Australian Journal of Basic and Applied Sciences, 1(4): 769-775, 2007
ISSN 1991-8178

Prediction of Transport Properties of Anisaldehyde – Benzene Mixture at 303.15K, 313.15K and 323.15K

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Abstract: The studies of density, excess molar volume, excess enthalpy and viscosity 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. Density (ρ) excess enthalpy (H^E) and viscosity (η) have been measured for the binary liquid mixture of Anisaldehyde +benzene over the entire composition range and diffusivity at 0.5mole fraction at 303.15K,313.15K and 323.15K Excess molar volume (V^E) and viscosity deviations (Δη), have been calculated. The appropriate models were used to correlate the measured properties. It was found that in all the cases, the experimental data obtained fitted with the values correlated by the corresponding models very well. The molecular interactions existing between the components were discussed.

Key words: Binary solvents, Diffusivity, Excess enthalpy, Excess molar volume, Transport, Viscosity deviations.

INTRODUCTION

Binary liquid mixtures due to their unusual behavior have attracted considerable attention (Ewing, M.B., *et al.,* 1970). 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. 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, process simulation, solution theory and molecular dynamics (Mchaweh, A., *et al.,* 2004). These properties are important from practical and theoretical point of view to understand liquid theory and provide information about molecular interactions. 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 and also in the preparation of a polymer containing pendant unsaturation. We have reported transport properties of pure anisaldehyde and benzene as well as for the binary system constituted by these two chemicals at a temperature of 303.15K, 313.15K and 323.15K. From these experimental results excess molar volume (V^E) and viscosity deviations (Δη) from the ideal behavior over the entire mole fraction range were calculated. The viscosity values have been fitted to McAllister model (McAllister, R. A, 1960). Viscosity deviations excess enthalpy and excess volume were fitted to Redlich-Kister type (Redlich.O.Kister and A.T., 1948) equation. Diffusivity values were fitted in laddha 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 (Mehdihasan, *et al.,*

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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.

Density:

Densities of the liquid mixtures were measured by using an Ostwald –Sprengel type pycnometer (Reilly, J., and W. Northman, 1978) having a bulk volume of 25cm^3 and a capillary diameter of about 1mm. The pycnometer was calibrated at 303.15 K with doubly distilled water.

Excess Molar Volume:

The excess molar volume can be computed from experimental density data using the relationship

$$V^E = (x_1M_1 + x_2M_2) / \rho_m - (x_1M_1 / \rho_1 + x_2M_2 / \rho_2) \quad (1)$$

Where x_1 and x_2 refers to the mole fraction of components 1 and 2. ρ_1 and ρ_2 refers to the density of components 1 and 2. ρ_m is the density of mixture.

Viscosity:

The Kinematic viscosities were measured at the desired temperature using Ostwald viscometer. The viscometer was calibrated using water. After the charged mixture had attained bath temperature, flow time has been measured. The flow measurements were made with an electronic stopwatch with a precision of 0.01sec. In the calculation of viscosity, two constants a and b of the viscometer in the relation

$$\nu = (at) - (b/t) \quad (2)$$

were obtained by measuring the flow time at a temperature. The kinematic viscosity were correlated by means of McAllister model considering three-body interaction, which for a two component mixture gives

$$\ln \nu = x_1^3 \ln \nu_1 + 3 x_1^2 x_2 \ln \nu_{12} + 3 x_1 x_2^2 \ln \nu_{21} + x_2^3 \ln \nu_2 - \ln(x_1 + x_2 M_2 / M_1) + 3x_1^2 x_2 \ln ((2+M_2 / M_1) / 3) + x_2^3 \ln (M_2 / M_1) + 3 x_1 x_2^2 \ln ((1+ 2 M_2 / M_1)/3) \quad (3)$$

Where ν and x_2 respectively. ν_1 and ν_2 refers to the kinematic viscosity of pure liquids 1 and 2 respectively. ν_{12} and ν_{21} represent the interaction parameters obtained by multiple regression analysis. M_1 and M_2 refer to the molecular weight of the two components respectively. The viscosity deviations can be calculated as

$$\Delta \eta = \eta - (x_1 \eta_1 + x_2 \eta_2) \quad (4)$$

where η, η_1, and η_2, are the dynamic viscosities of the mixture and those of the pure components 1 and 2 respectively. The percentage deviation was calculated by

$$d = \{(\nu_{exp} - \nu_{cal}) / \nu_{cal} \} 100 \quad (5)$$

The average deviation (AD) was calculated from the relation ship

$$AD = (\Sigma d^2 / N)^{1/2} \quad (6)$$

Excess Enthalpy:

In the present investigation, the H^E data have been obtained using a displacement calorimeter. The calorimeter used in this work is basically of the same type as used (Tsao, C.C., and Smith, 1953). The description of the apparatus and standard experimental procedure was given (Rajendran, M., *et al.,* 1989).

The calorimeter is essentially a doubled- walled Dewar flask. The performance of the calorimeter and its reliability for the measurement of enthalpy of mixing values were ascertained by determining the enthalpy of mixing for benzene + cyclohexane. The results compared well within 2% with literature data. The excess enthalpy of mixing can be calculated by using the formula Q= Vit where V=The resistance across the heater in volts, I is the current passing through the heater in amperes and t is the time in seconds. The H^E is obtained by dividing the energy-supplied value by the total moles involved for the particular mole fraction. All the measurements described above were performed at least three times, and the results were averaged to give the final values. The calculated excess molar volume, excess enthalpy and viscosity deviation for the binary system of this investigation have been correlated using Redlich Kister equation by the method of least square.

$$V^E \text{ or } \eta = x_1 x_2 \Sigma a_i (x_1 - x_2)^1 \quad (7)$$

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

Diffusivity:

In the present investigation, the D_{AB} data have been obtained using a diaphragm cell. The diaphragm cell used in this work is basically of the same type as used by Laddha and the description of the apparatus and standard experimental procedure was given (Amourdam. M.J., and G.S. Laddha. 1967). Diffusion was allowed to occur for a preliminary period of 4to 5hours to establish the concentration gradient across the diaphragm. The cell constant was found by calibrating the cell with 0.1N HCl diffusing in to pure water at a temperature of 303.15 K in a constant temperature bath. The average value of the cell constant determined was 0.2586. The cell constant so found was consistent to 0.1%. The test solutions from each compartment was analyzed by UV Spectrometer. The performance of the diffusivity cell and its reliability for the measurement of diffusivity coefficient values were ascertained by determining the diffusivity coefficient of toluene + cyclohexane. Diaphragm cell equation for the measurement of diffusion coefficient may be expressed as follows assuming unidirectional diffusion and quasi steady state in the diaphragm.

$$D = 1 / \beta t \, \Delta Ci \, \ln / \Delta Ci^f \quad (8)$$

ΔCi = initial concentration difference, $Ci_A - Ci_B$

ΔCi^f =Final concentration difference $Ci^f_A - Ci^f_B$

The experimental data on binary diffusivities at 0.5 are recorded and compared with the predicted values according to the following equation.

$$(D_{AB} \mu_B / T) (V_A)^{1/3} = \{(K/6\pi) (4\pi N/3)^{1/3}\} V_B / V_A \quad (9)$$

The results compared well within 3% with literature data.

RESULTS AND DISCUSSIONS

Table 1 lists the measured density ρ, kinematic viscosity η and excess enthalpy of anisaldehyde and benzene at 303.15K, 313.15K and 323.15K with the corresponding excess molar volume and viscosity deviations. Table 2 lists diffusivity values of the system at 303.15K, 313.15K and 323.15K. Table 3 shows the McAllister constants and average deviation values of the system .Redlich – Kister constants for the deviation of viscosity, excess molar volume and excess molar enthalpy were presented in Table 4. In Figure 1 the excess molar volume for anisaldehyde and benzene increases as temperature increases for all the mole fractions. It can be summarized that V^E 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 values of V^E (Changsheng vang, Hexilal and peisheng ma, 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 V^E 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 positive V^E values are due to declustering of aldehyde in the presence of benzene, repulsive forces due to the electronic charges of both components (Hiannie, D and J. Suryadi, 2005). Because of the mutual structure disrupting interactions of the solvent and co solvent, the volume of the mixture gradually increases (Savitha, T. and Sathyanarayana. D, 2004). The negative values of V^E are due to the compression in free volume is considered to occur, making the mixture more compressible than the ideal mixture which ultimately culminates into negative values of V^E. In Figure 2, the deviations in viscosity for anisaldehyde and benzene are negative for all the mole fractions and at 303.15K, 313.15K and 323.15K. The viscosity of the mixture strongly depends on the entropy of mixture,

Table 1: Experimental densities excess molar volume, kinematic viscosities, it's deviation and excess enthalpy of anisaldehyde – benzene mixture at 303.15K,313.15K and 323.15K.

X_1	ρ	V^E	η	Δη	H^E
	g /cc	(cc/g mol)	m.Pa.s		$Jmol^{-1}$
		303.15 K			
0.0000	0.8720	0.0000	0.6605	0.0000	0.0
0.1198	0.8750	-0.2114	0.7965	-0.2740	44.1
0.2141	0.9010	-0.2560	0.8478	-0.4590	101.6
0.3951	0.9610	-0.3052	1.0618	-0.6983	224.2
0.4081	0.9660	-0.4204	1.0789	-0.7138	315.4
0.5214	1.0002	-0.5159	1.3105	-0.7660	330.2
0.6605	1.0410	-0.3844	1.6805	-0.7444	320.1
0.7314	1.0590	-0.2078	1.9294	-0.6731	242.5
0.8195	1.0812	-0.1252	2.3089	-0.5143	111.7
0.9316	1.1100	-0.1909	2.9038	-0.2002	070.9
1.0000	1.1250	0.0000	3.2753	0.0000	0.0
		313.15K			
0.0000	0.8450	0.0000	0.6780	0.0000	0.0
0.1198	0.8740	-0.1002	0.7443	-0.2082	89.1
0.2141	0.9009	-0.2448	0.7965	-0.3721	155.5
0.3951	0.9608	-0.2833	0.9734	-0.6100	252.2
0.4081	0.9655	-0.3659	0.9981	-0.6151	258.1
0.5214	1.0000	-0.3000	1.1441	-0.7287	288.2
0.6605	1.0400	-0.2769	1.4390	-0.7525	283.5
0.7314	1.0580	-0.1003	1.6348	-0.7192	258.8
0.8195	1.0810	-0.1037	1.9553	-0.6006	204.2
0.9316	1.1090	-0.0836	2.5081	-0.3047	104.2
1.0000	1.1190	0.0000	2.9695	0.0000	0.0
		323.15K			
0.0000	0.8280	0.0000	0.6900	0.0000	0.0
0.1198	0.8730	0.0112	0.6646	-0.1648	99.5
0.2141	0.8980	0.0795	0.6914	-0.3108	171.5
0.3951	0.9572	0.1116	0.8478	-0.4859	275.3
0.4081	0.9610	0.1272	0.8732	-0.4844	285.0
0.5214	0.9950	0.2437	0.9981	-0.5670	318.2
0.6605	1.0362	0.2420	1.2396	-0.5803	311.1
0.7314	1.0550	0.2232	1.4042	-0.5456	284.0
0.8195	1.0790	0.1113	1.6805	-0.4307	224.1
0.9316	1.1080	0.0238	2.0864	-0.2301	102.0
1.0000	1.1140	0.0000	2.4418	0.0000	0.0

Table 2: Experimental and calculated diffusivity of anisaldehyde – benzene mixture at 303.15K,313.15K and 323.15K.

X_1	T	$\Delta Ci^I \times 10^3$	$\Delta Ci^f \times 10^3$	Time $x10^{-4}$	Dexp $x10^5$	Dcalx10^5
		g.mol/cc	g.mol/cc	sec	Cm^2 / sec	Cm^2 / sec
0.5000	303.15 K	5.745	5.740	1.1700	0.0204	0.0202
0.5000	313.15 K	7.053	7.049	1.0200	0.0223	0.0220
0.5000	323.15 K	7.141	7.138	0.7200	0.0230	0.0254

Table 3: McAllister Constants for the viscosity and average deviation of anisaldehyde – benzene at 303.15K,313.15K and 323.15K

Temperature	McAllister Constants		Average deviation (AD)
	A	B	%
303.15 K	1.790449	0.778247	0.4592
313.15 K	1.280254	0.862052	0.5372
323.15 K	1.149001	0.731632	0.5223

Table 4: Redlich-Kister Constants for Excess volume, deviation of viscosity and excess enthalpy of Anisaldehyde – benzene at 303.15K,313.15K and 323.15K

	a_0	a_1	σ
		303.15K	
Excess volume	-1.6846	-0.1047	0.8740
Deviation of viscosity	-3.0382	-0.4856	0.5733
Excess enthalpy	990.49	338.74	0.4141
		313.15 K	
Excess volume	-1.1320	0.203473	0.8650
Deviation of viscosity	-3.0080	-1.643429	0.4795
Excess enthalpy	1153.47	437.52	0.5150
		323.15 K	
Excess volume	0.6328	0.3217	0.9120
Deviation of viscosity	-2.3256	-1.1196	0.4148
Excess enthalpy	1252.45	409.76	0.8150

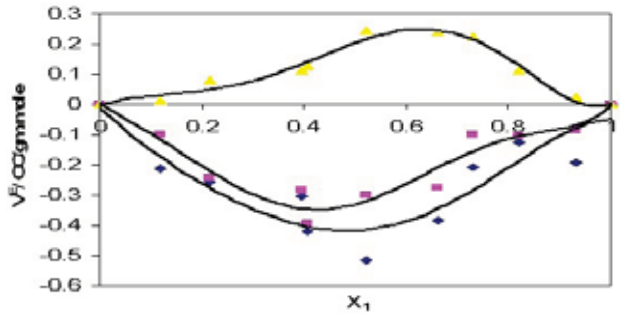

Fig. 1: Plot of V^E against X_1 of Anisaldehyde - benzene mixture at 303.15 K (◊), 313.15K(□) and 323.15 K (Δ).

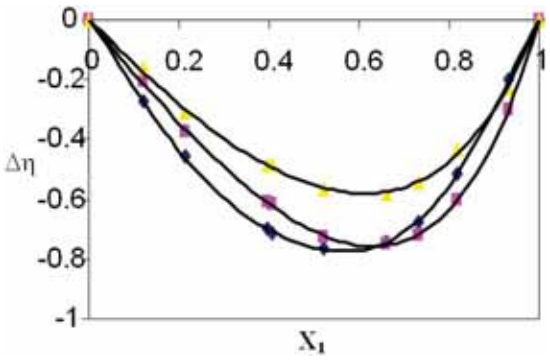

Fig. 2: Plot of of Δη against X_1 of Anisaldehyde - benzene mixture at 303.15 K (◊), 313.15K(□) and 323.15 K (Δ).

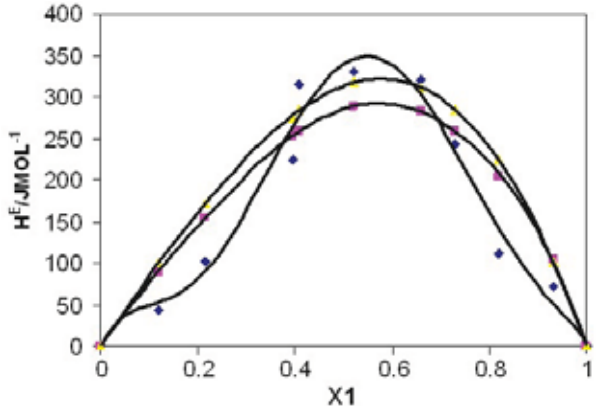

Fig. 3: Excess enthalpy of Anisaldehyde - benzene mixture at 303.15 K(◊), 313.15K(□) and 323.15 K (Δ).

which is related with liquid's structure and enthalpy (Rene, A. and C. Clara 2006), consequently with molecular interactions between the components of the mixture. Therefore the viscosity deviation depends on molecular interactions as well as on the size and shape of the molecules. For positive deviations of Raoult's law and without strong specific interactions, the viscosity deviations are negative. Figure 3 shows the excess enthalpy of mixing of the system is positive. Anisaldehyde-benzene is a nonpolar-nonpolar solvent. Its intermolecular attraction is due to vanderwall's forces. The measurement of enthalpy of mixing is endothermic illustrating cohesive forces within each solvent, which must be overcome for miscibility. It is an energy demanding process. If there is a strong interaction the excess enthalpy would have been exothermic. But it is supposed to be weak, as the excess enthalpy is largely endothermic.

Conclusion:

Experimental data of the density, viscosity, excess enthalpy and diffusivity of anisaldehyde and benzene mixture have been measured at 303.15K, 313.15K and 323.15K. These data have been used to compute the excess properties of the system. Negative deviations were observed for Δ η, positive deviations were observed for H^E V^E values are increasing as temperature increases. 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 interactions between anisaldehyde and benzene mixture lead to weak dispersion type effect. These properties are important from theoretical point of view to understand liquid theory and provide information about molecular interactions. These data will be useful in pharma, perfume and insecticide industries for handling and mixing processes. It is clear that McAllister equation can represent the viscosity values, Redlich kister polynomial equations can represent the excess volume viscosity deviation and excess enthalpy, and Laddha equation can represent diffusivity values very well.

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