Excess Molar Volumes and Surface Tensions of 1,2,4-Trimethylbenzene and 1,3,5-Trimethylbenzene with 1-Butanol, 2-Methyl-1-propanol, 2-Butanol, and 2-Methyl-2-propanol at 298.15 K

Chuanrong Pan, Gangfeng Ouyang,* Jielan Lin, Yun Rao, Xiuhuan Zhen, Guizeng Lu, and Zhongqi Huang

School of Chemistry and Chemical Engineering, Sun Yat-sen University, Guangzhou 510275, China

Densities for binary mixtures of (1,2,4-trimethylbenzene + 1-butanol, 2-methyl-1-propanol, 2-butanol, and 2-methyl-2-propanol and 1,3,5-trimethylbenzene + 1-butanol, 2-methyl-1-propanol, 2-butanol, and 2-methyl-2-propanol) 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

The surface tension and density of liquids and liquid mixtures are important physical properties because they play an important role in the mass and heat transfer at an interface such as in liquid−liquid extraction, gas absorption, distillation, and condensation. One of our research directions is xylene and trimethylbenzene separation. In previous papers, the excess molar volumes and surface tensions at 298.15 K for 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) systems were reported.[1−3] In this paper, surface tensions and densities for 1,2,4-trimethylbenzene +1-butanol, 2-methyl-1-propanol, 2-butanol, or 2-methyl-2-propanol and 1,3,5-trimethylbenzene + 1-butanol, 2-methyl-1-propanol, 2-butanol, or 2-methyl-2-propanol at 298.15 K are reported.

Experimental Section

1,2,4-Trimethylbenzene (ACROS Organics), 1,3,5-trimethylbenzene (ACROS Organics), 1-butanol (GuangZhou Chem., China), 2-methyl-1-propanol (ShangHai Chem., China), 2-butanol (ACROS Organics), and 2-methyl-2-propanol (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%), 1-butanol (99.86%), 2-methyl-1-propanol (99.88%), 2-butanol (99.90%), and 2-methyl-2-propanol (99.80%), as determined by a PE auto system XL gas chromatograph. All of the chemicals were prepared by a molecular sieve treatment, and all of the mixtures were measured by mass using an Ohaus E12140 balance with an accuracy 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 error 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 is 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 surrounding, d_e is the largest diameter of the drop, and H is a correction factor that depends on the sharpness of the drop. 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 the 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[d]
1,3,5-trimethylbenzene	0.86103	0.86109[b]	28.09	27.54[d]
1-butanol	0.80580	0.80575[c]	24.18	24.93[d]
2-methyl-1-propanol	0.79783	0.79790[e]	22.30	22.54[d]
2-butanol	0.80234	0.80241[f]	23.46	22.62[30, d]
			22.14[30]	
2-methyl-2-propanol	0.78085	0.78120[g]	20.13	20.10[g]

[a] Reference 7. [b] Reference 8. [c] Reference 9. [d] Reference 10. [e] Reference 11. [f] Reference 12. [g] Reference 13.

Result and Discussion

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

$$V^E = \frac{x_1M_1 + x_2M_2}{\rho} - x_1\frac{M_1}{\rho_1} - x_2\frac{M_2}{\rho_2} \tag{2}$$

where M_i represents the molar mass of component i, ρ and ρ_i are the densities of the mixture and component i,

* Corresponding author. E-mail: cesoygf@zsu.edu.cn.

10.1021/je049807n CCC: $27.50
Published on Web 10/16/2004

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

x_1	V^E / cm^3·mol^{-1}	x_1	V^E / cm^3·mol^{-1}	x_1	V^E / cm^3·mol^{-1}	x_1	V^E / cm^3·mol^{-1}
			xCH$_3$CH$_2$CH$_2$CH$_2$OH + (1− x)1,2,4-C$_6$H$_3$(CH$_3$)$_3$				
0.0499	0.048	0.2992	0.164	0.5498	0.120	0.8001	0.035
0.1013	0.101	0.3503	0.162	0.5985	0.105	0.8501	0.021
0.1492	0.130	0.4009	0.154	0.6501	0.087	0.9002	0.009
0.2002	0.149	0.4491	0.145	0.6987	0.070	0.9503	0.003
0.2499	0.160	0.5012	0.132	0.7499	0.051		
			xCH$_3$CH$_2$CH$_2$CH$_2$OH + (1 − x)1,3,5-C$_6$H$_3$(CH$_3$)$_3$				
0.0493	0.077	0.3002	0.211	0.5484	0.186	0.7999	0.095
0.1006	0.132	0.3487	0.213	0.6005	0.172	0.8500	0.074
0.1512	0.169	0.4003	0.211	0.6500	0.158	0.9010	0.047
0.2011	0.190	0.4535	0.206	0.6993	0.137	0.9506	0.019
0.2514	0.203	0.5001	0.198	0.7497	0.118		
			xCH$_3$CH(CH$_3$)CH$_2$OH + (1 − x)1,2,4-C$_6$H$_3$(CH$_3$)$_3$				
0.0509	0.093	0.3002	0.272	0.5488	0.278	0.8002	0.146
0.1004	0.162	0.3487	0.286	0.6002	0.258	0.8506	0.109
0.1530	0.205	0.3996	0.295	0.6508	0.237	0.8984	0.071
0.2018	0.235	0.4494	0.297	0.6989	0.210	0.9496	0.033
0.2490	0.254	0.4995	0.289	0.7484	0.180		
			xCH$_3$CH(CH$_3$)CH$_2$OH + (1 − x)1,3,5-C$_6$H$_3$(CH$_3$)$_3$				
0.0512	0.114	0.3006	0.326	0.5480	0.344	0.7998	0.217
0.1028	0.183	0.3529	0.342	0.6002	0.327	0.8504	0.172
0.1517	0.233	0.4019	0.356	0.6495	0.312	0.9006	0.122
0.1994	0.273	0.4494	0.359	0.6990	0.286	0.9485	0.064
0.2514	0.301	0.4995	0.358	0.7501	0.250		
			xCH$_3$CH$_2$CH(CH$_3$)OH + (1 − x)1,2,4-C$_6$H$_3$(CH$_3$)$_3$				
0.0497	0.127	0.2985	0.389	0.5486	0.385	0.7999	0.221
0.1008	0.223	0.3492	0.408	0.6008	0.362	0.8496	0.171
0.1486	0.282	0.4008	0.416	0.6505	0.332	0.9002	0.116
0.2010	0.332	0.4506	0.410	0.6994	0.295	0.9489	0.063
0.2507	0.368	0.4997	0.402	0.7503	0.264		
			xCH$_3$CH$_2$CH(CH$_3$)OH + (1 − x)1,3,5-C$_6$H$_3$(CH$_3$)$_3$				
0.0508	0.144	0.2986	0.460	0.5484	0.486	0.8009	0.294
0.1010	0.250	0.3488	0.484	0.6004	0.462	0.8504	0.234
0.1511	0.326	0.4007	0.500	0.6508	0.433	0.9002	0.160
0.2007	0.387	0.4495	0.504	0.6991	0.398	0.9505	0.074
0.2500	0.424	0.5017	0.501	0.7496	0.353		
			x(CH$_3$)$_3$COH + (1 − x)1,2,4-C$_6$H$_3$(CH$_3$)$_3$				
0.0498	0.165	0.3001	0.497	0.5494	0.613	0.7993	0.374
0.1000	0.269	0.3510	0.536	0.6006	0.595	0.8500	0.296
0.1496	0.348	0.4002	0.562	0.6502	0.566	0.9003	0.197
0.2007	0.409	0.4496	0.590	0.6991	0.509	0.9499	0.101
0.2495	0.453	0.5005	0.607	0.7491	0.451		
			x(CH$_3$)$_3$COH + (1 − x)1,3,5-C$_6$H$_3$(CH$_3$)$_3$				
0.0502	0.168	0.2995	0.594	0.5483	0.751	0.7995	0.538
0.1015	0.298	0.3484	0.645	0.6005	0.747	0.8501	0.432
0.1482	0.386	0.3995	0.686	0.6502	0.730	0.9002	0.315
0.2007	0.472	0.4490	0.717	0.6987	0.692	0.9509	0.155
0.2509	0.537	0.4992	0.746	0.7500	0.627		

Table 3. Least-Squares Parameters and Standard Deviations

	A_0	A_1	A_2	A_3	A_4	s^a
1-butanol + 1,2,4-trimethylbenzene	0.5313	0.5486	0.1816	0.1012	−0.1439	0.0024
1-butanol + 1,3,5-trimethylbenzene	0.7893	0.3787	0.2516	0.3253	0.0970	0.0015
2-methyl-1-propanol +1,2,4-trimethylbenzene	1.1536	0.2835	−0.1140	0.4977	0.4710	0.0038
2-methyl-1-propanol + 1,3,5-trimethylbenzene	1.4216	0.1933	0.0998	0.3275	0.4877	0.0033
2-butanol + 1,2,4-trimethylbenzene	1.6066	0.5012	0.1815	0.2967	0.3743	0.0029
2-butanol + 1,3,5-trimethylbenzene	1.9944	0.3027	0.2928	0.4706	0.1770	0.0033
2-methyl-2-propanol + 1,2,4-trimethylbenzene	2.4295	−0.3429	−0.2572	1.3514	0.8539	0.0033
2-methyl-2-propanol + 1,3,5-trimethylbenzene	2.9728	−0.7036	−0.4664	0.9346	0.1696	0.0034

[a] Given in units of cm^3·mol^{-1}.

and x_i is the molar fraction of component i. Experimental excess molar volumes V^E for eight binary mixtures (1,2,4-trimethylbenzene + 1-butanol, 2-methyl-1-propanol, 2-butanol, or 2-methyl-2-propanol and 1,3,5-trimethylbenzene + 1-butanol, 2-methyl-1-propanol, 2-butanol, or 2-methyl-2-propanol) 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 squares with all points weighted equally to the smoothing equation[6]

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

The parameters A_0, A_1, A_2, A_3, and A_4 and the standard deviations are given in Table 3. Table 4 lists the surface

Table 4. Surface Tensions σ at 298.15 K[a]

x_1	σ	$\delta\sigma$	x_1	σ	$\delta\sigma$	x_1	σ	$\delta\sigma$	x_1	σ	$\delta\sigma$
xCH$_3$CH$_2$CH$_2$CH$_2$OH + (1 − x)1,2,4-C$_6$H$_3$(CH$_3$)$_3$						xCH$_3$CH$_2$CH$_2$CH$_2$OH + (1 − x) 1,3,5-C$_6$H$_3$(CH$_3$)$_3$					
0.1013	28.81	0.07	0.5985	26.65	0.43	0.1006	27.92	0.22	0.5001	25.99	0.25
0.2002	28.42	0.19	0.6987	26.08	0.37	0.2011	27.65	0.35	0.6005	25.53	0.17
0.2992	28.04	0.31	0.8001	25.49	0.30	0.3002	27.33	0.41	0.6993	25.05	0.09
0.4009	27.61	0.39	0.9002	24.86	0.17	0.4003	26.91	0.39	0.7999	24.58	0.01
0.5012	27.15	0.44				0.5001	26.46	0.33			
xCH$_3$CH(CH$_3$)CH$_2$OH + (1 − x)1,2,4-C$_6$H$_3$(CH$_3$)$_3$						xCH$_3$CH(CH$_3$)CH$_2$OH + (1 − x)1,3,5-C$_6$H$_3$(CH$_3$)$_3$					
0.1004	28.42	−0.13	0.6002	24.72	−0.36	0.1028	27.65	0.16	0.6002	24.88	0.27
0.2018	27.54	−0.31	0.6989	24.16	−0.23	0.1994	27.21	0.27	0.6990	24.25	0.21
0.3002	26.70	−0.46	0.8002	23.60	−0.09	0.3006	26.67	0.32	0.7998	23.61	0.15
0.3996	25.95	−0.52	0.8984	22.98	−0.03	0.4019	26.09	0.33	0.9006	22.97	0.09
0.4995	25.29	−0.49				0.4995	25.51	0.31			
xCH$_3$CH$_2$CH(CH$_3$)OH + (1 − x)1,2,4-C$_6$H$_3$(CH$_3$)$_3$						xCH$_3$CH$_2$CH(CH$_3$)OH + (1 − x)1,3,5-C$_6$H$_3$(CH$_3$)$_3$					
0.1008	28.58	−0.09	0.6008	25.59	−0.18	0.1010	27.77	0.15	0.6004	25.49	0.18
0.2010	27.94	−0.15	0.6994	25.07	−0.13	0.2007	27.36	0.20	0.6991	24.98	0.13
0.2985	27.32	−0.20	0.7999	24.56	−0.06	0.2986	26.94	0.23	0.8009	24.45	0.07
0.4008	26.71	−0.22	0.9002	24.02	−0.02	0.4007	26.47	0.24	0.9002	23.94	0.02
0.4997	26.15	−0.21				0.5017	25.99	0.22			
x(CH$_3$)$_3$COH + (1 − x)1,2,4-C$_6$H$_3$(CH$_3$)$_3$						x(CH$_3$)$_3$COH + (1 − x)1,3,5-C$_6$H$_3$(CH$_3$)$_3$					
0.1000	28.12	−0.22	0.6006	23.23	−0.54	0.1015	27.18	−0.10	0.6005	23.02	−0.29
0.2007	27.00	−0.42	0.6991	22.46	−0.41	0.2007	26.24	−0.25	0.6987	22.32	−0.21
0.3001	25.92	−0.59	0.7993	21.70	−0.26	0.2995	25.35	−0.36	0.7995	21.61	−0.12
0.4002	24.93	−0.67	0.9003	20.96	−0.08	0.3995	24.51	−0.40	0.9002	20.86	−0.06
0.5005	24.06	−0.63				0.4992	23.75	−0.37			

[a] σ and $\delta\sigma$ are given in units of mN·m^{-1}.

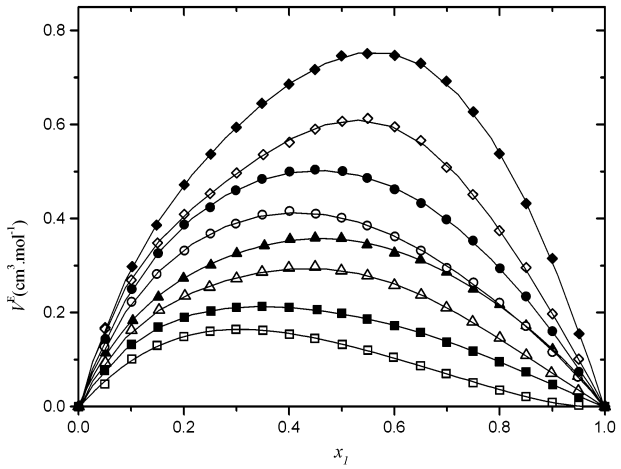

Figure 1. Excess molar volumes V^E for (x)*n*-butanol: □, + (1 − x) 1,2,4-trimethylbenzene; ■, + (1 − x)1,3,5-trimethylbenzene. (x)*iso*-butanol: △, + (1 − x)1,2,4-trimethylbenzene; ▲, + (1 − x)1,3,5-trimethylbenzene. (x)*sec*-butanol: ○, + (1 − x)1,2,4-trimethylbenzene; ●, + (1 − x)1,3,5-trimethylbenzene. (x)*tert*-butyl alcohol: ◇, + (1 − x)1,2,4-trimethylbenzene; ◆, + (1 − x)1,3,5-trimethylbenzene at 298.15 K.

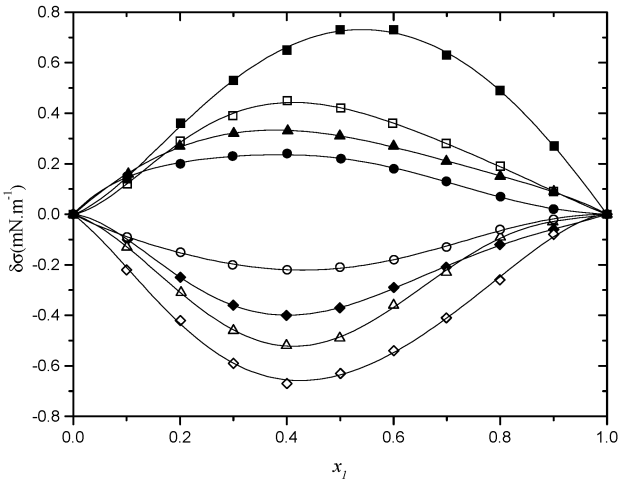

Figure 2. Surface tension deviations $\delta\sigma$ for (x)*n*-butanol: □, + (1 − x)1,2,4-trimethylbenzene; ■, + (1 − x)1,3,5-trimethylbenzene. (x)*i*-butanol: △, + (1 − x)1,2,4-trimethylbenzene; ▲, + (1 − x)1,3,5-trimethylbenzene. (x)*sec*-butanol: ○, + (1 − x)1,2,4-trimethylbenzene; ●, + (1 − x)1,3,5-trimethylbenzene. (x)*t*-butyl alcohol: ◇, + (1 − x)1,2,4-trimethylbenzene; ◆, + (1 − x)1,3,5-trimethylbenzene at 298.15 K.

tensions and surface tension deviations for eight binary mixtures (1,2,4-trimethylbenzene + 1-butanol, 2-methyl-1-propanol, 2-butanol, or 2-methyl-2-propanol and 1,3,5-trimethylbenzene + 1-butanol, 2-methyl-1-propanol, 2-butanol, or 2-methyl-2-propanol) at 298.15 K. The surface tension deviations $\delta\sigma$ are defined by[5]

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

The result of V^E values at 298.15 K from Figure 1 shows that they are all positive for these eight binary mixtures. The maximum values of V^E for them follow the order 1-butanol + 1,2,4-trimethylbenzene < 1-butanol + 1,3,5-trimethylbenzene < 2-methyl-1-propanol +1,2,4-trimethylbenzene < 2-methyl-1-propanol + 1,3,5-trimethylbenzene < 2-butanol + 1,2,4-trimethylbenzene < 2-butanol + 1,3,5-trimethylbenzene < 2-methyl-2-propanol + 1,2,4-trimethylbenzene < 2-methyl-2-propanol + 1,3,5-trimethylbenzene. It is obvious that the packing effect plays a more important role than the association between aromatic molecules and the hydroxide radical of the four kinds of alcohol molecules, which results in positive V^E values. Because 2-methyl-2-propanol has a stronger packing effect than the other molecules, the V^E values of 2-methyl-2-propanol + trimethylbenzene are more positive than those of 1-butanol, 2-methyl-1-propanol, or 2-butanol + trimethylbenzene.

Figure 2 shows that the surface tension deviations $\delta\sigma$ at 298.15 K are positive for mixtures of 1-butanol + 1,3,5-trimethylbenzene, 2-methyl-1-propanol + 1,3,5-trimethylbenzene, 2-butanol + 1,3,5-trimethylbenzene, and 1-butanol + 1,2,4-trimethylbenzene. The maximum values (at about x = 0.4 or 0.5) of $\delta\sigma$ for them follow the order

2-butanol + 1,3,5-trimethylbenzene < 2-methyl-1-propanol + 1,3,5-trimethylbenzene < 1-butanol + 1,2,4-trimethylbenzene < 1-butanol + 1,3,5-trimethylbenzene. It also shows that the surface tension deviations $\delta\sigma$ at 298.15 K are negative for mixtures of 2-methyl-2-propanol + 1,2,4-trimethylbenzene, 2-methyl-1-propanol + 1,2,4-trimethylbenzene, 2-methyl-2-propanol + 1,3,5-trimethylbenzene, and 2-butanol + 1,2,4-trimethylbenzene. The minimum values (at about $x = 0.4$) of $\delta\sigma$ follow the order 2-methyl-2-propanol + 1,2,4-trimethylbenzene < 2-methyl-1-propanol + 1,2,4-trimethylbenzene < 2-methyl-2-propanol +1,3,5-trimethylbenzene < 2-butanol + 1,2,4-trimethylbenzene.

The surface tension deviation $\delta\sigma$ can be considered to result from the following: One is association between an aromatic molecule and the hydroxide radical of butanol, one is a packing effect, and another is a dipolar−dipolar interaction. For the binary systems with positive deviation, the $\sigma-\pi$ bond formed between an aromatic molecule and the hydroxide radical of butanol is more dominant than the packing effect. Conversely, for the binary systems with negative deviation, because 2-methyl-2-propanol is a large molecule with steric hindrance, the packing effect is more dominant than the $\sigma-\pi$ bond formed by an aromatic molecule and the hydroxide radical of butanol, which results in a decrease in surface tension.

Supporting Information Available:

Density data of 1,2,4-trimethylbenzene and 1,3,5-trimethylbenzene with *n*-butanol, *iso*-butanol, *sec*-butanol, and *tert*-butanol at 298.15 K. This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited

(1) Ouyang, G.; Huang, Z.; Ou, J.; Wu, W.; Kang, B. Excess Molar Volumes and Surface Tensions of Xylene with 2-Propanol or 2-Methyl-2-propanol at 298.15 K. *J. Chem. Eng. Data* **2003**, *48*, 195−197.

(2) Ouyang, G.; Yang, Y.; Lu, S.; Huang, Z.; Kang, B. Excess Molar Volumes and Surface Tensions of Xylene with Acetone or 2-Butanone at 298.15K. *J. Chem. Eng. Data* **2004**, *49*, 330−332.

(3) Ouyang, G.; Lu, G.; Pan C.; Yang Y.; Huang, Z.; Kang, B. Excess Molar Volumes and Surface Tensions of Xylene with Isopropyl Ether or Methyl *tert*-Butyl Ether at 298.15K. *J. Chem. Eng. Data* **2004**, *49*, 732−734.

(4) Menke, T. J.; Funke, Z.; Maier, R. D.; Kressler, J. Surface Tension Measurements on Ethene−Butene Random Copolymers and Different Polypropenes. *Macromolecules* **2000**, *33*, 6120−6125.

(5) Eulogio, J.; Herminio, C.; Luisa, S.; Carlos, F. Surface Tensions, Refractive Indexes and Excess Molar Volumes of Hexane + 1-Alkanol Mixtures at 298.15 K. *J. Chem. Eng. Data* **2000**, *45*, 862−866.

(6) Wang, H. J.; Zhu, C.; Chen, M. Z.; Liu, H. L. Excess volumes of (a polar liquid + an aromatic hydrocarbon) at the temperature 298.15 K. *J. Chem. Thermodyn.* **1995**, *27*, 991−996.

(7) Andrzej, A. Excess volumes of (phenol +butyl benzene or propylbenzene or isopropyl benzene or 1,2,4-trimethylbenzene or ethyl benzene) at 318.15 and 348.15K. *J. Chem. Thermodyn.* **1990**, *22*, 55−60.

(8) Wilhelm, E.; Faradjzadeh, A.; Grolier, J.-P. E. Molar excess heat capacities and excess volumes of 1,2-dichloroehane + cyclooctane, + mesitylene, and + terachloromethane. *J. Chem. Thermodyn.* **1979**, *11*, 979−984.

(9) Romole, F.; Fabio, C. Excess Molar Enthapise and Excess Molar Volumes of Binary Mixtures Containing Dimethyl Carbonate + Four Buthanol Isomers at (288.15, 298.15, and 313.15 K). *J. Chem. Eng. Data* **1999**, *44*, 44−47.

(10) Dean, J. A. *Lange's Handbook of Chemistry*, 15th ed.; McGraw-Hill: New York, 1999.

(11) Rosa, M.; Burguet, M. C.; Natalia, M.; Francisca, G.-U. Densities, Refractive Indices, and Excess Molar Volumes of Binary and Ternary Systems Containing Isobutyl Alcohol, Ethanol, 2-Methylpentane, and Methyl *tert*-Butyl Ether at 298.15 K. *J. Chem. Eng. Data* **2000**, *45*, 585−589.

(12) Ignacio, G.; Ana, M.; Felix, M.; Joses, U. Experimental Viscosities and Viscosity Predictions of the Ternary Mixture (Cyclohexane + 1,3-Dioxolane + 2-Butanol) at 298.15 and 313.15 K. *J. Chem. Eng. Data* **2000**, *45*, 751−755.

(13) *TRC Databases for Chemistry and Engineering − Thermodynamic Tables, version 1998-2s*. Thermodynamic Research Center: Texas A&M University System, College Station, TX, 1998.

Received for review May 24, 2004. Accepted August 30, 2004. This project was supported by the National Key Basic Research and Development Program of China, no. G 2000026302.

JE049807N