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Density and Viscosities for the Binary Mixtures of 1, 4-Dioxane and Benzene or Chlorobenzene at 303.15, 308.15, 313.15 K and a Pressure of 0.1MPa

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Abstract

Densities (ρ) and Viscosities (η) of binary mixtures of 1, 4-dioxane and benzene or chlorobenzene have been measured as a function of mole fraction at atmospheric pressure and at different temperatures of (303.15, 308.15and 313.15) K. These values have been used to calculate the excess molar volume (VE) and the viscosity deviations (Δη) and Grunberg – Nissan interaction constant (d') of the binary mixtures. The viscosity values were fitted to the models of McAllister, Krishnan-Laddha, Jouyban – Acree model. The excess values were correlated using the Redlich-Kister polynomial equation to obtain their coefficients and standard deviations. It was found that in all cases the experimental data obtained fitted with the values correlated by the corresponding model very well. The molecular interactions existing between the components were also discussed.

Keywords: Viscosity, density, molecular interactions, deviations.

Introduction

The thermodynamic properties of a binary mixture such as viscosity and density are important from practical and theoretical points of view to understand liquid theory. Their properties are extremely useful for the design of process equipment in chemical industries. 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 and viscosity 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]. 1, 4-dioxane is used as a stabilizer in aluminium containers and solvent in inks and adhesives. Benzene is used in the production of drugs. Benzoin prepared from benzaldehyde is used as "tincture benzoin" in medicine for throat infection. In the present paper, it has been reported density (ρ) and viscosity (η) of pure 1, 4-dioxane and benzene or chlorobenzene as well as for the binary system constituted by these two chemicals at temperatures of 303.15, 308.15 and 313.15 K. The viscosity values have been fitted to McAllister[4], Krishnan-Laddha[5], Jouyban–Acree model model[6]. The deviation values have been fitted to Redlich-Kister[7] type equation. Literature survey showed that no measurements have been previously reported for the mixture studied in this paper.

Material and Methods

The 1, 4-dioxane of cited purity of 99.5 % and benzene, chlorobenzene with purity of 99.5 % were obtained from Loba chemicals and dried over anhydrous calcium chloride and fractionally distilled before use. Binary mixtures were gravimetrically prepared with a Shimadzu Corporation Japan type BL 2205 electronic balance with an uncertainty of 0.01 g. Care was taken to avoid evaporation and contamination during mixing. The resulting mole fraction uncertainty was estimated to be less than ±0.0001. All the measurements described below were performed at least three times, and the results presented are the average.

Density: A double- arm pycnometer with a bulb of 25 cm^3 and a capillary of an internal diameter of about 1mm is used to measure the densities (ρ) of pure liquids and binary mixtures. The pycnometer filled with air bubbles free liquids is kept in a thermostat with a thermal stability of ±0.01K for over 30 min to attain thermal equilibrium. The precision of the density measurements was estimated to be ± 0.0003 g ·$cm^{-3.}$

Kinematic Viscosity: The kinematic viscosities were measured with Ostwald viscometer previously calibrated using water. The time was measured with a precision of 0.01 s, and the uncertainty in the viscosity was estimated to be less than 0.0002 mPa·s. The kinematic viscosity was obtained from the working equation: $v=at-b/t$ (1)

Where the two constants *a* and *b* were obtained by measuring the flow time *t* of benzene.

Results and Discussion

The experimental values of densities (ρ) and viscosities (η) of 1, 4-Dioxane with benzene, chlorobenzene and their binary mixtures at various temperatures are listed in table 1 and 2.

Excess molar volumes V^E were calculated from the measured densities (ρ) by using equation

$$V^E=(x_1M_1+x_2M_2)/\rho_m-(x_1M_1/\rho_1+x_2M_2/\rho_2) \quad (2)$$

where ρ_m is the density of the mixture and M_1,ρ_1, x_1 and M_2,ρ_2,x_2 are molecular mass, density and mole fractions of pure 1, 4-dioxane(1) and benzene, chlorobenzene(2) respectively. The uncertainty in the measurement of V^E was found to be $\pm 0.002 cm^3mol^{-1}$. The deviations in viscosities, $\Delta\eta$, was computed using the relationship

$$\Delta\eta=\eta - (x_1\eta_1 + x_2\eta_2) \quad (3)$$

where η is the dynamic viscosity of the mixture and η_1,x_1 and η_2,x_2 are the viscosity and mole fractions of pure 1, 4-Dioxane (1) and benzene, chlorobenzene(2), respectively. The uncertainty in the measurement of $\Delta\eta$ was found to be ±0.001. The viscosities of mixtures of 1, 4-dioxane (1) and benzene, chlorobenzene (2) have been correlated with the model proposed by McAllister [4] for a two-component mixture considering three body interactions.

$$\ln\nu = x_1^3 \ln\nu_1 + 3x_1^2 x_2 \ln\nu_{12} + 3x_1 x_2^2 \ln\nu_{21} + x_2^3 \ln\nu_2 - \ln(x_1 + x_2 M_2/M_1) + 3x_1^2 x_2 \ln((2 + M_2/M_1)/3) + x_2^3 \ln(M_2/M_1) + 3x_1 x_2^2 \ln((1 + 2M_2/M_1)/3) \quad (4)$$

In equation 4, ν_1 and ν_2 refer to the kinematic viscosity of pure liquids 1 and 2 having mole fractions x_1 and x_2, respectively. The parameters ν_{12} and ν_{21} represent the interaction parameters obtained by multiple regression analysis, while M_1 and M_2 are the molar mass of the components.

The kinematic viscosity was correlated by means of the Krishnan and Laddha [5] model for a two-component mixture, which gives

$$\ln\nu = x_1 \ln\nu_1 + x_2 \ln\nu_2 + x_1 \ln M_1 + x_2 \ln M_2 + \ln(x_1M_1 + x_2M_2 - 2.30 x_1 x_2(B + C(x_1 - x_2)...)) \quad (5)$$

where *B* and *C* are interaction parameters.

Jouyban et. al[6] proposed a model for correlating the thermal properties of liquid mixtures at various temperatures

$$\ln Y_{m,T} = f_1 \ln y_1 + f_2 \ln y_2 + f_1 f_2 \Sigma[A_J(f_1 - f_2)^J / T] \quad (6)$$

Where $Ym,_T$, $y_{1,T}$, and $y_{2,T}$ are the viscosity of the mixture and solvents 1 and 2 at temperature *T*, respectively. A_J is the model constant

The excess molar volumes and deviations of viscosity were fitted to a Redlich–Kister(7) equation of the type

$$Y = x_1x_2 \Sigma A_i(x_1 - x_2)^i \quad (7)$$

where *Y* is either V^E and $\Delta\eta$ and *n* is the degree of polynomial. Coefficients Ai were obtained by fitting equation 7 to experimental results using a least-squares 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

$$S(Y) = [\Sigma(A_{exp} - A_{cal})^2 / (N - n)]^{1/2} \quad (8)$$

Where *N* is the number of data points and *n* is the number of coefficients. The calculated values of coefficients along with the standard deviation (*S*) are given in table 5 and 6. Interaction parameters and standard deviations of the McAllister model of 1, 4-dioxane (1) and benzene, chlorobenzene (2) mixture at (303.15, 308.15 and 313.15) K are presented in table 3 and 4.

Interaction parameters and standard deviations of the McAllister model and Krishnan and Laddha model for the viscosity of 1,4-dioxane and benzene or chlorobenzene mixture at (303.15, 313.15, and 323.15) K are presented in table 5 and 6. Constants and standard deviations of the Jouban-Acree model of the 1,4-dioxane and benzene or chlorobenzene at (303.15, 313.15, and 323.15) K are presented in table 7 and 8.

The variation of excess volumes with the mole fraction of 1,4-dioxane with benzene and chlorobenzene at (303.15, 308.15 and 313.15) K are represented in figures 1-2. The excess molar volume of 1, 4-dioxane with benzene is negative[8], but for the other binary mixtures containing chlorobenzene is positive[9] over the whole range of mole fraction. The sign of excess volume of a system depends on the relative magnitude of expansion/contraction on mixing of two liquids. If the factors causing expansion dominate the contraction factors, the V^E becomes positive. On the other hand if the contraction factors dominate the expansion factors, then V^E become negative. The factors that are responsible for expansion in volume are as follows, i. Loss of dipolar association, ii. The geometry of molecular structure, which does not allow fitting of one component into other component, iii. Steric hindrance, which opposes the proximity of the constituent molecules. The negative V^E values arise due to dominance of the following factors. i. Chemical interaction between constituent chemicals. ii. Accommodation of molecules of one component into the interstitials of the molecules of the other component. iii. Geometry of the molecular structure that favors fitting of the component molecules with each other. The negative V^E values in the mixtures under study indicate that interactions between molecules of the mixtures are stronger than interactions between molecules in the pure liquids and that associative force dominate the behavior of the solution.

The results of variation in viscosity deviations of binary systems consisting of 1,4-dioxane with benzene and chlorobenzene at temperatures of 303.15K, 308.15K, and 313.15K are represented in figure 3-4 shows positive and negative deviations[10] over the entire range of mole fraction. The viscosity of the mixture strongly depends on the entropy of mixture, which is related with liquid's structure and enthalpy. Consequently with the molecular interactions between the components of the mixtures. Therefore the viscosity deviation depends on molecular interactions as well as on the size and shape of the molecules.

Table-1
Experimental Densities and viscosities of 1, 4 Dioxane (1) + Benzene (2) at 303.15, 308.15 and 313.15 K

	303.15 K		308.15 K		313.15 K	
X_1	Density (g/cc)	η/ mpa.s	Density (g/cc)	η/ mpa.s	Density (g/cc)	η/ mpa.s
0.0000	0.8649	0.5407	0.8488	0.5221	0.8418	0.5040
0.1047	0.8788	0.5807	0.8599	0.5608	0.8594	0.5463
0.2083	0.8943	0.6280	0.8744	0.5963	0.8668	0.5644
0.3109	0.9196	0.6665	0.8807	0.6185	0.8750	0.5923
0.4124	0.9306	0.6946	0.8907	0.6420	0.8830	0.6182
0.5128	0.9428	0.7426	0.9026	0.6698	0.8917	0.6379
0.6122	0.9640	0.7934	0.9155	0.7072	0.8985	0.6692
0.7106	0.9740	0.8534	0.9357	0.7604	0.9072	0.6947
0.8080	0.9971	0.9363	0.9520	0.8282	0.9273	0.7531
0.9045	1.0090	1.0133	0.9793	0.9147	0.9512	0.8243
1.0000	1.0271	1.0958	1.0169	1.0094	1.0128	0.9446

Table-2
Experimental Densities and viscosities of 1, 4 Dioxane (1) + chlorobenzene (2) at 303.15, 308.15 and 313.15 K

	303.15 K		308.15 K		313.15 K	
X_1	Density (g/cc)	η/ mpa.s	Density (g/cc)	η/ mpa.s	Density (g/cc)	η/ mpa.s
0	1.1366	0.7558	1.1086	0.7206	1.0822	0.6809
0.1047	1.1201	0.7673	1.0944	0.7252	1.0710	0.6952
0.2083	1.0937	0.7748	1.0741	0.7371	1.0618	0.7152
0.3109	1.0796	0.7878	1.0660	0.7545	1.0551	0.7289
0.4124	1.0721	0.8043	1.0630	0.7744	1.0495	0.7498
0.5128	1.0642	0.8436	1.0513	0.8026	1.0449	0.7810
0.6122	1.0562	0.8672	1.0442	0.8150	1.0393	0.7943
0.7106	1.0479	0.8929	1.0389	0.8484	1.0339	0.8273
0.808	1.0401	0.9395	1.0333	0.8786	1.0268	0.8341
0.9045	1.0342	0.9652	1.0258	0.9050	1.0210	0.8534
1	1.0271	1.0958	1.0169	1.0094	1.0100	0.9420

Table-3
Parameters of the Redlich Kister Constants and standard deviations S for Excess molar Volume and viscosity deviations of 1,4-Dioxane (1) + Benzene (2)

T/K	A1	A2	A3	A4	A5	A6	A7	S
	Excess Molar Volume							
303.15	-56.509	-27.653	66.619	26.913	-15.736	0.7609	5.6556	0.2113
308.15	-67.92	-34.501	74.331	30.247	- 18.49	4.2666	12.104	0.2120
313.15	-87.369	- 102.92	76.667	98.355	- 3.6776	5.0706	14.481	0.8709
	Viscosity Deviations							
303.15	1.328	0.0171	- 1.5746	0.2169	0.5935	- 0.2341	-0.3483	0.005
308.15	1.3354	0.6588	- 1.3364	- 0.3553	0.4108	-0.3047	- 0.4107	0.002
313.15	1.842	1.8177	- 1.5655	- 1.6702	0.0816	- 0.1671	-0.3602	0.011

Table-4
Parameters of the Redlich Kister Constants and standard deviations S for Excess Volume of 1,4-Dioxane (1) + Chloro benzene (2)

T/K	A1	A2	A3	A4	A5	A6	A7	S
	Excess molar Volume							
303.15	19.75	-9.324	-44.93	18.79	18.32	-9.362	6.85	0.2217
308.15	11.15	4.818	- 26.09	1.381	10.04	6.102	4.877	0.1487
313.15	-87.369	- 102.9	76.667	98.355	-3.677	5.0706	15.481	0.1391
	Viscosity Deviations							
303.15	4.434	2.343	- 5.013	2.612	0.981	0.255	-0.408	0.020
308.15	3.841	1.527	-4.342	- 1.654	0.811	0.116	-0.314	0.015
313.15	3.451	1.8	- 4.045	- 2.032	0.778	0.224	- 0.187	0.012

Table-5
Parameters of McAllister constants for 1, 4 Dioxane (1) + Benzene (or) chlorobenzene (2) System at 303.15K, 308.15K and 313.15K

	1, 4 Dioxane (1) + Benzene (2)			1, 4 Dioxane (1) + Chlorobenzene (2)		
T/K	A	B	S	A	B	S
303.15K	0.7773	0.7655	0.0127	0.7499	0.7640	0.0152
308.15K	0.7343	0.7370	0.0080	0.7269	0.7357	0.0127
313.15K	0.6889	0.7215	0.0037	0.7175	0.7304	0.0037

Table-6
Parameters of the Krishnan and Laddha Constants and standard deviations S for the viscosity of 1,4-Dioxane (1) + Benzene (or) chlorobenzene (2)

	1, 4 Dioxane (1) + Benzene (2)				1, 4 Dioxane (1) + Chlorobenzene (2)			
T/K	A1	A2	A3	S	A1	A2	A3	S
303.15	-0.1243	0.0702	0.0943	0.0430	-0.0519	0.0855	0.1489	0.1459
308.15	-0.1606	0.0836	0.1012	0.0078	-0.023	0.0627	0.1282	0.0675
313.15	-0.1387	0.105	0.0991	0.0210	-0.0003	0.0801	0.0752	0.0626

Table-7
Parameters of the Jouyban Acree model Constants and standard deviations S for the viscosity of 1, 4Dioxane (1) + Benzene (2)

T/K	A1	A2	A3	A4	A5	A6	A7	S
303.15	11694	-2606.2	- 13119	2844.8	2156	-229.06	-738.22	0.4590
308.15	-65.449	78.811	58.256	13.025	75.979	-91.992	- 68.85	0.0008
313.15	-6087.9	3534.4	6983.1	3818.1	-1164.5	266.98	271.41	0.3138

Table-8
Parameters of the Jouyban Acree model Constants and standard deviations S for the viscosity of 1,4-Dioxane (1) + Chloro Benzene (2)

T/K	A1	A2	A3	A4	A5	A6	A7	S
303.15	11694	- 2606.2	- 13119	2844.8	2156.3	- 229.06	- 738.22	0.4344
308.15	1270.9	489.62	- 1476.6	- 522.58	293.32	29.991	- 88.943	0.3707
313.15	-6087.9	3534.4	6983.1	- 3818.1	-1164.5	266.98	271.41	0.3295

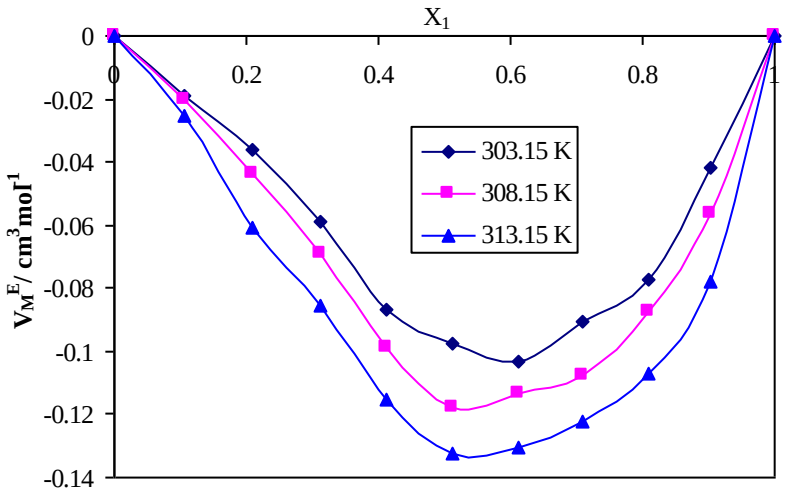

Figure-1
Excess Molar Volume (V^E) for [1,4-Dioxane (1) + Benzene (2)] :♦ T=303.15 K; ■ T=308.15K; : ▲ 313.15K

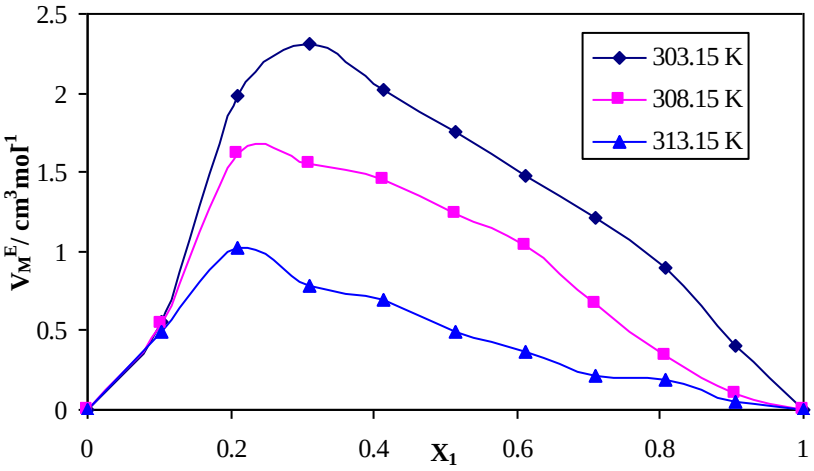

Figure-2
Excess Molar Volume (V^E) for [1,4-Dioxane (1) + Chloro benzene (2)] :♦ T=303.15 K; ■ T=308.15K; : ▲ 313.15K

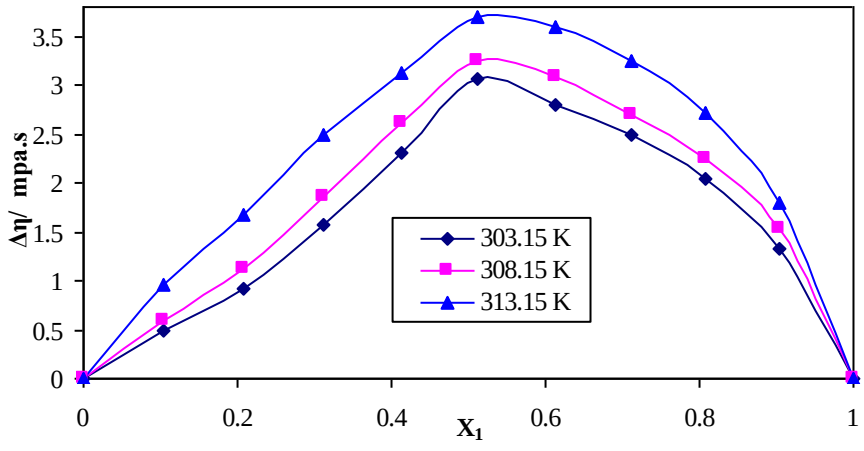

Figure-3
Deviation in viscosity (Δη) for [1,4-Dioxane (1) +Benzene (2)] :♦ T=303.15 K; ■ T=308.15K; : ▲ 313.15K

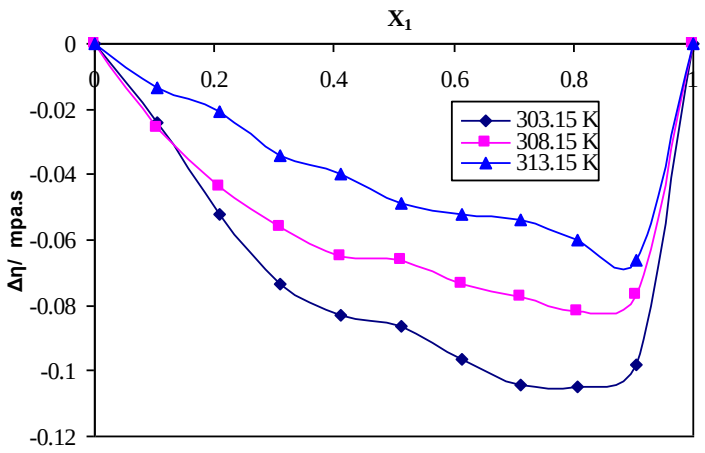

Figure-4
Deviation in viscosity (Δη) for [1,4-Dioxane (1) + Chloro benzene (2)] :♦ T=303.15 K; ■ T=308.15K; : ▲ 313.15K

Conclusions

Viscosities (η) and Densities (ρ) for the binary liquid mixture of 1, 4-Dioxane with Benzene, Chlorobenzene, Bromobenzene and Ethylbenzene system was found out as a function of mole fraction at atmospheric pressure and at temperatures of 303.15K, 308.15K, and 313.15K. From the density (ρ) and viscosity (η) data, the values of excess molar volumes (V^E) and the viscosity deviations ($\Delta\eta$) were determined at 303.15K, 308.15K, and 313.15K. Excess molar volumes (V^E) and the viscosity deviations ($\Delta\eta$) were used to predict the intermolecular interactions in the mixtures. McAllister, Krishnan-Laddha, Jouyban – Acree models were used to correlate the kinematic viscosity of the systems. The excess volume and viscosity deviation data were fitted by means of the Redlich-kister equation. It was found that in all cases the experimental data obtained, matches with the McAllister model and Redlich-Kister equation with a high degree of precision.

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