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# Refractive indices, Ultrasonic velocities, Surface Tension and Thermo acoustical parameters of Anisaldehyde + Benzene at 313.15 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 ($\sigma$) have been measured for the binary liquid mixture of Anisaldehyde +benzene over the entire composition range at 313.15 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:** Anisaldehyde; refractive indices; ultrasonic velocity; thermo acoustical; surface tension.

## 1. 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 ultrasonic 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 velocities have been very widely used to study binary liquid mixtures [3]. Para anisaldehyde is chemically known as 4-methoxy benzaldehyde and used in perfume and pharmaceutical industries. Para anisaldehyde and benzene mixture is used as insecticides, comprising gel formulations for vapor producing systems. This mixture is also used in the titration calorimetry and reaction calorimetry. We have reported

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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 313.15K. From these experimental results acoustical impedance(Z), isentropic compressibility ($\beta_s$), intermolecular free length ($L_f$), degree of intermolecular attraction ($\alpha$), molar sound velocity (R), molar compressiblity or Wada's constant (W), refractive index deviation ($\delta n_D$), ultrasonic velocity deviation ($\delta u$), intermolecular free length deviation ($\delta L_f$), acoustical impedance deviation ($\delta Z$), and isentropic compressibility deviation ($\delta\beta_s$) were derived over the entire mole fraction range. The values have been fitted to Redlich-Kister type [4] equation. Literature survey showed that no measurements have been previously reported for the mixture studied in this paper.

## 2. Material and Methods

The chemicals used were of analytical grade and obtained from lobo chemicals. All the components were dried over anhydrous potassium carbonate and fractionally distilled [5]. 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 indices

Refractive indices were measured using thermostatically controlled Abbe refractometer (Atago 3T) with accuracy less than 0.0001units.A minimum of three independent readings were taken for each composition and the average value was considered in all the calculations. 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 solutions were pre thermostated at the temperature of the experience before the experiments to achieve a quick thermal equilibrium. 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.

### 2.2. 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

$$\delta u = u - ( x_1 u_1 + x_2 u_2) \quad (2)$$

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 impedance (Z) was calculated by the equation,

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

Where $\rho$ is the density of mixture and u is the ultrasonic velocity of the mixture.

The isentropic compressibility ($\beta_s$) was calculated by the equation

$$\beta s = 1/ \rho u2 \quad (4)$$

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 $\beta_s$ is the isentropic compressiblity.

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

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

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 [6].

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 ($\delta L_f$), 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 $\beta_s$ )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 by the method of least square.

$$A^E = x_1 x_2 \Sigma a_i ( x_1 - x_2 )^I \quad (10)$$

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

In each case the optimum number of coefficients is ascertained from an examination of the variation in standard deviation (S). Standard deviation was calculated using the relation

$$S = \{\sum (A_{exp} - A_{cal})^2 / (N-n)\}^{½} \quad (11)$$

Where N is the number of data points and n is the number of coefficients.

### 2.3. Surface tension

Surface tension was determined using drop volume tensiometer described in detail [7] which also discussed procedure and handling of data. The precision capillary is connected to a dosing system. It is located in one of the two liquid phases involved and forces the second liquid phase in to first liquid phase through the capillary. From the flow rate and number of drops, surface tension of each drop is calculated for pure liquid and the binary mixture over the whole composition range. All the samples were equilibrated to 313.15 K under atmospheric pressure. It was calibrated with distilled water. The accuracy of the surface tension measurement was estimated to be $0.1 mNm^{-1.}$ This can be calculated as

$$\sigma = Vdrop (\rho_H - \rho_L) g / \pi d \quad (12)$$

σ = Surface tension, V= Volume of drop, d=Dia of capillary g = Acceleration. due to gravity.

## 3. Results and discussion

Table 1 summarizes the comparison of density, refractive index and ultrasonic velocity data for liquids at 313.15K with the literature. Table 2 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 313.15 K with the corresponding Refractive index deviation ($\delta n_D$) and ultrasonic velocity deviation (δu). Table 3 lists Acoustical impedance (Z), isentropic compressibility ($\beta_s$), molar compressiblity (W), molar sound velocity (R), intermolecular free length ($L_f$), degree of intermolecular attraction (α), intermolecular free length deviation ($\delta L_f$), acoustical impedance deviation (δZ), and isentropic compressibility deviation ($\delta\beta_s$) of Anisaldehyde – benzene mixture at 313.15 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 4. A detailed observation of the Table 2 shows that the surface tension of the mixture increases with the mole fraction. According to Karla Granados [8] strong interaction in the liquid mixture decreases the σ value of the mixture. This means that interactions in the mixture are not strong and hence rise in the σ value was observed when mole fraction increases. It has been observed that ultrasonic velocity increases with mole fraction. This means that interaction in the mixture is not strong and hence increases with mole fraction. Ultrasound waves are high frequency mechanical waves. Their velocity in a medium depends inversely on density and the compressibility of the medium. More over the variation in ultrasonic velocity depends on the intermolecular free length on mixing. On the basis of a model for sound propagation proposed by Eyring and Kincaid [9], ultrasonic velocity increases on decrease of intermolecular free length and vice versa. It has been observed that intermolecular free length decreases for the system studied. It has also been observed that the refractive index deviation shows positive values for the entire mole fraction. It may be noted that such values are due to the electronic perturbation of the individual molecules during mixing and therefore depend very much on the nature of the mixing molecules. Table 3 shows the intermolecular free length ($L_f$) values decreases with mole fraction. Decrease in intermolecular free lengths leads to positive deviation in sound velocity and negative deviation in compressibility. This indicates that the molecules are nearer in the system. The molar sound velocity (R) acoustical impedance (Z) and molar compressibility (W) were increasing linearly with mole fraction indicating solute-solvent interactions [10] may occur in the system. 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 $\delta L_f$, $\delta n_D$ and δu were positive over the entire range of mole fraction for anisaldehyde+benzene mixture at 313.15 K. Similar trend of positive ultrasonic velocity deviation has been reported for cyclohexanone +benzene[11]. 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 [12]. 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. Our study shows that anisaldehyde- benzene system follows the above mentioned second factor and hence physical intermolecular forces are weak and the sign of excess values are positive or negative. In the present investigation the behavior of these systems has

been interpreted qualitatively. In this binary mixture, it is assumed that on addition of benzene to p-anisaldehyde, molecules may break in to several dipoles which in turn may induce dipole moment in the neighboring aromatic hydrocarbons forming the molecular association. The nature of $\delta z$ and $\delta L_f$ play vital role in assessing the compactness due to molecular rearrangement .The molecular interactions in liquid mixture may also be due to interstitial accommodation [13] leading to more compact structure making $\delta Z$ and $\delta\beta_s$ negative. The positive deviation of $\delta L_f$, $\delta n_D$ and $\delta u$ is an indicative of weak interaction involving dispersion forces [14]. The degree of intermolecular attraction ($\alpha$) has also been evaluated to study the structural variations and the nature of interaction occurring in the system. It has been observed that the maximum value of $\alpha$ occurs at nearly mole fraction of 0.6. This suggests the presence of intermolecular interaction in the system.

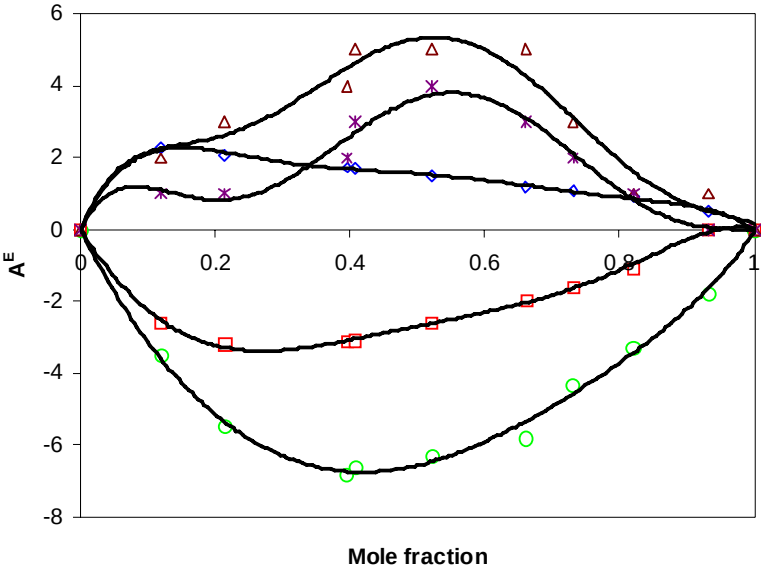


Figure 1. Excess values at 313.15 K. (a)○ $\delta Z$ x $10^1$ (b)□ $\delta\beta_s$ x$10^6$ (c) ◊ $\delta L_f$ x $10^9$ (d)* $\delta$ $n_D$ x$10^4$ (e) Δ $\delta u$

Table 1. Comparision of density, refractive index and ultrasonic velocity data for liquids at 313.15K with the literature.

| Pure liquids | $\rho$ / g/cc | | $n_D$ | | u / m.s$^{-1}$ | |
|---|---|---|---|---|---|---|
| | Exp. | Lit. | Exp. | Lit. | Exp. | |
| Anisaldehyde | 1.119 | - | 1.5480 | - | 1631 | - |
| Benzene | 0.845 | 0.875[a] | 1.4982 | 1.4921[a] | 408 | 423[b] |

[a] ref 15 [b]ref 16

Table 2. Experimental Density (ρ), refractive indices ($n_D$), ultrasonic velocities (u), surface tension (σ), refractive index deviation ($\delta n_D$) and ultrasonic velocity deviation (δu) of Anisaldehyde – benzene mixture at 313.15 K.

| $X_1$ | $\rho$ / g/cc | $n_D$ | u / $m.s^{-1}$ | $\sigma$/$m.N.m^{-1}$ | $\delta$u | $\delta n_D$ |
|---|---|---|---|---|---|---|
| | | | 313.15 K | | | |
| 0.0000 | 0.845 | 1.4821 | 408 | 20.20 | 0 | 0.0000 |
| 0.1198 | 0.874 | 1.4899 | 536 | 28.08 | 2 | 0.0001 |
| 0.2141 | 0.900 | 1.4963 | 672 | 35.14 | 3 | 0.0001 |
| 0.3951 | 0.960 | 1.5100 | 895 | 44.92 | 4 | 0.0002 |
| 0.4081 | 0.965 | 1.5110 | 912 | 45.50 | 5 | 0.0003 |
| 0.5214 | 1.000 | 1.5200 | 1050 | 49.70 | 5 | 0.0004 |
| 0.6605 | 1.040 | 1.5280 | 1220 | 54.71 | 5 | 0.0003 |
| 0.7314 | 1.058 | 1.5320 | 1305 | 61.74 | 3 | 0.0002 |
| 0.8195 | 1.081 | 1.5370 | 1411 | 68.21 | 1 | 0.0001 |
| 0.9316 | 1.109 | 1.5434 | 1523 | 71.22 | 1 | 0.0000 |
| 1.0000 | 1.119 | 1.5480 | 1631 | 82.14 | 0 | 0.0000 |

Table 3. Acoustical impedance (Z), isentropic compressibility ($\beta_s$), molar compressiblity (W), molar sound velocity (R), intermolecular free length ($L_f$), degree of intermolecular attraction ($\alpha$), intermolecular free length deviation ($\delta L_f$), acoustical impedence deviation ($\delta Z$), and isentropic compressibility deviation ($\delta\beta_s$) of Anisaldehyde – benzene mixture at 313.15 K.

| $X_1$ | Z | $\beta^S$x106 $Kg.m^2s^{-1}$ | W | R $m^2N^{-1}$ | $L_f$ x 109 | αm | $\delta L_f$ x 109 | δZ | $\delta\beta_s$ x106 |
|---|---|---|---|---|---|---|---|---|---|
| 0.0000 | 344 | 7.10 | 530 | 672 | 2.50 | 0.00 | 0.00 | 00.0 | 0.000 |
| 0.1198 | 485 | 3.70 | 560 | 780 | 1.80 | 0.79 | 2.40 | -35.0 | -2.580 |
| 0.2141 | 605 | 2.45 | 613 | 856 | 1.47 | 1.50 | 2.21 | -55.0 | -3.200 |
| 0.3951 | 859 | 1.29 | 702 | 989 | 1.06 | 2.85 | 1.83 | -68.0 | -3.100 |
| 0.4081 | 880 | 1.24 | 707 | 998 | 1.04 | 2.96 | 1.80 | -66.0 | -3.090 |
| 0.5214 | 1050 | 0.90 | 760 | 1060 | 0.89 | 3.52 | 1.56 | -63.0 | -2.600 |
| 0.6605 | 1260 | 0.64 | 823 | 1160 | 0.75 | 3.82 | 1.27 | -58.0 | -1.980 |
| 0.7314 | 1380 | 0.55 | 857 | 1210 | 0.69 | 3.63 | 1.12 | -43.0 | -1.590 |
| 0.8195 | 1520 | 0.46 | 890 | 1260 | 0.64 | 3.01 | 0.94 | -33.0 | -1.081 |
| 0.9316 | 1680 | 0.38 | 908 | 1330 | 0.58 | 1.39 | 0.54 | -18.0 | 0.001 |
| 1.0000 | 1820 | 0.33 | 981 | 1390 | 0.54 | 0.00 | 0.00 | 00.0 | 0.000 |

Table 4. Redlich-Kister Constants for the deviations of refractive index, ultrasonic velocity intermolecular free length, acoustical impedance and isentropic compressibility of Anisaldehyde – benzene at 313.15 K

| | Redlich-KisterConstants | | | |
|---|---|---|---|---|
| | $a_0$ | $a_1$ | $a_2$ | S |
| $\delta n_D$ | 0.009345 | -0.002554 | 0.006168 | 0.86 |
| $\delta u$ | 17.7020 | 9.3217 | -3.8598 | 0.64 |
| $\delta Lf$ | 92 | -66 | 16 | 1.12 |
| $\delta Z$ | -276.11 | -131.97 | 54.64 | 1.21 |
| $\delta\beta s$ | -12.34 | -30.03 | 12.43 | 0.44 |

## 4. Conclusion

Experimental data of the density, refractive index, ultrasonic velocity and surface tension of anisaldehyde and benzene mixture have been measured at 313.15 K. These data have been used to compute the excess properties of the system. Negative deviations were observed for $\delta Z$ and $\delta\beta_s$. The positive deviations were observed for $\delta L_f$, $\delta n_D$ and $\delta u$. It may be concluded that the interactions resulting in the interstitial accommodation of benzene in to p-anisaldehyde are the predominant factor over dipole – dipole and dipole induced–dipole interaction. The intermolecular interactions between anisaldehyde and benzene mixture leads to weak dispersive type. It is clear that Redlich kister polynomial equation can represent the refractive index deviation ($\delta n_D$), ultrasonic velocity deviation ($\delta u$) intermolecular free length deviation ($\delta L_f$), acoustical impedance deviation ($\delta Z$), and isentropic compressibility deviation ($\delta\beta_s$) very well by standard deviation values.

## References

[ 1] Ewing, M. B., Levian, B. J., and Marsh, K. N. 1970. Excess enthalpies, excess volume and excess Gibbs free energy for mixtures of cyclooctane +cyclopentane at 288. 15, 298. 15 and 308.15K. *Journal of Chemical Thermodynamics,* 2: 689 - 691.

[ 2] Mchaweh, A., Alsaygh, A., and Moshfeghian, M. A. 2004. A simplified method for calculating saturated liquid densities. *Fluid phase equilibria*, 224: 157-167.

[ 3] Yadava, S. S., and Anirudh, Y. 2005. Ultrasonic study on binary liquid mixtures between some bromoalkanes and hydrocarbons. *Ultrasonics*, 43: 732-735.

[ 4] Redlich, O., and Kister, A. T. 1948. Algebraic representation of thermodynamic Properties and the classification of solutions. *Industrial & Engineering Chemistry,* 40: 345-350.

[ 5] Kamila, S., Chakravarthy, V., and Jena, S. 2004. Studies on acoustic behavior, viscosity, and density of some commercial extractants and their molecular interaction with diluent, modifier and extractant. *Journal of Solution Chemical*, 33: 365-380.

[ 6] Jacobson, B. 1952. Compressiblity of binary liquid mixtures. *Acta Chemica Scandinavica,* 6:485-487.

[ 7] Pineiro, A., Brocas, P., Amigo, A., Pinto, M and Bravo, R. 1999. Surface tension and refractive indices of tetrahydrofurans and n-alkanes at 298.15 K. *Journal of Chemical Thermodynamics*, 31:931-942.

[ 8] Karla Granados and Jesus Gracia Fredrique.2006. Refractive index, surface tension and density of aqueous mixture of carboxylic acids at 298.15K. *Journal of Chemicl and Engineering Data,* 51:1473-1478.

[ 9] Eyring, H., and Kincaid, J. F. 1938. Free volume and free angle ratio of molecules in liquids, *Journal of Chemical Physics,* 6: 620-625.

[10] Baluja, S., and Oja, S. 2001. Studies of some acoustical properties in binary solutions. *Fluid phase equilibria*, 178: 233-238.

[11] Aralaguppi, M., I, Jadar, C. V., and Aminabhavi, T. M. 1999. Density, refractive index, viscosity, and speed of sound in binary mixtures of cyclohexanone with benzene, methylbenzene, 1,4-dimethylbenzene, 1,3,5-trimethylbenzene, and methoxybenzene in the temperature interval (298.15 to 308.15) K. *Journal of Chemicl and Engineering Data,* 44: 446-450.

[12] Kiyohara, O., and Benson, G. C. 1979. Ultrasonic speeds and isentropic Compressibility of n alkanol +n heptane mixture at 298.15 K. *Journal of Chemical Thermodynamics,* 11:861-873.

[13] Yang, C., Lal, H., and Ma, P. 2006. Density and viscosity of binary mixtures of diethyl carbonate with alcohols at 293.15 to 363.15 K and predictive results by unifac visco group contribution method, *Journal of Chemicl and Engineering Data,* 51:1345-1358.

[14] Susmita, K., Satyaban, J and Bipin, B. S. 2005. Studies on some thermo acoustical parmeters in binary liquid mixtures of phosphoric acid with different diluents at temperature 303.15K : Ultrasonic study. *Journal of Chemical Thermodynamics*, 37: 820-825.

[15] Kyu, J. H., Jong, H. O., and So-Jin, P. 2006. Densities and viscosities of ternary systems of methyl tert –butyl ether +methanol+benzene and their sub binary systems *Journal of Chemicl and Engineering Data*, 51: 1339-1344.

[16] Viswanathan, S., Rao, M. A., and Prasad, D. H. L. 2000. Densities and viscosities of binary liquid mixture of anisole or methyl tertiary butyl ether with benzene, chlorobenzene, benzonitrile and nitrobenzene *Journal of Chemicl and Engineering Data,* 45:764-770.