J. Chem. Eng. Data **2004,** *49,* 1839−1842

Excess Molar Volumes and Surface Tensions of Trimethylbenzene with Tetrahydrofuran Tetrachloromethane and Dimethyl Sulfoxide at 298.15 K

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Densities of binary mixtures of (tetrahydrofuran + 1,2,4-trimethylbenzene, tetrahydrofuran + 1,3,5-trimethylbenzene, tetrachloromethane + 1,2,4-trimethylbenzene, tetrachloromethane + 1,3,5-trimethylbenzene, dimethyl sulfoxide + 1,2,4-trimethylbenzene, and dimethyl sulfoxide + 1,3,5-trimethylbenzene) have been determined over the entire concentration range at 298.15 K, and excess molar volumes have been derived. Surface tensions of these binary mixtures have been measured at 298.15 K by the pendant drop method, and the values of the surface tension deviation for these mixtures were also calculated.

Introduction

For the purpose of finding proper ways to separation xylene and trimethylbenzene, we chose different organic solutions to determine excess functions of binary systems. The work presented here is a continuing series after reporting the excess molar volumes and surface tensions at 298.15 K of xylene + alkanol (2-propanol and 2-methyl-2-propanol), xylene + alkone (acetone and 2-butanone), and xylene + ether (isopropyl ether and methyl *tert*-butyl ether).[1−3]

Experimental Section

1,2,4-Trimethylbenzene (ACROS Organics), 1,3,5-trimethylbenzene (ACROS Organics), tetrahydrofuran (GuangZhou Chem., China), tetrachloromethane (TianJin Chem., China), and dimethyl sulfoxide (TianJin Chem., China) were of high grade. The mass fraction purities of the substances were 1,2,4-trimethylbenzene (99.20%), 1,3,5-trimethylbenzene (99.30%), tetrahydrofuran (99.99%), tetrachloromethane (99.60%), and dimethyl sulfoxide (99.32%), as determined by a PE autosystem XL gas chromatograph. All of the chemicals were placed over molecular sieves, and all of the mixtures were prepared by mass using an Ohaus E12140 balance with an error of ±0.1 mg.

Densities of the pure liquids and their mixture were measured with an Anton Paar DMA 4500 vibrating tube densimeter, thermostated at (298.15 ± 0.01) K. The densimeter uncertainty was $\pm 5 \times 10^{-5}$ g·cm^{-3}. The surface tensions of the pure liquids and their mixtures were determined by the pendant drop method using a Dataphysics OCA20 contact angle and surface tension measuring device. This instrument provides a computer-controlled display (CCD) video camera to take pictures and an electronic syringe unit to inject samples, so the surface tension of the sample can be determined very quickly. The surface tension was given by[4]

$$\sigma = \frac{g \Delta\rho d_e^2}{H} \tag{1}$$

where g is the gravitational acceleration, $\Delta\rho$ is the density difference between the droplet and the surroundings, d_e is the largest diameter of the drop, and H is a correction factor that depends on the sharpness of the drop. The sharpness correction factor H is calculated by the Young−Laplace equation and is performed via computer. The software needs only the density data and a picture of the drop of liquid to calculate the surface tension. The error of the instrument is ±0.05 mN·m^{-1} (±0.1 K). The densities and surface tensions of the pure compounds are given in Table 1 and compared with literature values.

Table 1. Physical Properties of the Pure Components at 298.15 K

	ρ/g·cm^{-3}		σ/mN·m^{-1}	
substance	exptl	lit	exptl	lit
1,2,4-trimethylbenzene	0.87164	0.87174[a]	29.25	29.19[f]
1,3,5-trimethylbenzene	0.86103	0.86109[b]	28.09	27.54[f]
tetrahydrofuran	0.88206	0.88197[c]	27.04	26.50[f]
tetrachloromethane	1.58380	1.58429[d]	26.76	26.43[f]
dimethyl sulfoxide	1.09554	1.095560[e]	42.09	42.86[f]

[a] Reference 8. [b] Reference 9. [c] Reference 10. [d] Reference 11. [e] Reference 12. [f] Reference 13.

Result and Discussion

Excess molar volumes were determined from the density data[5]

$$V^E = \frac{x_1 M_1 + x_2 M_2}{\rho} - x_1 \frac{M_1}{\rho_1} - x_2 \frac{M_2}{\rho_2} \tag{2}$$

where M_i is the molar mass of component i, ρ and ρ_i are the densities of the mixture and component i, respectively, and x_i is the molar fraction of component i. Experimental excess molar volumes V^E for six binary mixtures (tetrahydrofuran + 1,2,4-trimethylbenzene, tetrahydrofuran + 1,3,5-trimethylbenzene, tetrachloromethane + 1,2,4-trimethylbenzene, tetrachloromethane + 1,3,5-trimethylbenzene, dimethyl sulfoxide + 1,2,4-trimethylbenzene, and dimethyl sulfoxide + 1,3,5-trimethylbenzene) at 298.15 K are listed in Table 2 and graphically presented in Figure 1. The experimental results were fit by the method of least

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10.1021/je0497294 CCC: $27.50

Table 2. Experimental Excess Molar Volumes V^E at 298.15 K

x_1	V^E / $cm^3 \cdot mol^{-1}$	x_1	V^E / $cm^3 \cdot mol^{-1}$	x_1	V^E / $cm^3 \cdot mol^{-1}$	x_1	V^E / $cm^3 \cdot mol^{-1}$
$xC_4H_8O + (1 - x)1,2,4\text{-}C_6H_3(CH_3)_3$							
0.0530	−0.035	0.3003	−0.133	0.5478	−0.165	0.7996	−0.103
0.0988	−0.068	0.3502	−0.146	0.6005	−0.159	0.8497	−0.090
0.1497	−0.090	0.3995	−0.156	0.6504	−0.148	0.9006	−0.067
0.2018	−0.106	0.4484	−0.161	0.6986	−0.132	0.9505	−0.042
0.2489	−0.118	0.5002	−0.165	0.7487	−0.121		
$xC_4H_8O + (1 - x)1,3,5\text{-}C_6H_3(CH_3)_3$							
0.0481	0.001	0.3002	0.011	0.5501	0.019	0.7989	0.015
0.1006	0.003	0.3501	0.013	0.6010	0.020	0.8496	0.012
0.1509	0.005	0.4000	0.015	0.6506	0.020	0.9000	0.008
0.2021	0.007	0.4489	0.017	0.7003	0.019	0.9491	0.004
0.2495	0.009	0.5004	0.018	0.7498	0.017		
$xCCl_4 + (1 - x)1,2,4\text{-}C_6H_3(CH_3)_3$							
0.0496	0.055	0.3001	0.289	0.5502	0.385	0.7985	0.231
0.0996	0.104	0.3495	0.332	0.5987	0.369	0.8494	0.185
0.1492	0.161	0.4006	0.359	0.6498	0.342	0.9011	0.121
0.1986	0.208	0.4521	0.380	0.6986	0.309	0.9505	0.069
0.2485	0.249	0.5007	0.386	0.7489	0.271		
$xCCl_4 + (1 - x)1,3,5\text{-}C_6H_3(CH_3)_3$							
0.0499	0.083	0.2994	0.461	0.5505	0.470	0.7970	0.257
0.1009	0.195	0.3503	0.495	0.5995	0.441	0.8500	0.202
0.1492	0.281	0.4007	0.505	0.6496	0.403	0.9012	0.145
0.2014	0.351	0.4500	0.503	0.6988	0.354	0.9502	0.080
0.2504	0.414	0.4998	0.497	0.7493	0.307		
$x(CH_3)_2SO + (1 - x)1,2,4\text{-}C_6H_3(CH_3)_3$							
0.0474	−0.028	0.3007	−0.163	0.5496	−0.175	0.7992	−0.083
0.1007	−0.066	0.3485	−0.173	0.6012	−0.161	0.8477	−0.065
0.1517	−0.095	0.3995	−0.184	0.6504	−0.148	0.9013	−0.041
0.2007	−0.128	0.4523	−0.187	0.6992	−0.125	0.9499	−0.020
0.2501	−0.148	0.5010	−0.183	0.7506	−0.106		
$x(CH_3)_2SO + (1 - x)1,3,5\text{-}C_6H_3(CH_3)_3$							
0.0530	0.021	0.3027	0.108	0.5497	0.116	0.8003	0.063
0.1023	0.047	0.3517	0.116	0.6003	0.107	0.8489	0.051
0.1481	0.064	0.4010	0.122	0.6502	0.097	0.8998	0.032
0.1987	0.084	0.4504	0.124	0.6990	0.086	0.9505	0.015
0.2513	0.096	0.4999	0.121	0.7502	0.076		

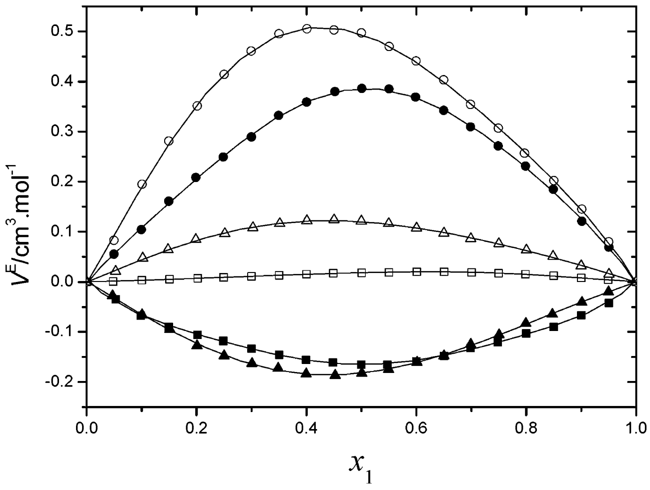

Figure 1. Excess molar volumes V^E for ■, (*x*)tetrahydrofuran + (1 − *x*)1,2,4-trimethylbenzene; □, (*x*)tetrahydrofuran + (1 − *x*)1,3,5-trimethylbenzene; ●, (*x*)tetrachloromethane + (1 − *x*)1,2,4-trimethylbenzene; ○, (*x*)tetrachloromethane + (1 − *x*)1,3,5-trimethylbenzene; ▲, (*x*)dimethyl sulfoxide + (1 − *x*)1,2,4-trimethylbenzene; △, (*x*)dimethyl sulfoxide + (1 − *x*)1,3,5-trimethylbenzene at 298.15 K.

squares with all points weighted equally to the smoothing equation:[6]

$$V^E = x(1 - x)\sum_{i=0}^{k} A_i(1 - 2x)^i \tag{3}$$

The parameters A_0, A_1, A_2, A_3, and A_4 and the standard deviations are given in Table 3. The surface tension deviations $\delta\sigma$ are defined by[5]

$$\delta\sigma = \sigma - x_1\sigma_1 - x_2\sigma_2 \tag{4}$$

Table 4 lists the surface tensions and surface tension deviations for six binary mixtures (tetrahydrofuran + 1,2,4-trimethylbenzene, tetrahydrofuran + 1,3,5-trimethylbenzene, tetrachloromethane + 1,2,4-trimethylbenzene, tetrachloromethane + 1,3,5-trimethylbenzene, dimethyl sulfoxide + 1,2,4-trimethylbenzene, and dimethyl sulfoxide + 1,3,5-trimethylbenzene) at 298.15 K as graphically presented in Figure 2 for tetrahydrofuran + 1,2,4-trimethylbenzene, tetrahydrofuran + 1,3,5-trimethylbenzene, tetrachloromethane + 1,2,4-trimethylbenzene, and tetrachloromethane + 1,3,5-trimethylbenzene, and Figure 3 presents the data for dimethyl sulfoxide + 1,2,4-trimethylbenzene and dimethyl sulfoxide + 1,3,5-trimethylbenzene.

The result of V^E values at 298.15 K from Figure 1 shows that they are positive for tetrahydrofuran + 1,3,5-trimethylbenzene, dimethyl sulfoxide + 1,3,5-trimethylbenzene, tetrachloromethane + 1,2,4-trimethylbenzene, and tetrachloromethane + 1,3,5-trimethylbenzene. The maxmum values of V^E for them follow the order tetrahydrofuran + 1,3,5-trimethylbenzene < dimethyl sulfoxide + 1,3,5-trimethylbenzene < tetrachloromethane + 1,2,4-trimethylbenzene < tetrachloromethane + 1,3,5-trimethylbenzene. It also can be seen that the values are negative for dimethyl

Table 3. Least-Squares Parameters and Standard Deviations

	A_0	A_1	A_2	A_3	A_4	$\frac{s}{\text{cm}^3\cdot\text{mol}^{-1}}$
tetrahydrofuran + 1,2,4-trimethylbenzene	−0.6597	0.0036	0.2104	0.0097	−0.5340	0.0025
tetrahydrofuran + 1,3,5-trimethylbenzene	0.0727	0.0508	0.0041	0.0242	−0.0227	0.0002
tetrachloromethane + 1,2,4-trimethylbenzene	1.5434	−0.0870	−0.7303	−0.0721	0.5625	0.0034
tetrachloromethane + 1,3,5-trimethylbenzene	1.9778	0.7466	−0.2132	−0.6910	0.0172	0.0044
dimethyl sulfoxide + 1,2,4-trimethylbenzene	−0.7296	−0.2421	0.2231	0.1165	−0.0028	0.0023
dimethyl sulfoxide + 1,3,5-trimethylbenzene	0.4803	0.1436	−0.0728	−0.1063	−0.0132	0.0017

Table 4. Surface Tensions σ at 298.15 K

	σ	$\delta\sigma$		σ	$\delta\sigma$		σ	$\delta\sigma$		σ	$\delta\sigma$
x_1	mN·m^{-1}		x_1	mN·m^{-1}		x_1	mN·m^{-1}		x_1	mN·m^{-1}	
$x\text{C}_4\text{H}_8\text{O} + (1 - x)1,2,4\text{-C}_6\text{H}_3(\text{CH}_3)_3$						$x\text{C}_4\text{H}_8\text{O} + (1 - x)1,3,5\text{-C}_6\text{H}_3(\text{CH}_3)_3$					
0.0988	29.11	0.08	0.6005	28.29	0.37	0.0481	27.88	−0.10	0.6010	27.23	−0.23
0.2018	29.00	0.20	0.6986	28.01	0.30	0.2021	27.72	−0.16	0.7003	27.15	−0.20
0.3003	28.88	0.29	0.7996	27.68	0.20	0.3002	27.57	−0.20	0.7989	27.09	−0.16
0.3995	28.73	0.36	0.9006	27.34	0.08	0.4000	27.44	−0.23	0.9000	27.06	−0.09
0.5002	28.53	0.39				0.5004	27.32	−0.24			
$x\text{CCl}_4 + (1 - x)1,2,4\text{-C}_6\text{H}_3(\text{CH}_3)_3$						$x\text{CCl}_4 + (1 - x)1,3,5\text{-C}_6\text{H}_3(\text{CH}_3)_3$					
0.0496	29.13	0.13	0.5987	28.24	0.48	0.1009	27.77	−0.19	0.5995	26.91	−0.38
0.0996	29.04	0.28	0.6986	27.89	0.38	0.2014	27.53	−0.29	0.6988	26.86	−0.30
0.1986	28.89	0.39	0.7985	27.54	0.28	0.2994	27.29	−0.40	0.7970	26.83	−0.20
0.3001	28.72	0.47	0.9011	27.13	0.12	0.4007	27.1	−0.46	0.9012	26.81	−0.08
0.4006	28.50	0.50				0.4998	26.99	−0.44			
$x(\text{CH}_3)_2\text{SO} + (1 - x)1,2,4\text{-C}_6\text{H}_3(\text{CH}_3)_3$						$x(\text{CH}_3)_2\text{SO} + (1 - x)1,3,5\text{-C}_6\text{H}_3(\text{CH}_3)_3$					
0.1007	28.48	−2.06	0.6012	29.34	−5.62	0.1023	27.3	−2.22	0.6003	30.09	−6.40
0.2007	28.77	−3.06	0.6992	29.35	−4.49	0.1987	26.92	−3.95	0.6990	32.05	−5.83
0.3007	28.81	−4.30	0.7992	30.04	−3.42	0.3027	26.7	−5.63	0.8003	34.77	−4.52
0.3995	29.10	−5.28	0.9013	35.71	−1.85	0.4010	27.41	−6.29	0.8998	37.92	−2.77
0.5010	29.46	−6.22				0.4999	28.4	−6.69			

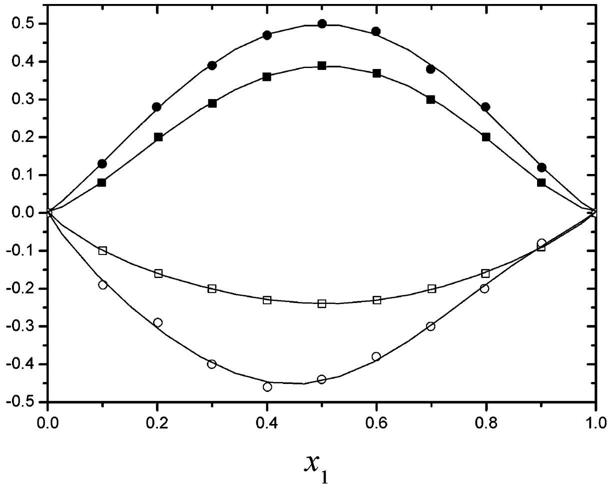

Figure 2. Surface tensions deviation $\delta\sigma$ for ■, (x)tetrahydrofuran + (1 − x)1,2,4-trimethylbenzene; □, (x)tetrahydrofuran + (1 − x)1,3,5-trimethylbenzene; ●, (x)tetrachloromethane + (1 − x)1,2,4-trimethylbenzene; ○, (x)tetrachloromethane + (1 − x)1,3,5-trimethylbenzene at 298.15 K.

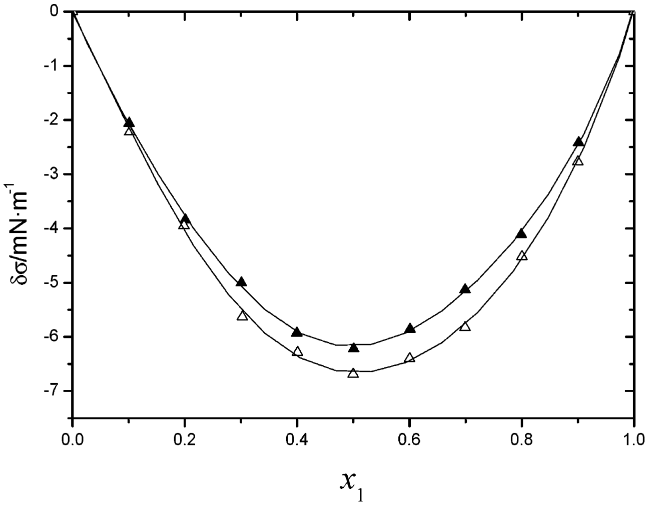

Figure 3. Surface tensions deviation $\delta\sigma$ for ▲, (x)dimethyl sulfoxide + (1 − x)1,2,4-trimethylbenzene; △, (x)dimethyl sulfoxide + (1 − x)1,3,5-trimethylbenzene at 298.15 K.

sulfoxide + 1,2,4-trimethylbenzene and tetrahydrofuran + 1,2,4-trimethylbenzene. The minimum values of V^E for them follow the order dimethyl sulfoxide + 1,2,4-trimethylbenzene < tetrahydrofuran + 1,2,4-trimethylbenzene < dimethyl sulfoxide + 1,3,5-trimethylbenzene.

Figures 2 and 3 show that the surface tension deviations $\delta\sigma$ at 298.15 K are positive for tetrahydrofuran + 1,2,4-trimethylbenzene and tetrachloromethane + 1,2,4-trimethylbenzene, following the order at the minimum values tetrahydrofuran + 1,2,4-trimethylbenzene < tetrachloromethane + 1,2,4-trimethylbenzene. At the same time, we can see they are negative for dimethyl sulfoxide + 1,3,5-trimethylbenzene, dimethyl sulfoxide + 1,2,4-trimethylbenzene, tetrachloromethane + 1,3,5-trimethylbenzene, and tetrahydrofuran + 1,3,5-trimethylbenzene, following the order dimethyl sulfoxide + 1,3,5-trimethylbenzene < dimethyl sulfoxide < 1,2,4-trimethylbenzene, tetrachloromethane < 1,3,5-trimethylbenzene and tetrahydrofuran < 1,3,5-trimethylbenzene.

The V^E values of tetrahydrofuran + 1,3,5-trimethylbenzene are small positive numbers, and the $\delta\sigma$ values are negative. The possible reason may be that there are no strong intermolecular forces between them because 1,3,5-trimethylbenzene is a symmetrical nonpolar molecule. Conversely, stronger forces exists for the system of tetrahydrofuran + 1,2,4-trimethylbenzene, so the values are negative. For the system of tetrachloromethane + trimethylbenzene, the V^E values are both positive, possibly owing to the packing effect, but the excess surface tension of tetrachloromethane + 1,2,4-trimethylbenzene is positive. Perhaps dipolar−dipolar interaction exists between them because 1,2,4-trimethylbenzene is a polar molecule. It was once reported that the excess volume of dimethyl sulfoxide + 1,3,5-trimethylbenzene at 303.15 K is positive; here we also found it to be positive at 298.15 K and the V^E value of dimethyl sulfoxide + 1,2,4-trimethylbenzene at 298.15 K to be negative. The two can also be explained by dipolar−dipolar interaction. We also got the obvious negative values of the excess surface tension. The surface tension value of dimethyl sulfoxide is too high; trimethylbenzene with relatively low values of the excess surface tension brings an obvious negative deviation.

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Received for review July 23, 2004. Accepted September 12, 2004. This project was supported by the National Key Basic Research and Development Program of China, no. G 2000026302.

JE0497294