Viscosities and Densities of Binary Mixtures of 1,4-Dioxane, Carbon Tetrachloride, and Butanol at 303.15 K, 308.15 K, and 313.15 K

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Viscosities and densities for 1,4-dioxane + carbon tetrachloride, carbon tetrachloride + butanol, and 1,4-dioxane + butanol have been measured as a function of mole fraction at atmospheric pressure and at temperatures of 303.15 K, 308.15 K, and 313.15 K. The calculated deviations in viscosities and excess volumes were reported. McAllister's three-body-interaction model and the Krishnan and Laddha model were used to correlate the kinematic viscosity of the systems. The excess volume data was fitted by means of the Redlich−Kister equation. It was found that in all cases the experimental data obtained fitted with the values correlated by the corresponding model very well.

Introduction

The physical 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 many types of transport and process equipment in chemical industries.

In the present paper, we report viscosity and density data for 1,4-dioxane + carbon tetrachloride, carbon tetrachloride + butanol, and 1,4-dioxane + butanol at temperatures of 303.15 K, 308.15 K, and 313.15 K and at atmospheric pressure. The experimental data were used to calculate deviations in viscosity $\Delta\eta$ and excess molar volumes V^E of the mixtures. The viscosity and excess molar volumes have been fitted to McAllister model,[4] the Krishnan and Laddha model,[2] and the Redlich−Kister[8] equation.

Experimental Section

Materials. The chemicals used were of analytical grade and obtained from Adlab. All components were further purified according to methods recommended by Riddick and Bunger.[8] The purities of the chemicals given in Table 1 were verified by the measurement of the density and viscosity at 303.15 K and are in good agreement with literature values.

Apparatus and Procedure. Densities of the liquid and liquid mixtures were measured with an Ostwold−Sprengal-type pyknometer[1] having a bulk volume of 25 cm^3 and an internal diameter of the capillary of about 1 mm.

The pyknometer was calibrated at 303.15 K with doubly distilled water. A thermostatically controlled well-stirred water bath whose temperature was controlled to ±0.01 K was used for all the measurements. Binary mixtures were prepared using an electronic balance Shimadzu Corporation, Japan Type BL2205 accurate to 0.01 g. The possible error in the mole fraction is estimated to be less than ±0.0001. The kinematic viscosities were measured at the desired temperature using an Oswald Viscometer supplied by SAI Scientific Company, Madras. The viscometer was calibrated using water, and the two constants a and b of the viscometer in the relation $\nu = (at) - (b/t)$ was obtained by measuring the flow time t with high-purity benzene at the working temperature. The averages of five sets of flow times were taken for the purpose of the calculations of viscosity. The flow time was measured with an accurate stopwatch having a precision of ±0.01 s. Viscosities are reproducible to ±0.003 mPa·S.

Table 1. Physical Properties' Data for Pure Liquids at the Temperature 303.15 K

chemicals	purity (mol %)	η/mPa·s		ρ/g·cm^{-3}	
		exp	literature	exp	literature
butanol	>99.0	2.282	2.271[5]	0.8057	0.8020[5]
1,4-dioxane	>99.4	1.0985	1.0937[3]	1.0223	1.0222[3]
carbon tetrachloride	>99.2	0.8689	0.8671[7]	1.5806	1.5821[7]

Results and Discussion

The experimental and literature values of physical properties of the pure liquids are shown in Table 1. The experimental viscosities, densities, and excess volumes at 303.15 K, 308.15 K, and 313.15 K are listed in Tables 2, 3, and 4.

Viscosity. The deviation in viscosities can be computed using the relationship

$$\Delta\eta = \eta - (x_1\eta_1 + x_2\eta_2) \quad (1)$$

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 kinematic viscosities were correlated by means of the McAllister model,[4] considering a three-body-interaction

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Table 2. Experimental Densities, ρ, Dynamic Viscosities, η, and Excess Molar Volume, V^E, for 1,4-Dioxane (1) + Carbon Tetrachloride (2) at 303.15 K, 308.15 K, and 313.15 K

x_1	ρ/g·cm^{-3}	η/mPa·s	V^E/cm^3·mol^{-1}	x_1	ρ/g·cm^{-3}	η/mPa·s	V^E/cm^3·mol^{-1}	x_1	ρ/g·cm^{-3}	η/mPa·s	V^E/cm^3·mol^{-1}
	T = 303.15 K				T = 308.15 K				T = 313.15 K		
0.0000	1.5806	0.8689	0.0000	0.0000	1.5757	0.8307	0.0000	0.0000	1.5709	0.8070	0.0000
0.1116	1.5206	0.9450	0.2541	0.1116	1.5173	0.8954	0.1437	0.1116	1.5132	0.8454	0.0987
0.2204	1.4623	0.9938	0.4177	0.2204	1.4586	0.9391	0.3246	0.2204	1.4551	0.8848	0.2337
0.3265	1.4053	1.0364	0.5104	0.3265	1.4011	0.9771	0.4365	0.3265	1.3969	0.9244	0.3808
0.4299	1.3490	1.0729	0.5541	0.4299	1.3448	1.0097	0.4732	0.4299	1.3409	0.9531	0.3972
0.5307	1.2943	1.1099	0.4870	0.5307	1.2905	1.0436	0.3696	0.5307	1.2869	0.9892	0.2711
0.6291	1.2409	1.1356	0.3286	0.6291	1.2362	1.0656	0.2631	0.6291	1.2325	1.0076	0.1724
0.7252	1.1874	1.1446	0.1615	0.7252	1.1824	1.0663	0.1219	0.7252	1.1779	0.9996	0.0875
0.7724	1.1611	1.1449	0.0433	0.7724	1.1559	1.0629	0.0174	0.7724	1.1509	0.9971	0.0205
0.8190	1.1344	1.1387	−0.0472	0.8190	1.1285	1.0578	−0.0259	0.8190	1.1232	0.9881	0.0013
0.8650	1.1077	1.1314	−0.1406	0.8650	1.1016	1.0521	−0.1026	0.8650	1.0960	0.9836	−0.0507
0.9105	1.0810	1.1233	−0.2373	0.9105	1.0747	1.0501	−0.1815	0.9105	1.0692	0.9785	−0.1375
0.9555	1.0526	1.1171	−0.2047	0.9555	1.0465	1.0458	−0.1610	0.9555	1.0412	0.9667	−0.1228
1.0000	1.0223	1.0985	0.0000	1.0000	1.0167	1.0295	0.0000	1.0000	1.0120	0.9575	0.0000

Table 3. Experimental Densities, ρ, Dynamic Viscosities, η, and Excess Molar Volume, V^E, for Carbon Tetrachloride (2) + Butanol (3) at 303.15 K, 308.15 K, and 313.15 K

x_2	ρ/g·cm^{-3}	η/mPa·s	V^E/cm^3·mol^{-1}	x_2	ρ/g·cm^{-3}	η/mPa·s	V^E/cm^3·mol^{-1}	x_2	ρ/g·cm^{-3}	η/mPa·s	V^E/cm^3·mol^{-1}
	T = 303.15 K				T = 308.15 K				T = 313.15 K		
0.0000	0.8057	2.2820	0.0000	0.0000	0.7972	1.9073	0.0000	0.0000	0.7955	1.6813	0.0000
0.0954	0.8850	2.0277	−0.1647	0.0954	0.8760	1.6985	−0.1206	0.0954	0.8739	1.4976	-0.0997
0.1918	0.9648	1.7085	−0.3491	0.1918	0.9555	1.4442	−0.2973	0.1918	0.9530	1.2934	-0.2611
0.2891	1.0445	1.4960	−0.5131	0.2891	1.0347	1.2764	−0.4068	0.2891	1.0317	1.1724	-0.3578
0.3875	1.1235	1.3561	−0.5938	0.3875	1.1138	1.1571	−0.4975	0.3875	1.1101	1.0694	-0.4034
0.4869	1.2012	1.2482	−0.5751	0.4869	1.1918	1.0959	−0.4758	0.4869	1.1876	1.0384	-0.3743
0.5874	1.2773	1.1567	−0.4438	0.5874	1.2685	1.0525	−0.3611	0.5874	1.2642	0.9981	-0.2832
0.6889	1.3522	1.0695	−0.2450	0.6889	1.3448	1.0037	−0.2259	0.6889	1.3409	0.9502	-0.1990
0.7401	1.3899	1.0250	−0.1685	0.7401	1.3827	0.9705	−0.1479	0.7401	1.3788	0.9211	-0.1303
0.7915	1.4271	1.0049	−0.0695	0.7915	1.4202	0.9552	−0.0450	0.7915	1.4159	0.8947	-0.0078
0.8432	1.4636	0.9778	0.0774	0.8432	1.4578	0.9211	0.0539	0.8432	1.4542	0.8727	0.0270
0.8952	1.5012	0.9554	0.1385	0.8952	1.4957	0.8975	0.1226	0.8952	1.4918	0.8612	0.1147
0.9475	1.5389	0.9164	0.1959	0.9475	1.5343	0.8787	0.1501	0.9475	1.5305	0.8346	0.1202
1.0000	1.5806	0.8689	0.0000	1.0000	1.5757	0.8307	0.0000	1.0000	1.5713	0.8072	0.0000

Table 4. Experimental Densities, ρ, Dynamic Viscosities, η, and Excess Molar Volume, V^E, for 1,4-Dioxane (1) + Butanol (3) at 303.15 K, 308.15 K, and 313.15 K

x_1	ρ/g·cm^{-3}	η/mPa·s	V^E/cm^3·mol^{-1}	x_1	ρ/g·cm^{-3}	η/mPa·s	V^E/cm^3·mol^{-1}	x_1	ρ/g·cm^{-3}	η/mPa·s	V^E/cm^3·mol^{-1}
	T = 303.15 K				T = 308.15 K				T = 313.15 K		
0.0000	0.8057	2.2820	0.0000	0.0000	0.7972	1.8947	0.0000	0.0000	0.7955	1.6813	0.0000
0.1066	0.8265	2.0114	0.1013	0.1066	0.8184	1.6830	0.0836	0.1066	0.8168	1.5218	0.0532
0.2116	0.8476	1.6350	0.1720	0.2116	0.8399	1.3617	0.1394	0.2116	0.8379	1.2812	0.1106
0.3151	0.8686	1.3702	0.2359	0.3151	0.8613	1.1651	0.1914	0.3151	0.8590	1.0938	0.1675
0.4171	0.8899	1.2430	0.2730	0.4171	0.8827	1.0811	0.2399	0.4171	0.8802	0.9963	0.2152
0.5177	0.9113	1.1645	0.2858	0.5177	0.9043	1.0316	0.2650	0.5177	0.9015	0.9565	0.2423
0.6169	0.9328	1.0930	0.2954	0.6169	0.9262	1.0073	0.2686	0.6169	0.9231	0.9426	0.2344
0.6659	0.9436	1.0639	0.2878	0.6659	0.9373	0.9903	0.2528	0.6659	0.9340	0.9289	0.2203
0.7146	0.9546	1.0382	0.2724	0.7146	0.9484	0.9768	0.2337	0.7146	0.9452	0.9190	0.1869
0.7630	0.9656	1.0160	0.2495	0.7630	0.9596	0.9543	0.2075	0.7630	0.9563	0.9043	0.1541
0.8111	0.9767	1.0147	0.2158	0.8111	0.9710	0.9484	0.1635	0.8111	0.9674	0.9234	0.1221
0.8588	0.9879	1.0306	0.1826	0.8588	0.9823	0.9507	0.1391	0.8588	0.9786	0.9384	0.0906
0.9062	0.9992	1.0646	0.1322	0.9062	0.9936	0.9793	0.1045	0.9062	0.9897	0.9315	0.0598
1.0000	1.0223	1.0983	0.0000	1.0000	1.0167	1.0295	0.0000	1.0000	1.0120	0.9575	0.0000

Table 5. Parameters and ADs of Equation 2

T/K	ν_{12}	ν_{21}	AD	T/K	ν_{12}	ν_{21}	AD	T/K	ν_{12}	ν_{21}	AD
1,4-Dioxane + Carbon Tetrachloride				Carbon Tetrachloride + Butanol				1,4-Dioxane + Butanol			
303.15	0.9946	0.7817	0.3821	303.15	0.8346	1.1638	1.4596	303.15	0.9254	1.4696	1.9320
308.15	0.9219	0.7398	0.3741	308.15	0.7889	0.9705	2.0045	308.15	0.9064	1.2087	2.3382
313.15	0.8851	0.6801	0.6510	313.15	0.7613	0.8965	1.1863	313.15	0.8931	1.1261	2.3344

model, which for two-component mixtures gives

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

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 viscosities 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 values of the parameters

Table 6. Krishnan and Laddha Constants for the Binary Systems Studied

T/K	B	C	D	AD	T/K	B	C	D	AD	T/K	B	C	D	AD
1,4-Dioxane + Carbon Tetrachloride					Carbon Tetrachloride + Butanol					1,4-Dioxane + Butanol				
303.15	−0.2182	0.0076	−0.0439	0.5212	303.15	0.2768	−0.1034	−0.2616	1.4323	303.15	0.5516	0.1514	−0.2190	1.8607
308.15	−0.1991	0.0066	−0.0308	0.5362	308.15	0.2966	−0.1504	−0.2715	1.5373	308.15	0.5245	0.0840	−0.1089	1.4114
313.15	−0.1972	−0.0421	0.0742	0.4146	313.15	0.2417	−0.1516	−0.1026	1.5261	313.15	0.4812	0.0592	−0.2891	1.1096

Table 7. Redlich−Kister Constants Obtained on Fitting the Excess Volume with Mole Fractions for the Binary Systems Studied

T/K	a_0	a_1	a_2	a_3	a_4	a_5	a_6	s
1,4-Dioxane + Carbon Tetrachloride								
303.15	2.0146	−1.8789	−1.5720	1.7272	−2.1664	−5.8227		1.9791
308.15	1.6537	−1.8939	−1.6352	2.4759	−0.4536	−4.1100	−2.400	1.6037
313.15	1.2700	−2.5116	−0.3627	7.7786	−4.8122	−9.5456	3.1570	1.2060
Carbon Tetrachloride + Butanol								
303.15	−2.2591	2.0147	3.4411	−2.6536	−4.4069	4.9085	6.8309	1.9510
308.15	−1.8570	1.3753	2.3721	−0.5499	−2.0002	1.9431	4.4698	1.5961
313.15	−1.4520	1.1409	0.6260	0.1183	2.0054	0.7952	1.0201	1.3414
1,4-Dioxane + Butanol								
303.15	1.1630	0.2956	0.1602	0.1023	0.0965	−0.1439		1.2744
308.15	1.0492	0.4514	−0.0642	−0.8640	−1.1333	0.7354	1.9357	1.1445
313.15	0.9636	0.3589	−0.7927	−0.9245	0.4222	0.8109		0.8432

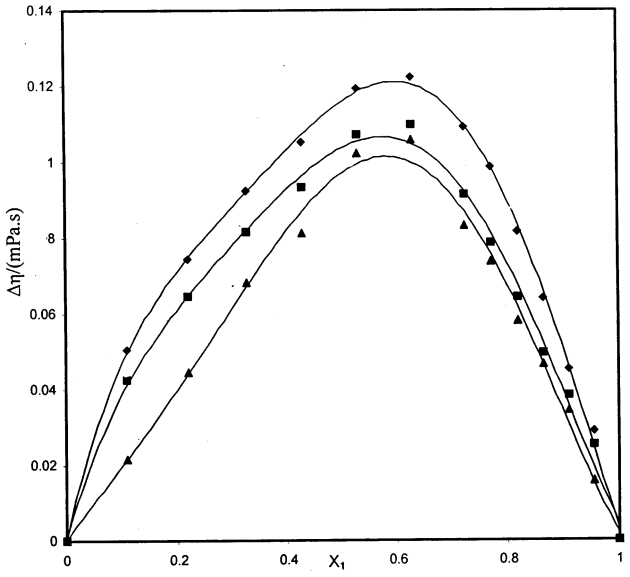

Figure 1. Deviations of viscosities of 1,4-dioxane (1) + carbon tetrachloride (2): ◆, 303.15 K; ■, 308.15 K; ▲, 313.15 K.

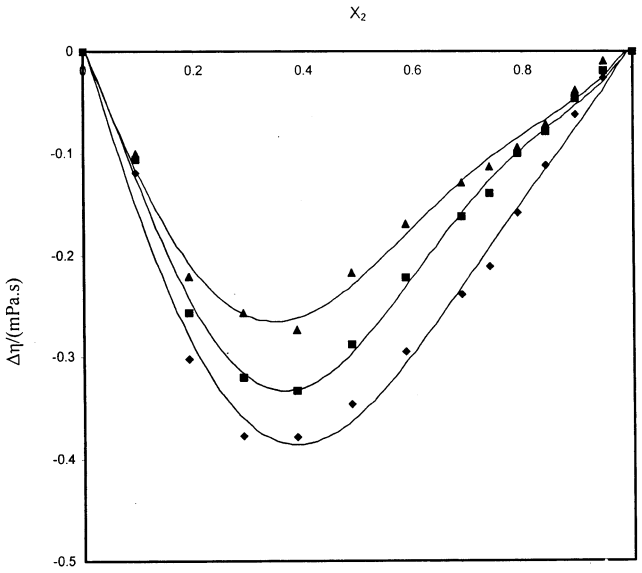

Figure 2. Deviations of viscosities of carbon tetrachloride (2) + butanol (3): ◆, 303.15 K; ■, 308.15 K; ▲, 313.15 K.

ν_{12} and ν_{21} are given in Table 5.

Krishnan and Laddha[2] have proposed an equation to predict viscosities of binary liquid mixtures based on Eyring's theory of absolute reaction rate. The equation is as follows

$$\ln \nu_{mix} = x_1 \ln \nu_1 + x_2 \ln \nu_2 + x_1 \ln M_1 + x_2 \ln M_2 - \ln(x_1M_1 + x_2M_2) - 2.303x_1x_2[B + C(x_1 - x_2) + D(x_1 - x_2)^2 + ...] \quad (3)$$

The values of the parameters *B*, *C*, and *D* are given in Table 6.

The percentage deviation was calculated by

$$d = ((\nu_{exp} - \nu_{cal})/\nu_{cal})100 \quad (4)$$

The average deviation (AD) was calculated from the relationship

$$AD = (\Sigma d^2/N)^{1/2} \quad (5)$$

In Figure 1, the physical interaction comprises mainly dispersion forces and nonspecific physical interactions giving a positive contribution. In Figures 2 and 3, the shape of deviation in viscosity observed in the carbon tetrachloride + butanol and 1,4-dioxane + butanol systems are attributed to varying interaction between a relatively large negative contribution due to chemical and structural effect as reported by Nikam.[6]

Excess Molar Volumes. The excess molar volumes (V^E) can be computed from experimental density data using the relationship

$$V^E = (x_1M_1 + x_2M_2)/\rho_m - (x_1M_1/\rho_1 + x_2M_2/\rho_2) \quad (6)$$

Where x_1 and x_2 refers to the mole fraction of components

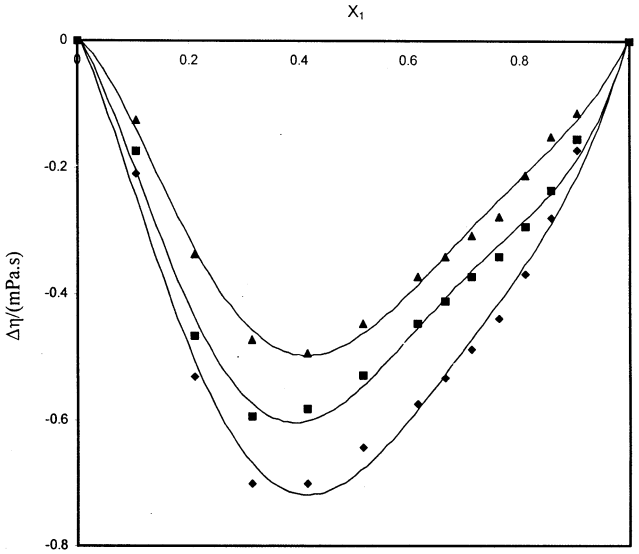

Figure 3. Deviations of viscosities of 1,4-dioxane (1) + butanol (3): ◆, 303.15 K; ■, 308.15 K; ▲, 313.15 K.

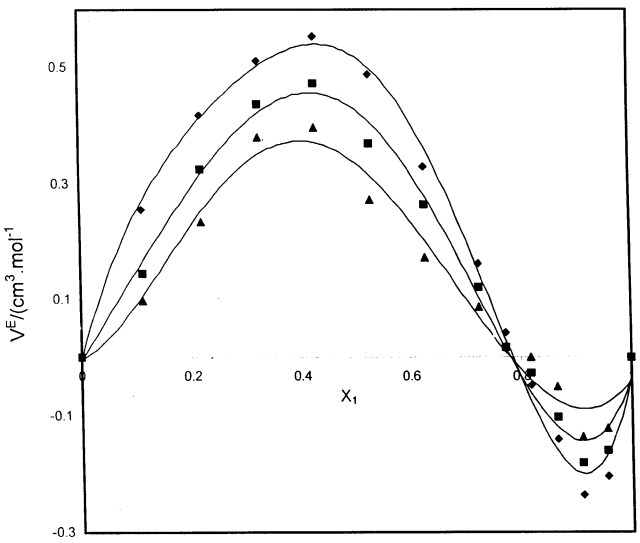

Figure 4. Excess molar volume of 1,4-dioxane (1) + carbon tetrachloride (2): ◆, 303.15 K; ■, 308.15 K; ▲, 313.15 K.

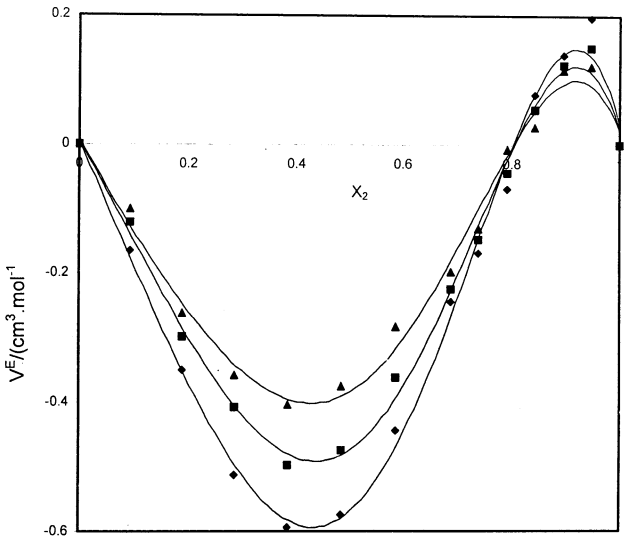

Figure 5. Excess molar volume of carbon tetrachloride (2) + butanol (3): ◆, 303.15 K; ■, 308.15 K; ▲, 313.15 K.

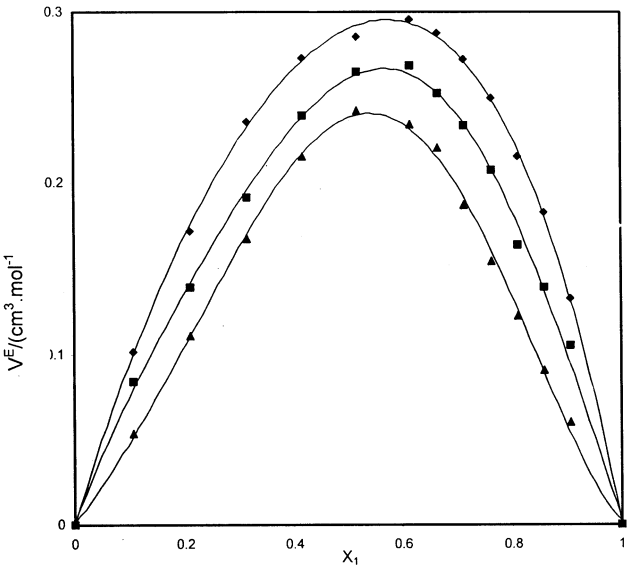

Figure 6. Excess molar volume of 1,4-dioxane (1) + butanol (3): ◆, 303.15 K; ■, 308.15 K; ▲, 313.15 K.

1 and 2. ρ_1 and ρ_2 refer to the density of components 1 and 2. ρ_m is the density of the mixture. For each mixture the excess molar volumes were fitted with Redlich−Kister equation[8]

$$V^E = x_1 x_2 \Sigma a_{i-1}(x_1 - x_2)^{i-1} \quad (7)$$

The coefficients a_{i-1} and standard deviations are listed in Table 7. The standard deviation was calculated by the following equation

$$\sigma(V^E) = [\Sigma(V^E_{exp} - V^E_{cal})^2/(N - m)]^{1/2} \quad (8)$$

where N is the number of experimental points and m is the number of coefficients in the corresponding equations.

In Figure 4, the V^E values are positive except at higher mole fractions of 1,4-dioxane. Positive values are attributed to changes in a free volume in the mixture of electron donor−acceptor-type interactions between 1,4-dioxane + carbon tetrachloride. In Figure 5, strong negative values are attributed for the mixture carbon tetrachloride + butanol except at higher mole fractions of carbon tetrachloride, which can be interpreted as a consequence of the strong attraction appearing between carbon tetrachloride + butanol. In Figure 6, the behavior of the 1,4-dioxane + butanol mixture may be attributed to the disruption of the hydrogen-bonded alcohol by the nonpolar 1,4-dioxane. The excess molar volumes decrease with increase in temperature.

Literature Cited

(1) Reilly, J.; Northman, W. *PhysioChem. Methods*, 1978, 88−90.
(2) Krishnan, M. R. V.; Laddha, G. S. Heat of Mixing and Vapor Liquid Equilibrium Data of Binary Liquid Mixtures−Prediction from Viscosity Data. *Ind. Chem. Eng., Trans 57*, 1963.
(3) Martin Contreras, S. Densities and Viscosities of Binary Mixtures of 1,4-Dioxane with 1-Propanol and 2-Propanol at (25, 30, and 40) °C. *J. Chem. Eng. Data* **2001**, *46*, 1149−1152.
(4) McAllister, R. A. The Viscosity of Liquid Mixtures. *AIChE J.* **1960**, *6*, 427−431.

(5) Indraswati, N.; Mudjijati; Wicaksana, F.; Hindarso, H. Measurements of Density and Viscosity of Binary Mixtures of Serval Flavor Compounds with 1-Butanol and 1-Pentanol at 293.15 K, 303.15 K, 313.15 K, and 323.15 K., *J. Chem. Eng. Data*. **2001**, *46*, 696−702.

(6) Nikam, P. S.; Jagdale, B. S. Densities and Viscosities of Binary Mixtures of Toluene with Methanol, Ethanol, Propan-l-ol, Butan-l-ol, Pentan-l-ol, and 2-Methylpropan-2-ol at (303.15, 308.15, 313.15) K. *J. Chem. Eng. Data*. **2000**, *45*, 559−563.

(7) Riddick, J. A.; Bunger, W. B.; Sakano, T. K. *Organic Solvents, Physical Properties and Methods of Purification*, 4th ed.; Wiley-Interscience: New York, 1986.

(8) Redlich, O.; Kister, A. T. Algebraic Representation of Thermodynamic Properties and the Classification of Solutions. *Ind. Eng. Chem*. **1948**, *40*, 345−348.

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