



## Thermo Acoustical Excess Parameters of Anisaldehyde-Toluene Mixture at 303.15, 308.15, 313.15 and 318.15 K

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The ultrasonic velocity, density and viscosity in binary liquid mixture of anisaldehyde + toluene have been determined at different temperatures from 303.15-318.15 K over the whole composition range. The data have been utilized to estimate the excess adiabatic compressibility ( $\beta^E$ ), excess volume ( $V^E$ ), excess intermolecular free length ( $L_r^E$ ), excess internal pressure ( $\pi^E$ ), excess enthalpy ( $H^E$ ) and excess viscosity ( $\eta^E$ ) at these 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.

**Key Words:** Binary mixtures, Excess enthalpy, Excess molar volume, Excess viscosity.

### INTRODUCTION

Binary liquid mixtures due to their unusual behaviour have attracted considerable attention in different fields. In chemical process industries materials are normally handled in fluid form and as a consequence, the physical, chemical and transport properties of fluids assume importance<sup>1,2</sup>. Thus data on some of the properties associated with the liquids and liquid mixtures like viscosity, density, excess enthalpy and excess volume find extensive application in chemical engineering design<sup>3,4</sup>. These properties are important from practical and theoretical point of view to understand liquid theory and provide information about molecular interactions.

Anisaldehyde is used in perfume and pharmaceutical industries. We have reported thermo acoustical properties of pure anisaldehyde and toluene as well as for the binary system constituted by these two chemicals at 303.15, 308.15, 313.15 and 318.15 K. From these experimental results excess adiabatic compressibility ( $\beta^E$ ), excess volumes ( $V^E$ ), excess intermolecular free length ( $L_r^E$ ), excess internal pressure ( $\pi^E$ ), excess enthalpy ( $H^E$ ) and excess viscosity ( $\eta^E$ ) over the entire mole fraction range were calculated.

### EXPERIMENTAL

Anisaldehyde and toluene are of AR grade and these were purified by usual methods<sup>5,6</sup>. Their boiling points agreed with literature values indicating that the liquids used in the present

study are of high purity. Other physical properties such as density ( $\rho$ ), ultrasonic velocity ( $U$ ) and viscosity ( $\eta$ ) are given in Table-1.

In order to carry out experiment on ultrasonic interferometer for ultrasonic velocity, specific gravity bottle for density, Oswald viscometer apparatus for coefficient of viscosity, the apparatus are standardized first with pure water and then with benzene. The results obtained are found to be good agreement with reported values (Table-1). In all the mixtures the mole fraction of 2nd compound toluene has been increased from 0 to 1. The ultrasonic velocity in liquid mixtures have been measured using an ultrasonic interferometer (Mittal enterprises, Model F-80X) working at 2 MHz frequency with an accuracy  $\pm 0.01$  %. The density and viscosity are measured by using specific gravity bottle and Oswald viscometer with an accuracy of  $\pm 0.5$  %. In all the above apparatus the temperature was maintained constant at 303.15, 308.15, 313.15 and 318.15 K using proportional temperature controller of accuracy  $\pm 0.01$  K.

**Theory:** The adiabatic compressibility has been determined by using the experimentally measured ultrasonic velocity ( $U$ ) and density ( $\rho$ ) 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:

TABLE-1  
PHYSICAL PROPERTIES OF ANISALDEHYDE AND TOLUENE

Liquid	$\rho$		U		$\eta$	
	Exptl.	Lit*	Exptl.	Lit*	Exptl.	Lit*
Anisaldehyde						
303.15 K	1.1252	1.1250 <sup>20</sup>	1694.33	–	3.2512	3.2753 <sup>20</sup>
308.15 K	1.1116	–	1670.67	–	3.1306	–
313.15 K	1.1095	1.1190 <sup>20</sup>	1631.33	1631 <sup>21</sup>	2.9614	2.9695 <sup>20</sup>
318.15 K	1.1047	–	1557.00	–	2.6822	–
Toluene						
303.15 K	0.8567	0.8566 <sup>22</sup>	1273.5	1276.8 <sup>23</sup>	0.5275	0.5372 <sup>22</sup>
308.15 K	0.8543	0.8649 <sup>17</sup>	1263.5	1268.4 <sup>17</sup>	0.5011	–
313.15 K	0.8510	–	1253.5	–	0.4846	–
318.15 K	0.8479	0.8567 <sup>17</sup>	1236.5	1242.5 <sup>17</sup>	0.4524	–

$$V = \frac{(X_1M_1 + X_2M_2)}{\rho} \quad (2)$$

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

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

where K = temperature dependent Jacobson's constant.

Enthalpy is calculated using the relation

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

Internal pressure ( $\Pi$ ) is calculated using the formula

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

The excess properties such as  $\beta^E$ ,  $V_m^E$ ,  $L_f^E$ ,  $H^E$  and  $\pi^E$  have been calculated using the equation

$$Y^E = Y_{mix} - [X_1Y_1 + X_2Y_2] \quad (6)$$

where  $Y^E$  is  $\beta^E$  or  $V_m^E$  or  $L_f^E$  or  $H^E$  or  $\pi^E$  and X represents mole fraction of the component and subscripts 1 and 2 stand for the components 1 and 2, respectively.

The excess thermodynamic functions are sensitively dependent not only on difference in intermolecular forces but different in the size of molecules. Internal pressure and free volumes are the fundamental properties of the liquid state which are initially studied by Hildebrand and Schott<sup>7,8</sup> and subsequently used to investigate molecular interactions of binary liquid mixtures. Thermodynamic and ultrasonic sound measurement are used to calculate the internal pressure, free volume and enthalpy of liquids and the effects of the change in composition and temperature on the excess free volume, internal pressure and enthalpy of the binary mixture have been evaluated by several researchers<sup>9-14</sup>. The study of excess values provides important information on molecular forces existing in the binary liquid mixtures. Depending upon the nature of the liquids whether they are polar or non-polar, the signs and magnitudes of these excess values can throw light on strength of interactions. The present paper reports the study of various thermo acoustic excess parameters.

## RESULTS AND DISCUSSION

The variation of excess compressibility of the mixture with mole fraction of toluene at all temperatures is shown in Fig. 1. Up to the mole fraction 0.5394 the excess compressibility values sign is negative after this the values sign is

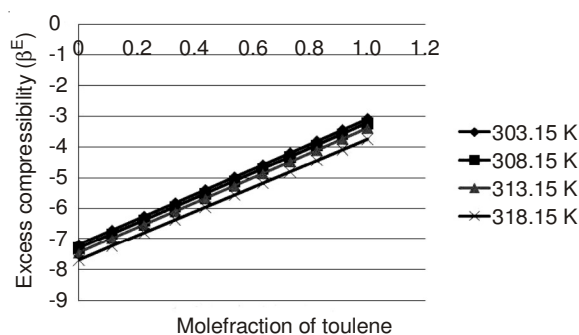


Fig. 1. Variation of excess compressibility with mole fraction of toluene for anisaldehyde + toluene system at different temperatures

positive at all temperatures. The values of  $\beta^E$  are positive and negative at different temperatures for the entire range of mole fraction of toluene. This trends suggests the presence of weak interactions between anisaldehyde and toluene. Fig. 1 shows that the excess values of adiabatic compressibility's are negative at lower mole fraction and positive for higher mole fraction of toluene in the present system. Fort and Moore<sup>15</sup> found that the negative value of excess compressibility's indicates greater interaction between the components of the mixtures and positive values in excess compressibility correspond to the existence of weak dispersive forces. Further the negative values of  $\beta^E$  is associated with a structure forming tendency while a positive value is taken to indicate a structure breaking tendency due to hetero-molecular interaction between the component molecules of the mixture.

Fig. 2 shows the variation of excess free length with mole fraction of toluene at different temperatures. Up to the mole fraction 0.5394 the excess free length values are negative and after that the values are positive. Similar like observations are noted for all four temperatures. The negative  $L_f^E$  values indicate the presence of strong interactions between unlike molecules. It is observed particular interactions only up to 0.5394 after this as temperature raises the value of  $L_f^E$  increases gradually. This further confirms the weak interactions between anisaldehyde and toluene. The Fig. 2 shows the variation of excess free length is negative up to a mole fraction 0.5394 and after this it is positive at all temperatures studied for the system. According to Ramamurthy *et al.*<sup>16</sup> negative values of excess intermolecular free length  $L_f^E$  indicate that sound waves cover longer distances due to decrease in intermolecular free length ascribing the dominant nature of hydrogen bond interaction between unlike molecules. Fort and Moore<sup>15</sup> indicated that

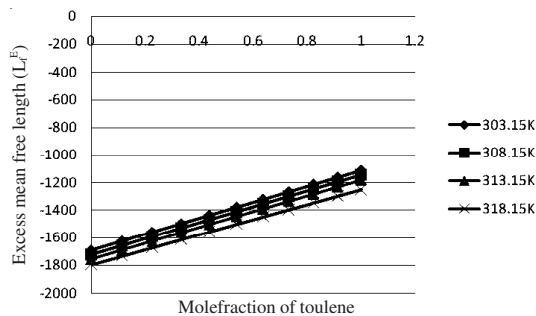


Fig. 2. Variation of excess mean free length with mole fraction of toluene for anisaldehyde + toluene system at different temperatures

the positive values of excess free length should be attributed to the dispersive forces and negative excess values should be due to charge transfer and hydrogen bond formation. In the present study the positive contribution at higher mole fractions shows a weak interaction.

Fig. 3 indicates excess molar volume of binary mixture with increase in mole fraction of toluene at different temperatures. It is observed that  $V_m^E$  of the mixture are negative at higher mole fraction of toluene. The same trends are observed at different temperatures. As mole fraction increases the excess molar volume decreases. The excess molar volume may be affected by three factors. The first factor is, the specific forces between the molecules, such as hydrogen bond, charge transfer complexes, breaking of hydrogen bonds and complexes bringing negative excess values. The second factor is the physical intermolecular forces, including electrostatic forces between charged particles and between a permanent dipole an induced dipole and forces of attraction and repulsion between non-polar molecules. Physical inter molecular forces are weak and the sign of excess values may be positive or negative, but the absolute values are small. Third factor is the structural characteristics of the component arising from geometrical fitting of one component into other structure due to the differences in shape and size of the components and free volume<sup>17</sup>. The magnitudes of these values are minimum. The negative values can be visualized by closer approach of the molecules in the liquid mixtures. This indicates the existence of specific interactions between the liquid components.

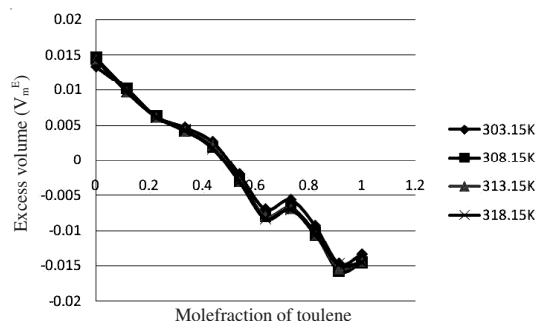


Fig. 3. Variation of excess molar volume with mole fraction of toluene for anisaldehyde + toluene system at different temperatures

Fig. 4 shows variation of excess free volume at different temperatures with increase in mole fraction of toluene. Excess free volume of the mixture increases with increase of mole fraction of toluene at all temperatures. This indicates the

presence of weak interactions. The values of  $V_f^E$  are found to be positive for higher mole fraction of toluene at all temperatures and vary non-linearly. For some binary liquid mixture, Fort and Moore<sup>15</sup> noticed that the negative excess free volume tends to decrease as the strength of the interaction between the unlike molecules increases. However, in the present investigation a trend is observed in such a way excess viscosity for the mixture is negative for the lower mole fraction of toluene and it is positive for higher mole fraction of toluene. Hence the non-linear character may be due to the disruption of molecular associations of dipole-dipole and dipole-induced dipole interactions.

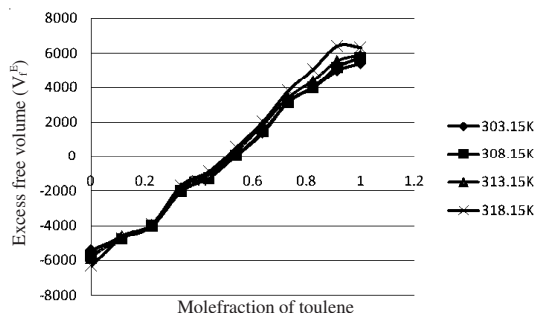


Fig. 4. Variation of excess free volume with mole fraction of toluene for anisaldehyde + toluene system at different temperatures

Fig. 5 indicates variation of excess internal pressure of binary mixture with increase in mole fraction of toluene at different temperatures. The excess values of  $\pi$  of the mixture decreases with the increase of mole fraction of toluene. The excess values of  $\pi$  shows both positive and negative deviations and hence suggesting weak inter molecular dispersive interaction between the components of the mixture. The excess internal pressures in Fig. 5 are negative at mole fraction of toluene greater than 0.334173. The same is observed at all temperatures. That is excess internal pressure of the mixture is found to be decreasing with increasing mole fraction of toluene. The negative values of  $\pi^E$  indicate that only dispersion and dipolar forces are operating with complete absence of specific interaction. The same is reported in the binary mixture alkanol with dimethyl sulphoxide (DMSO) by Palani *et al.*<sup>18</sup>.

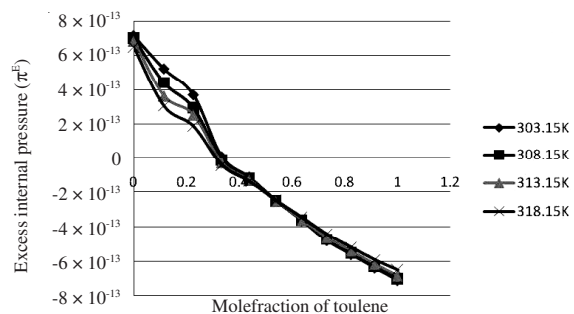


Fig. 5. Variation of excess internal pressure with mole fraction of toluene for anisaldehyde + toluene system at different temperatures

Fig. 6 shows the variation of excess enthalpy of the binary mixture with increase of mole fraction of toluene at four temperatures studied as mole fraction of toluene increases excess enthalpy of the mixture decreases. The magnitude of the excess enthalpy values is very less. This suggests that weak inter

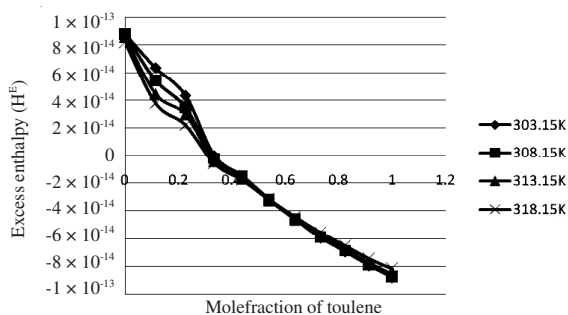


Fig. 6. Variation of excess enthalpy with mole fraction of toluene for anisaldehyde + toluene system at different temperatures

molecular dispersive forces exists between anisaldehyde and toluene.

The variation of excess acoustic impedance with mole fraction of toluene with different temperatures is shown in the Fig. 7. As the mole fraction of toluene increases the negative values of acoustic impedance of the mixture decreases. The negative values observed in this mixture suggests that rupture of hydrogen bond between anisaldehyde and toluene. This indicates the presence of weak interactions in the mixture.

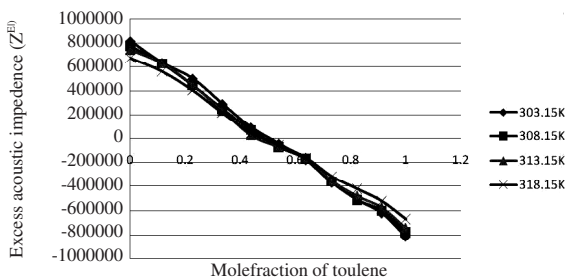


Fig. 7. Variation of excess acoustic impedance with mole fraction of toluene for anisaldehyde + toluene system at different temperatures

Fig. 8 shows the variation of excess viscosity at different temperatures. At all temperatures studied the excess viscosity of the mixture decreases positively in magnitude up to the mole fraction 0.33 of toluene. After this the excess viscosity of the mixture decreases negatively. The positive or negative values of  $V^E$  suggests the weak interactions.

The measurement of viscosity in binary mixture yields some reliable information in the study of molecular interaction. The thermodynamic excess properties are found to be more sensitive towards intermolecular interaction between component molecules of liquid mixtures. The sign and the extent of deviation of these properties from ideality depend on the strength of interaction between unlike molecule<sup>19</sup>.

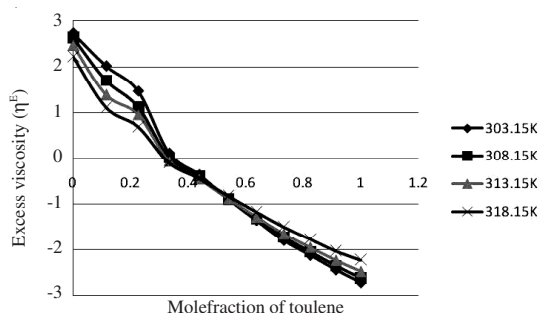


Fig. 8. Variation of excess viscosity with mole fraction of toluene for anisaldehyde + toluene system at different temperatures

According to Fort and Moore<sup>15</sup> the excess viscosity gives the strength of the molecular interaction between the interacting molecules. For systems where dispersion, induction and dipolar forces are operated by the values of excess viscosity are found to be negative, whereas the existence of specific interactions leading to the formation of complexes in liquid mixtures tend to make excess viscosity positive. In the present study at all temperatures, for the lower mole fraction of toluene, the excess viscosity of the liquid is positive upto a mole fraction of 0.3342. After this value the excess viscosity is negative through the whole range of mole fraction of toluene. The negative values of excess viscosity for the system can be attributed to the presence of the dispersion, induction and dipolar forces between the components.

## Conclusion

Experimental values of the ultrasonic velocity, density and viscosity of anisaldehyde and toluene mixture have been measured at 303.15, 308.15, 313.15 and 318.15 K. These data have been used to compute the excess properties of the system. Based on the deviations observed it may be concluded that there are weak interactions between anisaldehyde and toluene mixture.

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