Viscosities, Densities and Ultrasonic velocities of Methylbenzoate with 1-pentanol and 1-hexanol at 303.15 K

T. Sumathi¹, S. Vasanthi¹

¹Department of Physics, Annamalai University, Annamalai nagar-608002, Tamilnadu, India,

Abstract : Densities, viscosities and ultrasonic velocities of binary liquid mixtures of Methylbenzoate with 1-pentanol and 1-hexanol have been measured at 303.15 K. The experimental data have been used to calculate the various acoustical parameters namely adiabatic compressibility (β), free length (L₀), Internal pressure (πᵢ), acoustical impedance (Z) and the excess values of the above parameters have also been evaluated. The variation of these parameters with composition of the mixture helps us in understanding the nature and extent of interaction between unlike molecules in the mixtures.

Keywords: Ultrasonic velocity, Adiabatic compressibility, Binary system, Excess parameters.

1. Introduction

Knowledge of thermo acoustic properties is of great significance in understanding the physicochemical behavior and molecular arrangement in various liquid mixtures and solutions (Dhok et al., 2012). The practical applications of mixed solvents, rather than single solvent in industrial and biological processes have been recognized all over the world, as they provide a wide choice of solutions with appropriate properties (Ali et al., 2001). In recent years, the measurement of ultrasonic velocity has been successfully employed in understanding the nature of molecular interaction in pure liquids and liquid mixtures. The study of pure liquids and their properties cannot be altered continuously within a reasonable range by varying the concentration till an optimum value of some desired parameter is attained. This is only possible by considering the liquid mixtures and solutions which find direct applications in many chemical industries and technological processes (Nithiyanantham and Palaniappan, 2013).

Methylbenzoate is a colorless liquid that is poorly soluble in water, but miscible with organic solvents. It has a pleasant smell strongly reminiscent of the fruit of the feijoa tree and it is used in perfumery. It is also used as a solvent and as a pesticide which attract insects. Alcohols are strongly self-associated liquids with a three dimensional network of hydrogen and can be associated with any other group having some degree of polar attractions (Anwar Ali et al., 2004). The interaction of alcohol[s] with organic liquids is interesting due to its acidic nature. The O-H bonds in alcohols are polar and allow the release of the hydrogen atom as proton [H⁺]. Pentanol is used as a solvent for coating CDs and DVDs, another use is a replacement for gasoline. Hexanol is the odour of freshly mowed grass and is used in perfume industry. Owing to these considerations, an attempt has been made to elucidate the molecular interactions in the mixtures of 1-pentanol and 1-hexanol with methylbenzoate at 303.15 K. Further, the excess values of some of the acoustical and interaction parameters have been calculated from the measurements of ultrasonic velocity, density and viscosity of the mixtures. The excess parameters are used to explain intermolecular interaction in these binary mixtures.

2. Experimental technique

All the chemicals used were of Analytical reagent (AR) and spectroscopic reagent (SR) grades with minimum assay of 99.9%. The speeds of sound waves were obtained by using ultrasonic interferometer (Model No, F-81, M/S. Mittal enterprises, New Delhi) at a fixed frequency of 3 MHz with an accuracy of ± 2 ms⁻¹. An electronically digital operated constant temperature bath (RAAGA Industries, Madras 61) has been used to circulate water through the double walled measuring cell made up of steel containing the experimental solution at the desired temperature. The density of pure liquids and liquid mixtures was determined using a pycnometer by relative measurement method with an accuracy of ± 0.1 K (Model: SHIMADZU AX-200). The pycnometer was calibrated at 303.15K with double distilled water and gave an estimated reproducibility of ±0.0001 gcm⁻³. An Ostwald’s viscometer was calibrated with fresh conductivity water immersed in the water bath which was kept at the experimental temperature. The time of flow (t₀) of water and the time flow (tᵢ) of solution was measured with digital stop clock having an accuracy ± 3 x 10⁻⁶ Nsm⁻². The temperature around the viscometer was maintained with in ± 0.1 K in an electronically controlled thermostatic water bath. The various concentrations of the binary liquid mixtures were prepared in terms of mole fraction, such as 1-pentanol with methylbenzoate and 1-hexanol with methylbenzoate varied from 0.1 to 0.9.

2.1 Theory

From the measured values of density (ρ) and ultrasonic velocity (U), acoustic parameters like adiabatic compressibility (β), intermolecular free length (L₀), internal pressure (πᵢ) and acoustical impedance (Z) were calculated using the following relations (More et al., 2005).

\[ \beta = \frac{1}{\rho U^2} \]
\[ L_f = K_T \beta^{1/2} \]  
\[ \pi_i = bRT \left( \frac{K_i}{U} \right)^{1/2} \left( \frac{\rho^{2/3}}{M^{1/6}} \right) \]  
\[ Z = U \rho \]

Where \( K_T \) is the temperature dependent constant, \( K \) the temperature independent constant (\( K = 4.28 \times 10^9 \)), \( b \) a constant which is 2 for cubic packing, \( R \) the gas constant and \( T \) is the temperature in K. \( U \) and \( \rho \) are velocity and density of liquids.

The non-ideality of the liquid mixtures, the difference between the parameters of the real mixtures (\( A_{exp} \)) and those corresponding to an ideal mixture (\( A_{id} \)) values, namely excess parameters (\( A_E \)) of all the acoustic parameters were computed by the relation.

\[ A^E = A_{exp} - A_{id} \]

Where \( A_{id} = \sum_{i=1}^{n} A_i X_i \), \( A_i \) is any acoustical parameters and \( X_i \) the mole fraction of the liquid component \( i \).

3. Results and Discussion

Experimentally measured the values of density (\( \rho \)), viscosity (\( \eta \)) and ultrasonic velocity (\( U \)) for pure liquids and liquid mixture at 303.15 K are presented in Table 1&2. The binary liquid mixture were used to calculate the acoustical parameters such as adiabatic compressibility (\( \beta \)), free length (\( L_f \)), internal pressure (\( \pi_i \)) and acoustic impedance (\( Z \)) are presented in Table 3. In all the mixtures, the density and the ultrasonic velocity decreased with increasing mole fraction of 1-alkanol. The decrease in velocity and increase in compressibility were attributed to the formation of hydrogen bonds between solute and solvent molecules (Nemaniwar et al., 2013).

**Table 1 - Values of density (\( \rho \)), Viscosity (\( \eta \)), and velocity (\( U \)) of Pure liquids at 303.15K**

<table>
<thead>
<tr>
<th>Liquids</th>
<th>( \rho )Kgm(^{-3} )</th>
<th>( \eta \times 10^3 )NSm(^{-2} )</th>
<th>( U )ms(^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>I-Pentanol</td>
<td>806.14</td>
<td>2.4198</td>
<td>1253.7</td>
</tr>
<tr>
<td>I-hexanol</td>
<td>812.51</td>
<td>2.3619</td>
<td>1281.7</td>
</tr>
<tr>
<td>Methyl Benzoate</td>
<td>1062.84</td>
<td>1.1864</td>
<td>1365.4</td>
</tr>
</tbody>
</table>

**Table 2 - Values of density (\( \rho \)), Viscosity (\( \eta \)), and velocity (\( U \)) of systems I and II at 303.15 K**

<table>
<thead>
<tr>
<th>Mole fractions</th>
<th>( X_1 )</th>
<th>( X_2 )</th>
<th>( \rho )Kgm(^{-3} )</th>
<th>( \eta \times 10^3 )NSm(^{-2} )</th>
<th>( U )ms(^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>System I: 1-pentanol + Methyl Benzoate</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.1001</td>
<td>0.8999</td>
<td>971.43</td>
<td>1.4446</td>
<td>1372.6</td>
<td></td>
</tr>
<tr>
<td>0.2001</td>
<td>0.8000</td>
<td>950.15</td>
<td>1.4608</td>
<td>1356.6</td>
<td></td>
</tr>
<tr>
<td>0.3001</td>
<td>0.7001</td>
<td>929.60</td>
<td>1.4879</td>
<td>1348.1</td>
<td></td>
</tr>
<tr>
<td>0.4001</td>
<td>0.6001</td>
<td>888.56</td>
<td>1.4896</td>
<td>1344.8</td>
<td></td>
</tr>
<tr>
<td>0.5000</td>
<td>0.5000</td>
<td>878.53</td>
<td>1.4911</td>
<td>1329.8</td>
<td></td>
</tr>
<tr>
<td>0.6000</td>
<td>0.3999</td>
<td>832.57</td>
<td>1.5056</td>
<td>1309.3</td>
<td></td>
</tr>
<tr>
<td>0.7000</td>
<td>0.2998</td>
<td>827.41</td>
<td>1.5183</td>
<td>1298.5</td>
<td></td>
</tr>
<tr>
<td>0.7999</td>
<td>0.1998</td>
<td>822.11</td>
<td>1.5419</td>
<td>1281.5</td>
<td></td>
</tr>
<tr>
<td>0.8998</td>
<td>0.1001</td>
<td>815.44</td>
<td>1.5945</td>
<td>1258.6</td>
<td></td>
</tr>
<tr>
<td><strong>System II: 1-Hexanol + Methyl Benzoate</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.1001</td>
<td>0.9000</td>
<td>955.44</td>
<td>1.4844</td>
<td>1382.6</td>
<td></td>
</tr>
<tr>
<td>0.2000</td>
<td>0.8999</td>
<td>949.19</td>
<td>1.5335</td>
<td>1358.9</td>
<td></td>
</tr>
<tr>
<td>0.3002</td>
<td>0.7001</td>
<td>926.10</td>
<td>1.5991</td>
<td>1352.2</td>
<td></td>
</tr>
<tr>
<td>0.4000</td>
<td>0.6001</td>
<td>881.95</td>
<td>1.6032</td>
<td>1339.8</td>
<td></td>
</tr>
<tr>
<td>0.5001</td>
<td>0.5000</td>
<td>858.19</td>
<td>1.6721</td>
<td>1335.4</td>
<td></td>
</tr>
<tr>
<td>0.6004</td>
<td>0.3999</td>
<td>830.01</td>
<td>1.7669</td>
<td>1329.9</td>
<td></td>
</tr>
<tr>
<td>0.7000</td>
<td>0.2999</td>
<td>823.01</td>
<td>1.8396</td>
<td>1301.0</td>
<td></td>
</tr>
<tr>
<td>0.8001</td>
<td>0.2001</td>
<td>818.42</td>
<td>2.0337</td>
<td>1292.4</td>
<td></td>
</tr>
<tr>
<td>0.9002</td>
<td>0.0999</td>
<td>815.45</td>
<td>2.2139</td>
<td>1291.2</td>
<td></td>
</tr>
</tbody>
</table>
Adiabatic compressibility ($\beta$) increases by increase in mole fraction of 1-alkanol (Table 3). Loss of dipolar association and difference is size and shape of the component molecules, which leads to decrease in velocity and increasing compressibility (Rama Roa, 2004). The intermolecular free length is found to be a predominant factor in determining the nature of sound velocities variation in liquid mixtures and also in deciding the variations of ultrasonic parameters. Intermolecular free length depends on “$\beta$” and shows a similar behavior as that of compressibility (Table 3). Hence free length also increases but at a slower rate. On the basis of a model for sound propagation by Eyring and Kincaid, ultrasonic velocity should decrease if the intermolecular free length increases and vice versa (Eyring and Kincaid, 1938).

Table-3 Values of Adiabatic compressibility ($\beta$), Free length ($L_f$), Internal pressure ($\pi_i$), Acoustic impedance ($Z$), of system I and II at 303.15 K

<table>
<thead>
<tr>
<th>Mole fraction</th>
<th>$\beta \times 10^{10}$ Pa$^{-1}$</th>
<th>$L_f 10^{10}$m</th>
<th>$\pi_i \times 10^{-6}$ Pa</th>
<th>$Z \times 10^{-6}$ kgm$^{-1}$s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>X$_1$</td>
<td>X$_2$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.1001</td>
<td>0.8999</td>
<td>5.464</td>
<td>0.4664</td>
<td>335.6</td>
</tr>
<tr>
<td>0.2001</td>
<td>0.8000</td>
<td>5.724</td>
<td>0.4774</td>
<td>368.5</td>
</tr>
<tr>
<td>0.3001</td>
<td>0.7001</td>
<td>5.919</td>
<td>0.4854</td>
<td>384.5</td>
</tr>
<tr>
<td>0.4001</td>
<td>0.6001</td>
<td>6.317</td>
<td>0.5015</td>
<td>393.2</td>
</tr>
<tr>
<td>0.5000</td>
<td>0.5001</td>
<td>6.437</td>
<td>0.5062</td>
<td>410.8</td>
</tr>
<tr>
<td>0.6000</td>
<td>0.3999</td>
<td>7.006</td>
<td>0.5282</td>
<td>422.5</td>
</tr>
<tr>
<td>0.7000</td>
<td>0.2998</td>
<td>7.168</td>
<td>0.5342</td>
<td>447.7</td>
</tr>
<tr>
<td>0.7999</td>
<td>0.1998</td>
<td>7.631</td>
<td>0.5526</td>
<td>478.2</td>
</tr>
<tr>
<td>0.8998</td>
<td>0.1001</td>
<td>8.016</td>
<td>0.5687</td>
<td>517.4</td>
</tr>
<tr>
<td>0.1001</td>
<td>0.9000</td>
<td>5.475</td>
<td>0.4669</td>
<td>313.4</td>
</tr>
<tr>
<td>0.2000</td>
<td>0.8999</td>
<td>5.765</td>
<td>0.4867</td>
<td>327.0</td>
</tr>
<tr>
<td>0.3002</td>
<td>0.7001</td>
<td>5.941</td>
<td>0.4892</td>
<td>381.6</td>
</tr>
<tr>
<td>0.4000</td>
<td>0.6001</td>
<td>6.373</td>
<td>0.5028</td>
<td>383.6</td>
</tr>
<tr>
<td>0.5001</td>
<td>0.5000</td>
<td>6.534</td>
<td>0.5100</td>
<td>398.2</td>
</tr>
<tr>
<td>0.6004</td>
<td>0.3999</td>
<td>7.095</td>
<td>0.5319</td>
<td>414.9</td>
</tr>
<tr>
<td>0.7000</td>
<td>0.2999</td>
<td>7.174</td>
<td>0.5344</td>
<td>441.0</td>
</tr>
<tr>
<td>0.8001</td>
<td>0.2001</td>
<td>7.851</td>
<td>0.5543</td>
<td>462.8</td>
</tr>
<tr>
<td>0.9002</td>
<td>0.0999</td>
<td>8.109</td>
<td>0.5706</td>
<td>517.2</td>
</tr>
</tbody>
</table>

It is observed that internal pressure increases with increasing concentration of 1-ols (Table 3). The internal pressure increases due to the various degree of dispersive interaction and the coloumbic interaction existing between the component molecules (Sumathi and Umamaheswari, 2009). The magnitude of the adhesion increases with increasing mole fraction of 1-ol (Tabhane et al., 1999). The acoustic impedance ($Z$) (Table 3) decreases with increasing mole fraction of 1-pentanol and 1-hexanol. When an acoustical wave travel in a medium, there is a variation of pressure from particle to particle. The decrease in acoustic impedance with increase in mole fraction indicates significant interactions between the component molecules. This is an agreement with the results of Anwar Ali (Anwar Ali et al., 2001).

In order to highlight the presence of interaction between the molecules, it is essential to study the excess parameters. The deviation of a physical property of the liquid mixtures from the ideal behavior is a measure of the interaction between the molecules, which may be due to either adhesive or cohesive force. The values of excess adiabatic compressibility ($\beta^e$) (Fig.1) and excess free length ($L_f^e$) (Fig.2) changes from negative to positive as the mole fraction of 1-ols increases. It is evident that the $\beta^e$ and $L_f^e$ value are almost negative for lower 1-ols but the magnitude of negative values diminishes and the positive values increases with the increasing chain length of the alcohols. The values of $\beta^e$ and $L_f^e$ in terms of negative are enhanced by the following order; 1-pentanol > 1-hexanol. These results can be explained in terms of molecular interaction and structural effects. Positive $\beta^e$ and $L_f^e$ are due to the breaking of interactions and the corresponding disruption order in the pure components (Mousumi Das and Mahendra Nath Roy, 2006, Nikam et al., 2000, Ali and Nain, 2002).
In the study of liquid mixture the variations of the excess internal pressure ($\pi^E_i$) (Fig.3) may give some information regarding the nature and force existing between the molecules. According to Deshpande et al. (1968), the negative sign of excess internal pressure indicate the weak interaction, while the positive sign of excess internal pressure ($\pi^E_i$) indicates the strong bonding between the molecule (Subramanyan Naidu and Ravindra Prasad, 2002). The excess values of acoustic impedance ($Z^E_i$) changes from positive to negative as we increase the concentration of 1-ols (Fig.4). This may be indicative of the decreasing strength of interaction between the component molecules for 1-pentanol and for 1-hexanol, it exhibits positive values for all the mole fraction (Sumathi et al., 2011).
4. Conclusion

In the present investigation, the variation in the acoustic parameters and the sign and magnitude of the excess functions derived from the ultrasonic velocity, density and viscosity suggest the presence of molecular interaction in the binary mixture and is due to hydrogen bonding through polar oxygen atom of Methyl benzoate and hydrogen atom of alcohols. Perusal of the sign and magnitude of different parameters, it is concluded that the average strength of molecular interaction become weaker with rise in the chain length of the 1-alkanol and the order of the interaction is 1-pentanol > 1 – hexanol.

5. References