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

G. Pavan Kumar, Ch. Praveen Babu, K. Samatha

Ultrasonic Laboratory, Department of Physics, Andhra University, Visakhapatnam-530003.

Andhra Pradesh, India

E-mail address: pavan.phy@gmail.com

Keywords: Ultrasonic velocity; Density; Viscosity; molecular interactions

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 mixtures¹⁻³. 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 Chloro 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 assay 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 $\pm 0.1 \text{ ms}^{-1}$. 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 desired temperature. The density of pure liquids and liquid mixtures was determined using

density gravity bottle with accuracy of $\pm 0.1 \text{ Kg m}^{-3}$. An Ostwald's viscometer was used for the viscosity measurements with an accuracy of $\pm 0.0001 \text{ NSm}^{-2}$. The temperature around the viscometer and density gravity bottle was maintained within $\pm 0.1 \text{ K}$ 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 (L_f), 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})

$$\beta_{ad} = \frac{1}{\rho U^2} \quad (1)$$

2. Intermolecular free length (L_f)

$$L_f = K (\beta_{ad})^{1/2} \quad (2)$$

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	2.075×10^6	2.095×10^6	2.115×10^6	2.135×10^6

3. Specific acoustic impedance (Z)

$$Z = \rho U \quad (3)$$

4. Molar volume of the liquid mixture (V_m)

$$V_m = \frac{M_{eff}}{\rho_{mix}} \quad (4)$$

$$\text{Where } M_{eff} = \frac{M_1 X_1 + M_2 X_2}{X_1 + X_2}$$

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

$$R = V_m U^{1/3} \quad (5)$$

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

$$W = \frac{M_{eff}}{\rho \beta_{ad}^{1/7}} \quad (6)$$

7. Internal pressure (π)

$$\pi_i = bRT \left(\frac{k\eta}{U} \right)^{1/2} \frac{\rho^{2/3}}{M_{eff}^{7/6}} \quad (7)$$

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

8. Free volume (V_f)

$$V_f = \left(\frac{M_{eff} U}{k\eta} \right)^{3/2} \quad (8)$$

3. RESULTS AND DISCUSSION:

The experimentally measured values of Density (ρ), Ultrasonic velocity (U), Viscosity (η) and thermodynamic parameters like adiabatic compressibility (β_{ad}), Intermolecular free length (L_f), Acoustic impedance (Z), Molar volume (V_m), Rao's Constant (R), Wada's constant (W), Internal pressure (π) 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 temperature⁴⁻⁷. 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 creates induced dipole-induced dipole force of attraction between pair of atoms. This type of interaction is weaker which is given by the least ultrasonic velocity⁸.

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 system⁹⁻¹¹. 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 interaction¹²⁻¹⁴.

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 cell¹⁵⁻¹⁸. 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 π_i values with composition of P-CT. This indicates the presence of intermolecular interactions between the component molecules of the mixture¹⁹⁻²¹. 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 , ρ , β_{ad} , L_f , Z , V_m , R , W , η , π 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.

ACKNOELDGEEMENT

One of author's G. Pavan kumar sincerely thank the Union Grants Commission, India, for funding the current research work under UGC Scholarship Assistance Program (SAP) in the Department of Physics, Andhra University, Visakhapatnam.

Table: 1

Ultrasonic Velocity (U), Density (ρ), Adiabatic Compressibility (β_{ad}), Inter Molecular Free Length (L_f), 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	U ms ⁻¹	ρ Kg m ⁻³	$\beta_{ad} \times 10^{-10}$ N ⁻¹ .m ²	L_f 10 ⁻¹⁰ m	$Z \times 10^6$ Kg. m s ⁻²	$V_m \times 10^{-6}$ m ³ /mol	$R \times 10^{-7}$ (m ³ /mol) (m/s) ²	$W \times 10^{-7}$ (m ³ /mol) (Kg ⁻¹ ms ⁻²)	$\eta \times 10^{-3}$ N.S.m ⁻²	$\pi \times 10^{15}$ N.m ⁻²	$V_f \times 10^{-7}$ m ³ mol ⁻¹
303.15K											
0.0000	1287.6	852.81	7.0727	0.5518	1.0980	124.4942	6.2865	9.4141	0.5680	269.6515	4.2153
0.1808	1285.0	887.15	6.8257	0.5421	1.1400	123.6403	6.2392	9.3971	0.6136	279.5456	3.8359
0.3556	1282.5	921.50	6.5972	0.5329	1.1818	122.7976	6.1926	9.3785	0.6627	288.8453	3.5250
0.5247	1280.1	955.85	6.3853	0.5243	1.2234	121.9664	6.1467	9.3586	0.7149	297.6421	3.2657
0.6883	1277.4	990.20	6.1883	0.5161	1.2649	121.1468	6.1013	9.3374	0.7714	306.0074	3.0459
0.8466	1274.9	1024.5	6.0046	0.5084	1.3062	120.3375	6.0566	9.3151	0.8333	314.0152	2.8572
1.0000	1272.4	1058.9	5.8330	0.5011	1.3473	119.5396	6.0124	9.2917	0.9020	321.6713	2.6932
308.15K											
0.0000	1272.7	848.2	7.2786	0.5652	1.0795	125.1706	6.2962	9.4265	0.5420	268.3434	4.4440
0.1808	1269.2	882.61	7.0357	0.5556	1.1200	124.2822	6.2454	9.4051	0.5992	279.3015	3.9978
0.3556	1265.3	917.02	6.8113	0.5467	1.1603	123.4054	6.1953	9.3821	0.6564	289.5826	3.6380
0.5247	1261.6	951.43	6.6035	0.5383	1.2003	122.5416	6.1459	9.3577	0.7134	299.2978	3.3418
0.6883	1257.9	985.84	6.4106	0.5304	1.2400	121.6898	6.0972	9.3321	0.7703	308.5292	3.0935
0.8466	1254.2	1020.2	6.2310	0.5229	1.2795	120.8485	6.0491	9.3053	0.8278	317.3473	2.8824
1.0000	1250.5	1054.7	6.0632	0.5158	1.3189	120.0152	6.0015	9.2772	0.8850	325.8221	2.7004

Cont..

Temperatures at 313.15K and 318.15K.

X	U ms ⁻¹	ρ Kg m ⁻³	$\beta_{ad} \times 10^{-10}$ N ⁻¹ .m ²	$L_r \times 10^{-10}$ m	$Z \times 10^6$ Kg. m s ⁻² .s ⁻¹	$V_m \times 10^{-6}$ m ³ /mol	$R \times 10^{-7}$ (m ³ /mol) (m/s) ^{1/3}	$W \times 10^{-7}$ (m ³ /mol) (Kg ⁻¹ ms ²)	$\eta \times 10^{-3}$ N.s.m ⁻²	$\pi \times 10^{-6}$ N.m ⁻²	$V_r \times 10^{-6}$ m ³ mol ⁻¹
313.15K											
0.0000	1257.8	843.59	7.4928	0.5789	1.0610	125.8543	6.3058	9.4388	0.5230	268.4803	4.6062
0.1808	1253.9	878.12	7.2429	0.5692	1.1010	124.9223	6.2526	9.4144	0.5804	280.0641	4.1187
0.3556	1250.3	912.66	7.0124	0.5600	1.1408	124.0034	6.2001	9.3885	0.6378	290.9244	3.7292
0.5247	1246.1	947.19	6.7991	0.5514	1.1802	123.0985	6.1485	9.3611	0.6952	301.1765	3.4108
0.6883	1242.2	981.73	6.6012	0.5434	1.2195	122.2066	6.0975	9.3326	0.7526	310.9136	3.1457
0.8466	1238.3	1016.26	6.4171	0.5357	1.2584	121.3274	6.0473	9.3030	0.8100	320.2108	2.9214
1.0000	1234.4	1050.8	6.2455	0.5285	1.2971	120.4608	5.9978	9.2724	0.8675	329.1369	2.7290
318.15K											
0.0000	1242.9	838.98	7.7157	0.5930	1.0427	126.5462	6.3153	9.4510	0.4880	264.0907	5.0200
0.1808	1239.2	873.53	7.4546	0.5829	1.0824	125.5833	6.2610	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	3.5795
0.6883	1228.1	977.18	6.7843	0.5561	1.2001	122.7805	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	0.5406	1.2772	120.9908	6.0020	9.2779	0.8431	330.5185	2.8014

Molefraction of P-Chlorotoluene	Molefraction of P-Chlorotoluene	Molefraction of P-Chlorotoluene

303.15 308.15 313.15 318.15

Fig 10: Variation of Internal pressure with Molefraction of P-CT

Fig 11: Variation of Free volume with Molefraction of P-Chlorotoluene

References:

- [1] I.G. Mikhailov, J. Struct. Chem, 9, 332, 1968.
- [2] Donald L. Lamberson, Can. J. Chem, 49, 611, 1971.
- [3] N.G. Gereeze, Trans. Faraday Soc., 62, 112, 1966.
- [4] Kannappan A N and Palaniappan L, Ind. J. Phy., 73(B), 531, 1999.

-
- [5] Sadasiva Rao A, Vijayakumar Naidu B and Chawdoji Rao, J. Acous. Soc. Ind., 28, 303, 2000.
- [6] Ali A, Nain A K, Kuma N and Ibrahim M, Chinese J. Chem., 21, 253, 2003.
- [7] Bhatti S S and Singh D P, Ind. J. Pure and Appl. Phys., 21, 506, 1983.
- [8] M. Rastogi, A. Awasthi, M. Guptha and J. P. Shukla. Ind. J. Pure Appl. Phys., 40, 256, 2002.
- [9] David Hykes, Wayne R Hedrick and Dale E Stanch man, Ultra. Phy. Inst., (Newyork, Churchill Livinstone), 1st edn.1985.
- [10] Tabhane V A, Sangeetha Agarwal and Sharada Ghosh, Ind. J. pure and appl. Phy., 37, 583, 1999.
- [11] Ilaukhani H and Ghorbani R, J. Sol. Chem., 27, 141, 1998.
- [12] Arul G and Palanippan L, Ind. J. Pure and Appl. Phys., 39, 561, 2001.
- [13] Palanippan L, Ph. D. thesis Annamalai University, 1998.
- [14] Bhatti S S and Singh D P, Ind. J. Pure and Appl. Phys., 21, 506, 1983.
- [15] Y. Changsheng; G. He; H. Yifu; P. Ma. J. Chem. Eng. Data., 53, 1639, 2008.
- [16] Y. Changsheng; W. Xu; P. Ma. J. Chem. Eng. Data., 49, 1794, 2004.
- [17] A. Ali; A.K. Nain; V.K. Sharma; S. Ahmad. Phys. Chem. Liq., 42, 375, 2004.
- [18] N.N. Jyoti; I.A. Mrityunjaya; T.M. Aminabhavi; J. Chem. Eng. Data., 48, 628, 2003.
- [19] M.V. Rathnam; R. Rajeev Kumar Singh; M.S. Kumar. J. Chem. Eng. Data., 53, 265, 2008.
- [20] R. Thiyagarajan; P. Lakshmanan. C. R. Chim., 10, 1157, 2007.
- [21] T.S. Rao; N. Veeraiah; C. Rambabu. Indian J. Pure Appl. Phys., 40, 850, 2002.