Acoustical Studies on Binary Mixtures of Methyl Acrylate with Benzene and Mono-Substituted Benzenes At 313.15 K

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ABSTRACT:
Ultrasonic velocities and Densities of binary mixtures of Methyl Acrylate (MA) with Benzene and mono-substituted Benzenes like Benzene (B), Methyl benzene (MB), and Ethyl benzene (EB) have been measured at 313.15 K, by using these data, various acoustical parameters like Isentropic compressibility (Ks), Intermolecular free length (Lf), acoustic impedance (Z) and relative association (RA) were calculated, further by using these acoustical parameters, excess properties like excess ultrasonic velocities (uE), excess acoustic impedance (ZE), excess isentropic compressibility (KsE) and excess intermolecular free-length (LfE) were calculated and fitted to Redlich-Kister equation. The existence of intermolecular interactions between the components in the liquid mixtures was discussed.

Keywords: Ultrasonic velocity, density, methyl acrylate, benzene, methyl benzene, ethyl benzene, excess isentropic compressibility, excess intermolecular free-length, excess acoustic impedance, Redlich-Kister equation.

1. Introduction:
In the preparation of polymers, MA is used as a monomer, it has innumerable industrial applications. The study of physical property data on binary liquid mixtures with MA gained appreciable interest in the literature [1-3]. Thermodynamic and transport properties of liquid mixtures of MA + B, MA + MB, and MA + EB have been largely used to study the departure of a real mixture from ideality & inter-molecular interactions between the various species present in the liquid mixtures.

Over the last three decades, the ultrasonic study of liquid mixtures has gained much significance in assessing the nature of molecular interactions through the study of the physicochemical properties of such systems. Ultrasonic velocity and liquid mixture-related data is the most powerful tool in testing the theories of liquid state. Also, ultrasonic velocity data can be utilized to work out some useful properties of liquid mixtures which are not easily by other means. The measurement of ultrasonic velocity has been adequately employed as a versatile tool for investigating the physical properties of matter-solid, liquid, and gas.

These studies have extensive use in the textile, leather, and pharmaceutical industries, etc. Ultrasonic velocity measurement has proved useful in dealing with the problems of liquid structure and molecular...
interactions in liquid mixtures. This method has been applied both to pure liquids and to electrolyte solutions [4].

Given the above, the present investigation aims to measure the ultrasonic velocity of binary mixtures of MA + B, MA + MB, and MA + EB at 313.15 K, and using these results, excess ultrasonic velocity \( (u^E) \), excess acoustic impedance \( (Z^E) \), excess isentropic compressibility \( (K_s^E) \) and excess inter molecular free-length \( (L_f^E) \) were calculated and fitted to the Redlich-Kister equation.

2. Experimental Material and Methods:

Methyl Acrylate, Benzene, and mono-substituted Benzenes like Benzene (B), Methyl Benzene (MB), and Ethyl Benzene (EB) were purchased from E-Merck and used as purchased. Mixtures were prepared by mixing weighed amounts of the pure liquids adopting the method of the closed system by using Mettler balance with the precision of ± 0.1 mg. Mixtures were allowed to stand for some time before every measurement, to avoid air bubbles. The purity of the liquids was checked by comparing the values of densities and ultrasonic velocities with literature data (Table 1). The measurements were made with proper care in an AC room to avoid evaporation loss [5-7].

Table 1: Densities and ultrasonic velocities of pure liquids with literature values at 313.15 K

<table>
<thead>
<tr>
<th>Liquid</th>
<th>Density (ρ) x 10^{-3} Kg m^{-3}</th>
<th>Ultrasonic velocity (u) m s^{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>0.8574</td>
<td>0.8576 [4]</td>
</tr>
<tr>
<td>Methyl Benzene</td>
<td>0.8488</td>
<td>0.8587 [8]</td>
</tr>
<tr>
<td>Ethyl Benzene</td>
<td>0.8484</td>
<td>0.8486 [9]</td>
</tr>
<tr>
<td>Methyl Acrylate</td>
<td>0.9292</td>
<td>0.9292 [10]</td>
</tr>
</tbody>
</table>

The densities (ρ) of the liquids and their mixtures were determined using a bi-capillary pycnometer equipped with a capillary diameter of 0.85 mm, calibrated using double distilled water. Buoyancy corrections were meticulously applied, and the recorded density values were consistent within an error margin of ± 0.2 Kg m^{-3}. Ultrasonic velocity (u) measurements were conducted using a single-frequency (2 MHz) variable path interferometer, maintaining an accuracy of ± 0.03%. The experiments were performed in a thermostatically controlled water bath, employing a Schott Geräte Model CT 050/2, ensuring a well-stirred and constant temperature environment controlled to within ± 0.02 K for all measurements.

3. Results and Discussion:

From the measured density (ρ) and ultrasonic velocity (u), the various acoustical parameters such as \( K_s, Z, L_f, \) and \( R_A \) were calculated using the following equations 1, 2, 3 & 4 respectively, and are tabulated in Table 2 for the binary systems under study.

\[
K_s = \frac{1}{u^2} \rho \\
Z = \frac{\rho \ u}{u^2} \\
L_f = K(K_s)^{1/2} \\
\]

Where ‘K’ is Jacobson’s constant [11].

The excess functions \( Y^E \) have been calculated using the relation:
\[ Y^E = Y_{\text{mix}} - (X_1 Y_1 + X_2 Y_2) \] 

Where \( Y \) denotes \( u, Z, K_s, \) and \( L_f \), respectively. \( X \) is the mole fraction and suffixes 1 & 2 denote the components 1 & 2 in the binary mixture, and the values are given in Table 2.

The dependence of \( u^E, Z^E, K_s^E, \) and \( L_f^E \) on the mole fraction of Methyl acrylate (\( X_{\text{MA}} \)) for all three systems were fitted to the following Redlich-Kister equation by the least-squares method and the values are given in Table 2.

\[ Y^E = x(1 - x) \sum A_i (2x - 1)^i \] 

Where \( Y^E \) is \( u^E, Z^E, K_s^E, \) and \( L_f^E \) parameters. The parameters \( A_i \), obtained by a linear least squares polynomial fitting procedure, are also given in Table 3 together with the standard deviations (\( \sigma \)) values.

### Table 2: Values of \( \rho \), Ultrasonic Velocity (\( u \)), \( u^E \), \( Z^E X \), \( K_s^E \), and \( L_f^E \) for the binary liquid mixtures of Methyl Acrylate (MA) with Benzene and mono substituted Benzenes like Benzene (B), Methyl benzene (MB), and Ethyl benzene (EB) at 313.15 K.

<table>
<thead>
<tr>
<th>Mole fraction of MA (( X_{\text{MA}} ))</th>
<th>( \rho \times 10^{-3} ) Kg m(^{-3} )</th>
<th>( u ) m s(^{-1} )</th>
<th>( u^E ) m s(^{-1} )</th>
<th>( Z^E X \times 10^{-4} ) Kg m(^{2} ) s(^{-1} )</th>
<th>( K_s^E \times 10^{11} ) m(^{2} ) N(^{-1} )</th>
<th>( L_f^E \times 10^{12} ) m</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl Acrylate (MA) + Benzene (B)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.0000</td>
<td>0.8574</td>
<td>1236.2</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>0.0916</td>
<td>0.8646</td>
<td>1224.4</td>
<td>-0.9969</td>
<td>0.0586</td>
<td>-0.0614</td>
<td>-0.0139</td>
</tr>
<tr>
<td>0.1849</td>
<td>0.8718</td>
<td>1212.5</td>
<td>-1.7890</td>
<td>0.1039</td>
<td>-0.1107</td>
<td>-0.0247</td>
</tr>
<tr>
<td>0.2800</td>
<td>0.8789</td>
<td>1200.7</td>
<td>-2.3705</td>
<td>0.1360</td>
<td>-0.1472</td>
<td>-0.0326</td>
</tr>
<tr>
<td>0.3769</td>
<td>0.8861</td>
<td>1188.8</td>
<td>-2.7352</td>
<td>0.1549</td>
<td>-0.1706</td>
<td>-0.0374</td>
</tr>
<tr>
<td>0.4757</td>
<td>0.8933</td>
<td>1177.0</td>
<td>-2.8768</td>
<td>0.1609</td>
<td>-0.1803</td>
<td>-0.0392</td>
</tr>
<tr>
<td>0.5764</td>
<td>0.9005</td>
<td>1165.2</td>
<td>-2.7889</td>
<td>0.1540</td>
<td>-0.1756</td>
<td>-0.0378</td>
</tr>
<tr>
<td>0.6792</td>
<td>0.9077</td>
<td>1153.3</td>
<td>-2.4644</td>
<td>0.1343</td>
<td>-0.1559</td>
<td>-0.0332</td>
</tr>
<tr>
<td>0.7840</td>
<td>0.9148</td>
<td>1141.5</td>
<td>-1.8965</td>
<td>0.1020</td>
<td>-0.1206</td>
<td>-0.0254</td>
</tr>
<tr>
<td>0.8909</td>
<td>0.9220</td>
<td>1129.6</td>
<td>-1.0776</td>
<td>0.0572</td>
<td>-0.0689</td>
<td>-0.0144</td>
</tr>
<tr>
<td>1.0000</td>
<td>0.9292</td>
<td>1117.8</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>Methyl Acrylate (MA) + Methyl Benzene (MB)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.0000</td>
<td>0.8488</td>
<td>1242.4</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>0.1268</td>
<td>0.8568</td>
<td>1229.9</td>
<td>0.7826</td>
<td>0.1001</td>
<td>-0.2187</td>
<td>-0.0718</td>
</tr>
<tr>
<td>0.2463</td>
<td>0.8649</td>
<td>1217.5</td>
<td>1.3816</td>
<td>0.1779</td>
<td>-0.3911</td>
<td>-0.1280</td>
</tr>
<tr>
<td>0.3591</td>
<td>0.8729</td>
<td>1205.0</td>
<td>1.8009</td>
<td>0.2333</td>
<td>-0.5166</td>
<td>-0.1685</td>
</tr>
<tr>
<td>0.4657</td>
<td>0.8810</td>
<td>1192.6</td>
<td>2.0441</td>
<td>0.2665</td>
<td>-0.5942</td>
<td>-0.1933</td>
</tr>
<tr>
<td>0.5666</td>
<td>0.8890</td>
<td>1180.1</td>
<td>2.1148</td>
<td>0.2774</td>
<td>-0.6232</td>
<td>-0.2020</td>
</tr>
<tr>
<td>0.6623</td>
<td>0.8970</td>
<td>1167.6</td>
<td>2.0165</td>
<td>0.2661</td>
<td>-0.6025</td>
<td>-0.1947</td>
</tr>
<tr>
<td>0.7531</td>
<td>0.9051</td>
<td>1155.2</td>
<td>1.7526</td>
<td>0.2327</td>
<td>-0.5310</td>
<td>-0.1710</td>
</tr>
</tbody>
</table>
From Table 2, it is observed that the values of $u$, $Z$, $K_s$, and $L_f$ varied with the mole fraction of MA ($X_{MA}$). This indicates the presence of interactions between the components in these binary liquid mixtures. The excess functions which are a measure of the deviations from the ideal behavior are relatively more sensitive to the intermolecular interactions between the unlike molecules of the mixture than the pure acoustical parameters [12].
With this view in mind, the variations in excess acoustical parameters, like excess ultrasonic velocity, excess acoustic impedance, excess isentropic compressibility, and excess intermolecular free-length with mole fraction of methyl acrylate (X_{MA}) are examined from the Figs. 1 to 4 respectively.

**Fig:1:** Plots of excess Ultrasonic velocities (u^E) for various Benzene (- ◆ -) and mono-substituted Benzenes like Methyl Benzene (- ■ -), and Ethyl Benzene (- ▲ -) vs mole fraction of Methyl Acrylate (X_{MA}) at 313.15 K.

It is observed from Fig. 1 that excess ultrasonic velocity is positive for MA+ MB, and MA+EB liquid mixtures whereas the MA+B liquid mixture is slightly negative. In general, if the media is dense, the ultrasonic velocity value will be higher and if the media is less dense, the ultrasonic velocity value will be less. When we mix two liquids if they condense or compress more ultrasonic velocity will be more. For these mixtures, since the excess volume (V^E) values are negative [3, 4, and 13], this indicates the mixtures compressed more and it is natural to get positive excess ultrasonic velocities for these mixtures.

Another effect of interaction between the two components becomes more and more predominant as the alkyl group of the normal benzene becomes more due to their electron donation ability. Also, the size of benzene and mono-substituted benzene molecules increases from Benzene to Ethyl Benzene, which in turn makes a larger difference in the size of Methyl acrylate and benzene and mono-substituted benzene molecules. This gives more possibilities for more interstitial accommodation resulting in more compressed and more dense and decreased volume, it shows positive deviations of Excess ultrasonic velocity values.
Fig. 2: Plots of excess acoustic impedance ($Z^E$) for various Benzene (○ -) and mono-substituted Benzenes like Methyl Benzene (■ -), and Ethyl Benzene (▲ -) vs mole fraction of Methyl Acrylate ($X_{MA}$) at 313.15 K.

Fig. 2 shows a variation of $Z^E$ with a composition of liquid mixtures which exhibit positive deviations as expected as per equation (2) for $Z^E$ calculation.

The positive deviations in $u^E$ and $Z^E$ (Figs. 1 and 2) for all the systems under study are observed over the entire range of composition. These trends for these systems again support our view that the interactions between unlike molecules are quite possible and these values are in the following order:

$$(MA + B) < (MA + MB) < (MA + EB)$$

A similar observation was reported by Vijaya Lakshmi et al. [3] & Anil Kumar Nain [4] from their Intermolecular interactions in binary mixtures of methyl acrylate with benzene and mono-substituted benzenes.

Accordingly, it is evident from the Figs. 3 & 4 that, the negative excess isentropic compressibility and intermolecular free length are attributed to the presence of molecular interactions, possibly through electron donor-acceptor interactions leading to complex formation between unlike molecules. N. Chaudhary [14] and Ali et al. [15], Vijaya Lakshmi et al. [16], pointed out that, negative values of excess inter-molecular free length ($L^E_f$) indicates that sound waves cover longer distance due to a decrease in inter-molecular free length as a result of stronger donor-acceptor interactions between Methyl Acrylate with Benzene and mono substituted benzene molecules resulting in the large positive values of $K^E_s$ and $L^E_f$. 
Fig:3: Plots of Excess Isentropic Compressibility ($K_s^E$) for various Benzene (-تظاني) and mono-substituted Benzenes like Methyl Benzene (-●-), andEthyl Benzene (-▲-) vs mole fraction of Methyl Acrylate ($X_{MA}$) at 313.15 K.

The negative $K_s^E$ and $L_f^E$ values indicate the presence of strong interactions between unlike molecules, which may result in complex formation [17].

The polar nature of the two components Methyl Acrylate with benzenes and mono-substituted benzenes leads to the interaction between the electron-rich oxygen atom of the carbonyl group of Methyl Acrylate with the π-electrons of the aromatic ring of benzenes and substituted benzenes, forming donor-acceptor complexes between the two component molecules in the mixture which leads to a decrease in the intermolecular distances and increase in sound velocities, thereby decreasing the isentropic compressibility of the mixtures. The negative values obtained for the $K_s^E$ and $L_f^E$ are in the following order:

$$(MA + B) < (MA + MB) < (MA + EB)$$

Further, it is also observed from the experimental results that the negative contributions increase with the increase in substitution in benzene (-H, -CH₃, and -C₂H₅). The variation of $K_s^E$ and $L_f^E$ is qualitatively similar to that of excess volumes as discussed in viscosities studies [18-21].

The change in magnitude of negative values of $K_s^E$ and $L_f^E$ from benzene to methyl benzene to ethyl benzene shows that an increase in chain length of benzenes leads to less compressibility in homologous
series. This conclusion is supported by the observation made by Eswari Bai et al. [22], and Fort and Moore [23]. According to these workers, deviations in compressibility from ideality become increasingly negative as the strength of interactions between unlike molecules increase, for the same reason Vijaya Lakshmi et al. [3], observed negative compressibility for the mixtures of Methyl Acrylate with Benzene and substituted Benzenes at 308.15K from these ultrasonic studies.

Fig:4: Plots of excess isentropic compressibility ($L^E_f$) for various Benzene (-●-) and mono-substituted Benzenes like Methyl Benzene (-■-), and Ethyl Benzene (-▲-) vs mole fraction of Methyl Acrylate ($X_{MA}$) at 313.15 K.

4. Conclusion:
The dependence of ultrasonic velocity on the composition of the mixtures is satisfactorily explained. The trends in the variation of the parameters derived from ultrasonic velocity and the sign and extent of deviation of the excess function from rectilinear dependence on the composition of these mixtures suggest the presence of molecular interaction between the components of binary mixtures. The interactions are primarily due to the electron-donor acceptor interactions existing between the components of the mixtures. From the above ultrasonic studies conclude that $u^E$ and $Z^E$ values show positive and $K^E$ and $L^E_f$ values show negative for all binary liquid mixtures of methyl acrylate with benzene and mono-substituted benzenes in the following order,

$$(MA + B) < (MA + MB) < (MA + EB)$$

References:


