Evaluation of Excess Thermodynamic Parameters in a Binary Liquid Mixture (Cyclohexane + *O*-Xylene) at Different Temperatures

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Abstract: The ultrasonic velocity, density and viscosity in binary liquid mixture cyclohexane with *o*-xylene have been determined at different temperatures from 303.15 to 318.15 K over the whole composition range. The data have been utilized to estimate the excess adiabatic compressibility (β^E), excess volumes (V^E), excess intermolecular free length (L_f^E), excess internal pressure (π^E) and excess enthalpy (H^E) at the above temperatures. The excess values have been found to be useful in estimating the strength of the interactions in the liquid mixtures. Analysis of these parameters indicates that there are weak interactions among the components of the binary mixtures.

Keywords: Ultrasonic velocity, Binary mixtures, Excess thermodynamic parameters.

Introduction

Ultrasonic study of liquid and liquid mixtures has gained much importance during the last two decades in assessing the nature of molecular interactions and investigating the physicochemical behaviour of such systems. A survey of literature¹⁻⁴ indicates that excess values of ultrasonic velocity, adiabatic compressibility and molar volume in liquid mixtures are useful in understanding the interactions between the molecules. The adiabatic compressibility deviations are more related with structural effects and packing phenomena. The systematic investigations of these excess properties are therefore of great importance. The present investigation is a study of temperature variation of u , ρ , η , β , molar volume (V),

intermolecular free length (L_f), excess adiabatic compressibility (β^E), excess molar volume (V^E), excess intermolecular free length (L_f^E), excess internal pressure (π^E) and excess enthalpy (H^E) in cyclohexane + *o*-xylene.

Experimental

The chemicals were redistilled and purified by the standard methods described^{5,6}. Liquid mixtures of different known compositions were prepared by mixing measured amounts of the pure liquids in cleaned and dried flasks. Ultrasonic velocity was measured by a single crystal variable path interferometer (Mittal, Model F-81) at a frequency of 3 MHz. The accuracy of the velocity measurements is $\pm 5 \text{ ms}^{-1}$. The densities of pure liquids and liquid mixtures were measured by employing a specific gravity bottle at all the temperatures and weights were taken to an accuracy of $\pm 0.1 \text{ mg}$.

The Viscosities were measured with Ostwald viscometer. The viscometer was calibrated at each temperature using redistilled water. The measurements were made at all the temperatures with the help of thermostat with an accuracy of $\pm 0.1 \text{ K}$. Acoustical parameters such as adiabatic compressibility (β), intermolecular free length (L_f), molar volume (V_m), Enthalpy (H) and internal pressure (π) were calculated using standard equations.

Theory

The adiabatic compressibility has been determined by using the experimentally measured ultrasonic velocity (U) and density (ρ) by the following formula

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

The molar volumes of the binary mixtures were calculated using the equation

$$V = (X_1 M_1 + X_2 M_2) / \rho \quad (2)$$

Inter Molecular free length (L_f) was calculated by using the relation

$$L_f = K(\beta_{ad})^{1/2} \quad (3)$$

Where, K is temperature dependent Jacobson's constant². Enthalpy (H) is calculated using the relation

$$H = \Pi \cdot V_m \quad (4)$$

Internal pressure (Π) is calculated using the formula

$$\Pi = bRT \frac{(Kh)^{1/2}}{U} \rho^{2/3} \eta^{7/6} \quad (5)$$

The excess properties such as β^E , V_m^E , L_f^E , H^E and π^E have been calculated using the equation

$$Y^E = Y_{mix} - [X_1 Y_1 + X_2 Y_2] \quad (6)$$

Where Y^E is β^E or V_m^E or L_f^E or H^E or π^E , and X represents mole fraction of the component and subscripts 1 and 2 stand for the components 1 and 2.

Results and Discussion

The values of u , ρ , η , β , V and L_f for the binary system at different temperatures are given in Table 1.

Table 1. Ultrasonic velocity (u), density (ρ) and viscosity (η), adiabatic compressibility (β), molar volume (V_m), intermolecular free length (L_f) values for cyclohexane with *o*-xylene.

Temperature at 303.15 K						
X_1	$u \text{ ms}^{-1}$	$\rho \text{ Kg m}^{-3}$	$\eta / 10^{-3} \text{ Nsm}^{-2}$	$\beta \times 10^{12} \text{ m}^2 \text{ N}^{-1}$	$V_m \text{ cm}^3 \text{ mol}^{-1}$	$L_f \text{ \AA}^\circ$
0.0000	1235.6	0.7678	0.8224	85.3058	109.6119	0.5791
0.0908	1237.5	0.7768	0.7406	84.0621	110.9140	0.5749
0.1835	1243.6	0.7865	0.6960	82.2063	112.1388	0.5685
0.2781	1250.6	0.7975	0.6700	80.1706	113.2023	0.5614
0.3747	1259.0	0.8096	0.6540	77.9252	114.1358	0.5535
0.4734	1267.5	0.8222	0.6504	75.7054	115.0268	0.5455
0.5742	1274.7	0.8304	0.6558	74.1076	116.5612	0.5398
0.6772	1284.9	0.8368	0.6678	72.3779	118.3771	0.5334
0.7824	1300.5	0.8486	0.6820	69.6749	119.4594	0.5234
0.8900	1316.2	0.8614	0.6951	67.0067	120.4319	0.5132
1.0000	1338.7	0.8707	0.7051	64.0815	121.9249	0.5019
at 308.15 K						
0.0000	1206.1	0.7625	0.7539	90.1520	110.3738	0.5996
0.0908	1210.2	0.7731	0.6895	88.3109	111.4448	0.5934
0.1835	1218.7	0.7831	0.6525	85.9713	112.6257	0.5855
0.2781	1227.5	0.7946	0.6301	83.5235	113.6155	0.5771
0.3747	1237.3	0.8070	0.6135	80.9327	114.5035	0.5681
0.4734	1245.0	0.8194	0.6093	78.7345	115.4199	0.5603
0.5742	1254.2	0.8280	0.6135	76.7718	116.8990	0.5533
0.6772	1262.8	0.8349	0.6216	75.1008	118.6465	0.5473
0.7824	1278.6	0.8466	0.6327	72.2496	119.7416	0.5368
0.8900	1294.7	0.8600	0.6486	69.3633	120.6280	0.5259
1.0000	1315.0	0.8694	0.6652	66.5164	122.1072	0.5150
at 313.15 K						
0.0000	1188.7	0.7587	0.7042	93.2715	110.9266	0.6142
0.0908	1192.6	0.7711	0.6314	91.1762	111.7339	0.6073
0.1835	1201.8	0.7811	0.5997	88.6288	112.9141	0.5987
0.2781	1209.3	0.7930	0.5801	86.2194	113.8447	0.5906
0.3747	1219.5	0.8054	0.5718	83.4881	114.7310	0.5811
0.4734	1228.7	0.8181	0.5684	80.9494	115.5891	0.5722
0.5742	1237.6	0.8270	0.5701	78.9435	117.0404	0.5651
0.6772	1245.5	0.8337	0.5798	77.3219	118.8173	0.5593
0.7824	1261.8	0.8453	0.5925	74.2945	119.8258	0.5482
0.8900	1278.7	0.8585	0.6055	71.2342	120.8387	0.5368
1.0000	1297.5	0.8677	0.6211	68.4567	122.3464	0.5262
at 318.15 K						
0.0000	1168.1	0.7531	0.6562	97.3125	111.7514	0.6318
0.0908	1171.8	0.7668	0.5798	94.8148	112.3605	0.6242
0.1835	1181.1	0.7787	0.5491	92.0530	113.2621	0.6145
0.2781	1188.7	0.7907	0.5328	89.4967	114.1759	0.6059
0.3747	1198.0	0.8034	0.5233	86.7270	115.0166	0.5965

0.4734	1207.5	0.8158	0.5195	84.0702	115.9292	0.5873
0.5742	1216.0	0.8254	0.5209	81.9252	117.2672	0.5797
0.6772	1224.3	0.8329	0.5259	80.0900	118.9314	0.5732
0.7824	1240.1	0.8440	0.5355	77.0418	120.1105	0.5622
0.8900	1259.7	0.8567	0.5496	73.5534	121.0926	0.5493
1.0000	1278.7	0.8659	0.5691	70.6254	122.6008	0.5383

The plots of ultrasonic velocity against mole fraction of *o*-xylene at different temperatures are shown in Figure 1. These plots are almost linear with either positive or negative slope indicating the existence of very weak intermolecular attractions in these systems and there is a little deviation from ideal behavior. These forces may be of induced dipole induced dipole type.

Figure 1. Plots of ultrasonic velocity *versus* mole fraction of *o*-xylene with cyclohexane at different temperatures.

Excess values of adiabatic compressibility (β^E), molar volume (V_m^E), intermolecular free length (L_f^E), Enthalpy (H^E) and internal pressure (π^E) are calculated for the system investigated are presented in Table 2.

Table 2. Excess values of adiabatic compressibility (β^E), molar volume (V_m^E), intermolecular free length (L_f^E), enthalpy (H^E) and internal pressure (π^E) for cyclohexane with *o*-xylene.

Temperature at 303.15 K					
X_1	β^E	V_m^E	L_f^E	H^E	π^E
0.0000	0.0000	0.0000	-0.0037	0.00	0.00
0.0908	0.6839	0.1839	-0.0009	-19009.59	-187.68
0.1835	0.7953	0.2674	-0.0001	-28635.22	-282.02
0.2781	0.7679	0.1658	0.0002	-33079.01	-320.90
0.3747	0.5731	-0.0903	-0.0002	-34726.08	-328.20
0.4734	0.4474	-0.4142	-0.0005	-32571.97	-298.73
0.5742	0.9888	-0.1209	0.0016	-26742.32	-253.29
0.6772	1.4447	0.4271	0.0032	-19040.03	-197.00
0.7824	0.9754	0.2136	0.0014	-12147.85	-126.08
0.8900	0.5906	-0.1386	-0.0004	-5552.76	-3.16
1.0000	0.0000	0.0000	-0.0032	0.00	0.00
at 308.15 K					
0.0000	0.0000	0.0000	-0.0047	0.00	0.00

0.0908	0.2950	-0.0019	-0.0031	-16592.75	-157.48
0.1835	0.1378	0.0857	-0.0031	-25615.40	-245.89
0.2781	-0.0800	-0.0388	-0.0035	-30224.66	-285.47
0.3747	-0.3916	-0.2867	-0.0043	-33057.25	-303.70
0.4734	-0.2595	-0.5287	-0.0036	-31428.22	-281.62
0.5742	0.1605	-0.2314	-0.0021	-26663.17	-245.92
0.6772	0.9268	0.3100	0.0007	-20195.90	-200.48
0.7824	0.5691	0.1744	-0.0009	-14404.02	-141.65
0.8900	0.2347	-0.1958	-0.0025	-7361.82	-65.56
1.0000	0.0000	0.0000	-0.0041	0.00	0.00
at 313.15 K					
0.0000	0.0000	0.0000	-0.0058	0.00	0.00
0.0908	0.1474	-0.2373	-0.0046	-20734.84	-185.70
0.1835	-0.1088	-0.1215	-0.0050	-28883.09	-266.63
0.2781	-0.1769	-0.2755	-0.0047	-32851.84	-299.51
0.3747	-0.5151	-0.4949	-0.0056	-33297.45	-297.82
0.4734	-0.6075	-0.7643	-0.0057	-31765.24	-276.19
0.5742	-0.1117	-0.4632	-0.0039	-27672.53	-246.63
0.6772	0.8256	0.1400	-0.0006	-20391.32	-196.13
0.7824	0.4161	0.0508	-0.0023	-13971.94	-133.80
0.8900	0.0349	-0.2589	-0.0042	-7595.69	-65.45
1.0000	0.0000	0.0000	-0.0050	0.00	0.00
at 318.15 K					
0.0000	0.0000	0.0000	-0.0064	0.00	0.00
0.0908	-0.0857	-0.5596	-0.0055	-23578.41	-199.22
0.1835	-0.3834	-0.4941	-0.0063	-31857.42	-279.35
0.2781	-0.4218	-0.6112	-0.0060	-34774.78	-304.18
0.3747	-0.6179	-0.8212	-0.0063	-35350.15	-304.23
0.4734	-0.6438	-0.9798	-0.0062	-33607.99	-284.25
0.5742	-0.0984	-0.7345	-0.0042	-29243.33	-251.08
0.6772	0.8183	-0.1852	-0.0010	-23087.77	-208.85
0.7824	0.5857	-0.1435	-0.0021	-16775.10	-151.16
0.8900	-0.0215	-0.3225	-0.0048	-9581.94	-79.85
1.0000	0.0000	0.0000	-0.0054	0.00	0.00

The variation of β^E with mole fraction of *o*-xylene at different temperatures of study is shown in Figure 2.

Figure 2 shows the variation of excess adiabatic compressibility with mole fraction of *o*-xylene. β^E shows negative magnitude at lower mole fraction at all temperatures except 303.15 K. However, it becomes positive and of increase nature with increase in mole fraction of *o*-xylene. The positive excess compressibility suggests the medium is weakly packed. In the lower concentration of *o*-xylene β^E is negative it suggests the medium is highly packed. It may also because of spherical in shape of cyclohexane. Hence at higher mol fraction of *o*-xylene the packing environment is lost and the system may be having weak interaction. The same is reflected in variation in excess free length Figure 3.

The variation of V_m^E with mole fraction of *o*-xylene at different temperatures of study is shown in Figure.4.

Figure 2. Variation of excess compressibility with mole fraction at different temperatures.

Figure 3. Variation of excess free length with mole fraction at different temperatures.

Figure 4. Variation of excess molar volume with mole fraction at different temperatures.

It is observed that the values of V_m^E are negative at higher temperatures. The values are less at all the temperatures and minimum at $x_1 = 0.5742$ and maximum at $x_1 = 0.7824$. The negative values can be visualized as being due to a closer approach of the unlike molecules in the liquid mixtures, this indicating the existence of specific interactions between the liquid components. Since liquids having significantly different molecular sizes are considered, the V_m^E values show positive deviations at some places and negative at others. This signifies weak interactions.

The variation of H^E , π^E with mole fraction of *o*-xylene at different temperatures of study is shown in Figure 5 & 6.

Figure 5. Variation of excess enthalpy with mole fraction at different temperatures.

Figure 6. Variation of excess internal pressure with mole fraction at different temperatures.

The excess internal pressure is often discussed in terms of molecular interactions in liquid mixtures. The variation of excess internal pressure is entirely negative similar to the deviation in excess enthalpy and excess viscosity at all temperatures for cyclohexane with *o*-xylene. The less magnitude of these values suggests that weak interactions present in the system.

Conclusion

There are weak induced dipole-induced dipole interactions in binary mixture containing cyclohexane and *o*-xylene at temperatures 303.15, 308.15, 313.15 and 318.15 K.

References

1. Mehra R and Israni R, *Indian J Pure Appl Phys.*, 2000, **38**, 81.
2. Oswal S I and Patel N B, *J Chem Eng Data*, 1995, **40**, 845.
3. Anwar Ali and Nain A K, *Indian J Pure Appl Phys.*, 2001, **39**, 421.
4. Krestov G A, *Thermodynamics of Solvation* (Ellis Horwood, England), 1991, p.151.
5. Suryanarayanan C V and Kuppasamy J, *J Acous Soc India*, 1976, **4**, 75.
6. Suryanarayanan C V, *Indian J Chem.*, 1986, **25A**, 538.