Investigation of ultrasonic velocity and related thermo-acoustic parameters in ternary liquid mixture containing DEHPA + benzene + toluene at different temperatures

Manaswini Mishra¹, Upendra Nath Dash¹* and Nandita Swain²

¹Department of Chemistry, Institute of Technical Education and Research, SOA University, Bhubaneswar, Odisha, India
²Department of Chemistry, College of Basic Science and Humanities, OUAT, Bhubaneswar, Odisha, India

ABSTRACT

The measurements of ultrasonic velocity (U) and density (ρ) of the ternary mixture of Di-(2-ethyl- hexyl phosphoric acid), Benzene and Toluene are carried out for entire range of compositions of the mixtures at 298.15K – 313.15K and used to evaluate thermodynamic parameter such as isentropic compressibility (Kₛ), Intermolecular free length (Lf), acoustic impedance (Z), molar volume (Vm), Wada’s Constant (W) and Rao’s constant (R). Excess thermodynamic parameters, such as excess isentropic compressibility (ΔKₛ), excess free length (ΔLf), excess acoustic impendence (ΔZ) and excess velocity (ΔU) have been computed. The ultrasonic velocity has been calculated using various theoretical model and these theoretical relations have been discussed in the present system.

Key words: Ternary mixture, DEHPA, thermodynamic parameters, intermolecular interaction.

INTRODUCTION

Ultrasonic studies of liquid mixtures consisting of polar and non polar components are of considerable importance in introducing intermolecular interaction between the component molecules, and they find applications in several industrial and technological processes¹,² Di-(2-ethyl- hexyl) phosphoric acid (DEHPA) is one of the effective extract antemployed commercially in the solvent extraction processes to recover uranium, vanadium, yttrium, cobalt and Zinc³,⁵. The molecules of DEHPA, one of the components forming the ternary mixtures are polar and show non-ideal behaviors in mixtures. DEHPA is an acidic extract ant which cans deprotonate to form an anion. This hydrophobic anion can chelate a cat ion from an aqueous phase in solvent extraction and the chelate being suitable in the organic phase. In the present system, DEHPA has been treated with the organic aromatic diluents like benzene and toluene.

In the present study, ultrasonic velocities in the ternary mixtures have been estimated by calculating the excess properties and it gives the idea about the structural changes associated with the liquids. The experimental sound velocities have been compared with theoretical velocities predicted through various empirical relations, such as Nomotorelations⁶, Rao’s specific sound velocity relation⁷, Impedance dependence relation⁸, Danussomodel⁹, Van Deal and Vengeel Relation¹⁰. In our earlier work¹¹, the molecular interaction in ternary mixtures of di-(2- ethyl-hexyl) phosphoric acid with non-polar liquid namely benzene and m-xylene, the acoustical properties were studied. Hence this investigation has been carried out to study the physico -chemical properties of di-(2- ethyl- hexyl) phosphoric acid with benzene and toluene.
EXPERIMENTAL SECTION

All the chemicals used in this study were of Analytical Reagent grade and were obtained from E Merck chemicals limited, India. These chemicals were further purified by standard procedures and redistilled before use. Ternary mixtures were prepared by mass in airtight bottles. The mass measurements were performed on a digital top loading balance with a precision of 0.0001 g. Densities of pure liquids and their mixtures were determined with a specific gravity bottle of 25 ml capacity calibrated at four different temperatures from 298.15K to 313.15K. The increment in temperature was kept regular at 5K, with a view to ensuring measurable effects of temperature change on experimental observations. The maximum error in the density measurement was found to be ± 0.01 Kg m$^{-3}$. The ultrasonic velocity was determined using a single crystal variable path ultrasonic interferometer (F-81, Mittal Enterprises, New Delhi) working at frequency of 2 MHz with an accuracy of 0.5 m/s. The temperature of the sample was controlled by circulating water at the above temperature to an accuracy of ± 0.1K in an electronically controlled thermostatic water bath for the measurement of all the physical properties.

Theoretical aspects:

Various molecular interaction parameters such as isentropic compressibility ($K_s$), intermolecular Free length ($L_f$), acoustic impedance ($Z$), molar volume ($V_m$), Wada’s constant ($W$), Rao’s constant($R$) were determined using the following standard relations.

$$ K_s = \frac{1}{\rho U^2} $$

$$ L_f = k K_s^{1/2} $$

Where $k = (93.875 \pm 0.375 \times 10^{-9})$ is the Jacobson temperature dependent constant.

$$ Z = \rho U $$

$$ V_m = \sum_{i=1}^{3} \frac{x_i M_i}{\rho} $$

$$ W = V_m K_s^{-1/7} $$

$$ R = V_m U^{1/3} $$

The excess parameters ($\Delta Y$) such as $\Delta K_s$, $\Delta L_f$, $\Delta Z$, and $\Delta U$ are derived by the following expressions.

$$ \Delta Y = Y_{exp} - Y_{ideal} = Y_m - (x_1 Y_1 + x_2 Y_2 + x_3 Y_3) $$

Where $Y_m$ is the $K_s$, $L_f$, $Z$, $U$ of ternary mixture and $x$ is the mole fraction and subscripts 1, 2 and 3 refers to components of ternary system.

The theoretical values of ultrasonic velocity such as $U_N$, $U_R$, $U_{IDR}$, $U_V$ are calculated by the following relation 15-17

$$ U_N = \left( \frac{\sum x_i R_i}{\sum x_i V_i} \right)^{\frac{1}{2}} $$

Where $x_i$, $U_i$, $V_i$ are the respective mole fraction, ultrasonic velocity, molar volume and $R_i = V_i U_i^{1/3}$ the molar sound velocity of the $i^{th}$ component in the liquid mixture.

$$ U_R = \left( \sum x_i r_i \rho_i \right)^{\frac{1}{2}} $$

Where $r_i = U_i^{1/3} / \rho_i$ is the Rao’s specific sound velocity and $\rho_i$ is the density of the $i^{th}$ component of the mixture.

$$ U_{IDR} = \frac{\sum x_i Z_i}{\sum x_i \rho_i} $$
\[
\Delta U = (1/p) \left[ \frac{1}{1/M_i} \Sigma (x_i M_i \rho_i V_i) \right]^{1/2}
\]

(11)

\[
U_v = \left( \frac{X_1^2 + X_2^2 + X_3^2}{M_1 u_1^2 + M_2 u_2^2 + M_3 u_3^2} \right)^{1/2}
\]

(12)

The percentage of deviation is ultrasonic velocity between experimental and computed values can be calculated as

\[
\left( \frac{\Delta U}{U} \right) \% = \left( \frac{U_{exp} - U_{theo}}{U_{exp}} \right) \times 100
\]

(13)

REASULTS AND DISCUSSION

The measured values of the ultrasonic velocity \( U \), and density (\( \rho \)) of the ternary mixtures of DEHPA with two nonpolar solvents benzene and toluene at temperature range 298.15K – 313.15K are used to evaluate the values of isentropic compressibility (\( K_s \)), intermolecular free length (\( L_f \)), acoustic impedance (\( Z \)), molar volume (\( V_m \)), Wada’s constant (\( W \)) and Rao’s constant (\( R \)) are presented in the table-(1). The excess properties such as \( \Delta L_e \), \( \Delta K \), \( \Delta Z \) and \( \Delta U \) are described graphically in figures 1 to 4.

Table-1 Measured values of ultrasonic velocity (U) and density (\( \rho \)) of the ternary mixture of DEHPA with two nonpolar solvents benzene and toluene.

<table>
<thead>
<tr>
<th>( x_1 )</th>
<th>( x_2 )</th>
<th>( x_3 )</th>
<th>( \rho ) Kg m ( ^{-3} )</th>
<th>( U ) m/s</th>
<th>( K_s ) ( 10^6 )N m ( ^{-2} )</th>
<th>( L_f ) ( 10^3 ) m</th>
<th>( Z ) ( 10^9 ) Kgm ( ^{-1} ) s ( ^{-1} )</th>
<th>( V_m ) ( 10^3 ) m ( ^3 ) mol ( ^{-1} )</th>
<th>( W ) ( 10^3 ) m ( ^3 ) mol ( ^{-1} )(N m ( ^{-1} ))</th>
<th>( R ) ( 10^3 ) m ( ^3 ) mol ( ^{-1} )(N m ( ^{-1} ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.032</td>
<td>0.526</td>
<td>0.442</td>
<td>875.0</td>
<td>1233</td>
<td>5.7154</td>
<td>10.788</td>
<td>10.5291</td>
<td>0.2117</td>
<td>0.1129</td>
<td></td>
</tr>
<tr>
<td>0.069</td>
<td>0.511</td>
<td>0.420</td>
<td>885.8</td>
<td>1240</td>
<td>5.7322</td>
<td>10.983</td>
<td>11.3864</td>
<td>0.2297</td>
<td>0.1223</td>
<td></td>
</tr>
<tr>
<td>0.177</td>
<td>0.481</td>
<td>0.402</td>
<td>896.0</td>
<td>1254</td>
<td>5.7519</td>
<td>11.155</td>
<td>12.5374</td>
<td>0.2536</td>
<td>0.1349</td>
<td></td>
</tr>
<tr>
<td>0.176</td>
<td>0.446</td>
<td>0.378</td>
<td>904.0</td>
<td>1249</td>
<td>5.4771</td>
<td>11.291</td>
<td>13.9838</td>
<td>0.2835</td>
<td>0.1506</td>
<td></td>
</tr>
<tr>
<td>0.238</td>
<td>0.413</td>
<td>0.350</td>
<td>912.8</td>
<td>1252</td>
<td>5.4375</td>
<td>11.424</td>
<td>15.4740</td>
<td>0.3144</td>
<td>0.1668</td>
<td></td>
</tr>
<tr>
<td>0.323</td>
<td>0.372</td>
<td>0.305</td>
<td>925.4</td>
<td>1259</td>
<td>5.7303</td>
<td>11.651</td>
<td>17.4308</td>
<td>0.3554</td>
<td>0.1882</td>
<td></td>
</tr>
<tr>
<td>0.406</td>
<td>0.321</td>
<td>0.273</td>
<td>936.7</td>
<td>1264</td>
<td>5.3167</td>
<td>11.839</td>
<td>19.3375</td>
<td>0.3954</td>
<td>0.2091</td>
<td></td>
</tr>
<tr>
<td>0.544</td>
<td>0.261</td>
<td>0.195</td>
<td>947.3</td>
<td>1272</td>
<td>5.2536</td>
<td>12.049</td>
<td>22.5648</td>
<td>0.4630</td>
<td>0.2449</td>
<td></td>
</tr>
<tr>
<td>0.720</td>
<td>0.160</td>
<td>0.120</td>
<td>954.0</td>
<td>1293</td>
<td>5.1501</td>
<td>12.335</td>
<td>26.8034</td>
<td>0.5531</td>
<td>0.2920</td>
<td></td>
</tr>
</tbody>
</table>

\[ \rho = (1/\rho) \Sigma (x_i M_i \rho_i V_i) \]

(12)

\[ \rho = (1/\rho) \Sigma (x_i M_i \rho_i V_i) \]

(12)
Table-1 shows that, ultrasonic velocity and density increase with increase in mole fraction of DEHPA and decrease with increase in temperature. While isentropic compressibility $K_s$ and intermolecular free length $L_f$ decrease in concentration of DEHPA and increase with increase in the temperature. According to Kincaid and Earing (19), the ultrasonic velocity increases with decrease in the intermolecular free length and vice versa. The acoustic impedance ($Z$) increases with in concentration of DEHPA. The increase in acoustic impedance indicates the presence of bulkier or solvated ion due to interaction between unlike molecules which restrict the free flow of sound waves.

As DEHPA is a polar molecule and it exists as dimmers in pure form, and both benzene (C$_6$H$_6$) and toluene (C$_7$H$_8$) are nonpolar molecules and they are of ring type structure. The reduction of benzene and toluene creates the system ring structured molecules which occupy less space and increase the compactness. The molar volume $V_m$ increases with increase in mole fraction of DEHPA (Table-1). This reduces the net attractive forces. A continuous decrease in $K_s$ and $L_f$ and increase in acoustic impedance ($Z$) with concentration of DEHPA is a clear evidence for the existence of strong interactions like dipole-dipole, dipole-induced dipole, hydrogen bonding formation of charge transfer complexes etc. The increase in the values of $L_f$, $K_s$, $V_m$ and decrease in $Z$ with increase in temperature clearly reveals that the interaction becomes weaker with rise in temperature. Further, it is observed that the increasing trend of Wada’s constant ($W$) and Rao’s constant ($R$) with mole fraction of DEHPA indicate strong solute-solvent interaction.

Although all measured parameters indicate the existence of molecular interaction, probably the excess parameters rather offer better conformation in understanding the nature of molecular interaction in liquid mixtures. Figure-1 and Figure-2 indicate that, $\Delta L_f$ and $\Delta K_s$ are positive over the entire mole fraction range and even with rising of temperature in the ternary mixture. The positive deviation in $\Delta L_f$ and $\Delta K_s$ in ternary system has been attributed to dispersive forces that show weak interaction between the unlike molecules. The similar observation, we get in our previous work 9.

This result agrees with negative variation of $\Delta Z$ and $\Delta U$ in figure-3 and figure-4. The negative deviations indicate that there is weak interaction between the component molecules 19. The negative $\Delta U$ shows that, the mutual loss of dipolar association among DEHPA molecules between like and unlike molecules. Which create dispersive interaction between the component molecules. Thus, it may be concluded that, there are weak molecular interactions among the components of the mixture.

It is evident from Table-2 that there is good agreement between the experimental and calculated ultrasonic velocities even though assumption and approximation are made in the theory. In this ternary system, the suitability of these theories based on percentage deviation value is $U_{IDR} > U_{R} > U_{D} > U_{R} > U_{V}$.
Table – 2 Comparison between experimental and theoretical values of ultrasonic velocity with mole fraction (x$_1$) of DEHPA at 303.15K

<table>
<thead>
<tr>
<th>Mole fraction ( x$_1$)</th>
<th>U$_{exp}$ m/s</th>
<th>U$_{N}$ m/s</th>
<th>U$_{R}$ m/s</th>
<th>U$_{IDR}$ m/s</th>
<th>U$_{V}$ m/s</th>
<th>U$_{N}$ m/s</th>
<th>U$_{IDR}$ m/s</th>
<th>U$_{R}$ m/s</th>
<th>U$_{V}$ m/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.032</td>
<td>1214</td>
<td>1248.6</td>
<td>1272.9</td>
<td>1306.7</td>
<td>1286.6</td>
<td>1236.5</td>
<td>-5.8</td>
<td>-4.8</td>
<td>-7.3</td>
</tr>
<tr>
<td>0.069</td>
<td>1221</td>
<td>1256.9</td>
<td>1271.8</td>
<td>1307.6</td>
<td>1286.6</td>
<td>1198.6</td>
<td>-5.5</td>
<td>-4.1</td>
<td>-9.4</td>
</tr>
<tr>
<td>0.117</td>
<td>1226</td>
<td>1270.5</td>
<td>1263.7</td>
<td>1294.0</td>
<td>1288.6</td>
<td>1158.5</td>
<td>-5.5</td>
<td>-3.6</td>
<td>-11.2</td>
</tr>
<tr>
<td>0.176</td>
<td>1229</td>
<td>1280.0</td>
<td>1274.0</td>
<td>1303.7</td>
<td>1294.0</td>
<td>1158.5</td>
<td>-5.5</td>
<td>-3.2</td>
<td>-11.8</td>
</tr>
<tr>
<td>0.238</td>
<td>1232</td>
<td>1296.3</td>
<td>1283.3</td>
<td>1308.3</td>
<td>1303.7</td>
<td>1120.2</td>
<td>-5.6</td>
<td>-2.8</td>
<td>-14.0</td>
</tr>
<tr>
<td>0.323</td>
<td>1239</td>
<td>1307.2</td>
<td>1286.9</td>
<td>1316.1</td>
<td>1304.0</td>
<td>1089.0</td>
<td>-5.7</td>
<td>-2.8</td>
<td>-14.0</td>
</tr>
<tr>
<td>0.406</td>
<td>1246</td>
<td>1310.7</td>
<td>1262.8</td>
<td>1349.3</td>
<td>1306.6</td>
<td>1046.9</td>
<td>-5.1</td>
<td>-1.3</td>
<td>-15.5</td>
</tr>
<tr>
<td>0.544</td>
<td>1254</td>
<td>1315.2</td>
<td>1259.1</td>
<td>1347.1</td>
<td>1309.4</td>
<td>1043.4</td>
<td>-5.4</td>
<td>-0.4</td>
<td>-14.6</td>
</tr>
<tr>
<td>0.720</td>
<td>1266</td>
<td>1321.4</td>
<td>1258.4</td>
<td>1337.0</td>
<td>1324.5</td>
<td>1085.2</td>
<td>-3.8</td>
<td>1.6</td>
<td>-7.7</td>
</tr>
</tbody>
</table>

CONCLUSION

The present investigation shows that, weak molecular interaction exists in the ternary mixtures. The positive values of $\Delta K_s$, $\Delta L_f$ and negative values of $\Delta Z$ and $\Delta U$ in the ternary mixture indicate the presence of weak molecular interaction among the component of molecules in the mixture.

Among the five theories taken for the prediction of ultrasonic velocity, IDR is found to show better comparison with the experimental values for the system investigated.

Acknowledgement

The authors are grateful to the Chairman, Institute of Technical Education and Research (ITER), SOA University, Bhubaneswar for providing the necessary facilities to carry out the research work.

REFERENCES