Refractive Indices, Ultrasonic Velocities Surface

Tension and Thermo Acoustical

Parameters of Anisaldehyde+ Benzene at 323.15K

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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 323.15 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.

Keywords: Ultrasonic velocities, Thermo Acoustical Parameters, Binary solvents, Deviations, Surface tension, Refractive index

1. Introduction

Binary liquid mixtures due to their unusual behavior have attracted considerable attention (Marsh 1970). 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 (Mchaweh 2004). 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(Pandey 1977) 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 323.15K.   From these experimental results acoustical impedence(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 impedence 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 (Redlich.O.Kister 1948) equation. Literature survey showed that no measurements have been previously reported for the mixture studied in this paper.

2. Experimental

The chemicals used were of analytical grade and obtained from loba chemicals. All the components were dried over anhydrous potassium carbonate and fractionally distilled (Oswal 1995). 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.

2.1 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 thermostated water bath. Calibration was performed by measuring the refractive indices of doubly distilled water and propyl alcohol at defined temperatures. The sample mixture was directly injected in to the prism assembly of the instrument using a syringe. The change of refractive index over the composition range was obtained by

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

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

2.1.1 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 $0.1 ms^{-1}$

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

$$\delta u = u - (x_1 u_1 + x_2 u_2) \tag{2}$$

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,

$$Z = \rho u \tag{3}$$

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

$$\beta_s = 1/\rho u^2 \tag{4}$$

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

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

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

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

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

Where u is the ultrasonic velocity of the mixture.

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

$$L_f = K \beta_s^{½} \tag{7}$$

where   K is the Jacobson constant (Jacobson 1952).

The degree of intermolecular attraction (α) was calculated by the equation

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

where $u^2_{im} = 1/ \{ (x_1 M_1 + x_2 M_2)(x_1/M_1 u_1^2 + x_2/M_2 u_2^2) \}$

The δL_f, δZ, and $\delta \beta_s$ were derived over the entire mole fraction range by using the general equation

$$A^E = A - (Xi A_1 + (1-Xi) A_2) \tag{9}$$

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 experimental   data for the binary system of this investigation have been correlated using Redlich Kister

$$A^E = x_1 x_2 \Sigma a_i (x_1 - x_2)^I \tag{10}$$

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

2.1.2 Surface tension

Surface tension of pure liquids and binary mixtures over the whole composition range was determined using Interfacial tensiometer (ASTM D.971) with 1No. 4cm platinum ring as per IS 6104. All samples were equilibrated to (303.15, 313.15, and 323.15) K under atmospheric pressure. It was calibrated with distilled water. The accuracy of the surface tension measurement was estimated to be 0.03mNm^{-1}.

3. Results and discussion

Table 1 lists the measured, Density (ρ), refractive indices (n_D), ultrasonic velocities (u) and surface tension (σ) for the binary liquid mixture of Anisaldehyde -benzene over the entire composition range at 323.15 K with the corresponding Refractive index deviation (δn_D) and ultrasonic velocity deviation (δu). Table 2 lists Acoustical impedence (Z), isentropic compressibility (β_s), molar compressiblity (W), molar sound velocity (R), intermolecular free length (L_f), degree of intermolecular attraction (α), intermolecular free length deviation (δL_f), acoustical impedence deviation (δZ), and isentropic compressibility deviation ($\delta \beta_s$) of Anisaldehyde – benzene mixture at 323.15 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, ultrasonic velocity and surface tension values increases with the mole fraction. This means that interaction in the mixture is not strong and hence increases. As seen in figure 1, the values of δZ and $\delta \beta_s$ were negative over the entire range of mole fraction and the curves are symmetrical in nature. The values of δL_f, 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 (Changsheng vang 2006). 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 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 $\delta \beta_s$ 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 (Kiyohora 1979) leading to more compact structure making δZ and $\delta \beta_s$ negative. The positive deviation of δL_f, δn_D and δu is an indicative of weak interaction involving dispersion forces(Susmita 2005). The α has also been evaluated to study the structural variations and the nature of interaction occurring in the system.

4. 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 δZ and $\delta \beta_s$. It is clear that redlich kister polynomial equation can represent δn_D, δu, δL_f, δZ, $\delta \beta_s$ very well which is indicated by low standard deviation values.

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Table 1. Experimental Density (ρ), refractive indices (n$_D$), ultrasonic velocities (u), surface tension (σ), refractive index deviation (δn$_D$) and ultrasonic velocity deviation (δu) of Anisaldehyde – benzene mixture at 323.15 K.

X$_1$	ρ / g/cc	n$_D$	u / ms^{-1}	σ/m.N.m^{-1}	δu	δ n$_D$
				323.15 K		
0.0000	0.828	1.4691	388	16.21	0	0.0000
0.1198	0.873	1.4762	525	24.09	3	0.0002
0.2141	0.898	1.4835	632	31.13	4	0.0002
0.3951	0.957	1.4960	836	37.38	5	0.0004
0.4081	0.961	1.4965	852	38.51	6	0.0005
0.5214	0.995	1.5045	978	46.71	5	0.0005
0.6605	1.036	1.5138	1134	50.85	5	0.0003
0.7314	1.055	1.5183	1212	56.75	3	0.0002
0.8195	1.079	1.5241	1311	64.64	3	0.0001
0.9316	1.108	1.5316	1472	67.21	2	0.0001
1.0000	1.114	1.5362	1571	78.11	0	0.0000

Table 2. Acoustical impedence (Z), isentropic compressibility (β$_s$), molar compressiblity (W), molar sound velocity (R), intermolecular free length (L$_f$), degree of intermolecular attraction (α), intermolecular free length deviation (δL$_f$), acoustical impedence deviation (δZ), and isentropic compressibility deviation (δβ$_s$) of Anisaldehyde – benzene mixture at 323.15 K.

X$_1$	Z kgm^{2}s^{-1}	β$_S$ m^{2}N^{-1}	W	R	L$_f$ m	α	δL$_f$ x 10^9	δZ	δβ$_s$ x10^6
0.0000	321	8.02	487	674	2.66	0.00	0.00	00.0	0.000
0.1198	426	4.46	546	769	1.98	0.50	2.40	-66.0	-2.640
0.2141	560	2.70	606	841	1.54	1.43	2.21	-66.0	-3.670
0.3951	800	1.49	690	971	1.14	2.72	1.83	-85.0	-3.500
0.4081	818	1.43	697	980	1.12	2.82	1.80	-86.0	-3.450
0.5214	973	1.05	748	1040	0.96	3.42	1.56	-93.0	-2.970
0.6605	1174	0.75	809	1140	0.81	3.62	1.27	-94.0	-2.200
0.7314	1270	0.64	840	1180	0.75	3.42	1.12	-96.0	-1.770
0.8195	1414	0.53	878	1230	0.69	2.83	0.94	-78.0	-1.200
0.9316	1630	0.41	900	1320	0.60	1.46	0.54	-02.0	0.001
1.0000	1750	0.36	974	1380	0.56	0.00	0.00	00.0	0.000

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

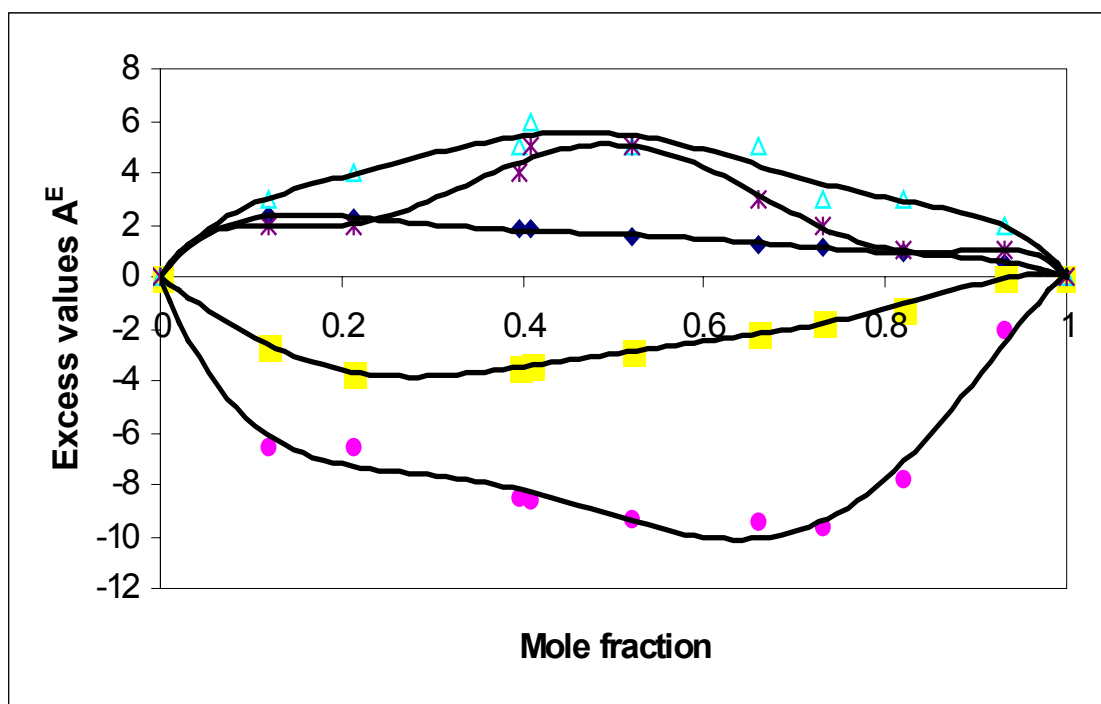|	Redlich - Kister Constants			
	a_0	a_1	a_2	σ
δn_D	0.001	-0.00	0.00	1.22
δu	23.10	-1.21	-2.41	1.22
δL_f	0.00	-0.00	-0.00	1.84
δZ	-405.9	140.2	-338.9	0.00
$\delta \beta_s$	-13.52	13.23	-31.96	0.99

Figure 1. Excess values at 323.15 K. (a)● $\delta Z \times 10^1$ (b)■ $\delta \beta_s \times 10^6$ (c) ♦ $\delta L_f \times 10^9$ (d)* $\delta n_D \times 10^4$ (e) Δ δu