Thermophysical properties of Para anisaldehyde with ethyl benzene at (303.15, 313.15 and 323.15) K.

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Abstract: Measurements of thermodynamic and transport properties have been adequately employed in understanding the nature of molecular systems and physico-chemical behavior in liquid mixtures. These properties are important from practical and theoretical point of view to understand liquid theory. Density (ρ),viscosity (η), refractive index (n) and surface tension (σ) have been measured for a binary liquid mixture of p-anisaldehyde +ethyl benzene over the entire composition range at 303.15 K, 313.15 K and 323.15 K The viscosity values have been fitted to McAllister model and Krishnan and Laddha model. The excess values were correlated using Redlich-Kister polynomial equation. It was found that in all cases, the data obtained fitted with the values correlated by the corresponding models very well. Comparison has been made between the models. The molecular interactions existing between the components were also discussed.

Keywords: Viscosity; Surface tension; Refractive index; Molecular interactions

1. Introduction

Binary liquid mixtures due to their unusual behavior have attracted considerable attention [1]. 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 Density, viscosity, refractive index and surface tension find extensive application in solution theory and molecular dynamics [2]. Such results are necessary for interpretation of data obtained from thermo chemical, electrochemical, biochemical and kinetic studies [3]. Para anisaldehyde is chemically known as 4-methoxy benzaldehyde and used in perfume and pharmaceutical industries. Para anisaldehyde and ethyl benzene mixture is used to prepare allyl anisole analog repellant (pesticides). In the present paper, we have reported density (ρ), viscosity (η), refractive index (n) and surface tension (σ) of pure p-anisaldehyde and ethyl benzene as well as for the binary system constituted by these two chemicals at temperatures of 303.15 K, 313.15 K and 323.15 K. The viscosity values have been fitted to McAllister [4] model and Krishnan and Laddha [5] model. The deviation values have been fitted to Redlich-Kister type [6] equation. Literature survey showed that no measurements have

been previously reported for the mixture studied in this paper.

2. Materials and methods

The chemicals used were of analytical reagent grade obtained from lobo chemicals and purified by standard procedures [7]. All the components were dried over anhydrous calcium chloride and fractionally distilled [8]. Binary solutions were prepared on percentage basis (v/v) by dissolving known volume of p-anisaldehyde in appropriate volume of ethyl benzene and measuring their masses on a Shimadzu Corporation Japan Type BL 2205 electronic balance accurate to 0.01 g. The possible uncertainty in the mole fraction was estimated to be less than ± 0.0001. All the measurements described below were performed at least three times and the results were averaged to give the final values.

2.1. Density

The densities were determined by using bicapillary pycnometer as described [9] and calibrated with deionised double distilled water with 0.9960×10^3 Kg.m^{-3} as its density at temperature 303.15 K. The pycnometer filled with air bubble free experimental liquids was kept in a transparent walled water bath to attain thermal equilibrium. The positions of the liquid level in the two arms were recorded with a help of traveling microscope which could read to 0.01mm. The precision density measurements were within ± 0.0003 g.cm^{-3}. The experimentally determined density data have been used to calculate the excess molar volumes, V^E, using the following equation

$$V^E = (x_1 M_1 + x_2 M_2)/\rho_m - (x_1 M_1/\rho_1 + x_2 M_2/\rho_2) \tag{1}$$

where x_1 and x_2 refer to the mole fraction of components 1 and 2. ρ_1, ρ_2 and ρ_m refer to the density of pure components 1, 2 and mixture respectively.

2.2. Kinematic viscosity

The Kinematic viscosities were measured at the desired temperature using Ostwald viscometer. The viscometer was calibrated using water. The liquid mixture was charged into the viscometer. After the 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

$$\nu = (at) - (b/t) \tag{2}$$

were obtained by measuring the flow time with high purity benzene at the working temperature. The calculated viscosities were fitted in Eq. (1) and constants were determined. The kinematic viscosity were correlated by means of McAllister model considering three-body interaction, which for a two component mixture gives

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

where ν refers to the kinematic viscosity of the mixture of components 1 and 2 having mole fractions x_1 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 kinematic viscosity were correlated by means of Krishnan and Laddha model for a two component mixture gives

$$\ln v = x_1 \ln v_1 + x_2 \ln v_2 + x_1 \ln M_1 + x_2 \ln M_2$$
$$+ \ln(x_1 M_1 + x_2 M_2 - 2.303 x_1 x_1 (B + C(x_1 x_2) + ..)$$
$$(4)$$

The viscosity deviations can be calculated as

$$\Delta \eta = \eta - (x_1 \eta_1 + x_2 \eta_2) \qquad (5)$$

where η, η_1, and η_2, are the dynamic viscosities of the mixture and those of the pure components 1 and 2 respectively.

2.3. Refractive index

Refractive indices were measured using thermostatically controlled Abbe refractometer with 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 sample mixture was directly injected in to the prism assembly of the instrument using a syringe. The solutions were pre thermo stated at the temperature of the experience before the experiments to achieve a quick thermal equilibrium. The excess deviation can be calculated as

$$\Delta n_D = n_{D} - (x_1 n_{D1} + x_2 n_{D2}) \qquad (6)$$

where n_D, n_{D1} and n_{D2} are the refractive index of the mixture, pure components 1 and 2 respectively.

2.4. 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}.

$$\Delta \sigma = \sigma - (x_1 \sigma - \sigma_1 + x_2 \sigma_2) \qquad (7)$$

where σ, σ_1 and σ_2 are the surface tension of the mixture, surface tension of pure components 1 and 2 respectively.

3. Results

Experimental data of density ρ, viscosity η, refractive index n_D and surface tension σ of para anisaldehyde and ethyl benzene system over the entire composition range at temperatures of 303.15 K, 313.15 K and 323.15 K have been listed in Table 1. The calculated quantities of excess molar volume V^E, viscosity deviation $\Delta\eta$, refractive index deviation Δn_D and surface tension deviation $\Delta\sigma$ of para anisaldehyde and ethyl benzene system over the entire composition range at 303.15 K, 313.15 K and 323.15 K have been presented in Table 2. The excess values of thermo physical properties and thermo acoustical parameters of binary liquid mixtures are fitted to a Redlich-Kister equation of the type

$$Y = x_1 x_2 \Sigma A_i (x_1 - x_2)^i \qquad (8)$$

where Y represents V^E, $\Delta\eta$, Δn_D $\Delta\sigma$ in the corresponding equation. Coefficients A_i were obtained by fitting equation to experimental values using a least square regression method. In each case, the optimum number of coefficients is ascertained from an examination of the variation in standard deviation (S). S was calculated using the relation

$$S(Y) = [\Sigma (A_{exp} - A_{cal})^2 / (N-n)]^{1/2} \qquad (9)$$

where N is the number of data points and n is the number of coefficients. The coefficients

and standard deviations of Redlich – Kister polynomial equation are presented in Tables 3. McAllister and Krishnan and Laddha constants for the viscosity of anisaldehyde – ethylbenzene at 303.15 K, 313.15 K, and 323.15 K are presented in Table 4.

Table 1. Experimental values of anisaldehyde-ethyl benzene mixture at 303.15 K, 313.15 K and 323.15 K.

X1	ρ/g/cc	η/mpa.s	n	σ/mN.m-1
		303.15K		
0.0000	0.8670	0.6770	1.4985	30.01
0.1220	0.9001	0.9950	1.5058	39.01
0.2521	0.9340	1.3400	1.5135	48.22
0.3444	0.9581	1.6712	1.5191	56.22
0.4232	0.9794	1.8805	1.5238	65.21
0.5670	1.0181	2.3511	1.5321	73.11
0.6909	1.0490	2.7114	1.5392	83.21
0.7861	1.0732	2.9142	1.5448	89.12
0.8278	1.0830	2.8114	1.5472	94.11
0.9434	1.1121	2.8170	1.5539	96.25
1.0000	1.1250	3.2753	1.5571	99.08
		313.15K		
0.0000	0.8420	0.5914	1.4901	29.04
0.1220	0.8777	0.9001	1.4975	37.06
0.2521	0.9135	1.2500	1.5051	46.28
0.3444	0.9400	1.5210	1.5109	54.24
0.4232	0.9621	1.7111	1.5155	63.22
0.5670	1.0010	2.2002	1.5240	72.15
0.6909	1.0350	2.5121	1.5311	82.28
0.7861	1.0641	2.6000	1.5366	87.22
0.8278	1.0721	2.6542	1.5389	93.18
0.9434	1.1041	2.8470	1.5456	95.22
1.0000	1.1192	2.9695	1.5488	98.45
		323.15K		
0.0000	0.8321	0.4841	1.4821	28.12
0.1220	0.8681	0.7221	1.4871	36.26
0.2521	0.9066	0.8811	1.4891	45.24
0.3444	0.9318	1.1554	1.4921	53.41
0.4232	0.9526	1.3521	1.4991	61.12
0.5670	0.9951	1.6782	1.5067	71.12
0.6909	1.0310	2.1446	1.5103	81.18
0.7861	1.0571	2.2728	1.5228	86.22
0.8278	1.0681	2.2942	1.5398	92.28
0.9434	1.1010	2.3471	1.5447	94.12
1.0000	1.1140	2.4418	1.5463	97.45

Table 2. Excess volume (V^E), viscosity deviation ($\delta\eta$), refractive index deviation (δn) of anisaldehyde-ethyl benzene mixture at 303.15 K, 313.15 K and 323.15 K.

X_1	V^E / cc/mol^{-1}	$\delta\eta$ / mpa.s	δn	$\Delta\sigma$
		303.15 K		
0.0000	0.0000	0.0000	0.0000	0.00
0.1220	-0.2573	0.0010	0.0001	0.05
0.2521	-0.3301	0.0081	0.0002	0.09
0.3444	-0.3595	0.0911	0.0004	0.42
0.4232	-0.4418	0.1000	0.0005	0.66
0.5670	-0.6518	0.1919	0.0003	0.72
0.6909	-0.5080	0.2222	0.0002	1.09
0.7861	-0.4178	0.1841	0.0002	1.19
0.8278	-0.3759	0.0545	0.0001	0.95
0.9434	-0.1921	0.0150	0.0001	0.55
1.0000	0.0000	0.0000	0.0000	0.00
		313.15 K		
0.0000	0.0000	0.0000	0.0000	0.00
0.1220	-0.3218	0.0184	0.0002	0.08
0.2521	-0.4803	0.0590	0.0002	0.11
0.3444	-0.6380	0.1095	0.0005	0.46
0.4232	-0.6680	0.1121	0.0005	0.71
0.5670	-0.7392	0.2602	0.0006	0.77
0.6909	-0.5446	0.2655	0.0004	1.04
0.7861	-0.4227	0.1391	0.0003	1.33
0.8278	-0.3923	0.0900	0.0002	0.99
0.9434	-0.2133	0.0621	0.0001	0.66
1.0000	-0.0000	0.0000	0.0000	0.00

Table 2. Excess volume (V^E), viscosity deviation ($\delta\eta$), refractive index deviation (δn) of anisaldehyde-ethyl benzene mixture at 303.15 K, 313.15 K and 323.15 K.(continued)

X_1	V^E / cc/mol^{-1}	$\delta\eta$ / mpa.s	δn	$\Delta\sigma$
		323.15 K		
0.0000	0.0000	0.0000	0.0000	0.00
0.1220	-0.4204	0.1571	0.0003	0.08
0.2521	-0.5820	0.1760	0.0003	0.11
0.3444	-0.7550	0.1916	0.0006	0.46
0.4232	-0.9974	0.3650	0.0007	0.71
0.5670	-0.8256	0.5504	0.0006	0.77
0.6909	-0.6957	0.4361	0.0005	1.04
0.7861	-0.5125	0.2711	0.0004	1.33
0.8278	-0.4976	0.1895	0.0002	0.99
0.9434	-0.4030	0.0961	0.0001	0.66
1.0000	0.000	0.0000	0.0000	0.00

Table 3. represents Redlich-Kister Constants for excess volume, and excess viscosity of Anisaldehyde-ethyl benzene at 303.15 K, 313.15K, and 323.15 K.

Temperature	Redlich-Kister Constants for Excess volume			
	a_0	a_1	a_2	S%
303.15 K	-2.1679	-1.6472	0.6453	0.43
313.15 K	-2.8652	-0.0815	0.0319	0.60
323.15 K	-3.3467	-0.7382	1.8842	0.50
	Redlich-Kister Constants for viscosity deviations			
303.15 K	0.4553		0.3751	-0.9575
313.15 K	0.6384		0.5674	-1.4467
323.15 K	1.4815		0.4126	-1.0533
	Redlich-Kister Constants for refractive index deviations			
303.15 K	-0.02	0.01	0.00	1.58
313.15 K	0.00	0.01	0.01	1.11
323.15 K	0.01	0.01	0.01	0.89
	Redlich-Kister Constants for surface tension deviations			
303.15 K	-14.4	3.59	5.67	1.67
313.15 K	-16.1	3.96	6.33	1.24
323.15 K	-16.5	4.12	6.48	1.01

Table 4. McAllister and Krishnan and Laddha constants for the viscosity of anisaldehyde-ethylbenzene at 303.15 K, 313.15K, and 323.15 K.

Temperature	Constants		
	A	B	S %
McAllister			
303.15 K	2.6423	2.1723	0.4
313.15 K	2.5344	2.0204	0.1
323.15 K	2.4914	1.2361	0.5
Krishnan and Laddha			
303.15 K	-0.5541	0.4884	1.8
313.15 K	-0.7000	0.2608	2.3
323.15 K	-0.6389	0.0438	4.7

Results and discussion

Table 1 summarizes experimentally determined densities (ρ), viscosities (η), refractive indices (n), and surface tensions (σ) of Anisaldehyde – ethyl benzene mixture at 303.15 K, 313.15 K and 323.15 K. A detailed observation of the Table 1 shows that the surface tension of a mixture increases when mole fraction increases and shows decreasing trend when temperature increases. According to Karla Granados[10] interaction in the liquid mixture decreases the σ value of the mixture. As can be seen from Table 2, it has also been observed that the refractive index deviation shows positive values for the entire mole fraction at 303.15 K, 313.15 K and 323.15 K. 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. Excess volume and viscosity deviation of anisaldehyde(1) + Ethylbenzene (2) at 303.15 K, 313.15 K and 323.15 K are plotted in Figure 1-4. The solid lines of figure 1-4 are the correlated results as shown. As seen in Figure 1 the excess molar volume values are negative and increases when temperature increases. 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 [11]. 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 (dispersion forces) and repulsion between non polar molecules. Physical intermolecular forces are weak and the sign of excess value 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 in to other structure due to the differences in shape and size of the components and free volume. In our present study the negative V^E values indicate that interactions between molecules are stronger than interactions between molecules in the pure liquids and that associative force dominate the behavior of the solution [12]. There fore in this system, 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 ethyl benzene are positive for all the mole

fractions at 303.15K, 313.15K and 323.15K. The viscosity of the mixture strongly depends on the entropy of mixture, which is related with liquid's structure and enthalpy [13], 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 negative deviations of Raoult's law and with strong specific interactions, the viscosity deviations are positive. A detailed observation shows that the deviations in refractive index are always positive for all the studied temperatures and for any composition. The variations of surface tension deviation with compositions of para anisaldehyde have been represented in Figure 4. A detailed observation of shows that the deviations of surface tension of a mixture show increasing trend when mole fraction and temperature increases. 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.
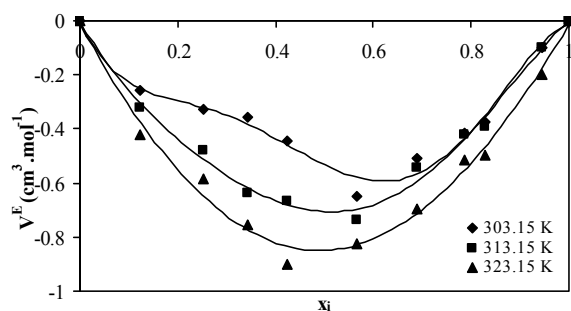

Figure 1. Plot of V^E against x_i for anisaldehyde in anisaldehyde(1) + Ethylbenzene (2) at 303.15 K, 313.15 K and 323.15 K.
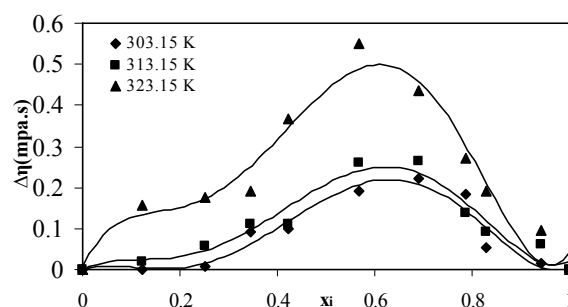

Figure 2. Plot of $\Delta\eta$ against x_i for anisaldehyde in anisaldehyde(1) + Ethylbenzene (2) at 303.15 K, 313.15 K and 323.15 K.
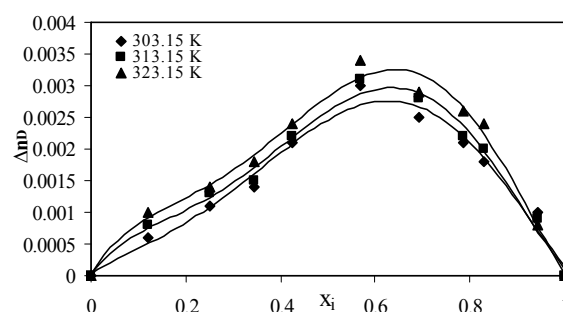

Figure 3. Deviations in refractive index (Δn_D) for para anisaldehyde and ethylbenzene at (303.15, 313.15 , 323.15) K.
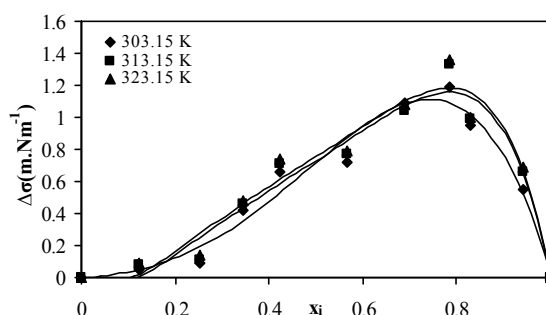

Figure 4. Deviations in surface tension ($\Delta\sigma$) for para anisaldehyde and ethylbenzene at (303.15, 313.15 , 323.15) K

4.Conclusion

Experimental data of the density, viscosity, refractive index and surface tension of

anisaldehyde and ethyl benzene mixtures have been measured over the entire composition range at 303.15 K, 313.15 K and 323.15 K. It has been observed that negative deviations were observed for excess volume where as positive deviations were observed for viscosity deviation at 303.15 K, 313.15 K and 323.15 K. It may be concluded that the interactions resulting in the interstitial accommodation of ethyl benzene in to p-anisaldehyde are the predominant factor over dipole – dipole and dipole induced–dipole interaction. The intermolecular interactions between anisaldehyde with ethyl benzene mixture leads to specific type. The excess values show a systematic change with increasing temperature. With an increase in temperature the intermolecular interactions between molecules become weak. At 323.15 K the intermolecular interaction become weak compared with 303.15 K and 313.15 K.

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