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Refractive indices, ultrasonic velocities surface tension and thermo acoustical parameters of anisaldehyde+benzene at 303.15 k.

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ABSTRACT

The studies of ultrasonic velocities, refractive indices and surface tension are being increasingly used as tools for investigation of the properties of pure components and the nature of intermolecular interactions between the liquid mixture constituents. Refractive indices (n_D), ultrasonic velocities (U) and surface tension (σ) have been measured for the binary liquid mixture of Anisaldehyde +benzene over the entire composition range at 303.15 K. This study involves the evaluation of different thermo acoustical parameters along with the excess properties. The Redlich-Kister model was used to correlate the measured properties. It was found that in all cases, the experimental data obtained fitted with the values correlated by the corresponding models very well. The molecular interactions existing between the components were also discussed.

Key words: Ultrasonic velocities, thermo acoustical parameters, binary solvents, deviations, surface tension, refractive index.

INTRODUCTION

Binary liquid mixtures due to their unusual behavior have attracted considerable attention[1]. Data on some of the properties associated with the liquids and liquid mixtures like refractive index, ultrasonic velocities and surface tension find extensive application in chemical engineering process simulation, solution theory and molecular dynamics[2]. These properties are important from practical and theoretical point of view to understand liquid theory. The review of literature on acoustical studies of solutions reveals that these measurements are used to estimate the different elastic properties of the molecule from which the type of molecular interactions can be very well understood. Ultrasonic velocity has proved to be useful in understanding the physico-chemical behavior of the particular system. Ultrasonic velocity have been very widely used now a days to study binary liquid mixtures[3]. We report refractive index, ultrasonic velocities and surface tension of pure anisaldehyde and benzene as well as for the binary system constituted by these two chemicals at temperatures of 303.15K. From these experimental results acoustical impedance(Z), isentropic compressibility (β_s), intermolecular free length (L_f), degree of intermolecular attraction (α), molar sound velocity (R), molar compressiblity or wada's constant (W), refractive index deviation (δn_D), ultrasonic velocity deviation (δu), intermolecular free length deviation (δL_f), acoustical impedance deviation (δZ), and isentropic compressibility deviation ($\delta\beta_s$) were derived over the entire mole fraction range. The values have been fitted to Redlich-Kister type equation. Literature survey showed that no measurements have been previously reported for the mixture studied in this paper.

MATERIAL AND METHODS

The chemicals used were of analytical grade and obtained from loba chemicals. All the components were dried over anhydrous potassium carbonate and fractionally distilled[4].A thermostatically controlled well-stirred water bath

whose temperature was controlled to ±0.01 K accuracy was used for all the measurements. All the measurements were done by using electronic balance Shimadzu Corporation Japan Type BL 2205 accurate to 0.01 g. The possible uncertainty in the mole fraction was estimated to be less than ± 0.0001.

Refractive index

Refractive indices were measured using thermostatically controlled Abbe refractometer with an accuracy less than 0.0001units. Water was circulated in to the prism of the refractometer by a circulation pump connected to an external thermo stated water bath. Calibration was performed by measuring the refractive indices of doubly distilled water and propyl alcohol at defined temperatures. The change of refractive index over the composition range was obtained by

$$\delta n_D = n_{D-} (x_1 n_{D1} + x_2 n_{D2}) \quad ...(1)$$

where n_D is the refractive index of the mixture and n_{D1} and n_{D2} are the refractive indices of the pure compounds.

Ultrasonic velocity

Speed of sound was measured by using a variable path, single crystal interferometer. (mittal Enterprises New Delhi). The interferometer was calibrated using toluene. The interferometer cell was filled with the test liquid, and water was circulated around the measuring cell from a thermostat. The uncertainty was estimated to be 0.1ms^{-1}.

The change of speed of sound on mixing were calculated by the equation

$$\delta u = u - (x_1u_1 + x_2u_2) \quad ...(2)$$

where u is the speed of sound of the mixture and u_1 and u_2 are the speed of the sound of the pure compounds. The acoustical impedence (Z) was calculated by the equation,

$$Z = \rho u \quad ...(3)$$

where ρ is the density of mixture and u is the ultrasonic velocity of the mixture.

The isentropic compressibility (β_s) was calculated by the equation

$$\delta_s = 1/ \rho u^2 \quad ...(4)$$

where ρ is the density of mixture and u is the ultrasonic velocity of the mixture.

The molar compressibility or Wada's constant (W), was calculated by the equation

$$W = (M / \rho) \beta_s^{-1/7} \quad ...(5)$$

where M is the relative molar mass and β_s is the isentropic compressiblity.

The molar sound velocity (R) was calculated by the equation

$$R = (M / \rho) u^{1/3} \quad ...(6)$$

where u is the ultrasonic velocity of the mixture.

The intermolecular free length (L_f) was calculated by the equation

$$L_f = K \beta_s^{½} \quad ...(7)$$

where K is the Jacobson constant {5}.The degree of intermolecular attraction (α) was calculated by the equation

$$\alpha = (u^2 / u^2_{im}) - 1 \quad ...(8)$$

where $u^2_{im} = 1/ \{ (x_1M_1 + x_2M_2)(x_1/M_1u_1^2 + x_2/ M_2u_2^2)\}$.The intermolecular free length deviation (δL_f), acoustical impedence deviation (δZ), and isentropic compressibility deviation ($\delta\beta_s$) were derived over the entire mole fraction range by using the general equation

$$A^E = A - (Xi A_1 + (1-Xi) A_2) \quad ...(9)$$

where A is the corresponding parameters (L_f, Z and β_s)of binary mixture and A_1 and A_2 are the corresponding pure component values. The experimentally determined data's for the binary system of this investigation have been correlated using Redlich Kister equation[6] by the method of least square.

$$A^E = x_1 x_2 \Sigma a_i (x_1 - x_2)^{1R} \quad ...(10)$$

where a's are constant, which are functions of system properties.

Surface tension

The drop volume method was employed to measure surface tension of binary mixture over the whole composition range. All samples were

equilibrated to 303.15 K under atmospheric pressure. It was calibrated with distilled water. The accuracy of the surface tension measurement was estimated to be 0.1mNm$^{-1.}$

RESULTS AND DISCUSSIONS

Table 1 lists the Experimental Density (ρ), refractive indices (n_D), ultrasonic velocities (u), surface tension (σ), Acoustical impedence (Z), isentropic compressibility (β_s), molar compressiblity (W), molar sound velocity (R), intermolecular free length (L_f) and degree of intermolecular attraction (α) of Anisaldehyde – benzene mixture at 303.15 K over the entire composition range at 303.15 K. Table 2 lists Refractive index deviation (δn_D), ultrasonic velocity deviation (δu), intermolecular free length deviation (δL_f), acoustical impedence deviation (δZ), and isentropic compressibility deviation ($\delta\beta_s$) of Anisaldehyde – benzene mixture at 303.15 K. Redlich-Kister Constants evaluated from the least square fit for the deviations of refractive index, ultrasonic velocity intermolecular free length, acoustical impedance and isentropic compressibility have been presented in Table 3. The refractive index, an ultrasonic velocity and surface tension value increases with the mole fraction. This means that interaction in the mixture is not strong and hence increases. As seen in Fig. 1, the values of δL_f and $\delta\beta_s$ were negative over the entire range of mole fraction and the curves are symmetrical in nature. The values of δn_D and δu were positive over the entire range of mole fraction. It can be summarized that excess values may be affected by three factors. The first factor is the specific forces between molecules, such as hydrogen bonds, charge transfer complexes, breaking of hydrogen bonds and complexes bringing negative excess values[7]. The second factor is the physical intermolecular forces, including electrostatic forces between charged particles and between a permanent dipole and so on induction forces between a permanent dipole and an induced dipole and forces of attraction and repulsion between non polar molecules. Physical intermolecular forces are weak and the sign

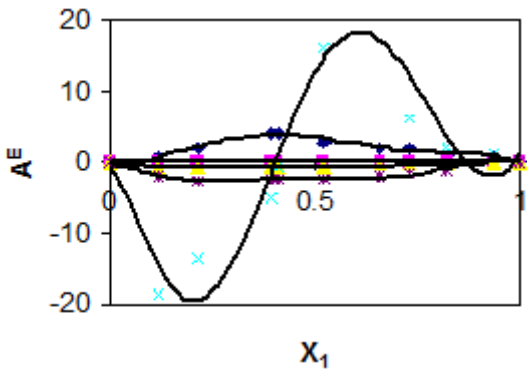

Fig. 1. Excess values at 303.15 K. (a)%δu (b) % δn_D (c) $\Delta\delta L_f$ x 10^9 (d) X δZ (e)*$\delta\beta_s$ x10^6

Table 1: Experimental Density (ρ), refractive indices (n_D), ultrasonic velocities (u), surface tension (σ), Acoustical impedence (Z), isentropic compressibility (β_s), molar compressiblity (W), molar sound velocity (R), intermolecular free length (L_f) and degree of intermolecular attraction (α) of Anisaldehyde – benzene mixture at 303.15 K

X_1	ρ/g/cc	n_D	u/ms^{-1}	σ/m. N.m^{-1}	Z/kg m^{2}s^{-1}	$\beta_{S\ x10}{}^{6}$ / m^{2}N^{-1}	W	R	L_f×10^9 m	α
					303.15 K					
0.0000	0.8690	1.5000	448	30.22	393	5.666	494	659	2.40	0.00
0.1198	0.8750	1.5059	596	36.48	552	3.036	556	755	1.64	0.74
0.2141	0.9010	1.5111	714	39.39	695	2.011	595	807	1.33	1.33
0.3951	0.9610	1.5207	934	59.29	950	1.120	693	947	0.99	2.51
0.4081	0.9660	1.5223	956	61.58	1000	1.040	696	984	0.96	2.62
0.5214	1.0002	1.5290	1093	66.22	1184	0.772	730	996	0.82	3.11
0.6605	1.0410	1.5342	1262	68.62	1376	0.575	818	1120	0.71	3.42
0.7314	1.0590	1.5380	1462	72.20	1614	0.426	879	1210	0.61	3.90
0.8195	1.0812	1.5419	1591	72.40	1787	0.357	931	1289	0.56	3.33
0.9316	1.1100	1.5470	1625	80.14	1818	0.339	980	1350	0.54	1.40
1.0000	1.1250	1.5500	1684	95.97	1890	0.313	1000	1400	0.52	0.00

Table 2 : Refractive index deviation (δn_D), ultrasonic velocity deviation (δu), intermolecular free length deviation (δL_f), acoustical impedence deviation (δZ), and isentropic compressibility deviation ($\delta\beta_s$) of Anisaldehyde – benzene mixture at 303.15 K.

X_1	δu	δn_D	δL_f x 10^9m	δZ kgm^{2}s^{-1}	$\delta\beta_s$ x10^6 m^{2}N^{-1}
0.0000	0	0.0000	0.00	0.00	0.00
0.1198	1	0.0002	-0.53	-18.50	-1.98
0.2141	2	0.0005	-0.66	-13.40	-2.50
0.3951	4	0.0010	-0.66	-04.92	-2.40
0.4081	4	0.0020	-0.66	-00.70	-2.40
0.5214	3	0.0030	-0.59	16.10	-2.10
0.6605	2	0.0020	-0.44	24.20	-1.55
0.7314	2	0.0015	-0.41	06.21	-1.32
0.8195	1	0.0010	-0.29	02.15	-0.92
0.9316	1	0.0005	-0.10	01.12	-0.34
1.0000	0	0.0000	0.00	0.00	0.00

Table 3: Redlich-Kister Constants for the deviations of refractive index, ultrasonic velocity intermolecular free length, acoustical impedence and isentropic compressiblity of Anisaldehyde – benzene at 323.15 K

	Redlich - Kister Constants		
	a_0	a_1	a_2
δn_D	0.00649	0.00348	-0.0084
δu	12.0783	0.76991	1.8593
δL_f	-2.8333	-4.4751	1.8531
δZ	-12.011	108.953	-263.12
$\delta\beta_s$	-10.197	-18.281	7.5963

of excess value may be positive and negative. Third factor is the structural characteristics of the component arising from geometrical fitting of one component in to other structure due to the differences in shape and size of the components and free volume. The nature of $\delta\alpha_s$ and δL_f play vital role in assessing the compactness due to molecular rearrangement .The molecular interactions in liquid mixture may also be due to interstitial accommodation[8] leading to more compact structure making δL_f and $\delta\beta_s$ negative. The positive deviation of δn_D and δu is an indicative of weak interaction involving dispersion forces[9]. The α has also been evaluated to study the structural variations and the nature of interaction occurring in the system.

Conclusion

Experimental data of the density, refractive index, ultrasonic velocity and surface tension of anisaldehyde and benzene mixture have been measured at 323.15 K. These data have been used to compute the excess properties of the system. Negative deviations were observed for δL_f and $\delta\beta_s$. It is clear that Redlich kister polynomial equation can represent the refractive index deviation (δn_D), ultrasonic velocity deviation (δu) intermolecular free length deviation (δL_f), acoustical impedance deviation (δZ), and isentropic compressibility deviation ($\delta\beta_s$) very well.

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