J. Chem. Eng. Data **2005,** *50,* 1047−1051

Measurements of Liquid−Liquid Equilibria for Quaternary Mixtures of Water, Methyl *tert*-Butyl Ether, and Diisopropyl Ether with Methanol or Ethanol

Yao Chen,* Zhongjuan Pan, and Yanhui Dong

Department of Chemistry, Jinan University, Guangzhou 510632, China

Experimental tie-line data for two quaternary mixtures of water + methyl *tert*-butyl ether + diisopropyl ether + methanol or ethanol were measured at 298.15 K and ambient pressure. The experimental quaternary liquid−liquid equilibrium data were successfully correlated by using a modified UNIQUAC model. The calculated results were further compared with those obtained from the extended UNIQUAC model of Nagata.

1. Introduction

Recently, there has been considerable interest in the use of fuel additives to improve gasoline performance as anti-knock agents and to reduce air pollution. Methyl *tert*-butyl ether (MTBE) is used mostly because of its low Reid vapor pressure and the availability of ethanol feedstock from renewable resources. However, MTBE has the drawbacks of easily dissolving in water and of difficult removal from water. In addition, it is resistant to microbial decomposition. These facts have promoted research on the possible use of other ethers of higher molecular weight that are harmless to the environment. Diisopropyl ether (DIPE) is effective in reducing automotive CO emissions and has been considered to be a good alternative to MTBE as an oxygenated additive. To assess the effect of the additives in gasoline reformulation, fundamental knowledge of the multicomponent phase equilibria of the mixtures containing these ether compounds is needed. Although many liquid−liquid equilibrium (LLE) investigations of ternary mixtures formed by MTBE or DIPE have been made,[1−6] LLE data of quaternary mixtures with MTBE and DIPE were not available in the literature.

In this work, we report two quaternary LLE data points for the water + MTBE + DIPE mixtures with methanol or ethanol measured at 298.15 K and ambient pressure. We present an accurate description of the experimental LLE data of the quaternary systems by using a modified UNIQUAC model[7] and an extended UNIQUAC model[8] that includes additional ternary and quaternary parameters coming from three-body and four-body interactions. For a reliable representation of the quaternary LLE system, the constituent ternary systems of water + MTBE + DIPE,[1] MTBE + methanol + water,[2] MTBE + ethanol + water,[3] water + methanol + DIPE,[4] and water + ethanol + DIPE[5] are necessary to obtain the ternary parameters. Vapor−liquid equilibrium (VLE) data and mutual solubilities of the constituent binary mixtures have been published.[1,6,9−15]

Table 1. Equilibrium Phase Compositions in Mole Fraction (x) for the Quaternary of Water (1) + Methanol (2) + Methyl *tert*-Butyl Ether (3) + Diisopropyl Ether (4) Mixtures at 298.15 K

organic phase			aqueous phase		
x_1	x_2	x_3	x_1	x_2	x_3
{x_1Water + x_2Methanol + x_3Methyl *tert*-Butyl Ether + (1 − x_1 − x_2 − x_3)Diisopropyl Ether}[a]					
$x_3' = 0.25$[b]					
0.023	0.011	0.190	0.962	0.038	0.000
0.034	0.039	0.189	0.901	0.099	0.000
0.043	0.096	0.167	0.877	0.123	0.000
0.061	0.128	0.164	0.827	0.172	0.000
0.087	0.162	0.143	0.755	0.232	0.005
0.096	0.210	0.134	0.724	0.233	0.006
0.200	0.258	0.100	0.689	0.290	0.007
0.293	0.290	0.075	0.634	0.330	0.010
0.288	0.336	0.064	0.603	0.357	0.012
$x_3' = 0.50$					
0.040	0.016	0.447	0.992	0.009	0.000
0.097	0.059	0.402	0.895	0.100	0.004
0.118	0.090	0.362	0.868	0.125	0.006
0.099	0.141	0.346	0.808	0.179	0.009
0.154	0.209	0.277	0.757	0.230	0.009
0.222	0.236	0.230	0.726	0.258	0.010
0.261	0.290	0.182	0.689	0.289	0.014
0.341	0.317	0.131	0.581	0.316	0.045
$x_3' = 0.75$					
0.056	0.019	0.668	0.991	0.003	0.007
0.059	0.048	0.641	0.932	0.061	0.007
0.094	0.115	0.566	0.867	0.121	0.012
0.117	0.168	0.504	0.813	0.175	0.010
0.256	0.201	0.380	0.763	0.220	0.015
0.362	0.256	0.258	0.716	0.257	0.022
0.392	0.274	0.214	0.713	0.271	0.013
0.438	0.319	0.171	0.640	0.309	0.041

[a] Obtained by mixing pure water and methanol with the binary mixtures of {x_3'methyl *tert*-butyl ether + (1 − x_3')diisopropyl ether }. [b] Mole fraction of methyl *tert*-butyl ether in the binary mixtures.

2. Experimental Section

Materials. Ethanol and methanol were supplied by the Guangzhou Chemical Reagent Factory with minimum mass fractions of 99.5% and 99.7%, respectively. DIPE was obtained from the Tianjin Chemical Reagent Institute with a mass fraction of 99.0%. MTBE was supplied by Tedia Company, Inc. with a nominal minimum mass fraction of 99.8%. Water was distilled twice.

---

* To whom correspondence should be addressed. E-mail: tlirq@jnu.edu.cn. Tel: +86-20-85220223. Fax: +86-20-85221697.

10.1021/je0500328 CCC: $30.25

Table 2. Equilibrium Phase Compositions in Mole Fraction (x) for the Quaternary Water (1) + Ethanol (2) + Methyl *tert*-Butyl Ether (3) + Diisopropyl Ether (4) Mixtures at 298.15 K

organic phase			aqueous phase		
x_1	x_2	x_3	x_1	x_2	x_3
{x_1Water + x_2Ethanol + x_3Methyl *tert*-Butyl Ether + $(1 - x_1 - x_2 - x_3)$Diisopropyl Ether}[a]					
$x_3' = 0.25$[b]					
0.038	0.009	0.184	0.974	0.023	0.002
0.063	0.039	0.177	0.950	0.045	0.002
0.076	0.065	0.172	0.929	0.066	0.002
0.092	0.128	0.158	0.904	0.091	0.002
0.149	0.170	0.134	0.894	0.101	0.002
0.206	0.214	0.114	0.872	0.120	0.003
0.323	0.276	0.078	0.831	0.158	0.004
0.446	0.297	0.050	0.815	0.175	0.004
0.482	0.324	0.035	0.771	0.203	0.007
$x_3' = 0.50$					
0.038	0.014	0.440	0.974	0.023	0.004
0.034	0.043	0.427	0.956	0.038	0.005
0.061	0.060	0.408	0.936	0.059	0.004
0.153	0.151	0.323	0.904	0.088	0.006
0.172	0.189	0.295	0.895	0.097	0.006
0.227	0.241	0.242	0.875	0.114	0.008
0.379	0.286	0.149	0.835	0.148	0.011
0.468	0.294	0.106	0.809	0.168	0.014
0.519	0.298	0.082	0.754	0.203	0.022
$x_3' = 0.75$					
0.080	0.036	0.649	0.973	0.021	0.007
0.086	0.065	0.624	0.956	0.036	0.007
0.136	0.103	0.550	0.929	0.063	0.008
0.173	0.165	0.485	0.911	0.079	0.011
0.270	0.197	0.388	0.903	0.092	0.005
0.377	0.219	0.290	0.876	0.102	0.019
0.583	0.217	0.144	0.834	0.145	0.018
0.612	0.248	0.101	0.818	0.154	0.022

[a] Obtained by mixing pure water and ethanol with the binary mixtures of {x_3'methyl *tert*-butyl ether + $(1 - x_3')$diisopropyl ether}. [b] Mole fraction of methyl *tert*-butyl ether in the binary mixtures.

Apparatus and Procedure. Quaternary LLE measurements were made at (298.15 ± 0.01) K. The quaternary mixtures were prepared by mixing the binary mixtures of MTBE and DIPE with water and then ethanol or methanol stepwise to cover the entire two-phase region. The mixtures in the equilibrium glass cell were stirred vigorously by using a magnetic stirrer for 3 h and were then allowed to settle for 3 h, which was sufficient to separate the mixtures into two layers. The headspace of the cell was filled with dry nitrogen gas to prevent contamination with moisture. The samples, withdrawn from the upper and lower phases in the cell by using a microsyringe, were analyzed by a gas chromatograph (GC-122) equipped with a thermal conductivity detector. A stainless steel column (2 m long, 3 mm i.d.) packed with Porapak QS was used to separate each component. The oven temperature of the injection port and detector was set at 483 K. The initial temperature and final temperature of the oven were kept at 453 K. The hydrogen flow rates for both the separation and reference columns were set at 1.0 $cm^3\ s^{-1}$. The peak area of the components, measured with a chromatopac (MR98S), was calibrated by gravimetrically prepared mixtures. Three analyses were made for each sample to obtain a mean value with a reproducibility of better than 0.1%. The mole fraction uncertainty was estimated to be 0.001. Tables 1 and 2 list experimental LLE results for the water + MTBE + DIPE + methanol or ethanol mixtures.

3. Calculations and Results

Calculation Procedure. The modified UNIQUAC model[7] and the extended UNIQUAC model[8] were employed to represent the experimental quaternary LLE data with binary and additional ternary and quaternary parameters.

The binary energy parameters for the miscible mixtures were obtained from the VLE data reduction according to the following thermodynamic equations by using a computer program described by Prausnitz et al.[16]

$$Py_i\varphi_i = x_i\gamma_iP_i^{s}\,\varphi_i^{s}\exp\left\{\frac{V_i^{L}(P - x_i\gamma_iP_i^{s})}{RT}\right\} \qquad (1)$$

$$\ln\varphi_i = \frac{(2\sum_j y_jB_{ij} - \sum_i\sum_j y_iy_jB_{ij})P}{RT} \qquad (2)$$

where P, x, y, and γ are the total pressure, the liquid-phase mole fraction, the vapor-phase mole fraction, and the activity coefficient, respectively. The pure component vapor pressure P^{s} was calculated by using the Antoine equation with coefficients taken from the literature.[3,6,17] The liquid molar volume V^{L} was obtained by a modified Rackett equation.[18] The fugacity coefficient φ was calcu-

Table 3. Calculated Results of Binary Phase Equilibrium Data Reduction

system(1 + 2)	T/K	no.[a]	model	a_{12}/K	a_{21}/K	$\sigma(P)$/kPa	$\sigma(T)$/K	$10^3\sigma(x)$	$10^3\sigma(y)$	lit.
ethanol + water	298.15	10	I[b]	212.17	−46.98	0.1	0.0	1.5	6.0	9
			II[c]	157.12	37.08	0.1	0.0	0.9	4.8	
ethanol + DIPE	344.17	9	I	−24.30	701.41	0.9	0.0	1.6	2.9	10
			II	−37.30	697.44	0.9	0.0	1.6	2.9	
ethanol + MTBE	328.06−351.34	54	I	−56.88	523.26	0.1	0.1	1.9	7.7	11
			II	−41.96	513.31	0.1	0.0	1.9	8.1	
methanol + water	298.14	13	I	−160.39	158.59	0.1	0.0	0.6	4.0	12
			II	−71.81	70.15	0.1	0.0	0.6	4.1	
methanol + DIPE	320.00	15	I	−86.75	614.83	0.2	0.0	0.9	4.1	13
			II	−139.87	608.60	0.2	0.0	0.9	4.1	
methanol + MTBE	313.15	37	I	−107.03	569.52	0.1	0.0	0.1	0.5	14
			II	−63.71	540.64	0.1	0.0	0.6	4.7	
MTBE + DIPE	338.05−325.95	12	I	−178.45	255.08	0.4	0.1	0.9	5.3	15
			II	−219.26	319.95	0.4	0.1	0.9	5.2	
DIPE + water	298.15	MS[d]	I	1590.60	166.68					6
			II	1075.00	163.26					
MTBE + water	298.15	MS	I	1196.10	173.24					1
			II	1023.70	399.09					

[a] Number of data points. [b] Modified UNIQUAC model. [c] Extended UNIQUAC model. [d] Mutual solubilities.

Table 4. Calculated Results for Ternary Liquid−Liquid Equilibria at 298.15 K

system(1 + 2 + 3)	no.[a]	model	ternary parameter			deviations/mol %		lit.
MTBE + methanol + water	8	I[b]	$\tau_{231} = -0.835$	$\tau_{132} = 0.943$	$\tau_{123} = -0.934$	0.33[d]	0.34[e]	2
		II[c]	$\tau_{231} = -0.815$	$\tau_{132} = 0.959$	$\tau_{123} = -0.952$	0.31	0.32	
MTBE + ethanol + water	8	I	$\tau_{231} = 1.347$	$\tau_{132} = -1.068$	$\tau_{123} = 0.747$	0.56	0.57	3
		II	$\tau_{231} = 0.4096$	$\tau_{132} = 0.567$	$\tau_{123} = 0.03$	0.74	0.77	
water + methanol + DIPE	7	I	$\tau_{231} = -1.226$	$\tau_{132} = 1.313$	$\tau_{123} = -0.893$	1.28	1.30	4
		II	$\tau_{231} = -0.383$	$\tau_{132} = -1.853$	$\tau_{123} = 6.000$	4.80	5.48	
water + ethanol + DIPE	9	I	$\tau_{231} = -0.422$	$\tau_{132} = 1.485$	$\tau_{123} = -1.746$	1.30	1.42	5
		II	$\tau_{231} = -1.034$	$\tau_{132} = -1.398$	$\tau_{123} = -1.252$	6.27	8.16	
water + MTBE + DIPE	9	I	$\tau_{231} = 0.011$	$\tau_{132} = -1.203$	$\tau_{123} = 3.848$	0.42	0.84	1
		II	$\tau_{231} = -0.566$	$\tau_{132} = 0.352$	$\tau_{123} = -11.168$	4.10	5.44	

[a] Number of tie lines. [b] Modified UNIQUAC model. [c] Extended UNIQUAC model. [d] Absolute arithmetic mean deviation. [e] Root-mean-square deviation.

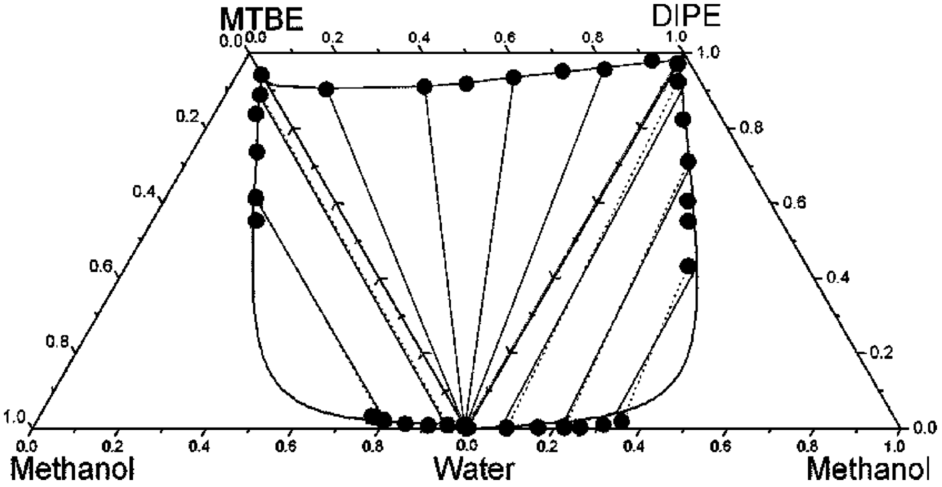

Figure 1. Experimental and calculated LLE data of three ternary mixtures (water + methanol + MTBE + DIPE) at 298.15 K. ●- - - ●, Experimental tie line; —, correlated by the modified UNIQUAC model with binary and ternary parameters.

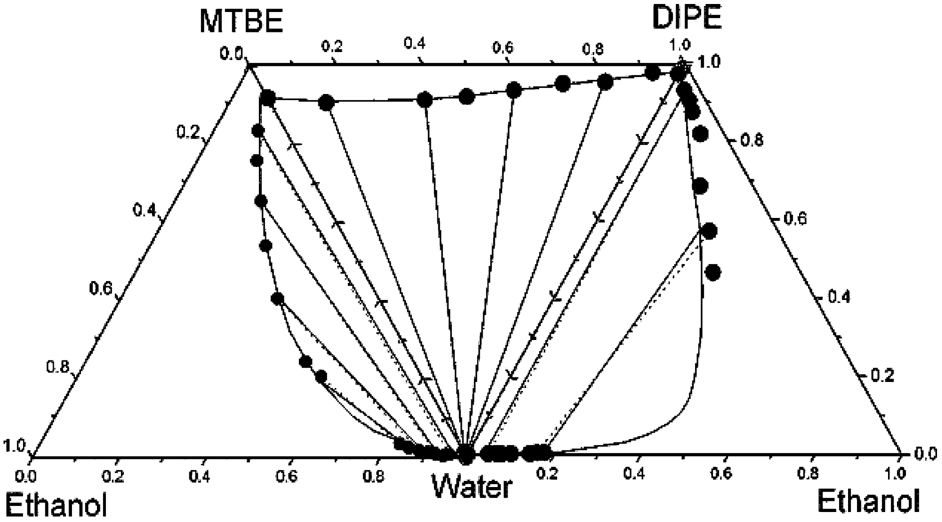

Figure 2. Experimental and calculated LLE of three ternary mixtures (water + ethanol + MTBE + DIPE) at 298.15 K. ●- - - ●, Experimental tie line; —, correlated by the modified UNIQUAC model with binary and ternary parameters.

lated from eq 2. The pure and cross second virial coefficients B were estimated by the method of Hayden and O'Connell.[19]

The binary energy parameters for the partially miscible mixtures were obtained by solving the following thermodynamic equations simultaneously.

$$(x_i\gamma_i)^{\mathrm{I}} = (x_i\gamma_i)^{\mathrm{II}} \tag{3}$$

$$\sum_i x_i^{\mathrm{I}} = 1 \text{ and } \sum_i x_i^{\mathrm{II}} = 1 \quad (\mathrm{I, II} = \text{two liquid phases}) \tag{4}$$

Table 5. Calculated Results for Quaternary Liquid−Liquid Equilibria at 298.15 K

system (1 + 2 + 3 + 4)	no.[a]	model	quaternary parameters		deviations/mol %	
water + methanol + MTBE + DIPE	25	I[b]	$\tau_{2341} = -4.301$ $\tau_{1243} = 4.909$	$\tau_{1342} = -0.056$ $\tau_{1234} = -0.597$	1.78[d]	2.35[e]
		II[c]	$\tau_{2341} = 20.450$ $\tau_{1243} = -20.269$	$\tau_{1342} = -11.474$ $\tau_{1234} = -0.014$	4.02	4.95
water + ethanol + MTBE + DIPE	26	I	$\tau_{2341} = -0.212$ $\tau_{1243} = 0.094$	$\tau_{1342} = -0.081$ $\tau_{1234} = 0.258$	2.08	2.63
		II	$\tau_{2341} = 15.286$ $\tau_{1234} = 0.868$	$\tau_{1342} = -10.418$ $\tau_{1243} = -0.852$	3.19	3.96

[a] Number of data points. [b] Modified UNIQUAC model. [c] Extended UNIQUAC model. [d] Absolute arithmetic mean deviation. [e] Root-mean-square deviation.

Ternary and quaternary LLE calculations were carried out using eqs 3 and 4. For the ternary systems of type I having a plait point, the two-parameter original UNIQUAC model predicts a generally larger solubility envelope than the experimental one, and the calculation results predicted with only binary parameters were not always good. It is necessary to correlate ternary and quaternary LLE using ternary and quaternary parameters in addition to binary ones. Ternary parameters τ_{231}, τ_{312}, and τ_{123} were obtained by fitting the two models to the ternary LLE data, and then quaternary parameters τ_{2341}, τ_{1342}, τ_{1243} and τ_{1234} were determined from the quaternary experimental LLE data using a simplex method[20] by minimizing the objective function

$$F = 10^2 \left\{ \frac{\sum_k \min \sum_i \sum_j (x_{ijk}^{\mathrm{exptl}} - x_{ijk}^{\mathrm{calcd}})^2}{M} \right\}^{0.5} \tag{5}$$

where min stands for the minimum values, $i = 1$ to 3 for ternary mixtures and $i = 1$ to 4 for quaternary mixtures, $j =$ phases I and II, $k = 1, 2,..., n$ (no. of tie lines), $M = 2ni$, and $x =$ the liquid-phase mole fraction.

Calculated Results. Table 3 presents the constituent binary energy parameters of the modified UNIQUAC and extended UNIQUAC models along with the root-mean-square deviations between the experimental and calculated values for pressure, σP, for temperature, σT, for liquid-phase mole fraction, σx, and for vapor-phase mole fraction, σy.

Table 4 shows the ternary parameters obtained by fitting the modified UNIQUAC and extended UNIQUAC models to the experimental ternary LLE data and the root-mean-square and absolute arithmetic mean deviations of the mole fraction of tie lines between the experimental and correlated results for these systems. Figures 1 and 2 compare the experimental and correlated LLE of the ternary mixtures making up the quaternary mixtures of water + MTBE + DIPE + methanol or ethanol systems at 298.15 K. Table 5 summarizes the correlated results for the quaternary mixtures obtained by fitting the modified UNIQUAC and extended UNIQUAC models with binary, ternary, and quaternary parameters to the quaternary LLE data and root-mean-square and absolute arithmetic mean deviations of the mole fraction of tie lines between the experimental and calculated results for the two quaternary systems. Absolute arithmetic mean deviations of the mole fraction of tie lines between the two quaternary experimental LLE and calculated results for the modified UNIQUAC model are 1.78 mol % and 2.08 mol %, respectively, whereas for the extended UNIQUAC model they are 4.02 mol % and 3.19 mol %, respectively. This indicates that the two models can accurately correlate the two quaternary experimental LLE data measured in this work. The quaternary LLE calculated results obtained by the modified UNIQUAC model give better agreement with experimental results.

Literature Cited

(1) Pan, Z. J.; Chen, Y. Ternary Liquid-Liquid Equilibrium for Mixtures of Water, Methyl *tert*-Butyl Ether and Diisopropyl Ether. *Guangdong Chem. Ind.* (*China*) **2005**, *1*, 30−32.

(2) Arce, A.; Blanco, A.; Blanco, M.; Soto, A.; Vidal, I. Liquid-Liquid Equilibria of Water + Methanol + (MTBE or TAME) Mixtures. *Can. J. Chem. Eng.* **1994**, *72*, 935−938.

(3) Arce, A.; Blanco, M.; Riveiro, R.; Vidal, I. Liquid-Liquid Equilibria of (MTBE or TAME) + Ethanol + Water Mixtures. *Can. J. Chem. Eng.* **1996**, *74*, 419−422.

(4) Dong, Y. H.; Chen, Y.; Pan, Z. J. Ternary and Quaternary Liquid−Liquid Equilibria of the Water + Methanol + Diisopropyl Ether and Water + Methanol + Diisopropyl Ether + Toluene Systems. *J. Chem. Ind. Eng.* (*China*), accepted for publication.

(5) Pan, Z. J.; Chen, Y.; Dong, Y. H.; Li, R. Q.; Tang, Y. Ternary Liquid-Liquid Equilibria for Mixtures of Water, Diisopropyl Ether and Toluene. *J. Jinan Univ., Nat. Sci. Med. Ed.* **2004**, *25*, 609−614.

(6) Arce, A.; Marchiaro, A.; Rodriguez, O.; Soto, A. Liquid−Liquid Equilibrium of Diisopropyl Ether + Ethanol + Water System at Different Temperatures. *J. Chem. Eng. Data* **2002**, *47*, 529−532.

(7) Tamura, K.; Chen, Y.; Tada, K.; Yamada, T.; Nagata, I. Representation of Multicomponent Liquid−Liquid Equilibria for Aqueous and Organic Solutions Using a Modified UNIQUAC Model. *J. Solution Chem.* **2000**, *29*, 463−488.

(8) Nagata, I. Modified of the Extended UNIQUAC Model for Correlating Quaternary Liquid-Liquid Equilibria Data. *Fluid Phase Equilib.* **1990**, *54*, 191−206.

(9) Hall, D. J.; Mash, C. J.; Penberton, R. C. Vapor-Liquid Equilibrium for the Systems Water + Methanol, Water + Ethanol, Methanol + Ethanol and Water + Methanol + Ethanol. *NPL Rep. Chem.* **1979**, *95*, 1−32.

(10) Lee, M.-J.; Hu, C.-H. Isothermal Vapor-Liquid Equilibria for Mixtures of Ethanol, Acetone, and Diisopropyl Ether. *Fluid Phase Equilib.* **1995**, *109*, 83−98.

(11) Arce, A.; Martinez-Ageitos, J.; Soto, A. VLE Measurements of Binary Mixtures of Methanol, Ethanol, 2-Methoxy-2-Methylpropane, and 2-Methoxy-2-Methylbutane at 101.32 kPa. *J. Chem. Eng. Data* **1996**, *41*, 718−723.

(12) Kooner, Z. S.; Phutela, R. C.; Fenby, D. V. Determination of the Equilibrium Constants Water-Methanol Deuterium Exchange Reactions from Vapour Pressure Measurements. *Aust. J. Chem.* **1980**, *33*, 9−13.

(13) Fárková, J.; Linek, J.; Wichterle, I. Isothermal Vapour-Liquid Equilibria and Excess Volumes in the Methanol-Aliphatic Ether Systems. *Fluid Phase Equilib.* **1995**, *109*, 53−65.

(14) Toghiani, R. K.; Toghiani, H.; Venkateswarlu, G. Vapor-Liquid Equilibria for Methyl *tert*-Butyl Ether + Methanol and *tert*-Amyl Methyl Ether + Methanol. *Fluid Phase Equilib.* **1996**, *122*, 157−168.

(15) Wisniak, J.; Embon, G.; Shafir, R. Isobaric Vapor−Liquid Equilibria in the Systems Methyl 1,1-Dimethylethyl Ether + 1,3-Dioxolane and Methyl 1,1-Dimethylethyl Ether + 2,2′-Oxybis-[propane]. *J. Chem. Eng. Data* **1997**, *42*, 673−676.

(16) Prausnitz, J. M.; Anderson, T. F.; Grens, E. A.; Eckert, C. A.; Hsieh. R.; O'Connell, J. P. *Computer Calculations for Multicomponent Vapor-Liquid and Liquid-Liquid Equilibria*; Prentice Hall: Englewood Cliffs, NJ, 1980.

(17) Riddick, J. A.; Bunger, W. B.; Sakano, T. K. *Organic Solvents*, 4th ed.; Wiley-Interscience: New York, 1986.

(18) Spencer, C. F.; Danner, R. P. Improved Equation for Prediction of Saturated Liquid Density.*J. Chem. Eng. Data* **1972**, *17*, 236−241.

(19) Hayden, J. G.; O'Connell, J. P. A Generalized Method for Predicting Second Virial Coefficient. *Ind. Eng. Chem. Process Des. Dev.* **1975**, *14*, 209−216.

(20) Nelder, J. A.; Mead, R. A Simplex Method for Minimization. *J. Comput.* **1965**, *7*, 308−313.

Received for review January 21, 2005. Accepted March 23, 2005. Supported by the Foundation of Ministry of Education of China (2002-247), Foundation of Scientific Research from Guangdong Province of China (2003C33101), and Foundation of Jinan University of China (640071).

JE0500328