J. Chem. Eng. Data **1995,** *40,* 1001−1004 **1001**

Densities and Excess Molar Volumes for Sulfolane + Ethylbenzene, Sulfolane + 1-Methylnaphthalene, Water + *N,N*-Dimethylformamide, Water + Methanol, Water + *N*-Formylmorpholine, and Water + *N*-Methylpyrrolidone

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Measurements of the densities have been made with a vibrating tube densimeter over the whole composition range for sulfolane + ethylbenzene and sulfolane + 1-methylnaphthalene at 313.15 and 333.15 K and water + *N,N*-dimethylformamide, water + methanol, water + *N*-formylmorpholine, and water + *N*-methylpyrrolidone at 283.15 and 313.15 K. Excess molar volumes (V^E) calculated from the measured densities show negative deviation from the ideal for these systems. For water + methanol and sulfolane + ethylbenzene, the values of V^E increase with increasing temperature, but for other systems, the values of V^E decrease with increasing temperature. The values of V^E were fitted to the polynomial function and correlated by means of the Peng−Robinson equation.

Introduction

Density and excess molar volume are significant for the design of new processes and the study of molecular interactions in binary liquid systems. The aim of this work is to make a contribution to the literature on the densities and excess molar volumes of binary liquid systems. This paper reports the densities and the excess molar volumes for sulfolane + ethylbenzene and sulfolane + 1-methylnaphthalene at 313.15 and 333.15 K and water + *N,N*-dimethylformamide, water + methanol, water + *N*-formylmorpholine, and water + *N*-methylpyrrolidone at 283.15 and 313.15 K. These data are not available in the literature except for water + methanol at 283.15 and 313.15 K and water + *N,N*-dimethylformamide at 313.15 K (Mikhail and Kimel, 1961; Lee et al., 1990; Della Volpe et al., 1986). The present density values were compared with the literature values. The Peng−Robinson equation (Peng and Robinson, 1976) and the polynomial function were used to correlate and fit the experimental excess molar volumes.

Experimental Section

The purities of the laboratory-distilled water and other chemicals obtained from Merck were over 99 mol % as specified on their labels. Their purities were verified by the measured densities of pure liquids in this work. All chemicals were degassed and used without further purification. Binary systems were prepared on a mass basis. The mole fraction error is estimated to be less than 2×10^{-4}.

Densities ϱ were measured with a vibrating tube densimeter, Anton Paar (DMA 602/60). The accuracy of the apparatus in temperature was maintained to ±0.01 K. The densimeter was calibrated with nonane and distilled and degassed water. The purity of nonane was over 99.99% and the accuracy in the densities at different temperatures given on the label was better than 3×10^{-3} kg/m^3. The density of any liquid is given by

$$\varrho = \varrho_w + b(\tau^2 - \tau_w^2) \qquad (1)$$

where τ is the period of vibration of the measured liquid and b is a constant for a particular oscillator determined by

$$b = (\varrho_n - \varrho_w)/(\tau_n^2 - \tau_w^2) \qquad (2)$$

ϱ_n, ϱ_w, τ_n, and τ_w are the densities and the periods of vibration of nonane and water, respectively. The accuracy in the density values measured with using this densimeter is estimated to be better than 5×10^{-2} kg/m^3.

Table 1. Comparison of the Densities of Some Pure Components Measured in This Work with Literature Values

component	T/K	$10^{-3}\varrho$(present)/ (kg·m^{-3})	$10^{-3}\varrho$(lit.)/ (kg·m^{-3})	lit.
water	283.15	0.9997	0.9997	*a*
			0.9997	*b*
	313.15	0.9922	0.9922	*a*
			0.9922	*b*
methanol	283.15	0.8005	0.8007	*c*
			0.8008	*d*
	313.15	0.7733	0.7740	*d*
			0.7726	*c*
N,N-dimethyl-formamide	313.15	0.9298	0.9294	*e*
sulfolane	313.15	1.2532	1.2528	*a*
	333.15	1.2359	1.2360	*a*
ethylbenzene	313.15	0.8496	0.8494	*c*
			0.8495	*d*
	333.15	0.8318	0.8315	*d*
			0.8316	*c*

[a] Riddick and Bunger (1970). [b] Kikuchi and Oikawa (1967). [c] TRC (1994). [d] Vargaftik (1975). [e] Della Volpe et al. (1986).

Results and Discussion

The density values of some pure components measured in this work are listed in Table 1 and compared with literature values. Table 1 shows that the differences between the present and literature data are less than 0.09%. The present and the literature density values for water + methanol at 283.15 and 313.15 K and water + *N,N*-dimethylformamide at 313.15 K are shown in Figure 1. The average deviations of the present data from the

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0021-9568/95/1740-1001$09.00/0

Table 2. Densities and Excess Molar Volumes for Six Binary Liquid Mixtures

x_1	$10^{-3}\varrho$/ (kg·m^{-3})	10^6V^E/ (m^3·mol^{-1})	x_1	$10^{-3}\varrho$/ (kg·m^{-3})	10^6V^E/ (m^3·mol^{-1})
Sulfolane (1) + Ethylbenzene (2)					
	313.15 K			333.15 K	
0.0000	0.8496	0.000	0.0000	0.8318	0.000
0.2007	0.9203	−0.712	0.2007	0.9027	−0.810
0.3980	0.9941	−0.988	0.3980	0.9762	−1.071
0.5992	1.0751	−0.987	0.5992	1.0573	−1.069
0.7938	1.1588	−0.675	0.7938	1.1415	−0.758
1.0000	1.2532	0.000	1.0000	1.2359	0.000
Sulfolane (1) + 1-Methylnaphthalene (2)					
	313.15 K			333.15 K	
0.0000	1.0038	0.000	0.0000	0.9890	0.000
0.2057	1.0434	−0.304	0.2057	1.0282	−0.314
0.4034	1.0856	−0.396	0.4034	1.0696	−0.366
0.5967	1.1322	−0.364	0.5967	1.1156	−0.324
0.7967	1.1876	−0.237	0.7967	1.1705	−0.204
1.0000	1.2532	0.000	1.0000	1.2359	0.000
Water (1) + *N,N*-Dimethylformamide (2)					
	283.15 K			313.15 K	
0.0000	0.9584	0.000	0.0000	0.9298	0.000
0.1040	0.9635	−0.291	0.1040	0.9350	−0.276
0.1875	0.9681	−0.511	0.1875	0.9397	−0.483
0.3069	0.9756	−0.795	0.3069	0.9474	−0.749
0.4102	0.9830	−1.000	0.4102	0.9550	−0.933
0.5072	0.9903	−1.124	0.5072	0.9627	−1.042
0.6099	0.9980	−1.162	0.6099	0.9710	−1.060
0.6860	1.0030	−1.106	0.6860	0.9769	−0.995
0.8169	1.0071	−0.784	0.8169	0.9848	−0.693
0.9200	1.0037	−0.342	0.9200	0.9882	−0.304
1.0000	0.9997	0.000	1.0000	0.9922	0.000
Water (1) + Methanol (2)					
	283.15 K			313.15 K	
0.0000	0.8005	0.000	0.0000	0.7733	0.000
0.1028	0.8215	−0.516	0.1028	0.7907	−0.342
0.2997	0.8561	−0.914	0.2193	0.8122	−0.667
0.4033	0.8764	−1.046	0.2997	0.8288	−0.870
0.5011	0.8943	−1.030	0.4033	0.8487	−0.958
0.6077	0.9167	−0.999	0.5011	0.8696	−1.006
0.6981	0.9357	−0.885	0.6077	0.8933	−0.962
0.7909	0.9537	−0.657	0.6981	0.9148	−0.862
0.8975	0.9742	−0.308	0.7909	0.9368	−0.663
1.0000	0.9997	0.000	0.8975	0.9629	−0.340
			1.0000	0.9922	0.000
Water (1) + *N*-Formylmorpholine (2)					
	283.15 K			313.15 K	
0.0000	1.1570	0.000	0.0000	1.1333	0.000
0.0854	1.1560	−0.129	0.0854	1.1323	−0.110
0.1933	1.1543	−0.279	0.1933	1.1305	−0.227
0.2942	1.1520	−0.396	0.2942	1.1284	−0.334
0.4229	1.1481	−0.540	0.4229	1.1245	−0.445
0.5029	1.1445	−0.607	0.5029	1.1211	−0.501
0.6349	1.1351	−0.664	0.6349	1.1122	−0.541
0.7103	1.1263	−0.653	0.7103	1.1039	−0.522
0.7906	1.1115	−0.581	0.7906	1.0904	−0.456
0.9030	1.0726	−0.347	0.9030	1.0555	−0.257
1.0000	0.9997	0.000	1.0000	0.9922	0.000
Water (1) + *N*-Methylpyrrolidone (2)					
	283.15 K			313.15 K	
0.0000	1.0410	0.000	0.0000	1.0144	0.000
0.1226	1.0434	−0.285	0.1226	1.0173	−0.299
0.2166	1.0463	−0.552	0.2166	1.0201	−0.535
0.3149	1.0496	−0.804	0.3149	1.0231	−0.742
0.4222	1.0535	−1.042	0.4222	1.0268	−0.940
0.5105	1.0567	−1.189	0.5105	1.0297	−1.048
0.5873	1.0591	−1.265	0.5873	1.0320	−1.099
0.7034	1.0600	−1.228	0.7034	1.0332	−1.034
0.8004	1.0543	−0.987	0.8004	1.0294	−0.810
0.9257	1.0271	−0.349	0.9257	1.0107	−0.281
1.0000	0.9997	0.000	1.0000	0.9922	0.000

literature data for water + methanol at 283.15 and 313.15 K and water + *N,N*-dimethylformamide at 313.15 K are 0.05%, 0.07%, and 0.03%, respectively.

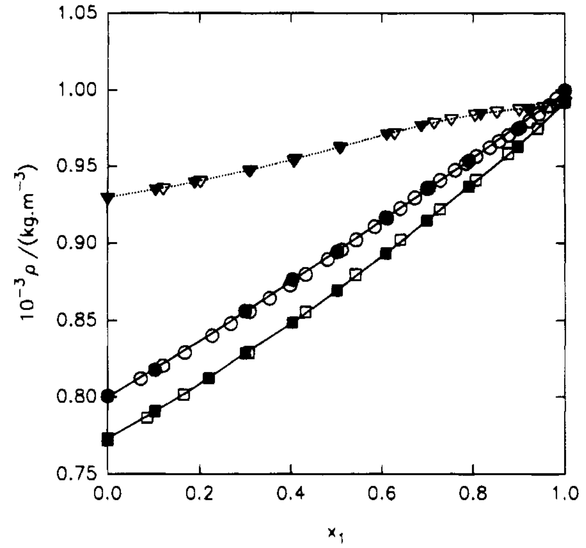

Figure 1. Densities for water + methanol: ●, this work and, ○, literature data (Lee et al., 1990) at 283.15 K; ■, this work and, □, literature data (Mikhail and Kimel, 1961) at 313.15 K. Densities for water + *N,N*-dimethylformamide at 313.15 K: ▼, this work, ▽, literature data (Della Volpe et al., 1986).

Table 3. Values of the Constants A_i in Eq 4 and the Standard Deviation $\sigma(V^E)$ for Six Binary Liquid Mixtures

T/K	A_0	A_1	A_2	A_3	$10^6\sigma(V^E)$/ (m^3·mol^{-1})
Sulfolane (1) + Ethylbenzene (2)					
313.15	−4.0939	−0.2362	−0.5222		0.014
333.15	−4.4099	−0.3088	−1.2123		0.019
Sulfolane (1) + 1-Methylnaphathalene (2)					
313.15	−1.5702	−0.3386	−0.2719		0.001
333.15	−1.4139	−0.5493	−0.5118		0.007
Water (1) + *N,N*-Dimethylformamide (2)					
313.15	−4.1814	1.6657	0.8584	−1.3504	0.008
283.15	−4.5350	2.1246	0.8418	−1.7137	0.013
Water (1) + Methanol (2)					
283.15	−4.2091	0.0911	−0.4324	−2.3647	0.020
313.15	−4.0959	0.0642	0.5526	−0.0919	0.018
Water (1) + *N*-Formylmorpholine (2)					
313.15	−2.0080	1.2086	−0.2656	−0.3895	0.003
283.15	−2.4298	1.5158	−0.6051	−0.1420	0.003
Water (1) + *N*-Methylpyrrolidone (2)					
313.15	−4.2663	2.4097	0.9705	−2.3134	0.024
283.15	−4.8542	3.3535	1.1695	−2.6503	0.035

The excess molar volumes V^E for various systems from the measured density are calculated from the following equation:

$$V^E = (x_1M_1 + x_2M_2)/\varrho_m - [(x_1M_1/\varrho_1) + (x_2M_2/\varrho_2)] \quad (3)$$

where x_i, ϱ_i, ϱ_m, M_i represent the mole fraction, the density of pure or mixture components, and the molar mass, respectively. The accuracy of V^E values is within 1×10^{-9} m^3/mol. The results obtained are listed in Table 2. Each set of excess molar volumes is fitted to the polynomial function

$$10^6V^E/(\text{m}^3\cdot\text{mol}^{-1}) = x_1x_2\sum_{i\geq 0}A_i(x_1 - x_2)^i \quad (4)$$

The constants A_i and the corresponding standard deviations $\sigma(V^E)$ are given in Table 3. These constants were used to obtain the calculated curves in Figures 2 and 3.

The values of V^E have been plotted in Figures 2 and 3, which show that the curves are sightly skewed to the left

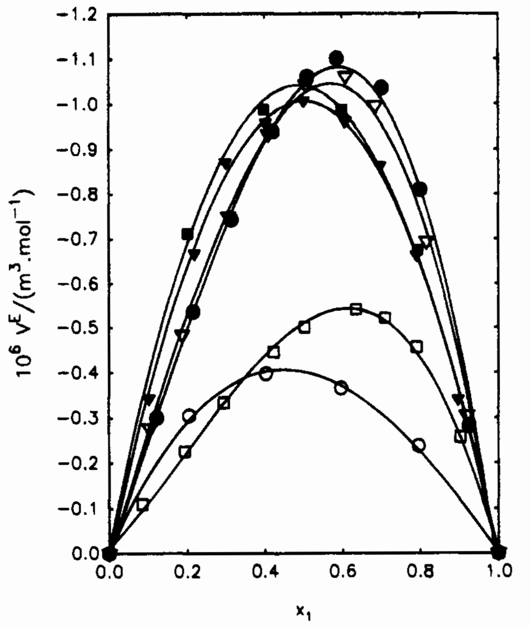

Figure 2. Excess molar volumes at 313.15 K for, ○, sulfolane + 1-methylnaphathalene; □, water + *N*-formylmorpholine; ▼, water + methanol; ■, sulfolane + ethylbenzene; ▽, water + *N*,*N*-dimethylformamide; and, ●, water + *N*-methylpyrrolidone. The curves were calculated from eq 4 with constants from Table 3.

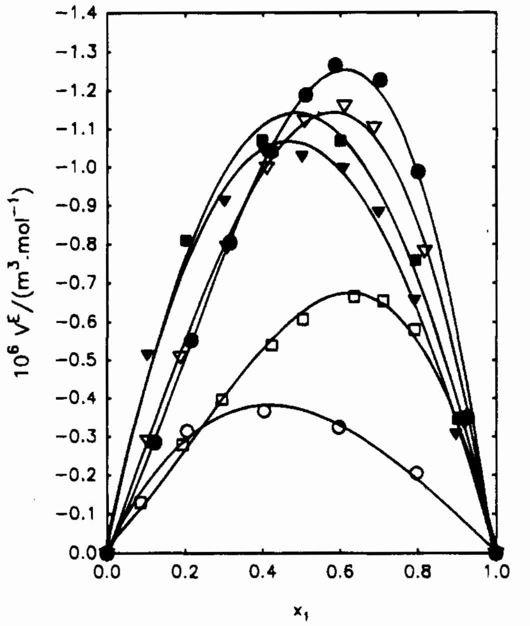

Figure 3. Excess molar volumes for, ○, sulfolane + 1-methylnaphathalene at 333.15 K; □, water + *N*-formylmorpholine at 283.15 K; ▼, water + methanol at 283.15 K; ■, sulfolane + ethylbenzene at 333.15 K; ▽, water + *N*,*N*-dimethylformamide at 283.15 K; and, ●, water + *N*-methylpyrrolidone at 283.15 K. The curves were calculated from eq 4 with constants from Table 3.

for the two systems including sulfolane and apparently skewed to the right for water + *N*,*N*-dimethylformamide, water + *N*-methylpyrrolidone, and water + *N*-formylmorpholine; they also show the fitted V^E curves together with the experimental points. Table 2 shows that values of V^E are negative for all mixtures. For water + methanol and sulfolane + ethylbenzene, the values of V^E increase with increasing temperature, but for other systems, the values of V^E decrease with increasing temperature.

By using the modified conventional mixing rules (Adach and Sugie, 1986, 1988), the excess molar volumes have been correlated by means of the Peng–Robinson equation (Peng and Robinson, 1976). The correlation is strongly dependent on the binary interaction parameters of the modified conventional mixing rules. Comparisons of correlated and experimental V^E for three liquid mixtures are shown in Figures 4 and 5. Average absolute deviations of the calculated results by means of the Peng–Robinson equation are 0.013, 0.041, and 0.023 for sulfolane + 1-methylnaphthalene, sulfolane + ethylbenzene, and water + methanol, respectively. These results clearly show that the results calculated by means of the Peng–Robinson equation are acceptable.

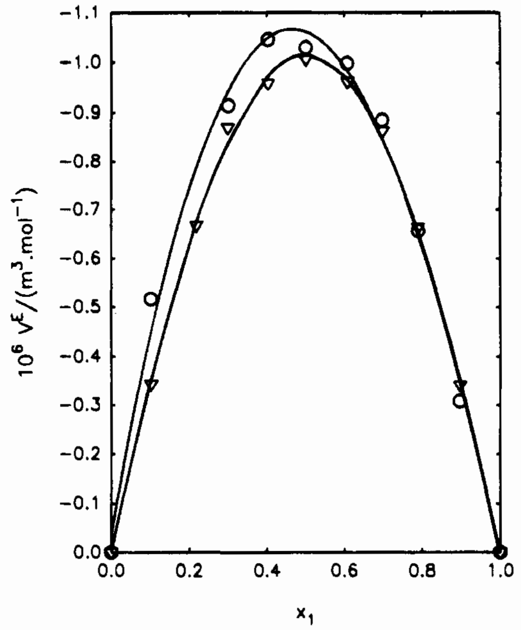

Figure 4. Comparison of experimental and calculated results by means of the Peng–Robinson equation with modified conventional mixing rules for water + methanol: ▽, 283.15 K; ○, 313.15 K.

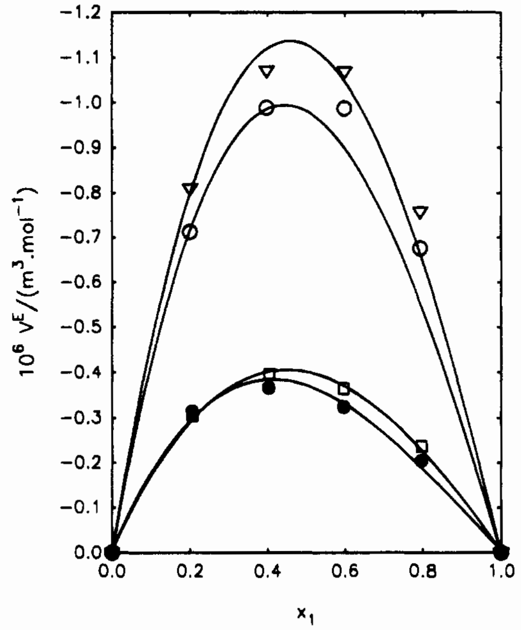

Figure 5. Comparison of experimental and calculated results by means of the Peng–Robinson equation with modified conventional mixing rules for sulfolane + 1-methylnaphathalene (●, 333.15 K; □, 313.15 K); and sulfolane + ethylbenzene (○, 313.15 K; ▽, 333.15 K).

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Received for review February 24, 1995. Accepted April 20, 1995.[⊗] The authors are very grateful for financial support from Deutscher Akademischer Austauchsdienst and for some literature data from the DIPPR project.

JE950050X

[⊗] Abstract published in *Advance ACS Abstracts,* June 15, 1995.