Thermodynamic Interactions of P-Chlorotoluene with 
P-xylene at 303.15 K, 308.15 K, 313.15 K and 318.15 K 

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ABSTRACT. Ultrasonic velocity, density and viscosity of the binary liquid mixtures of P-Chlorotoluene with p-xylene over the whole composition range at 303.15, 308.15, 313.15 and 315.15 K at frequency 2 MHz have been measured. Acoustical parameters such as adiabatic compressibility, intermolecular free length, impedance, molar volume, internal pressure, free volume, Rao constant and Wada constant. The acoustical parameters can be used to assess the strength of induced dipole-dipole interactions in this system studied.

1. INTRODUCTION

Ultrasonic velocities, densities, viscosities and derived thermodynamic and acoustical parameters are of considerable interest in understanding the intermolecular interactions in binary liquid mixtures\(^1\)-\(^3\). Ultrasonic investigation of liquid mixtures consisting of polar and non-polar components is of considerable importance in understanding inter molecular interaction between the component molecules and they find applications in several industrial and technological processes. When a polar liquid is mixed with non-polar liquid there may be three types of interactions, namely dipole-dipole, dipole-induced dipole and induced dipole-induced dipole interactions.

In recent years, ultrasonic technique has become a powerful tool for studying the molecular behaviour of liquid mixtures. This is because of its ability of characterizing physico chemical behaviour of liquid medium. Binary liquid mixtures due to their unusual behaviour have attracted considerable attention. Data on some of the properties associated with the liquids and liquid mixtures like density, viscosity and ultrasonic velocity find extensive applications in chemical engineering process simulation, solution theory and molecular dynamics. These measurements are used to study the molecular interactions in pure liquids, liquid mixtures and ionic interactions in solution comprising of either single or mixed solutes.

The study of solution properties of liquid mixtures consisting of polar as well as non-polar components finds application in industrial and technological processes. However, no attempt has been made to measure ultrasonic studies on P-Chlorotoluene with P-xylene. Introduction of a Choloro group into the toluene molecule may influence both sign and magnitude of acoustical studies of these liquids. Hence, we report here new experimental sound velocity data for three binary mixtures of P-Chlorotoluene with M, O, P-xylenes.

2. EXPERIMENTAL DETAILS

All the chemicals used were of Analytical Reagent (AR) grade with minimum array of 99.9%. The ultrasonic velocity (U) have been measured using an ultrasonic interferometer (Mittal Enterprises, Model F-81) working at 2 MHz frequency with an accuracy of ± 0.1 ms\(^{-1}\). An electronically digital operated constant temperature water bath has been used to circulate water through the double walled measuring cell made up of steel containing the experimental solution at the desire temperature. The density of pure liquids and liquid mixtures was determined using...
density gravity bottle with accuracy of ±0.1Kgm⁻³. An Ostwald’s viscometer was used for the viscosity measurements with an accuracy of ±0.0001 NSm⁻². The temperature around the viscometer and density gravity bottle was maintained within ±0.1K in an electronically operated constant temperature water bath. All the precautions were taken to minimize the possible experimental errors.

From the measured values of density (ρ) and ultrasonic velocity (U), Viscosity (η). The Adiabatic Compressibility (β_{ad}), Inter Molecular Free Length (Lf), Acoustical Impedance (Z), Molar Volume (V_m), Rao’s Constant (R), Wada’s constant (W), internal pressure (π) and free volume(V_f) were calculated by using the following standard relations.

1. Adiabatic compressibility (β_{ad})

\[ \beta_{ad} = \frac{1}{\rho U^2} \]  

2. Intermolecular free length (L_f)

\[ L_f = K \left( \beta_{ad} \right)^{\frac{1}{2}} \]  

Where k is temperature dependent constant called as Jacobson constant. The value of k at the working temperatures of the experiment were calculated (MKS units) and they are given below

| Temperature (K) | 303.15 | 308.15 | 313.15 | 318.15 |
|----------------|--------|--------|--------|--------|
| Value of K     | 2.075 x 10^6 | 2.095 x 10^6 | 2.115 x 10^6 | 2.135 x 10^6 |

3. Specific acoustic impedance (Z)

\[ Z = \rho U \]  

4. Molar volume of the liquid mixture (V_m)

\[ V_m = \frac{M_{eff}}{\rho_{mix}} \]  

Where \[ M_{eff} = \frac{M_1X_1 + M_2X_2}{X_1 + X_2} \]

5. Molar Sound Velocity or Rao’s Constant (R) can be calculated by the relation

\[ R = \frac{V_m U^{1/3}}{\eta} \]  

6. Molar compressibility or Wada’s constant (W) can be calculated by the relation

\[ W = \frac{M_{eff}}{\rho \beta_{ad}^{0.7}} \]  

7. Internal pressure (π)

\[ \pi_i = bRT \left( \frac{kT}{U} \right)^{1/2} \frac{\rho^{2/3}}{M^{7/6}} \]  

Here b is packing factor (b=2 ), K is a constant, which is independent of temperature and its value is 4.28 X 10^9 for all liquids, R (8.314 J/mol K) is universal gas constant and T is absolute temperature.
8. Free volume \((V_f)\)

\[
V_f = \left( \frac{M g U}{k \eta} \right)^{3/2}
\]

(8)

3. RESULTS AND DISCUSSION:

The experimentally measured values of Density \((\rho)\), Ultrasonic velocity \((U)\), Viscosity \((\eta)\) and thermodynamic parameters like adiabatic compressibility \((\beta_{ad})\), Intermolecular free length \((L_f)\), Acoustic impedance \((Z)\), Molar volume \((V_m)\), Rao’s Constant \((R)\), Wada’s constant \((W)\), Internal pressure \((\pi)\) and Free volume \((V_f)\) of P-Chlorotoluene with P-xylene binary liquid system at different temperatures at a frequency of 2MHz over the whole concentration of P-chlorotoluene with P-xylene are presented in Table-1.

Density increases with increasing the concentration of P-Chlorotoluene and also it decreases with increasing the temperature. It suggests that a solute-solvent interaction exist between P-Chlorotoluene and P-xylene system. In other words the decrease in density may be interpreted to the structure maker of the solvent due to H-bonding.

The ultrasonic velocity decreases with increase in the concentration of P-Chlorotoluene and decreases with increase in temperature\(^4\)-\(^7\). The decrease in velocity is perhaps due to structural changes occurring in the mixtures resulting in weakening of intermolecular forces. Further the ultrasonic velocity decreases with increase in temperature at any concentrations as rise in temperature leads to less disordered structure and more spacing between the molecules.

The induced dipole moment that create induced dipole–induced dipole force of attraction between pair of atoms. This type of interaction is weaker which is given by the least ultrasonic velocity\(^8\).

From the Table-1, the adiabatic compressibility and free length decreases with increasing mole fraction of the P-Chlorotoluene and increases with increasing temperature. Which suggest that making and breaking of H-bonding between molecules of the system\(^9\)-\(^11\). The intermolecular free length depends upon the intermolecular attractive and repulsive forces. Eyring and Kincaid have proposed that \(L_f\) is a predominating factor in determining the variation of ultrasonic velocity of solution. Hence it can be concluded that there is significant interaction between solute and solvent molecules due to which the structural arrangement is also affected. From the above parameters it is clear that there is a strong association between P-Chlorotoluene and P-xylene system.

The acoustic impedance \((Z)\) (which is the product of ultrasonic velocity and density of the solution) increases with increase in concentration of P-Chlorotoluene. It represents that there is strong interaction between the P-Chlorotoluene and P-xylene system.

In this system, viscosity increases with increasing molefraction of P-Chlorotoluene and decreases with increasing temperature. The decrease in density and viscosity with temperature indicates that decrease in intermolecular forces due to increase in thermal energy of the system, which cause increase in volume expansion and hence increase in free length. Viscosity increases with concentration of P-chlorotoluene confirms that increase of cohesive forces because of strong interaction\(^12\)-\(^14\).

The internal pressure decreases with increasing mole fraction of P-Chlorotoluene. The reduction in internal pressure may be due to the loosening of cohesive forces and adhesive force leading to breaking the structure of the solution. This gives the information regarding the nature and strength of forces existing between the molecules.

The free volume decreases with increase molefraction of P-Chlorotoluene. The free volume is the space available for the molecules to move in an imaginary unit cell\(^15\)-\(^18\). It clearly indicates the existence of intermolecular interaction, due to which the structural arrangement is considerably affected.
These binary systems exhibit non-linear increase/decrease in $U$, $V_f$, $Z$ and $\pi_i$ values with composition of P-CT. This indicates the presence of intermolecular interactions between the component molecules of the mixture$^{19-21}$. In order to substantiate the presence of interactions (either adhesive or cohesive forces) between the molecules.

4. CONCLUSION

The ultrasonic velocity, density and other related parameters were calculated. The existence of type of molecular interactions in solute-solvent is favoured in the system, confirmed from the $U$, $\rho$, $\beta_{ad}$, $L_f$, $Z$, $V_m$, $R$, $W$, $\eta$, $\pi$ and $V_f$ data. Weak dispersive type intermolecular interactions are confirmed in the systems investigated. All the experimental determinations of acoustic parameters are weakly correlated between P-Chlorotoluene with P-xylene.

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Table 1
Ultrasonic Velocity (U), Density (ρ), Adiabatic Compressibility (βad), Inter Moleculat Free Length (Ld), Acoustical Impedance (Z), Molar Volume (V_m), Rao’s Constant (R), Wada’s constant (W), Viscosity (η), Internal pressure (π) and free volume (V_f) for Molefraction of P-Chlorotoluene with P-xylene at different temperatures 303.15K and 308.15K.

| Mole Fraction X | 1287.6 | 303.15K | | | | | | |
|-----------------|--------|---------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| 0.0000          | 852.81 | 7.0727  | 0.5518          | 1.0980          | 124.4942        | 6.2865          | 9.4141          | 0.5680          | 269.6515        | 4.2153          |
| 0.1808          | 987.15 | 6.8257  | 0.5421          | 1.1400          | 133.6003        | 6.2392          | 9.3971          | 0.6136          | 279.5456        | 3.8359          |
| 0.3556          | 921.50 | 6.5972  | 0.5329          | 1.1818          | 122.7976        | 6.1926          | 9.3785          | 0.6627          | 288.8453        | 3.5250          |
| 0.5247          | 955.85 | 6.3853  | 0.5243          | 1.2234          | 121.9664        | 6.1467          | 9.3586          | 0.7149          | 297.6421        | 3.2657          |
| 0.6833          | 990.20 | 6.1883  | 0.5161          | 1.2649          | 121.1468        | 6.1013          | 9.3374          | 0.7714          | 306.0074        | 3.0459          |
| 0.8466          | 1024.9 | 6.0046  | 0.5084          | 1.3062          | 120.3375        | 6.0566          | 9.3151          | 0.8333          | 314.0152        | 2.8572          |
| 1.0000          | 1058.9 | 5.8330  | 0.5011          | 1.3473          | 119.5396        | 6.0124          | 9.2917          | 0.9020          | 321.6713        | 2.6932          |

| Mole Fraction X | 1272.7 | 308.15K | | | | | | |
|-----------------|--------|---------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| 0.0009          | 848.2  | 7.2788  | 0.5652          | 1.0975          | 125.1709        | 6.2962          | 9.4205          | 0.5420          | 268.3434        | 4.4440          |
| 0.1808          | 982.61 | 7.0557  | 0.5556          | 1.1200          | 124.2823        | 6.2454          | 9.4051          | 0.5992          | 279.3015        | 3.9978          |
| 0.3556          | 917.02 | 6.8113  | 0.5467          | 1.1603          | 123.4054        | 6.1953          | 9.3821          | 0.6564          | 288.5826        | 3.6380          |
| 0.5247          | 951.43 | 6.6035  | 0.5383          | 1.2003          | 122.5416        | 6.1459          | 9.3577          | 0.7134          | 299.2978        | 3.3418          |
| 0.6833          | 985.84 | 6.4106  | 0.5304          | 1.2400          | 121.6898        | 6.0972          | 9.3321          | 0.7703          | 308.5292        | 3.0935          |
| 0.8466          | 1020.2 | 6.2319  | 0.5229          | 1.2795          | 120.8485        | 6.0491          | 9.3053          | 0.8278          | 317.3473        | 2.8824          |
| 1.0000          | 1054.7 | 6.0632  | 0.5158          | 1.3189          | 120.0152        | 6.0015          | 9.2772          | 0.8850          | 325.8221        | 2.7001          |

Cont.
Temperatures at 313.15K and 318.15K.

| X     | U     | ρ      | $\beta_\alpha 10^{-10}$ | L $10^{10}$ | $Z \times 10^2$ | $V_\infty \times 10^4$ | R $10^7$ | W $10^5$ | g $10^3$ | $\pi \times 10^{-5}$ | $V \times 10^4$ |
|-------|-------|--------|--------------------------|-------------|-----------------|------------------------|----------|----------|----------|---------------------|-----------------|
|       | m⁻¹   | Kg⁻¹   | N⁻¹. m²                  | m⁻¹         | Kg. m⁻¹         | m²/mol                  | (m²/mol) | (m²/s)² | (m²/s)² | N.S. m⁻²            | m⁻¹ mol⁻¹       |
| 0.0000| 1257.8| 843.59 | 7.4928                   | 0.5789      | 1.0610         | 125.8543                | 6.3058   | 9.4388   | 0.5230   | 268.4803            | 4.6632          |
| 0.1808| 1253.9| 878.12 | 7.2429                   | 0.5692      | 1.1019         | 124.9223                | 6.2526   | 9.4144   | 0.5804   | 280.0641            | 4.1187          |
| 0.3556| 1250.3| 912.66 | 7.6124                   | 0.5600      | 1.1403         | 124.0034                | 6.2001   | 9.3885   | 0.6378   | 290.9244            | 3.7292          |
| 0.5247| 1246.1| 947.19 | 6.7991                   | 0.5514      | 1.1802         | 123.9085                | 6.1485   | 9.3611   | 0.6952   | 301.7765            | 3.1082          |
| 0.6883| 1242.2| 951.73 | 6.6012                   | 0.5434      | 1.2195         | 122.2066                | 6.0975   | 9.3326   | 0.7526   | 310.9136            | 3.1457          |
| 0.8466| 1238.3| 1016.36| 6.4171                   | 0.5357      | 1.2584         | 121.3274                | 6.0473   | 9.3066   | 0.8100   | 320.2108            | 2.9214          |
| 1.0000| 1234.4| 1050.8 | 6.2455                   | 0.5285      | 1.2971         | 120.4503                | 5.9978   | 9.2724   | 0.8675   | 329.1369            | 2.7290          |

|       | 1242.9 | 838.98 | 7.7157                   | 0.5930      | 1.0427         | 126.5462                | 6.3153   | 9.4516   | 0.4880   | 264.0907            | 5.0200          |
| 0.1808| 1239.2 | 873.53 | 7.4546                   | 0.5829      | 1.0824         | 125.5833                | 6.2510   | 9.4253   | 0.5471   | 276.9235            | 4.4210          |
| 0.3556| 1235.5 | 908.08 | 7.2138                   | 0.5734      | 1.1219         | 124.6341                | 6.2076   | 9.3981   | 0.6063   | 288.8846            | 3.9537          |
| 0.5247| 1231.8 | 942.63 | 6.9910                   | 0.5645      | 1.1611         | 123.7004                | 6.1549   | 9.3696   | 0.6655   | 300.1213            | 3.5895          |
| 0.6883| 1228.1 | 977.18 | 6.7843                   | 0.5561      | 1.2001         | 122.7905                | 6.1030   | 9.3399   | 0.7247   | 310.7501            | 3.2731          |
| 0.8466| 1224.4 | 1011.73| 6.5921                   | 0.5481      | 1.2388         | 121.8746                | 6.0519   | 9.3090   | 0.7839   | 320.8624            | 3.0177          |
| 1.0000| 1220.8 | 1046.2 | 6.4135                   | 0.5466      | 1.2772         | 120.9903                | 6.0020   | 9.2779   | 0.8431   | 330.5185            | 2.8014          |
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