s,i}$, $V^o_i$, $\alpha^o_i$, and $C_{p,i}$ are isentropic compressibility, molar volume, coefficient of isobaric thermal expansion and molar heat capacity respectively, for pure component i. $\alpha^o_i$ 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 specific acoustic impendence (Z), intermolecular free length ($L_f$), available volume ($V_a$), intrinsic pressure ($\pi_{int}$), can be calculated, which provides better insight in understanding of molecular interactions in pure and binary liquids mixtures, which are given by relations,

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

$$L_f = K(\kappa_s)^{1/2} \quad (7)$$

$$V_a = V_m [1-(u_{expt}/u_\infty)] \quad (8)$$

Where K is the temperature dependent constant whose values are $1.976\times10^{-6}$ at 298.15 K respectively, $u_\infty$ = 1600 m/s.

For binary liquid mixtures intrinsic pressure can be given as,

$$\pi_i = bRT\,(K\eta_{12}/u_{12})^{1/2}(\rho_{12}^{2/3}/M_{12}^{7/6}) \quad (9)$$

Where b is packing factor, K is a temperature independent constant having value of $4.28 \times 10^9$, R is gas constant and $\eta_{12}$, $u_{12}$, $\rho_{12}$ are viscosity, ultrasonic velocity and density of mixture.

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, $L_f$, Va, $\pi_{int}$ 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 ($\pi_{int}^E$).

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

$$M_A = [(u/\Sigma x_1 u_1)^2 - 1] \quad (11)$$

$$R = (M/\rho)\,u^{1/3} \quad (12)$$

Where M is average molecular weight.

All these thermodynamic parameters are represented in Table 1.

**Table 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 ($V_a^E$), Excess intrinsic pressure ($\pi_{int}^E$), Molecular association ($M_A$) and Rao's constant (R) for Acrylates (1) + Decane-2-ol (2)**

| $X_1$ | u ($m.s^{-1}$) | $\Delta\kappa_s$ ($TPa^{-1}$) | $Z^E$ ($Kg.m^{-2}.s^{-1}$) | $L_f^E$ (m) | $V_a^E$ ($m^3.mol^{-1}$) | $\pi_{int}^E$ (atm) | $M_A$ | R |
|---|---|---|---|---|---|---|---|---|
| | Methyl Acrylate (1) + Decane-2-ol (2) | | | | | | | |
| 0 | 1423 | 0 | 0 | 0 | 0 | 0 | 0 | 2.169 |
| 0.05520 | 1409 | 6.03 | -5.31 | 0.001 | 0.909 | -329.25 | -0.001 | 2.100 |
| 0.09968 | 1397 | 11.25 | -9.58 | 0.002 | 1.651 | -389.80 | -0.003 | 2.044 |
| 0.15545 | 1383 | 16.80 | -14.02 | 0.003 | 2.369 | -529.99 | -0.004 | 1.975 |
| 0.19985 | 1372 | 20.94 | -17.23 | 0.003 | 2.854 | -562.79 | -0.005 | 1.921 |
| 0.25536 | 1358 | 26.10 | -21.15 | 0.004 | 3.397 | -664.82 | -0.006 | 1.852 |
| 0.29995 | 1347 | 29.79 | -23.83 | 0.005 | 3.736 | -674.09 | -0.007 | 1.797 |
| 0.35553 | 1333 | 34.33 | -27.08 | 0.005 | 4.098 | -743.49 | -0.008 | 1.729 |
| 0.39986 | 1323 | 36.46 | -28.37 | 0.005 | 4.202 | -730.56 | -0.007 | 1.676 |
| 0.45375 | 1310 | 39.42 | -30.25 | 0.006 | 4.330 | -767.73 | -0.008 | 1.610 |
| 0.49990 | 1299 | 41.31 | -31.30 | 0.006 | 4.351 | -742.01 | -0.008 | 1.554 |
| 0.55543 | 1285 | 43.82 | -32.81 | 0.007 | 4.360 | -750.99 | -0.009 | 1.487 |
| 0.59990 | 1275 | 43.86 | -32.47 | 0.007 | 4.189 | -698.83 | -0.008 | 1.434 |
| 0.65497 | 1262 | 43.70 | -31.93 | 0.007 | 3.948 | -688.06 | -0.008 | 1.368 |
| 0.69991 | 1252 | 42.02 | -30.37 | 0.006 | 3.634 | -620.14 | -0.007 | 1.315 |
| 0.75553 | 1239 | 39.40 | -28.13 | 0.006 | 3.207 | -586.54 | -0.007 | 1.248 |
| 0.79992 | 1229 | 35.71 | -25.26 | 0.006 | 2.770 | -498.38 | -0.006 | 1.196 |
| 0.85547 | 1217 | 28.76 | -20.09 | 0.004 | 2.106 | -446.86 | -0.004 | 1.131 |
| 0.89989 | 1207 | 22.09 | -15.30 | 0.003 | 1.536 | -338.33 | -0.003 | 1.078 |
| 0.95554 | 1195 | 10.73 | -7.32 | 0.002 | 0.704 | -265.68 | -0.001 | 1.013 |
| 1 | 1185 | 0 | 0 | 0 | 0 | 0 | 0 | 0.961 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | Ethyl Acrylate (1) + Decane-2-ol (2) | | | | | |
| 0 | 1423 | 0 | 0 | 0 | 0 | 0 | 0 | 2.169 |
| 0.05544 | 1407 | 5.38 | -3.98 | 0.001 | 0.925 | -282.76 | -0.003 | 2.110 |
| 0.09990 | 1395 | 8.87 | -6.31 | 0.001 | 1.502 | -343.50 | -0.003 | 2.063 |
| 0.15533 | 1380 | 13.16 | -9.11 | 0.001 | 2.152 | -465.34 | -0.005 | 2.005 |
| 0.19980 | 1368 | 16.42 | -11.17 | 0.001 | 2.601 | -499.37 | -0.006 | 1.958 |
| 0.25555 | 1353 | 20.33 | -13.55 | 0.002 | 3.089 | -587.81 | -0.007 | 1.900 |
| 0.29991 | 1341 | 25.55 | -19.09 | 0.003 | 3.509 | -608.66 | -0.008 | 1.860 |
| 0.35543 | 1326 | 26.80 | -17.33 | 0.003 | 3.749 | -654.33 | -0.009 | 1.797 |
| 0.39998 | 1314 | 29.32 | -18.71 | 0.003 | 3.946 | -643.55 | -0.010 | 1.751 |
| 0.45545 | 1300 | 31.11 | -19.40 | 0.003 | 4.022 | -672.71 | -0.010 | 1.694 |
| 0.49994 | 1289 | 31.95 | -19.55 | 0.003 | 4.001 | -644.45 | -0.009 | 1.649 |
| 0.55540 | 1275 | 32.76 | -19.62 | 0.003 | 3.923 | -648.26 | -0.009 | 1.592 |
| 0.59993 | 1263 | 33.88 | -20.12 | 0.003 | 3.875 | -601.16 | -0.010 | 1.547 |
| 0.65550 | 1249 | 33.47 | -19.54 | 0.003 | 3.644 | -583.15 | -0.010 | 1.491 |
| 0.69990 | 1239 | 31.13 | -17.72 | 0.003 | 3.298 | -522.80 | -0.008 | 1.447 |
| 0.75555 | 1225 | 29.10 | -16.31 | 0.003 | 2.920 | -483.82 | -0.007 | 1.391 |
| 0.79990 | 1214 | 26.48 | -14.68 | 0.003 | 2.541 | -406.96 | -0.007 | 1.347 |
| 0.85546 | 1201 | 21.12 | -11.43 | 0.002 | 1.937 | -351.09 | -0.005 | 1.292 |
| 0.89987 | 1190 | 16.58 | -8.91 | 0.002 | 1.439 | -260.48 | -0.004 | 1.248 |
| 0.95548 | 1177 | 8.31 | -4.33 | 0.001 | 0.683 | -187.76 | -0.002 | 1.194 |
| 1 | 1167 | 0 | 0 | 0 | 0 | 0 | 0 | 1.15 |
| | | | Butyl Acrylate (1) + Decane-2-ol (2) | | | | | |
| 0 | 1423 | 0 | 0 | 0 | 0 | 0 | 0 | 2.169 |
| 0.05547 | 1410 | 2.05 | -1.67 | 0.000 | 0.475 | -199.02 | -0.001 | 2.132 |
| 0.09983 | 1400 | 3.41 | -2.81 | 0.000 | 0.781 | -266.84 | -0.002 | 2.103 |
| 0.15555 | 1387 | 5.40 | -4.42 | 0.000 | 1.174 | -367.77 | -0.003 | 2.066 |
| 0.19982 | 1377 | 6.64 | -5.36 | 0.000 | 1.418 | -410.00 | -0.004 | 2.037 |
| 0.25543 | 1364 | 8.54 | -6.82 | 0.001 | 1.733 | -478.99 | -0.006 | 2.001 |
| 0.29996 | 1354 | 9.62 | -7.58 | 0.001 | 1.908 | -499.63 | -0.006 | 1.972 |
| 0.35555 | 1342 | 10.40 | -8.03 | 0.001 | 2.033 | -542.03 | -0.006 | 1.936 |
| 0.39981 | 1332 | 11.37 | -8.68 | 0.001 | 2.151 | -542.26 | -0.007 | 1.907 |
| 0.45546 | 1320 | 11.90 | -8.92 | 0.001 | 2.199 | -559.40 | -0.007 | 1.871 |
| 0.49996 | 1311 | 11.60 | -8.54 | 0.001 | 2.144 | -543.44 | -0.006 | 1.843 |
| 0.55552 | 1299 | 11.81 | -8.55 | 0.001 | 2.117 | -537.32 | -0.006 | 1.807 |
| 0.59994 | 1289 | 12.31 | -8.83 | 0.001 | 2.108 | -503.56 | -0.007 | 1.779 |
| 0.65548 | 1277 | 12.19 | -8.61 | 0.001 | 2.004 | -476.50 | -0.007 | 1.743 |
| 0.69989 | 1268 | 11.27 | -7.84 | 0.001 | 1.832 | -430.00 | -0.006 | 1.715 |
| 0.75544 | 1257 | 9.57 | -6.50 | 0.001 | 1.554 | -385.12 | -0.004 | 1.680 |
| 0.79991 | 1247 | 9.40 | -6.36 | 0.001 | 1.418 | -324.87 | -0.005 | 1.652 |
| 0.85445 | 1236 | 7.42 | -4.93 | 0.001 | 1.092 | -262.88 | -0.004 | 1.617 |
| 0.89988 | 1227 | 5.32 | -3.47 | 0.000 | 0.776 | -192.22 | -0.003 | 1.589 |
| 0.95499 | 1216 | 2.49 | -1.55 | 0.000 | 0.362 | -114.33 | -0.001 | 1.554 |
| 1 | 1207 | 0 | 0 | 0 | 0 | 0 | 0 | 1.526 |
| | | | Methyl Methacrylate (1) + Decane-2-ol (2) | | | | | |
| 0 | 1423 | 0 | 0 | 0 | 0 | 0 | 0 | 2.169 |
| 0.05544 | 1408 | 5.37 | -4.42 | 0.001 | 0.883 | -272.85 | -0.002 | 2.109 |
| 0.09990 | 1397 | 8.74 | -7.06 | 0.001 | 1.408 | -328.02 | -0.003 | 2.061 |
| 0.15533 | 1383 | 13.04 | -10.35 | 0.002 | 2.024 | -444.31 | -0.004 | 2.002 |
| 0.19980 | 1371 | 17.03 | -13.43 | 0.002 | 2.538 | -472.89 | -0.006 | 1.954 |
| 0.25555 | 1357 | 20.90 | -16.21 | 0.003 | 2.996 | -558.51 | -0.006 | 1.896 |
| 0.29991 | 1346 | 23.64 | -18.09 | 0.003 | 3.283 | -567.02 | -0.007 | 1.849 |
| 0.35543 | 1332 | 27.02 | -20.38 | 0.004 | 3.590 | -622.68 | -0.008 | 1.790 |
| 0.39998 | 1321 | 29.22 | -21.76 | 0.004 | 3.752 | -612.26 | -0.008 | 1.743 |
| 0.45545 | 1308 | 30.85 | -22.58 | 0.004 | 3.811 | -643.63 | -0.008 | 1.686 |
| 0.49994 | 1297 | 32.40 | -23.46 | 0.004 | 3.855 | -614.20 | -0.008 | 1.639 |
| 0.55540 | 1284 | 33.01 | -23.52 | 0.004 | 3.766 | -621.98 | -0.008 | 1.582 |
| 0.59993 | 1273 | 33.69 | -23.76 | 0.005 | 3.691 | -576.51 | -0.008 | 1.536 |
| 0.65550 | 1260 | 33.01 | -22.94 | 0.004 | 3.454 | -563.69 | -0.008 | 1.478 |
| 0.69990 | 1250 | 31.40 | -21.56 | 0.004 | 3.175 | -503.64 | -0.007 | 1.433 |
| 0.75555 | 1237 | 29.09 | -19.68 | 0.004 | 2.799 | -471.69 | -0.006 | 1.376 |
| 0.79990 | 1227 | 25.91 | -17.35 | 0.003 | 2.401 | -396.83 | -0.005 | 1.331 |
| 0.85546 | 1214 | 21.43 | -14.19 | 0.003 | 1.876 | -347.38 | -0.005 | 1.275 |
| 0.89987 | 1204 | 16.32 | -10.70 | 0.002 | 1.368 | -260.57 | -0.004 | 1.230 |
| 0.95548 | 1192 | 7.77 | -5.03 | 0.001 | 0.626 | -192.67 | -0.001 | 1.174 |
| 1 | 1182 | 0 | 0 | 0 | 0 | 0 | 0 | 1.129 |

***Empirical Relations for Ultrasonic Velocity:-***

I. Nomoto's Relation:-

The formula proposed by Nomoto [11] is based on assumption of linearity of molecular sound velocity versus mole fraction and additivity of molar volume in liquid mixture. An empirical formula for the sound velocity in liquid mixtures based on the assumption of the linearity of the molecular sound velocity,

$$R = x_1R_1 + x_2R_2 \quad (13)$$

Where $R_1$, $R_2$ are molar sound velocities and $x_1$, $x_2$ 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 the relation. Hence, ultrasonic velocity (u) is given by,

$$u = (R/V)^3 = [(x_1rR_1 + x_2 R_2)/ (x_1V_1 + x_2V_2)]^3 \quad (14)$$

II. Van Dael's Relation:-

According to Vangeel [12] assumption, adiabatic compressibility (βs) of mixture is,

$$\beta s_{(im)} = \phi_1 v_1 \beta s_{(1)} / v_{im} + \phi_2 v_2 \beta s_{(2)} / v_{im} \quad (15)$$

Where v represent volume fraction.

III. Collision Factor Theory:-

Schaffs [13, 14] on basis of CFT gave following relation for sound velocity in liquids,

$$u = u_\infty Srf = u_\infty SB/V \quad (16)$$

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

IV. Free Length Theory:-

The sound velocity in mixtures can be evaluated from Jacobson's formula [15, 16],

$$u_{mix} = K/ ( L_f(mix)\rho_{(mix)}^{1/2}) \quad (17)$$

Where K is a temperature dependent constant, $L_{f(mix)}$ is intermolecular free length of mixture and $\rho_{mix}$ is density of mixture.

The calculated ultrasonic velocities using various theories along with theirs percentage error are summarized in Table 2.

**Table 2 Comparison of experimental ultrasonic velocity with various theories like NOMOTO, VAN, CFT and FLT with errors for Acrylates (1) + Decane-2-ol (2)**

| $X_1$ | Ultrasonic Velocity | | | | | % Errors for Ultrasonic Velocity | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Expt. | NOM | VAN | CFT | FLT | NOM | VAN | CFT | FLT |
| | Methyl Acrylate (1) + Decane-2-ol (2) | | | | | | | | |
| 0 | 1423 | 1423 | 1423 | 1423 | 1335 | 0 | 0 | 0 | 38.451 |
| 0.05520 | 1409 | 1416 | 1380 | 1413 | 1321 | 0.261 | 4.378 | 0.065 | 38.974 |
| 0.09968 | 1397 | 1411 | 1350 | 1405 | 1313 | 0.935 | 11.488 | 0.311 | 35.876 |
| 0.15545 | 1383 | 1403 | 1317 | 1394 | 1302 | 2.076 | 22.827 | 0.686 | 34.153 |
| 0.19985 | 1372 | 1397 | 1294 | 1386 | 1293 | 3.204 | 32.076 | 1.049 | 32.858 |
| 0.25536 | 1358 | 1388 | 1270 | 1375 | 1283 | 4.925 | 42.292 | 1.633 | 30.873 |
| 0.29995 | 1347 | 1381 | 1253 | 1367 | 1274 | 6.362 | 49.187 | 2.111 | 29.402 |
| 0.35553 | 1333 | 1372 | 1234 | 1355 | 1263 | 8.342 | 55.123 | 2.814 | 27.271 |
| 0.39986 | 1323 | 1363 | 1221 | 1346 | 1255 | 9.359 | 59.036 | 3.074 | 26.365 |
| 0.45375 | 1310 | 1353 | 1208 | 1335 | 1245 | 10.823 | 60.418 | 3.570 | 24.578 |
| 0.49990 | 1299 | 1344 | 1199 | 1325 | 1237 | 11.787 | 59.636 | 3.910 | 22.933 |
| 0.55543 | 1285 | 1331 | 1189 | 1312 | 1227 | 13.042 | 55.397 | 4.453 | 20.715 |
| 0.59990 | 1275 | 1321 | 1183 | 1302 | 1218 | 12.966 | 51.628 | 4.370 | 19.758 |
| 0.65497 | 1262 | 1307 | 1178 | 1288 | 1209 | 12.716 | 44.512 | 4.349 | 17.894 |
| 0.69991 | 1252 | 1295 | 1175 | 1277 | 1201 | 11.665 | 38.172 | 3.962 | 16.883 |
| 0.75553 | 1239 | 1278 | 1172 | 1262 | 1191 | 10.108 | 28.852 | 3.493 | 15.246 |
| 0.79992 | 1229 | 1264 | 1172 | 1250 | 1183 | 8.224 | 21.488 | 2.858 | 14.197 |
| 0.85547 | 1217 | 1245 | 1173 | 1233 | 1173 | 5.294 | 12.971 | 1.819 | 13.226 |
| 0.89989 | 1207 | 1228 | 1175 | 1220 | 1165 | 3.092 | 6.844 | 1.081 | 12.226 |
| 0.95554 | 1195 | 1205 | 1180 | 1201 | 1155 | 0.730 | 1.584 | 0.252 | 11.343 |
| 1 | 1185 | 1185 | 1185 | 1185 | 1146 | 0 | 0 | 0 | 10.667 |
| | Ethyl Acrylate (1) + Decane-2-ol (2) | | | | | | | | |
| 0 | 1423 | 1423 | 1423 | 1423 | 1335 | 0 | 0 | 0 | 38.451 |
| 0.05544 | 1407 | 1414 | 1387 | 1411 | 1323 | 0.264 | 2.073 | 0.076 | 35.349 |
| 0.09990 | 1395 | 1407 | 1361 | 1401 | 1315 | 0.726 | 5.974 | 0.192 | 33.233 |
| 0.15533 | 1380 | 1397 | 1332 | 1389 | 1304 | 1.586 | 11.931 | 0.409 | 30.481 |
| 0.19980 | 1368 | 1389 | 1312 | 1379 | 1295 | 2.443 | 16.889 | 0.620 | 28.397 |
| 0.25555 | 1353 | 1379 | 1289 | 1366 | 1285 | 3.689 | 22.415 | 0.943 | 25.552 |
| 0.29991 | 1341 | 1370 | 1273 | 1351 | 1254 | 4.779 | 25.969 | 0.599 | 42.008 |
| 0.35543 | 1326 | 1359 | 1254 | 1343 | 1266 | 6.179 | 29.100 | 1.629 | 20.523 |
| 0.39998 | 1314 | 1349 | 1241 | 1332 | 1258 | 7.268 | 30.472 | 1.949 | 18.317 |
| 0.45545 | 1300 | 1337 | 1227 | 1319 | 1248 | 8.089 | 31.463 | 2.122 | 16.229 |
| 0.49994 | 1289 | 1326 | 1217 | 1308 | 1240 | 8.462 | 31.306 | 2.168 | 14.733 |
| 0.55540 | 1275 | 1313 | 1206 | 1294 | 1230 | 8.761 | 29.567 | 2.231 | 12.682 |
| 0.59993 | 1263 | 1301 | 1198 | 1283 | 1222 | 9.142 | 26.586 | 2.435 | 10.628 |
| 0.65550 | 1249 | 1286 | 1189 | 1268 | 1212 | 8.748 | 22.719 | 2.350 | 8.772 |
| 0.69990 | 1239 | 1273 | 1184 | 1256 | 1204 | 7.573 | 19.866 | 1.935 | 7.877 |
| 0.75555 | 1225 | 1256 | 1178 | 1241 | 1195 | 6.460 | 14.793 | 1.701 | 6.128 |
| 0.79990 | 1214 | 1242 | 1174 | 1228 | 1187 | 5.240 | 10.793 | 1.403 | 4.999 |
| 0.85546 | 1201 | 1223 | 1171 | 1212 | 1177 | 3.301 | 6.428 | 0.876 | 3.86 |
| 0.89987 | 1190 | 1207 | 1169 | 1199 | 1170 | 1.972 | 3.238 | 0.557 | 2.882 |
| 0.95548 | 1177 | 1185 | 1167 | 1182 | 1161 | 0.494 | 0.690 | 0.156 | 1.911 |
| 1 | 1167 | 1167 | 1167 | 1167 | 1152 | 0 | 0 | 0 | 1.639 |
| | Butyl Acrylate (1) + Decane-2-ol (2) | | | | | | | | |
| 0 | 1423 | 1423 | 1423 | 1423 | 1335 | 0 | 0 | 0 | 38.451 |
| 0.05547 | 1410 | 1413 | 1403 | 1412 | 1333 | 0.061 | 0.249 | 0.021 | 29.505 |
| 0.09983 | 1400 | 1406 | 1388 | 1403 | 1331 | 0.166 | 0.743 | 0.045 | 24.155 |
| 0.15555 | 1387 | 1396 | 1370 | 1392 | 1329 | 0.395 | 1.468 | 0.114 | 17.265 |
| 0.19982 | 1377 | 1388 | 1357 | 1383 | 1328 | 0.592 | 2.119 | 0.168 | 12.615 |
| 0.25543 | 1364 | 1377 | 1341 | 1371 | 1327 | 0.932 | 2.768 | 0.280 | 7.458 |
| 0.29996 | 1354 | 1369 | 1330 | 1362 | 1326 | 1.167 | 3.272 | 0.348 | 4.329 |
| 0.35555 | 1342 | 1358 | 1316 | 1350 | 1325 | 1.370 | 3.859 | 0.392 | 1.615 |
| 0.39981 | 1332 | 1349 | 1305 | 1341 | 1324 | 1.594 | 4.040 | 0.467 | 0.321 |
| 0.45546 | 1320 | 1337 | 1293 | 1329 | 1324 | 1.730 | 4.219 | 0.499 | 0.096 |
| 0.49996 | 1311 | 1328 | 1284 | 1320 | 1324 | 1.679 | 4.373 | 0.450 | 0.961 |
| 0.55552 | 1299 | 1316 | 1273 | 1308 | 1324 | 1.711 | 4.120 | 0.465 | 3.773 |
| 0.59994 | 1289 | 1306 | 1264 | 1298 | 1325 | 1.774 | 3.649 | 0.510 | 7.644 |
| 0.65548 | 1277 | 1294 | 1255 | 1286 | 1326 | 1.685 | 3.064 | 0.501 | 14.438 |
| 0.69989 | 1268 | 1283 | 1247 | 1276 | 1326 | 1.448 | 2.661 | 0.418 | 21.234 |
| 0.75544 | 1257 | 1270 | 1239 | 1264 | 1328 | 1.073 | 2.125 | 0.289 | 31.827 |
| 0.79991 | 1247 | 1259 | 1232 | 1254 | 1329 | 0.949 | 1.414 | 0.288 | 43.591 |
| 0.85445 | 1236 | 1245 | 1225 | 1241 | 1332 | 0.587 | 0.841 | 0.178 | 59.79 |
| 0.89988 | 1227 | 1234 | 1219 | 1231 | 1334 | 0.305 | 0.448 | 0.091 | 75.611 |
| 0.95499 | 1216 | 1219 | 1212 | 1218 | 1337 | 0.070 | 0.102 | 0.022 | 99.013 |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 1207 | 1207 | 1207 | 1207 | 1339 | 0 | 0 | 0 | 119.746 |
| | | | | Methyl Methacrylate (1) + Decane-2-ol (2) | | | | | |
| 0 | 1423 | 1423 | 1423 | 1423 | 1335 | 0 | 0 | 0 | 38.451 |
| 0.05544 | 1408 | 1415 | 1389 | 1412 | 1326 | 0.244 | 1.847 | 0.078 | 34.319 |
| 0.09990 | 1397 | 1408 | 1364 | 1403 | 1318 | 0.644 | 5.422 | 0.174 | 32.369 |
| 0.15533 | 1383 | 1399 | 1337 | 1391 | 1308 | 1.417 | 10.856 | 0.371 | 29.321 |
| 0.19980 | 1371 | 1392 | 1318 | 1382 | 1301 | 2.366 | 14.975 | 0.654 | 26.373 |
| 0.25555 | 1357 | 1382 | 1296 | 1370 | 1292 | 3.528 | 20.033 | 0.969 | 23.16 |
| 0.29991 | 1346 | 1374 | 1281 | 1361 | 1285 | 4.472 | 23.470 | 1.215 | 20.797 |
| 0.35543 | 1332 | 1364 | 1263 | 1349 | 1276 | 5.748 | 26.450 | 1.577 | 17.713 |
| 0.39998 | 1321 | 1355 | 1251 | 1339 | 1269 | 6.651 | 27.973 | 1.826 | 15.396 |
| 0.45545 | 1308 | 1343 | 1237 | 1326 | 1261 | 7.354 | 29.078 | 1.963 | 12.968 |
| 0.49994 | 1297 | 1334 | 1228 | 1316 | 1254 | 8.001 | 28.477 | 2.161 | 10.821 |
| 0.55540 | 1284 | 1321 | 1217 | 1303 | 1246 | 8.217 | 27.085 | 2.184 | 8.589 |
| 0.59993 | 1273 | 1310 | 1210 | 1292 | 1240 | 8.431 | 24.632 | 2.299 | 6.63 |
| 0.65550 | 1260 | 1296 | 1202 | 1279 | 1233 | 7.987 | 21.249 | 2.173 | 4.725 |
| 0.69990 | 1250 | 1283 | 1197 | 1267 | 1227 | 7.174 | 18.246 | 1.914 | 3.506 |
| 0.75555 | 1237 | 1267 | 1191 | 1253 | 1220 | 6.071 | 13.720 | 1.658 | 1.961 |
| 0.79990 | 1227 | 1254 | 1188 | 1241 | 1214 | 4.763 | 10.242 | 1.273 | 1.182 |
| 0.85546 | 1214 | 1236 | 1185 | 1225 | 1207 | 3.190 | 5.877 | 0.888 | 0.345 |
| 0.89987 | 1204 | 1220 | 1183 | 1213 | 1201 | 1.823 | 3.067 | 0.513 | 0.045 |
| 0.95548 | 1192 | 1200 | 1182 | 1196 | 1195 | 0.411 | 0.714 | 0.107 | 0.05 |
| 1 | 1182 | 1182 | 1182 | 1182 | 1190 | 0 | 0 | 0 | 0.43 |

Deviation in isentropic compressibility ($\Delta\kappa_s$) were fitted to Redlich-Kister [17] polynomial equation of type,

$$Y = x_1x_2 \sum_{i}^{n} a_i (x_1 - x_2)^i \qquad (18)$$

where Y is $\Delta\kappa_s$ and n is the degree of polynomial. Coefficient $a_i$ was obtained by fitting equation (19) to experimental results using a least squares regression method. In each case, optimum number of coefficients is ascertained from an examination of variation in standard deviation ($\sigma$).

$\sigma$ was calculated using relation,

$$\sigma(Y) = \left[ \frac{\sum (Y_{expt} - Y_{calc})^2}{N - n} \right]^{1/2} \qquad (19)$$

where N is number of data points and n is number of coefficients. The calculated values of the coefficients $a_i$ along with the standard deviations ($\sigma$) are given at 298.15 K in Table 3.

**Table 3 Adjustable parameters of Redlich-Kister Polynomial Equation for deviation in isentropic compressibility for Acrylates (1) + Decane-2-ol (2)**

| Property | $a_0$ | $a_1$ | $a_2$ | $a_3$ | $a_4$ | $\sigma$ |
|---|---|---|---|---|---|---|
| $\Delta\kappa_s$ /(TPa$^{-1}$) | Methyl Acrylate (1) + Decane-2-ol (2) | | | | | |
| | 58.4230 | 35.9430 | 25.0119 | -4.2558 | -22.9234 | 0.28388 |
| | Ethyl Acrylate (1) + Decane-2-ol (2) | | | | | |
| | 20.0120 | 15.3601 | -6.4729 | 5.6403 | 22.6601 | 0.66040 |
| | Butyl Acrylate (1) + Decane-2-ol (2) | | | | | |
| | -0.7841 | 4.1070 | 7.6155 | 0.8304 | -10.9231 | 0.31658 |
| | Methyl Mathacrylate (1) + Decane-2-ol (2) | | | | | |
| | 36.6692 | 22.6216 | 4.1846 | -4.3274 | 3.4808 | 0.30463 |

Jouyban Acree [18, 19] recently proposed model for correlating ultrasonic velocities of liquid mixtures at various temperatures. The proposed equation is,

$$\ln y_{mT} = f_1 \ln y_{1T} + f_2 \ln y_{2T} + f_1 f_2 \sum [A_j (f_1 - f_2)^j / T] \qquad (20)$$

Where $y_{mT}$, $y_{1T}$ and $y_{2T}$ is ultrasonic velocities of mixture, solvents 1 and 2 at temperature T, respectively, $f_1$and $f_2$ 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,

$$APD = (100/N) \sum [(| y_{expt} - y_{cal} |)/ y_{expt})] \quad (21)$$

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 4.

**Table 4 Adjustable parameters of Jouyban-Acree Model Equation for ultrasonic velocity for Acrylates (1) + Decane-2-ol (2)**

| Property | $a_0$ | $a_1$ | $a_2$ | $a_3$ | $a_4$ | σ | APD |
|---|---|---|---|---|---|---|---|
| | | | Methyl Acrylate (1) + Decane-2-ol (2) | | | | |
| | 0.0818 | -0.2291 | -1.8521 | 0.5625 | 3.2343 | 1313.8158 | 0.0178 |
| | | | Ethyl Acrylate (1) + Decane-2-ol (2) | | | | |
| u ($m.s^{-1}$) | 0.0988 | 0.0216 | -1.0346 | -0.4437 | 1.2038 | 1310.0579 | 0.0201 |
| | | | Butyl Acrylate (1) + Decane-2-ol (2) | | | | |
| | -0.0444 | -0.2932 | -0.9405 | 0.7343 | 1.9723 | 1329.7640 | 0.0197 |
| | | | Methyl Methacrylate (1) + Decane-2-ol (2) | | | | |
| | 0.0404 | 0.1906 | -0.6552 | -0.5028 | 1.0571 | 1318.5762 | 0.0205 |

## RESULTS AND DISCUSSION

Thermodynamic functions are highly useful in understanding the interaction in binary liquid mixtures. Figure 1 shows graphical variation of deviation in isentropic compressibility ($\Delta\kappa_s$) of acrylates with decane-2-ol at 298.15 K.

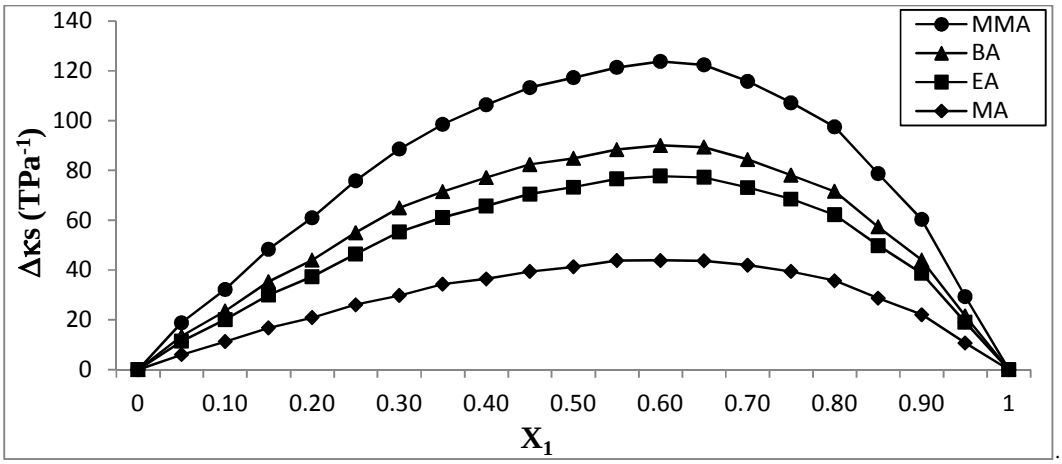


**Figure 1 Variation of deviation in isentropic compressibility for Acrylates (1) + Decane-2-ol (2)**

In present study of binary liquid mixtures, values of $\Delta\kappa_s$ are found to be positive for all mixtures. $\Delta\kappa_s$ attributed to relative strength of effects which influenced free space, according to which positive $\Delta\kappa_s$ arise 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 $\Delta\kappa_s$. This effect will be counteracted by changes of free volume in real mixtures.

Kiyohara and Benson [20] have suggested that is resultant of several opposing effects.

Deviation in isentropic compressibility can be interpreted as:-
1. Increase in free volume in mixture compared to pure components due to rupture of alkanols aggregates with addition of second component.
2. Interstitial accommodation of acrylate molecules in aggregates of alkanols.

Positive values of deviation in isentropic compressibility suggest a mixture is more compressible than corresponding ideal one. In binary liquid mixtures, an expansion in free volume makes mixture more compressible than ideal mixtures.

Figure 2 shows graphical variation of excess specific acoustic impendence ($Z^E$) with mole fraction acrylates with decane-2-ol at 298.15 K, which clearly indicates exactly reverse graphical variation of deviation in isentropic compressibility ($\Delta\kappa_s$).

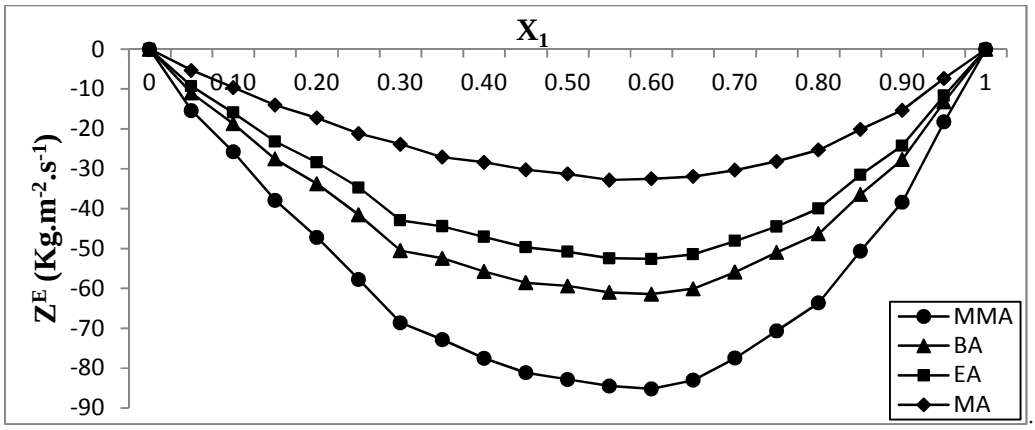


**Figure 2 Variation of excess specific acoustic impedance for Acrylates (1) + Decane-2-ol (2)**

Deviations in $Z^E$ more negative, as length of carbon chain in acrylates increases. Observed negative values of $Z^E$ in curves and opposite behaviour in $\Delta\kappa_s$ curves reinforce that, structure breaking effect and weak interactions between unlike molecules dominates. In present case, negative values of $Z^E$ represent weak interactions are dominant over dispersion forces.

Figure 3 represents graphical comparison of excess available volume ($V_a^E$) of present binary liquid mixtures. Positive values of $V_a^E$ over entire range of composition mean strong molecular interactions.

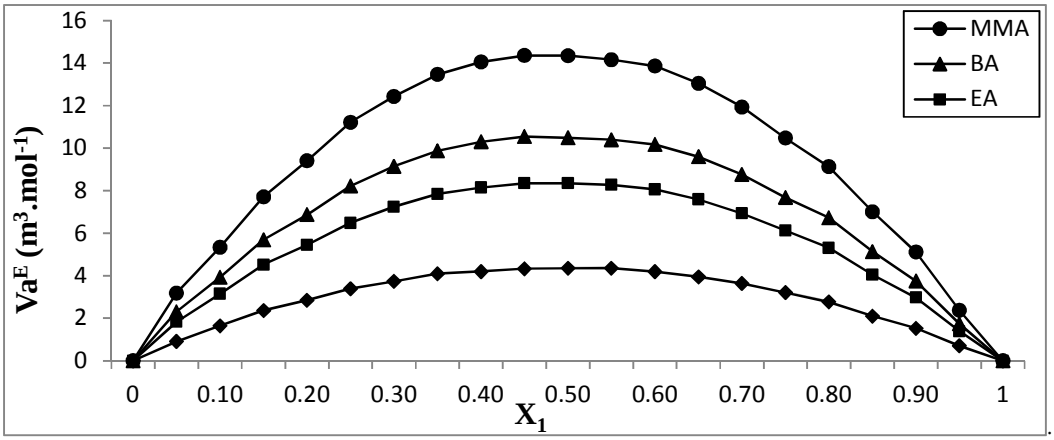


**Figure 3 Variation of excess available volume for Acrylates (1) + Decane-2-ol (2)**

Graphical variation of excess internal pressure ($\pi_{int}^E$) for acrylates with decane-2-ol represented in Figure 4 at 298.15 K.

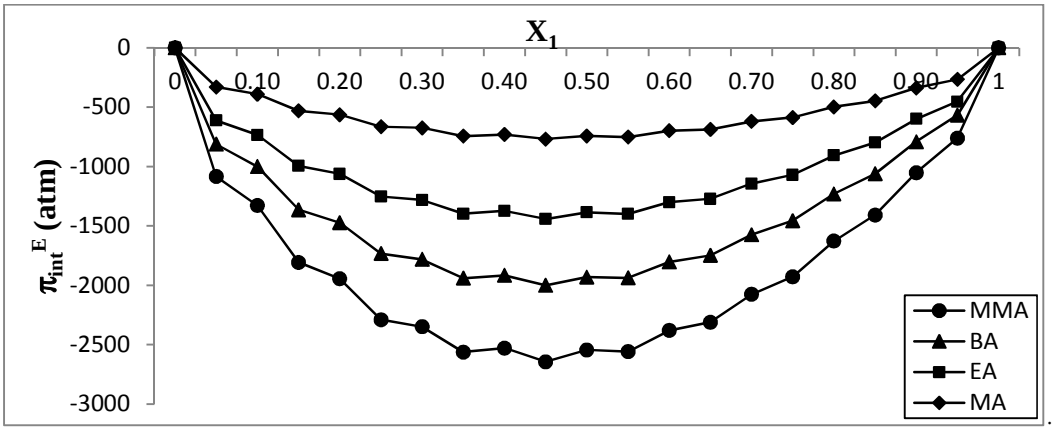


**Figure 4 Variation of excess intrinsic pressure for Acrylates (1) + Decane-2-ol (2)**

Values of $\pi_{int}^{E}$ are found to be negative in all binary liquid mixtures. Less magnitude of $\pi_{int}^{E}$ suggests that, weak type 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.

Table 1 represents variation of excess intermolecular free length ($L_f^E$) for acrylates with decane-2-ol. Values of $L_f^E$ 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.

Computed values ultrasonic velocities with the average percentage errors for all binary liquid mixtures have been calculated theoretically over entire mole fraction range using Nomoto, Van Deal, collision factor theory (CFT) and Jacobson's free length theory (FLT) at 298.15 K and are summarized in Table 2. A close scrutiny of the result indicates that CFT does succeed in computing the ultrasonic velocity value for all the mixtures studied in the present investigation to a greater degree of accuracy as compared with Nomoto, Van Deal and FLT. Nomoto and CFT show positive and van Deal theory shows negative deviations for the prediction of theoretical ultrasonic velocities. FLT seems to be not suitable for comparison purpose, as it shows large negative deviations from experimental values for almost all binary liquid mixtures investigated. Free length theory is generally not applicable to systems having self associated components.

Evaluated values of derived thermodynamic parameter such as deviation isentropic compressibility ($\Delta\kappa_s$) were fitted to Redlich-Kister polynomial equation at 298.15 K and are represented as in Table 3 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. Tomiska [21, 22] has described the mathematical procedure to transform a power expansion, such as that of Redlich-Kister, into an orthogonal series [23].

Experimentally measured fundamental thermodynamic properties such as ultrasonic velocity were correlated using recently proposed Jouyban-Acree model. The constants (Aj) calculated from the least square analysis along with the average percentage deviation (APD) are presented in Table 4. The proposed model provides reasonably accurate calculations for ultrasonic velocity of binary liquid mixtures.

## CONCLUSION

In present paper, an attempt is made to measure fundamental thermodynamic property like ultrasonic velocity and various derived thermodynamic parameters of binary liquid mixtures of methyl acrylate, ethyl acrylate, butyl acrylate and methyl methacrylate with decane-2-ol at 298.15 K. Positive values of $\Delta\kappa_s$ decides compactness due to molecular arrangement. Negative values of $Z^E$ represent the weak interactions are dominant over dispersion forces. $L_f^E$ values increase with increase of chain length in acrylates. Positive values of $V_a^E$ mean strong molecular interactions. Negative values of $\pi_{int}^{E}$ suggest weak types of intermolecular interactions are present in present binary

liquid mixtures. Nomoto, CFT show positive and van Deal theory, free length theory shows negative deviations for the prediction of theoretical ultrasonic velocities.

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