Theoretical Prediction of Ultrasonic Velocity in Organic Liquid Mixtures

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Abstract: Theoretical values of ultrasonic velocity in the binary mixtures of cyclohexanone with 2-propanol and 2-methyl-2-propanol have been evaluated at 303 K using Nomoto’s relation, collision factor theory, free length theory, ideal mixture relation, Junjie’s method. Theoretical values are compared with the experimental values and the validity of the theories are checked by applying the chi-square test for goodness of fit and by calculating the average percentage error (APE).

Keywords: Ultrasonic velocity, Binary mixtures and Theoretical prediction.

Introduction

Measurement of ultrasonic velocity gives the valuable information about the physico-chemical behaviour of the liquid and liquid mixtures. Several relations, semi-empirical formula and theories are available for the theoretical computation of ultrasonic velocity in liquid and liquid mixtures1-5. Further, the best suitable theory for the given molecular system under study is also picked out by calculating the average percentage error and chi-square test at 1% and 5% levels.

Experimental

The ultrasonic velocity was measured at 303 K using a single crystal interferometer with a high degree of accuracy operating at a frequency of 2 MHz. The density was measured at 303 K using specific gravity bottle by the standard procedure.

Theory

The following are relations/theories used for the prediction of ultrasonic velocity in the binary liquid mixtures.
Nomoto’s relations (NOM)

\[
U_{\text{NOM}} = \left[ \frac{X_1R_1 + X_2R_2}{X_1R_2 + X_2R_1} \right]^{3/2}
\]  
(1)

Where, Molar sound velocity, 
\[
R_i = \frac{m_i}{d_i^{1/3}}; \quad R_2 = \frac{m_2}{d_2^{1/3}}
\]

Molar volume, 
\[
V_i = \frac{m_i}{d_i} ; \quad V_2 = \frac{m_2}{d_2}
\]

Collision factor theory (CFT)

\[
U_{\text{CFT}} = u_m \left[ \frac{(X_1S_1 + X_2S_2)(X_1S_1 + X_2S_2)}{V_m} \right]
\]  
(2)

Where, Molar volume of mixture, 
\[
V_m = \frac{X_1m_1 + X_2m_2}{d_{\text{exp}}}
\]

Actual volume, 
\[
B = \frac{4}{3} \pi r_3 N
\]

Molecular radius, 
\[
r = \left[ \frac{3b}{16\pi N} \right]^{1/3}
\]

Vander waal’s constant, 
\[
b = \frac{m}{d} \left[ 1 - \frac{RT}{mu^2} \left( \sqrt{1 + \frac{mu^2}{3RT}} - 1 \right) \right]
\]

Temperature dependent constant, 
\[
u_\alpha = 1600 \text{ m/sec}, \quad N \text{ is the Avagadro’s number.}
\]

Free length theory (FLT)

\[
U_{\text{FLT}} = \frac{K}{L_{mix}^{1/2}d_{\text{exp}}^{1/2}}
\]  
(3)

Where, 
\[
L_{mix} = 2 \left[ V_m - (X_1V_{01} + X_2V_{02}) \right] \left( X_1Y_1 + X_2Y_2 \right)
\]

Molar volume at absolute zero, 
\[
V_{0i} = V_i u_i / u_w ; \quad V_{02} = V_2 u_2 / u_w
\]

Surface area per mole, 
\[
y_1 = \frac{2(V_1 - V_{01})}{L_{f1}} , \quad y_2 = \frac{2(V_2 - V_{02})}{L_{f2}}
\]

Ideal mixture relation(IMR)

\[
U_{\text{IMR}} = \left[ \frac{1}{X_1m_1 + X_2m_2} \right]^{1/2} \left[ \frac{X_1V_1}{m_1u_1^2} + \frac{X_2V_2}{m_2u_2^2} \right]^{-1/2}
\]  
(4)

Junjie’s method(JM)

\[
U_{\text{JM}} = \left[ \frac{X_1V_1 + X_2V_2}{(X_1m_1 + X_2m_2)^{1/2}} \right] \left[ \frac{X_1V_1}{d_1u_1^2} + \frac{X_2V_2}{d_2u_2^2} \right]^{-1/2}
\]  
(5)

Where, 1, 2, represents the first and second component of the liquid mixture and the other symbols have their usual meanings.
Theoretical Prediction of Ultrasonic Velocity

Results and Discussion
The experimental values along with the values calculated theoretically using Nomoto’s relation, collision factor theory, free length theory, ideal mixture relation and Junjie’s method for the systems: (i) cyclohexanone + 2-propanol and (ii) cyclohexanone + 2-methyl-2-propanol at 303 K are given in Table 1 & 2 respectively. The validity of the theories is checked by applying Chi-square test and by calculating average percentage error.

Chi-square test for goodness of fit
The ‘goodness of fit’ of the theories for the binary liquid mixtures under study is evaluated. For example, in both the binary liquid systems, the number of degrees of freedom is 6. For this, the Chi-square value for ‘goodness of fit’ at 1% level is equal to 16.81 and at 5% level is equal to 12.59. According to Karl Pearson, the Chi-square value is calculated using the formula,

\[ \chi^2 = \sum_{i=1}^{n} \frac{(U_{\text{mix(obs)}} - U_{\text{mix(cal)}})^2}{U_{\text{mix(cal)}}} \]  

For (n-1) degrees of freedom, where, n is the number of data used.

Average percentage error (APE)
The average percentage Error is calculated using the relation,

\[ \text{APE} = \frac{1}{n} \sum \frac{(U_{\text{mix(obs)}} - U_{\text{mix(cal)}})}{U_{\text{mix(obs)}}} \times 100\% \]

Where, \( n \) - number of data used.
\( U_{\text{mix(obs)}} \) = experimental values of ultrasonic velocities.
\( U_{\text{mix(cal)}} \) = computed values of ultrasonic velocities.

It can be seen from Table 1 & 2 that the theoretical values of ultrasonic velocity computed by various theories show deviation from experimental values. The reason may be the limitations and approximations incorporated in these theories.

Table 1. Experimental and computed values of \( U_{\text{mix}} \) for cyclohexanone + 2-propanol system.

<table>
<thead>
<tr>
<th>Mole fraction of cyclohexanone ( (X_1) )</th>
<th>( U_{\text{exp}} ) ( \text{ms}^{-1} )</th>
<th>( U_{\text{NOM}} ) ( \text{ms}^{-1} )</th>
<th>( U_{\text{CFT}} ) ( \text{ms}^{-1} )</th>
<th>( U_{\text{FLT}} ) ( \text{ms}^{-1} )</th>
<th>( U_{\text{IMR}} ) ( \text{ms}^{-1} )</th>
<th>( U_{\text{JM}} ) ( \text{ms}^{-1} )</th>
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</thead>
<tbody>
<tr>
<td>0.0000</td>
<td>1113.4</td>
<td>1113.4</td>
<td>1113.4</td>
<td>1113.4</td>
<td>1113.4</td>
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<td>1241.0</td>
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<td>5.178</td>
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<td>Chi-Square</td>
<td>0.133</td>
<td>9.539</td>
<td>37.252</td>
<td>4.908</td>
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</table>

Table 1 shows that the Chi-square value and APE value are minimum for Nomoto’s relation than those obtained by other theories. However for the binary mixtures of cyclohexanone+2-methyl-2-propanol, these values are minimum for CFT. This may be due the fact that Nomoto’s relation and Collision factor theory holds good for self associated polar liquids. When two liquids are mixed, the interaction between the molecules of the two liquids takes place because of the presence of various forces like dispersive force, charge transfer, hydrogen bonding dipole-dipole and dipole-induced dipole interactions. Hence the observed deviation shows that the molecular interaction is taking place between the unlike molecules in the liquid mixture.
Table 2. Experimental and computed values of $U_{mix}$ for cyclohexanone+2-methyl-2-propanol system.

<table>
<thead>
<tr>
<th>Mole fraction of cyclohexanone ($X_1$)</th>
<th>$U_{exp}$ ms$^{-1}$</th>
<th>$U_{NOM}$ ms$^{-1}$</th>
<th>$U_{CFT}$ ms$^{-1}$</th>
<th>$U_{FLT}$ ms$^{-1}$</th>
<th>$U_{IMR}$ ms$^{-1}$</th>
<th>$U_{JM}$ ms$^{-1}$</th>
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<td>APE</td>
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<td>0.726</td>
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<td>3.789</td>
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<td>Chi-Square</td>
<td>1.317</td>
<td>0.823</td>
<td>23.942</td>
<td>19.302</td>
<td>11.243</td>
<td></td>
</tr>
</tbody>
</table>

Conclusion

It may be concluded that Nomoto’s relation is best suited for the binary mixtures of cyclohexanone+2-propanol and collision factor theory holds good for cyclohexanone + 2-methyl-2-propanol. The observed deviation of theoretical values of velocity from the experimental values is attributed to the presence of intermolecular interactions in the systems studied.

References

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