Asian Journal of Chemistry Vol. 20, No. 5 (2008), 3381-3386

Viscosity and Excess Volume of Anisaldehyde-Nitrobenzene at 303.15 K, 313.15 K and 323.15 K

R. BASKARAN† and T.R. KUBENDRAN*
Department of Chemical Engineering, Alagappa College of Technology
Anna University, Chennai-600 025, India
E-mail: trkuben@annauniv.edu; trkubendran@yahoo.co.in

Densities (ρ) and viscosities (η) have been measured for the binary liquid mixture of anisaldehyde + nitrobenzene over the entire composition range at 303.15, 313.15 and 323.15 K. 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 cases, the experimental data obtained fitted very well with the values correlated by the corresponding models. The molecular interactions existing between the components were discussed.

Key Words: Excess molar volume, Transport, Binary solvents, Viscosity deviations.

INTRODUCTION

In chemical process industries materials are normally handled in fluid form and as a consequence, the physical, chemical, thermodynamic and transport properties of fluids assume importance. Thus data on some of the properties associated with the liquids and liquid mixtures like viscosity, density and excess volume find extensive application in chemical engineering design. These properties are important from practical and theoretical point of view to understand liquid theory and provide information about molecular interactions. We report here the thermodynamic properties of pure anisaldehyde and nitrobenzene as well as for the binary system constituted by these two chemicals at temperatures of 303.15, 313.15 and 323.15 K. From these experimental results excess volume (V^E) and viscosity deviations (Δη) from the ideal behaviour over the entire mole fraction range were calculated. The viscosity values have been fitted to McAllister[1] model. Viscosity deviations and excess volume were fitted to Redlich-Kister[2] type equation.

---

†Department of Chemical Engineering, St. Joseph's College of Engineering, Old Mahabalipuram Road, Chennai-600 119, India. E-mail: rbaskaran2000@yahoo.com

EXPERIMENTAL

The chemicals used were of analytical grade and obtained from Loba chemicals. All components were dried over anhydrous potassium carbonate and fractionally distilled[3]. 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. The possible uncertainty in the mole fraction was estimated to be less than ± 0.0001.

Densities of the liquid mixtures were measured by using an Ostwald-Sprengel type pycnometer[4] having a bulk volume of 25 cm^3 and a capillary diameter of about 1 mm. The pycnometer was calibrated at ± 303.15 K with doubly distilled water.

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 ± 0.01 s. All the measurements described above were performed at least three times and the results were averaged to give the final values.

RESULTS AND DISCUSSION

Table-1 listed the measured density (ρ) and kinematic viscosity (η) at 303.15, 313.15 and 323.15 K with the corresponding excess molar volume and viscosity deviations.

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

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

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.

In the calculation of viscosity, two constants a and b of the viscometer in the relation $\nu = (at)–(b/t)$ were obtained by measuring the flow time with high purity benzene at the working temperature. The viscosity deviations can be calculated as

$$\Delta\eta = \eta–(x_1\eta_1 + x_2\eta_2)$$

where η, η_1 and η_2, are the dynamic viscosities of the mixture and those of the pure components 1 and 2, respectively. Table-2 lists the McAllister and Redlich-Kister constants for the viscosity and deviation of viscosity. Redlich-Kister constants for excess volume were presented in Table-3.

The kinematic viscosity were correlated by means of McAllister model considering three-body interaction, for a two component mixture gives

TABLE-1
EXPERIMENTAL DENSITIES, EXCESS MOLAR VOLUMES, KINEMATIC VISCOSITIES AND ITS DEVIATION OF ANISALDEHYDE-NITROBENZENE MIXTURE AT 303.15, 313.15 AND 323.15 K

Mole fraction (X_1)	Density (ρ) (g/cc)	Excess volume (V^E) (cc/gmol)	Kinematic viscosity (mpa.s)		Deviation (Δη)
			ν (exp.)	ν (calcd.)	
			303.15 K		
0.0714	1.200	0.1322	1.8167	1.8094	0.0012
0.1333	1.199	0.1826	1.9069	1.9098	0.0059
0.2352	1.189	0.2158	2.0864	2.0904	0.0134
0.3157	1.181	0.2495	2.2423	2.2440	0.0427
0.4901	1.166	0.2878	2.5963	2.5944	0.1226
0.5235	1.163	0.2954	2.6623	2.6614	0.1361
0.6059	1.158	0.2858	2.8271	2.8219	0.1713
0.7936	1.151	0.2359	3.1226	3.1275	0.1718
0.8849	1.132	0.1720	3.2317	3.2241	0.1373
0.9389	1.128	0.1013	3.2579	3.2590	0.0787
1.0000	1.125	0.0000	3.2753	3.2753	0.0000
			313.15 K		
0.0714	1.196	0.1045	1.4646	1.4620	-0.0296
0.1333	1.191	0.1391	1.5431	1.5407	-0.0495
0.2352	1.179	0.1635	1.6805	1.6863	-0.0740
0.3157	1.172	0.2075	1.8167	1.8145	-0.0657
0.4901	1.158	0.2528	2.1243	2.1245	-0.0351
0.5235	1.153	0.2686	2.1979	2.1873	-0.0146
0.6059	1.149	0.2650	2.3317	2.3442	-0.0117
0.7936	1.134	0.1914	2.7063	2.6878	0.0647
0.8849	1.125	0.1394	2.8381	2.8311	0.0515
0.9389	1.120	0.0836	2.9257	2.9030	0.0533
1.0000	1.119	0.0000	2.9695	2.9695	0.0000
			323.15 K		
0.0714	1.185	0.0598	1.3434	1.3440	0.0040
0.1333	1.182	0.0906	1.4158	1.4169	0.0046
0.2352	1.169	0.1221	1.5431	1.5424	0.0026
0.3157	1.163	0.1541	1.6462	1.6454	0.0109
0.4901	1.147	0.2203	1.8754	1.8742	0.0345
0.5235	1.144	0.2344	1.9204	1.9181	0.0402
0.6059	1.140	0.2433	2.0192	2.0247	0.0419
0.7936	1.129	0.1675	2.2423	2.2501	0.0437
0.8849	1.121	0.1106	2.3533	2.3443	0.0472
0.9389	1.118	0.0532	2.3976	2.3934	0.0278
1.0000	1.114	0.0000	2.4418	2.4418	0.0000

TABLE-2
McALLISTER AND REDLICH-KISTER CONSTANTS FOR THE VISCOSITY AND DEVIATION IN VISCOSITY OF ANISALDEHYDE-NITROBENZENE AT 303.15, 313.15 AND 323.15 K

Temp. (K)	McAllister constants		Redlich-Kister constants for deviations				
	A	B	a_0	a_1	a_2	a_3	σ
303.15	3.2592	2.2463	-2.6258	1.4081	-2.0235	-2.1879	2.0921
313.15	2.6719	1.7870	-2.1266	1.5660	-1.8889	-2.3150	2.1656
323.15	2.2127	1.6905	-1.8425	1.0730	-0.2458	-1.3715	1.6869

TABLE-3
REDLICH-KISTER CONSTANTS FOR EXCESS VOLUME OF ANISALDEHYDE-NITROBENZENE AT 303.15, 313.15 AND 323.15 K

Temp. (K)	Redlich-Kister constants for excess volume				
	a_0	a_1	a_2	a_3	σ
303.15	-1.494	0.377	0.089	-0.003	0.854
313.15	-1.353	0.376	0.083	-0.003	0.793
323.15	-1.213	0.374	0.086	-0.001	1.023

$$\ln \nu = x_1^3 \ln \nu_1 + 3x_1^2 x^2 \ln \nu_{12} + 3x_1x_2^2 \ln \nu_{21} + x_2^3 \ln \nu_2 - \ln(x_1 + x_2 M_2/M_1) + 3x_1^2 x_2 \ln[(2 + M_2/M_1)/3] + x_2^3 \ln(M_2/M_1) + 3x_1x_2^2 \ln[(1+2 M_2/M_1)/3]$$

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 experimentally determined excess volume and viscosity deviation data for the binary system of this investigation have been correlated using Redlich Kister equation by the method of least square.

$$H^E / J\ mol^{-1} = x(1-x)\sum_{i=0}^{j} h_i (2x-1)^i$$

In Fig. 1, the deviations in viscosity for 303.15 K is positive. The negative deviations at 313.15 K for 0.0-0.6 mole fraction and positive deviation from 0.7 -.0 mole fraction. The viscosity deviations are almost constant for 323.15 K. This could be an indication of the findings of Kabadi *et al.*[5] in which they mention that positive deviations of the viscosity results from hydrogen bonding interactions more than from dissociation effects. The positive deviations corresponds to binary system that exhibits negative deviations from Raoult's law[6]. The viscosity of the mixture strongly depends on the entropy of mixture, which is related with liquid's structure and enthalpy[7,8] and 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.

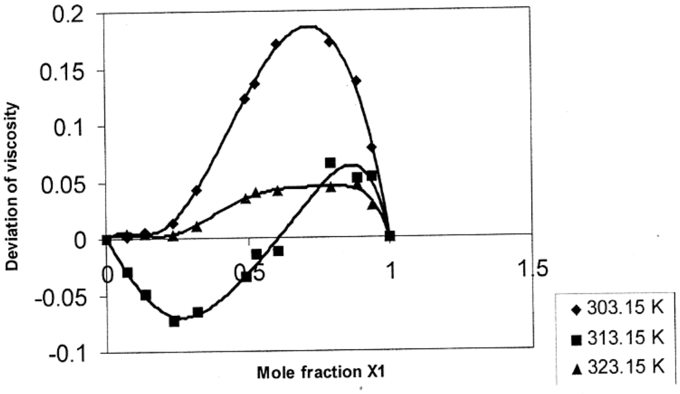

Fig. 1. Deviation of viscosity of anisaldehyde-nitrobenzene mixture at 303.15, 313.15 and 323.15 K

In Fig. 2 the excess molar volume increases with decrease in temperature. The positive V^E values are due to several factors such as declustering of aldehyde in the presence of benzene, repulsive forces due to the electronic charges of both components[9]. Because of the mutual structure disrupting interactions of the solvent and cosolvent, the volume of the mixture gradually increases[10].

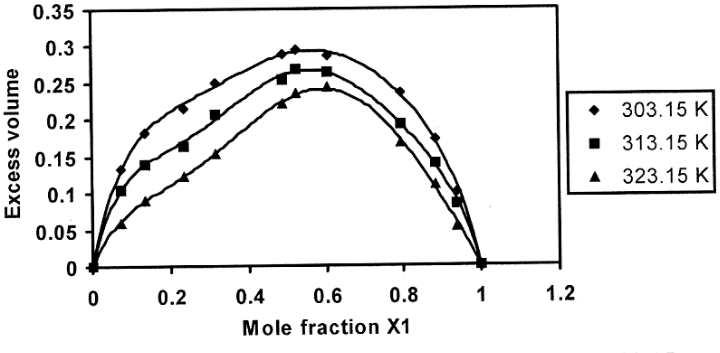

Fig. 2. Excess volume of anisaldehyde-nitrobenzene mixture at 303.15, 313.15 and 323.15 K

REFERENCES

1. R.A. McAllister, *AIChE J.*, **6**, 427 (1960).
2. A.T. Redlich and O. Kister, *Ind. Eng. Chem.*, **40**, 345 (1948).
3. S.L. Oswal and N.B. Patel, *J. Chem. Eng. Data*, **40**, 845 (1995).
4. J. Reilly and W. Northman, Physio Chemical Methods, p. 88 (1978).
5. U.R. Kapadi, D.G. Hundiwale, N.B. Patil and M.K. Lande, *Fluid Phase Equilib.*, **201**, 335 (2002).
6. T.R. Kubendran, R. Baskaran and L. Meyyappan, *Proc. Chemcon*, **1**, 184 (2006).
7. W. Kauzman and H. Eyring, *J. Am. Chem. Soc.*, **62**, 3113 (1940).
8. A. Rene and C. Clara, *J. Chem. Eng. Data*, **51**, 1473 (2006).
9. D. Hiannie and I. Suryadi, *J. Chem. Eng. Data*, **50**, 1343 (2005).
10. T. Savitha and N. Sathyanarayana, *Asian J. Chem.*, **16**, 1721 (2004).

(*Received*: 24 March 2007; *Accepted*: 31 January 2008) AJC-6266