Density, Ultrasonic Velocity, Isentropic Compressibility, Molar Volumes and Related Excess Parameters Studies on Ethyl Acetate with 1-Ethanol at 303K, 308K, And 313K

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Abstract
A binary liquid mixture that consists of ethyl acetate and 1-ethanol has been prepared at various concentrations by the mole fraction method. The ultrasonic velocity and density have been determined at 303K, 308K and 313K. From the experimental data, the excess isentropic compressibility, excess molar volumes, excess internal pressures, and excess molar enthalpy have been computed. The variations were observed as polynomial and fitted to the Redlich-Kister polynomial functions. By using this function, adjustable parameters and the standard deviations have been calculated. The experimental and theoretical data reveal that the existence of the intermolecular interactions between the selected liquid system. The partial molar compressibility’s and partial molar volume also calculated at infinite dilution of the system. In general, the intermolecular forces have tended to the variations in the magnitude and sign of the excess parameters. The excess molar volume ($v^\text{E}$), excess isentropic compressibility ($\kappa_s^E$), excess internal pressure ($\pi^E$), and the enthalpy ($\mu^E$) show the negative magnitude at the entire range of concentrations and temperatures. The significant variations of these parameters with the mole fraction of ethyl acetate have been analysed. Furthermore, the strength of the intermolecular interactions decreased with increasing the experimental temperatures as 303K > 308K > 313K.

Introduction
The intermolecular forces acting between the molecules take a vital role in the interactions between the functional groups present in the binary as well as the ternary liquid mixtures. Due to the variations of these forces and the temperature of the solutions, thermo dynamical properties of the liquid system are also significantly changed. The study of
the changes in the ideal and excess parameters at various temperatures in the entire concentrations leads to provoke the nature of intermolecular interactions, molecular structure, and intermolecular forces acting in the liquid systems.\textsuperscript{1-3}

In recent years, determination of various physicochemical properties such that molar volume, density, ultrasonic velocity of the pure liquids and the binary systems are used as one of the reliable methods to investigate the strength and nature of the bonding formations among the molecules.\textsuperscript{4-6} Moreover, the volumetric properties depend upon the temperature of the systems have reported as a functional indicator of the presence of the intermolecular interactions.\textsuperscript{7,8} The excess internal pressure also considerable changes with the interactions, recent reports of various liquid mixtures\textsuperscript{9-11} furnish the impact of the excess internal pressure insight of the intermolecular forces acting among the molecules as a function of temperature of the system.

Ethyl acetate is one of the ester group compounds. It acts as a solvent in the column chromatography. Furthermore, ethyl acetate acts as a building block in the synthesis process of bulk materials having spectacular applications in the pharmaceutical, polymers, fragrances. Alcohols are self-associated organic compounds, have widely used in chemical and pharmaceutical and applied research.\textsuperscript{12} The 1-ethanol behaves as both H-bond donor and acceptor. The ethyl acetate acts as H-bond acceptor. The prospect of hydrogen bonding between the hydroxyl group of 1-ethanol and the carbonyl group of the ethyl acetate gives the significant importance of the chosen liquid system. The present work is an attempt to study the excess molar volume \((\pi_1^E)\), excess isentropic compressibility \((\Delta k_i^E)\), excess internal pressure \((\pi_i^E)\), excess molar enthalpy(HE), partial molar volume \((V_{m1}, V_{m2})\), and partial molar compressibility’s \((k_1, k_2)\) and their excess values \((V_{m1}^E, V_{m2}^E, \beta_{m1}^E, \beta_{m2}^E)\) of ethyl acetate and 1-ethanol over the entire composition at 303K, 308K, and 313K.

Materials and Methods
The various concentrations of ethyl acetate and 1-ethanol solutions were prepared by the mole fraction method. An electronic mass balance (OHAUS- AR 2104) with accuracy of \(\pm 1 \times 10^{-4} \) g was used to measure the masses of the solvents. Air tight, sample bottles were used to avoid the evaporation and avoid the atmospheric moisture. The Analytical Reagent (AR grade) chemicals which are used in the study were obtained from Ranboxy Fine Chemicals Pvt Ltd (India). These chemicals were purified by following the standard procedure prescribed by Perrin and Armarego.\textsuperscript{13} A pycnometer with a bulb volume of 10 ml and capillary diameter 0.1cm was used to determine the densities of the liquid mixtures and calibrated with the double distilled water. A constant temperature bath, INSREF-India, modelIRI-016C was used to maintain the experimental temperature of the accuracy \(\pm 0.1K\). The concurrent values of the density were noted with the precision \(\pm 0.001 \text{ kg m}^{-3}\). A single frequency (2MHz) ultrasonic interferometer with the uncertainty \(\pm 1 \text{ ms}^{-1}\) was used to gauge the ultrasonic velocity of the pure and mixtures. It was calibrated with the double distilled water and carbon tetrachloride.

Theory
The various physicochemical parameters were determined by the standard relations\textsuperscript{14-17} as listed below,

\[
\text{Excess molar volume} = \left( \frac{x_1 M_1 + x_2 M_2}{\rho_{mix}} \right) - \left( \frac{x_1 M_1 + x_2 M_2}{\rho_1 + \rho_2} \right) 
\]

...(1)

Here \(x_1\) and \(x_2\) are mole fractions; \(M_1\) and \(M_2\) are molar masses; \(\rho_1\) and \(\rho_2\) are densities of ethyl acetate and 1-ethanol respectively. \(\rho\) is the density of liquid mixtures.

Isentropic compressibility of the solution \(k_i = \frac{1}{u^2 \rho} \)

...(2)

Here \(u\) is the ultrasonic velocity.

\[
\text{Excess isentropic compressibility} = \Delta k_i^E = k_i - k_i^{id} 
\]

...(3)

Here, \(k_i^{id}\) is the ideal value of the isentropic compressibility

\[
\text{Excess internal pressure} = \pi_i^E = \pi_{i,mix} - \sum_{i=1}^{2} x_i \pi_i 
\]

...(4)

Here, \(x_i\) is the mole fraction of the components (In this study, \(x_1\) denotes the mole fraction of ethyl acetate and \(x_2\) represents the mole fraction of 1-ethanol).
Excess enthalpy \( H^E_m = \sum_{i=1}^{2} x_i \pi_i V_i - \pi_{mix} V_{mix} \) ...(5)

Here \( x_i \) is the internal pressure of the liquid, \( V_i \) is the volume of the liquid, \( \pi_{mix}, V_{mix} \) are the internal pressure and volume of the mixture.

Molar isentropic compressibility \( K_s = K_s V_s \) ...(6)

Excess molar isentropic compressibility

\[
K^E_s = K_s - \sum_{i=1}^{2} x_i K_{s,i}
\]  ...(7)

The excess parameters were fitted with Redlich-Kister polynomial as the following relations,

\[
Y^E = x_1 x_2 \sum_{i=1}^{2} a_i (1 - 2x)^{i-1}
\]  ...(8)

The \( a_i \) represents the coefficients of the polynomial.

\[
\sigma(Y^E) = \left[ \frac{\sum(Y_{exp} - Y_{cal})^2}{n - p} \right]^{1/2}
\]  ...(9)

Here \( Y_{exp} \) is the experimental data and \( Y_{cal} \) is the theoretical data. The \( n \) denotes the total number of experimental values and \( p \) is the number of coefficients.

The average partial molar volume of ethyl acetate \((\bar{V}_{m,1}^E)\) and 1-ethanol\((\bar{V}_{m,2}^E)\) are given as below, 1 denotes the first component ethyl acetate and 2 represents the second component 1-ethanol,

\[
\bar{V}_{m,1}^E = V_{m,1}^* + x_2 \left( \frac{\partial V_{m,1}^E}{\partial x_1} \right)_{T, p}
\]  ...(10)

\[
\bar{V}_{m,2}^E = V_{m,2}^* - x_1 \left( \frac{\partial V_{m,2}^E}{\partial x_1} \right)_{T, p}
\]  ...(11)

The average partial molar isentropic compressibility of the selected components at the constant temperature (T) and atmospheric pressure are given in equ (12) and equ (13) respectively

\[
\bar{K}_{m,1}^E = K_{s,1}^E + x_2 \left( \frac{\partial K_{s,1}^E}{\partial x_1} \right)_{T, p}
\]  ...(12)

\[
\bar{K}_{m,2}^E = K_{s,2}^E - x_1 \left( \frac{\partial K_{s,2}^E}{\partial x_1} \right)_{T, p}
\]  ...(13)

The molar volume at the infinite dilution can be derived from the equ (14) and equ (15) for the ethyl acetate and 1-ethanol respectively.

\[
V_{m,1}^* = V_{m,1}^* + x_2 \sum_{i=0}^{\infty} A_i (1 - 2x_1)^i - 2x_1 x_2 \sum_{i=0}^{\infty} A_i (1 - 2x_1)^i
\]  ...(14)

\[
V_{m,2}^* = V_{m,2}^* + x_1 \sum_{i=0}^{\infty} A_i (1 - 2x_2)^i + 2x_1^2 x_2 \sum_{i=0}^{\infty} A_i (1 - 2x_2)^i
\]  ...(15)

Results and Discussions

The experimental observations of density (\( \rho \)), ultrasonic velocity (U), and the calculated the isentropic compressibility of the entire concentrations of ethyl acetate and 1-ethanol are listed in Table1. In this study, the density (\( \rho \)) of the liquid mixtures increased with the ethyl acetate concentrations. Moreover, densities decreasing with increase the experimental temperature. This trend suggested the dissociation of the dipoles in the liquid system.

In general, the ultrasonic velocity varies with the medium and intermolecular forces acting between the solute- solvent systems. Furthermore, the increasing cluster of molecules with the increasing mole fraction of the ethyl acetate leads to the increasing ultrasonic velocity (U) linearly in the liquid mixtures. Since, the increasing temperature rupture the molecular forces, the ultrasonic velocities, decreased with the increasing the entire temperature range. Obviously, the isentropic compressibility inversely related with the density and ultrasonic velocity of the liquid system.\(^{16-20}\) Thus, the isentropic compressibility values are increasing with the temperature from 303K to 313K.

The molar volume, partial molar volume of the pure liquids and the partial excess molar volume at the infinite solutions with their excess values are listed in Table 2.
In this present work, the partial molar volume at the infinite dilutions ($\overline{V}$) are relatively smaller than that of the molar volume of the pure liquid components ($V$) respectively. This result suggested that the pure component’s molar volume is the resultant of the actual molar volume and free molar volume that arises due to the formation of self association and the intramolecular forces acting within the molecules. Similar trends observed in the molar isentropic compressibility and the partial molar isentropic compressibility’s and their excess values are obtained at the entire temperature ranges as specified in Table3.

Table 1: Density ($\rho$), Ultrasonic velocity ($U$), and isentropic compressibility ($k_s$) of ethyl acetate and 1-ethanol at 303K, 308K, and 313K

<table>
<thead>
<tr>
<th>$X_1$</th>
<th>$\rho$ (kgm$^{-3}$)</th>
<th>$U$ (ms$^{-1}$)</th>
<th>$k_s$ $10^{-10}$ (m$^2$N$^{-1}$)</th>
<th>$\rho$ (kgm$^{-3}$)</th>
<th>$U$ (ms$^{-1}$)</th>
<th>$k_s$ $10^{-10}$ (m$^2$N$^{-1}$)</th>
<th>$\rho$ (kgm$^{-3}$)</th>
<th>$U$ (ms$^{-1}$)</th>
<th>$k_s$ $10^{-10}$ (m$^2$N$^{-1}$)</th>
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<tr>
<td></td>
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<td>313K</td>
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<td>308K</td>
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<td>10.1635</td>
<td>786</td>
<td>1109</td>
<td>10.3446</td>
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<td>9.8030</td>
<td>800</td>
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<td>10.0006</td>
<td>795</td>
<td>1111</td>
<td>10.1907</td>
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<td>9.6044</td>
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<td>864</td>
<td>1125</td>
<td>9.1450</td>
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<td>8.8805</td>
<td>872</td>
<td>1125</td>
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Table 2: The molar volume, partial molar volume, excess partial molar volume at infinite dilution of ethyl acetate and 1-ethanol at 303K, 308K and 313K

<table>
<thead>
<tr>
<th>Temperature</th>
<th>$\overline{V}_1^*$ (m$^3$ mol$^{-1}$)</th>
<th>$\overline{V}_{n1}$ (m$^3$ mol$^{-1}$)</th>
<th>$\overline{V}^E_{n1}$ (m$^3$ mol$^{-1}$)</th>
<th>$\overline{V}_2^*$ (m$^3$ mol$^{-1}$)</th>
<th>$\overline{V}_{n2}$ (m$^3$ mol$^{-1}$)</th>
<th>$\overline{V}^E_{n2}$ (m$^3$ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>303K</td>
<td>100.88</td>
<td>99.75</td>
<td>-1.13</td>
<td>93.95</td>
<td>92.61</td>
<td>-1.34</td>
</tr>
<tr>
<td>308K</td>
<td>103.59</td>
<td>101.95</td>
<td>-1.64</td>
<td>96.87</td>
<td>95.79</td>
<td>-3.21</td>
</tr>
<tr>
<td>313K</td>
<td>105.45</td>
<td>103.35</td>
<td>-2.10</td>
<td>97.77</td>
<td>97.36</td>
<td>-3.17</td>
</tr>
</tbody>
</table>

Table 3: The molar isentropic compressibility, partial compressibility, excess partial molar compressibility at infinite dilution of ethyl acetate and 1-ethanol at 303K, 308K and 313K

<table>
<thead>
<tr>
<th>Temperature</th>
<th>$K_{n1}$ $10^{-10}$ (m$^2$N$^{-1}$)</th>
<th>$K^E_{n1}$ $10^{-10}$ (m$^2$N$^{-1}$)</th>
<th>$K_{n2}$ $10^{-10}$ (m$^2$N$^{-1}$)</th>
<th>$K^E_{n2}$ $10^{-10}$ (m$^2$N$^{-1}$)</th>
<th>$K_{n3}$ $10^{-10}$ (m$^2$N$^{-1}$)</th>
<th>$K^E_{n3}$ $10^{-10}$ (m$^2$N$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>303K</td>
<td>10.11</td>
<td>10.15</td>
<td>-0.04</td>
<td>8.73</td>
<td>8.76</td>
<td>-0.03</td>
</tr>
<tr>
<td>308K</td>
<td>10.32</td>
<td>10.39</td>
<td>-0.07</td>
<td>8.88</td>
<td>8.94</td>
<td>-0.06</td>
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<tr>
<td>313K</td>
<td>10.54</td>
<td>10.57</td>
<td>-0.03</td>
<td>9.06</td>
<td>9.17</td>
<td>-0.11</td>
</tr>
</tbody>
</table>
The Redlich-Kister\textsuperscript{23} polynomial coefficients ($a_1$, $a_2$, $a_3$, $a_4$, $a_5$) are calculated along with the standard deviations $\sigma(Y^E)$ of the excess values of the selected parameters are as shown in Table 4.

Table 4: Redlich-Kister polynomial coefficients with the standard deviations of the excess parameters ($V_m^E$, $\Delta k_i^E$, $\pi_i^E$, $H_m^E$) of ethylacetate and 1-ethanol at 303K, 308K, and 313K

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Parameters</th>
<th>$a_1$</th>
<th>$a_2$</th>
<th>$a_3$</th>
<th>$a_4$</th>
<th>$a_5$</th>
<th>$\sigma(Y^E)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>303K</td>
<td>$V_m^E$ (m$^3$mol$^{-1}$)</td>
<td>-0.471</td>
<td>-0.311</td>
<td>-0.231</td>
<td>-0.451</td>
<td>-0.095</td>
<td>0.033</td>
</tr>
<tr>
<td></td>
<td>$\Delta k_i^E$ 10$^{-10}$ (m$^2$N$^{-1}$)</td>
<td>-0.341</td>
<td>-0.329</td>
<td>-0.113</td>
<td>-0.321</td>
<td>-0.023</td>
<td>0.025</td>
</tr>
<tr>
<td></td>
<td>$\pi_i^E$ 10$^{-12}$ Nm$^{-2}$</td>
<td>-0.341</td>
<td>-0.385</td>
<td>-0.120</td>
<td>-0.321</td>
<td>-0.016</td>
<td>0.032</td>
</tr>
<tr>
<td></td>
<td>$H_m^E$ 10$^{-20}$ (J mol$^{-1}$)</td>
<td>-1.027</td>
<td>-0.464</td>
<td>0.163</td>
<td>-1.007</td>
<td>-0.299</td>
<td>0.045</td>
</tr>
<tr>
<td>308K</td>
<td>$V_m^E$ (m$^3$mol$^{-1}$)</td>
<td>-0.789</td>
<td>-0.160</td>
<td>0.185</td>
<td>-0.769</td>
<td>-0.321</td>
<td>0.037</td>
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<tr>
<td></td>
<td>$\Delta k_i^E$ 10$^{-10}$ (m$^2$N$^{-1}$)</td>
<td>-1.187</td>
<td>-0.503</td>
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<td>-1.167</td>
<td>-0.427</td>
<td>0.046</td>
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<tr>
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<td>$\pi_i^E$ 10$^{-12}$ Nm$^{-2}$</td>
<td>-0.272</td>
<td>-0.642</td>
<td>0.525</td>
<td>-0.252</td>
<td>-0.661</td>
<td>0.034</td>
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<tr>
<td></td>
<td>$H_m^E$ 10$^{-20}$ (J mol$^{-1}$)</td>
<td>-0.326</td>
<td>-1.022</td>
<td>0.956</td>
<td>-0.306</td>
<td>-1.092</td>
<td>0.040</td>
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<tr>
<td>313K</td>
<td>$V_m^E$ (m$^3$mol$^{-1}$)</td>
<td>-0.358</td>
<td>-1.480</td>
<td>1.380</td>
<td>-0.338</td>
<td>-1.516</td>
<td>0.048</td>
</tr>
<tr>
<td></td>
<td>$\Delta k_i^E$ 10$^{-10}$ (m$^2$N$^{-1}$)</td>
<td>-0.110</td>
<td>-0.128</td>
<td>-0.150</td>
<td>-0.090</td>
<td>-0.014</td>
<td>0.031</td>
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<tr>
<td></td>
<td>$\pi_i^E$ 10$^{-12}$ Nm$^{-2}$</td>
<td>-0.044</td>
<td>-0.106</td>
<td>-0.237</td>
<td>-0.024</td>
<td>-0.101</td>
<td>0.035</td>
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<tr>
<td></td>
<td>$H_m^E$ 10$^{-20}$ (J mol$^{-1}$)</td>
<td>-0.010</td>
<td>-0.051</td>
<td>-0.346</td>
<td>-0.030</td>
<td>-0.210</td>
<td>0.030</td>
</tr>
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</table>

All the coefficients are found in negative magnitude and the standard deviations are in negligible values are obtained in the entire temperature range. This data validated the precision of the measurements and theoretical calculations.

The deviations of the excess molar volume ($V_m^E$), excess isentropic compressibility ($\Delta k_i^E$), excess internal pressure ($\pi_i^E$) and the enthalpy ($H_m^E$) at 303K, 308K, and 313K are plotted against the mole fraction of ethyl acetate as displayed in Fig 1(a-d) respectively.

The deviations of the excess parameters are useful to interpret the intermolecular interactions among the unlike molecules. In general, the positive values of the excess values revealed that the dispersion forces. More over, the negative values of the excess parameters suggested that the dipole-dipole, charge transfer interaction, and hydrogen bonding formation between the liquid system.\textsuperscript{24}

The Fig 1(a-d) signifies that all the excess parameters show the negative sign, and the magnitudes vary with the entire concentrations and temperature range. At a critical mole fraction ($x_1 \sim 0.7$), the negative excess values increased with the increasing the concentrations of ethyl acetate. The change in the variations suggested the 1:1 complex formation of the ethyl acetate and 1-ethanol at the entire range of temperatures. The changes in the experimental and the excess parameters confirmed that (i) Breakdown of the self association takes place with increasing 1-ethanol concentrations, (ii) While increasing the
temperature, dispersive force increased between the molecules, (iii) At a critical mole fraction \( x_1 \approx 0.7 \), the negative excess deviation decreased with increasing the concentrations of ethyl acetate. This trend reveals the weakened hydrogen bonding formation between \((\text{C=O} \ldots \text{H-O})\) functional group present in the liquid mixtures. The negative excess parameters were decreasing with increase the experimental temperature. This result suggested that the strength of intermolecular interactions decreased with the increase the temperature and found in the order 303K > 308K > 313K.

Fig 1: (a) Excess molar volume, (b) Excess isentropic compressibility, (c) Excess internal pressure, (d) Excess enthalpy against the mole fraction of ethyl acetate at 303K, 308K, and 313K

**Conclusion**
The ethyl acetate and 1-ethanol mixtures were prepared at various concentrations at 303K, 308K, and 313K. Physico chemical parameters such that the density, ultrasonic velocity of the selected components were measured. Using the experimental results, the excess isentropic compressibility, excess molar volumes, excess internal pressures, and excess molar enthalpy were calculated. More over the excess parameters also evaluated. The excess parameters were fitted with the Redlich-Kister polynomial functions. The hydrogen bonding between the functional groups was stronger at the 1-ethanol rich concentrations and weaker with ethyl acetate molecules. The strength of the
intermolecular interactions were decreasing with the temperature as 303K>308K>313K.

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Conflict of Interest
The authors do not have any conflict of interest.

References


