J. Chem. Eng. Data **2005,** *50,* 2031−2034

Ternary and Quaternary Liquid−Liquid Equilibria of Water + Methanol + Diisopropyl Ether and Water + Methanol + Diisopropyl Ether + Toluene Mixtures

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Experimental tie line data of one quaternary mixture for water + methanol + diisopropyl ether + toluene system and one constituent ternary mixtures for the water + methanol + diisopropyl ether system were measured at a temperature of 298.15 K and ambient pressure. The experimental ternary and quaternary liquid−liquid equilibrium data were successfully correlated by using a modified UNIQUAC model including multibody interaction parameters in addition to binary ones. The calculated results were further compared with those obtained from the extended UNIQUAC model of Nagata.

Introduction

Various ethers have been suggested as fuel additives either alone or with other ethers or alcohols because they can enhance the octane rating and reduce air pollution. Methyl *tert*-butyl ether (MTBE) is currently the primary oxygenated compound being used in lead-free gasoline. However, there has been a growing concern over the past few years about contamination of groundwater by MTBE due to leaking storage tanks and pipelines. Therefore, it is very important to have some other oxygenates to use as alternative gasoline additives. Diisopropyl ether (DIPE) is an ideal fuel additive to replace MTBE because of its high octane number and lower vapor pressure. It has been considered a good alternative to MTBE as a blending agent in reformulated gasoline because of its antiknocking effect. Studies of phase equilibria of muticomponent systems consisting of oxygenated compounds, such as MTBE and DIPE, have gained interest in recent years, as can be seen in the literature.[1−7]

In this work, liquid−liquid equilibria (LLE) measurements were performed for one quaternary system of water + methanol + DIPE + toluene and one ternary system of water + methanol + DIPE at a temperature of 298.15 K and ambient pressure. The experimental LLE data were correlated by means of the modified UNIQUAC[8] and extended UNIQUAC models[9] including mutibody parameters coming from multicomponent intermolecular interactions, in addition to binary parameters. For a reliable representation of the quaternary LLE system, the constituent ternary systems of water + DIPE + toluene,[10] water + methanol + toluene,[5] and water + methanol + DIPE are necessary to obtain the ternary parameters. Vapor−liquid equilibrium (VLE) data and mutual solubilities of the constituent binary mixtures have been published.[4,11−15]

Experimental Section

Materials. Methanol and toluene were purchased from the Guangzhou Chemical Reagent Factory, with minimum mass fractions of 99.7 % and 99.5 %, respectively. DIPE was obtained from the Tianjin Chemical Reagent Institute with nominal minimum mass fraction of 99.0 %. All chemicals were used without further purification. The GC analysis did not detect appreciable peaks and gave mass fractions of 99.7 % for toluene, 99.4 % for DIPE, and more than 99.8 % for methanol. Water was distilled twice with mass fraction of 99.9 %.

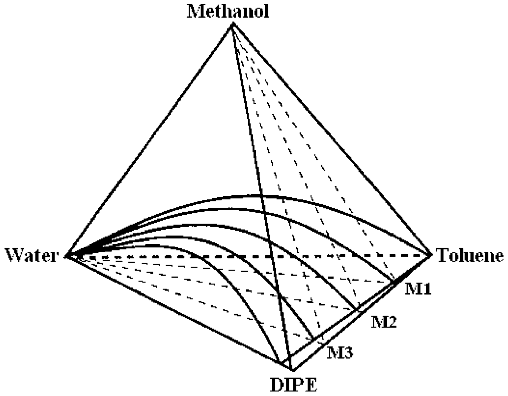

Figure 1. Phase equilibria of (water + methanol + DIPE + toluene). M1, M2, and M3 denote quaternary section planes.

Apparatus and Procedure. Ternary and quaternary LLE measurements were made at (298.15 ± 0.01) K. The quaternary mixtures were prepared by mixing the binary mixtures of DIPE and toluene, whose compositions are M1, M2, and M3 with water, and then methanol stepwise to cover the two-phase regions. The approximate values of M1, M2, and M3 are 0.25, 0.50, and 0.75, respectively, as shown in Figure 1, indicating the mole fraction of DIPE in the binary DIPE + toluene mixtures. Figure 1 shows schematically a tetrahedron to depict three planes of the quaternary LLE for the water + methanol + DIPE + toluene system. About 70 cm^3 of ternary or quaternary mixtures located in the equilibrium glass cell was stirred vigorously by using a magnetic stirrer for 3 h and 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 conduc-

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10.1021/je050258a CCC: $30.25

Table 1. Equilibrium Phase Compositions in Mole Fraction (x) for Ternary Mixtures of Water (1) + Methanol (2) + Diisopropyl Ether (3) at 298.15 K

organic phase			aqueous phase		
x_1	x_2	x_3	x_1	x_2	x_3
0.0289	0.0000	0.9711	0.9980	0.0000	0.0020
0.0516	0.0233	0.9251	0.9085	0.0906	0.0009
0.0907	0.0861	0.8232	0.8335	0.1642	0.0023
0.1344	0.1546	0.7110	0.7740	0.2231	0.0029
0.1878	0.2051	0.6071	0.7368	0.2600	0.0032
0.2144	0.2329	0.5527	0.6801	0.3094	0.0105
0.2741	0.2929	0.4330	0.6340	0.3473	0.0187

Table 2. Equilibrium Phase Compositions in Mole Fraction (x) for Quaternary Mixtures of Water (1) + Methanol (2) + Diisopropyl Ether (3) + Toluene (4) Mixtures at 298.15 K[a]

organic phase			aqueous phase		
x_1	x_2	x_3	x_1	x_2	x_3
		M1 = 0.25			
0.0048	0.0128	0.2308	0.8512	0.1464	0.0024
0.0089	0.0320	0.2222	0.8318	0.1656	0.0026
0.0100	0.0559	0.2246	0.8056	0.1908	0.0033
0.0129	0.0651	0.2132	0.7515	0.2430	0.0052
0.0145	0.0686	0.2140	0.7161	0.2764	0.0066
0.0127	0.0886	0.2020	0.6410	0.3505	0.0077
0.0132	0.0981	0.1929	0.6237	0.3652	0.0092
		M2 = 0.50			
0.0272	0.0378	0.4137	0.8740	0.1237	0.0023
0.0583	0.0876	0.4124	0.8464	0.1474	0.0062
0.0579	0.0949	0.3884	0.8209	0.1700	0.0091
0.0941	0.1635	0.3225	0.7533	0.2371	0.0092
0.0989	0.1752	0.3003	0.7365	0.2513	0.0114
0.1057	0.2064	0.2884	0.6897	0.2983	0.0112
0.1247	0.2335	0.2905	0.6414	0.3464	0.0113
0.1353	0.2558	0.2812	0.6034	0.3793	0.0157
		M3 = 0.75			
0.0522	0.0361	0.6708	0.8749	0.1221	0.0030
0.0565	0.0746	0.6449	0.8502	0.1439	0.0059
0.0671	0.0900	0.6330	0.8332	0.1608	0.0060
0.0739	0.1226	0.5925	0.7909	0.2019	0.0072
0.0697	0.1581	0.5619	0.7382	0.2523	0.0095
0.0993	0.2046	0.4944	0.6904	0.2970	0.0126
0.1032	0.2371	0.4770	0.6572	0.3280	0.0148
0.1384	0.3297	0.3753	0.6411	0.3418	0.0157
0.1625	0.3527	0.3561	0.6074	0.3681	0.0224

[a] {x_1 water + x_2 methanol + x_3 diisopropyl ether + $(1 - x_1 - x_2 - x_3)$ toluene}.

Table 3. Structural Parameters for Pure Components

component	r	q	q' [a]	q' [b]
water	0.92	1.40	1.283	0.96
methanol	1.43	1.43	1.482	1.00
DIPE	4.74	4.09	$q^{0.75}$	$q^{0.20}$
toluene	3.92	2.97	$q^{0.75}$	$q^{0.20}$

[a] Modified UNIQUAC model. [b] Extended UNIQUAC model.

tivity 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 483.15 K. The initial temperature and final temperature of the oven were kept at 453.15 K. The hydrogen flow rates for both the separation and reference columns were set at 1.1 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 the experimental ternary and quaternary tie line results for water + methanol + DIPE and water + methanol + DIPE + toluene systems at 298.15 K.

Calculation and Results

Calculation Procedure. The experimental ternary and quaternary LLE results were accurately correlated by using the modified UNIQUAC and extended UNIQUAC models with binary and additional ternary as well as quaternary parameters.

The extended UNIQUAC model has been described in detail elsewhere.[9] The binary parameter τ_{ji} defined by the binary energy parameter a_{ji} is expressed as

$$\tau_{ji} = \exp\left(-\frac{a_{ji}}{T}\right) \tag{1}$$

The modified UNIQUAC model[8] is expressed by both the combinatorial contribution given by a modified form of Gmehling et al.[16] and the residual contribution modified by introducing the third parameter C to the residual term of the extended UNIQUAC model. The adjustable binary parameter τ_{ji} is given as following equation:

$$\tau_{ji} = \exp\left(-\frac{a_{ji}}{CT}\right) \tag{2}$$

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.:[17]

$$Py_i\varphi_i = x_i\gamma_i P_i^{\mathrm{s}}\,\varphi_i^{\mathrm{s}}\exp\left\{\frac{V_i^{\mathrm{L}}(P - x_i\gamma_i P_i^{\mathrm{s}})}{RT}\right\} \tag{3}$$

$$\ln\varphi_i = \frac{(2\sum_j y_j B_{ij} - \sum_i\sum_j y_i y_j B_{ij})P}{RT} \tag{4}$$

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 literatures.[18,19] The liquid molar volume (V^{L}) was obtained by a modified Rackett equation.[20] The fugacity coefficient (φ) was calculated from eq 4. The pure and cross second virial coefficients B were estimated by the method of Hayden and O'Connell.[21]

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

$$(x_i\gamma_i)^{\mathrm{I}} = (x_i\gamma_i)^{\mathrm{II}} \tag{5}$$

$$\sum_i x_i^{\mathrm{I}} = 1 \text{ and } \sum_i x_i^{\mathrm{II}} = 1 \quad (\mathrm{I, II} = \text{two liquid phases}) \tag{6}$$

Ternary and quaternary LLE calculations were also carried out using eqs 5 and 6. Following Sørensen and Arlt,[22] the quaternary experimental data exhibit type II quaternary LLE behavior as shown in Figure 1 and are composed of two ternary LLE mixtures of type I having only one immiscible binary pairs, the water + methanol + toluene and water + methanol + DIPE systems, and one ternary LLE mixture type II having two immiscible binary pairs, the water + DIPE + toluene system. For the ternary

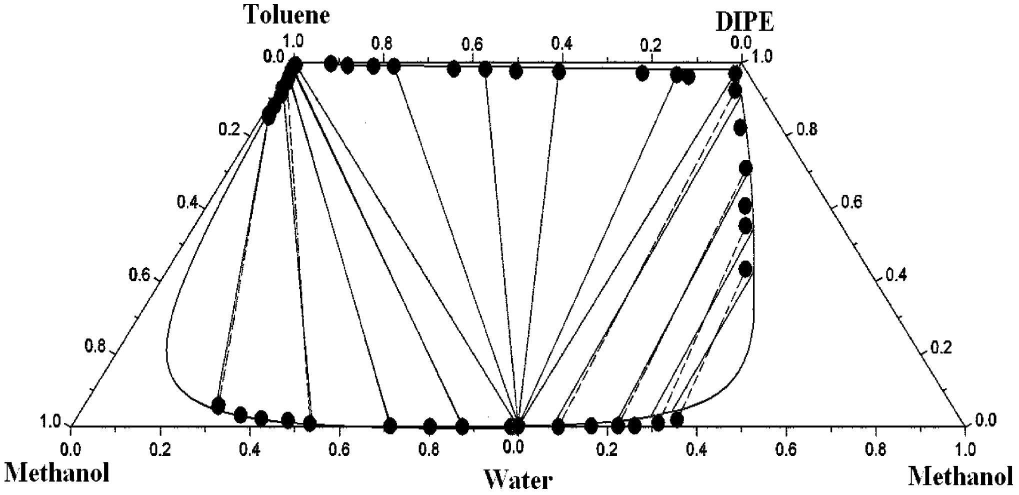

Figure 2. Experimental and calculated LLE data of three ternary mixtures making up (water + methanol + DIPE + toluene) at 298.15 K. ● − ●, experimental tie lines; —, correlated by the modified UNIQUAC model with binary and ternary parameters taken from the Tables 4 and 5.

Table 4. 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
methanol + water	298.14	13	I[b]	−160.39	158.59	0.1	0.0	0.6	4.0	11
			II[c]	−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	12
			II	−139.87	608.60	0.2	0.0	0.9	4.1	
methanol + toluene	318.05	11	I	19.30	906.82	0.1	0.0	0.1	3.0	13
			II	93.98	867.82	0.2	0.0	0.7	3.1	
toluene + DIPE	339.70−381.19	15	I	580.63	−310.42	0.9	0.4	5.0	15.0	14
			II	662.21	−390.72	1.0	0.4	6.0	14.9	
DIPE + water	298.15	MS[d]	I	1590.60	166.68					4
			II	1209.00	158.70					
toluene + water	298.15	MS	I	1713.30	752.99					15
			II	1540.70	1053.90					

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

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

system (1 + 2 + 3)	no.[a]	model	τ_{231}	τ_{132}	τ_{123}	rms[d]/mol %		lit.
water + methanol + DIPE	7	I[b]	−1.2263	1.3131	−0.8928	1.65[e]	1.30[f]	this work
		II[c]	−0.3833	−1.8533	6.0000	12.79	5.48	
water + methanol + toluene	11	I	−0.5529	−1.0604	1.3912	2.80	0.56	5
		II	−0.6123	−0.4948	0.7860	2.34	0.71	
water + toluene + DIPE	12	I	0.2258	0.3533	−3.0509	0.51	0.19	10
		II	−0.0708	−0.0116	−0.1330	6.51	5.94	

[a] Number of tie lines. [b] Modified UNIQUAC model. [c] Extended UNIQUAC model. [d] Root mean square deviation. [e] Predicted results using only binary parameters. [f] Correlated results using binary and ternary parameters.

Table 6. Calculated Results for Quaternary Liquid−Liquid Equilibria at 298.15 K

system (1 + 2 + 3 + 4)	no.[a]	model	τ_{2341}	τ_{1342}	τ_{1243}	τ_{1234}	rms[d]/mol %	
water + methanol + DIPE + toluene	24	I[b]	−2.9372	3.3320	14.2872	−11.3468	2.24[e]	1.67[f]
		II[c]	−0.4400	−9.3692	10.2752	−39.7380	2.97	2.50

[a] Number of data points. [b] Modified UNIQUAC model. [c] Extended UNIQUAC model. [d] Root mean square deviation. [e] Predicted results using binary and ternary parameters alone. [f] Correlated results using binary, ternary, and quaternary parameters.

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 so good. It is necessary to correlate ternary and quaternary LLE using ternary and quaternary parameters in addition to binary ones. The additional ternary parameters τ_{231}, τ_{312}, and τ_{123} were obtained by fitting the two models to the ternary experimental LLE data. Then the quaternary parameters τ_{2341}, τ_{1342}, τ_{1243}, and τ_{1234} were determined from the quaternary experimental LLE data using a simplex method[23] by minimizing the objective function:

$$F = 10^2 \cdot \left\{ \frac{\sum_k \min \sum_i \sum_j (x_{ijk}^{\text{exptl}} - x_{ijk}^{\text{calcd}})^2}{M} \right\}^{0.5} \tag{7}$$

where min stands for the minimum values; $i = 1$ to 3 stands for ternary mixtures; i = 1 to 4 stands for quaternary mixtures; j = phases I and II; k = 1, 2, ...; n (number of tie lines); $M = 2ni$; and x = (the liquid-phase mole fraction).

Calculated Results. Table 3 shows the molecular–structural volume and area parameters, r and q. The value for DIPE is taken from Arce et al.[4] and the others are from Prausnitz et al.[17] The interaction correction factor (q') was fixed to obtain a good representation for all binary VLE systems and mutual solubilities. The value for self-associating components was taken from the literature,[8,9] while that for nonassociating components was set to $q' = q^{0.75}$ in the modified UNIQUAC model and $q' = q^{0.20}$ in the extended UNIQUAC model. The third parameter C of eq 2 was obtained to reproduce the binary VLE and ternary LLE results as well as possible, fixed empirically as 0.65 in previous work.[8] Once q and C were set, an optimum set of the binary energy parameters was obtained using eqs 3−6 by the method of maximum likelihood principle.[17] Table 4 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 5 presents the ternary parameters obtained in fitting the modified UNIQUAC and extended UNIQUAC models to the experimental ternary LLE systems and the root mean square deviation of the mole fraction of tie lines between the experimental and calculated results for the ternary LLE systems. It seems that the modified UNIQUAC model with the only binary parameters predicts the ternary LLEs more successfully than the extended UNIQUAC model. These models can give a much more accurate representation for the ternary LLEs by including the ternary parameters in addition to the binary ones. Figure 2 compares the experimental tie lines of the ternary mixtures making up the quaternary water + methanol + DIPE + toluene system at 298.15 K with those correlated by the modified UNIQUAC model. The figure shows good agreement between ternary experiment LLE results and correlated results.

Table 6 summarizes the quaternary calculated results predicted by the modified UNIQUAC and extended UNIQUAC models with the binary and ternary parameters without using quaternary parameters, together with those obtained in fitting the modified UNIQUAC model and the extended UNIQUAC model with binary, ternary, and quaternary parameters to the quaternary LLE data. The root mean square deviations predicted using the binary and ternary parameters are slightly large for the water + methanol + DIPE + toluene system, but both models can describe accurately the quaternary experimental LLE data by the correlation involving the additional quaternary parameters.

Conclusions

Liquid−liquid equilibrium tie line data were measured for one ternary system of water + methanol + DIPE and one quaternary system of water + methanol + DIPE + toluene at 298.15 K. The correlated results using the modified UNIQUAC model for the experimental ternary LLE data are slightly better than those obtained from the extended UNIQUAC model. The calculated results obtained by both the modified UNIQUAC and extended UNIQUAC models having binary, ternary, and quaternary parameters are in good agreement with the experiment LLE results.

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Received for review July 5, 2005. Accepted September 7, 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).

JE050258A