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(Liquid + Liquid) Equilibria of Oxygenate Fuel Additives with Water: (Water + Diisopropyl Ether + 2,2,4-Trimethylpentane + Ethanol) and (Water + Diisopropyl Ether + 2,2,4-Trimethylpentane + 2-Propanol)

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The tie line of (water + ethanol + diisopropyl ether + 2,2,4-trimethylpentane), (water + 2-propanol + diisopropyl ether + 2,2,4-trimethylpentane), and (water + 2-propanol + 2,2,4-trimethylpentane) have been measured at a temperature of 298.15 K and ambient pressure. The experimental ternary and quaternary (liquid + liquid) equilibria were correlated with the modified UNIQUAC activity coefficient model including binary and multibody interaction parameters.

Introduction

Presently, several fuel oxygenates such as methanol, ethanol, methyl *tert*-butyl ether (MTBE), ethyl *tert*-butyl ether (ETBE), *tert*-amyl methyl ether (TAME), and diisopropyl ether (DIPE) are added to gasoline to enhance the octane number and to reduce air pollution. MTBE is used mostly because of its low vapor pressure and the availability of the feedstock ethanol from renewable resources. However, MTBE has the drawbacks of dissolving easily in water, being difficult to remove from water, and being resistant to microbial decomposition. These facts have promoted research on the possible use of ethers of higher molar mass that are environmentally friendly. DIPE is an ideal fuel additive to replace MTBE because of its high octane number, lower vapor pressure, and reducing automotive CO emissions. The phase equilibria of mixtures containing oxygenated compounds such as MTBE, TAME, and DIPE have been reported in the literature.[1−5]

In this paper, we report the (liquid + liquid) equilibrium (LLE) data for (water + 2-propanol + TMP), (water + DIPE + TMP + ethanol), and (water + DIPE + TMP + 2-propanol) at a temperature of 298.15 K and ambient pressure. The experimental results are reproduced by the modified UNIQUAC model,[6] including ternary and quaternary parameters obtained from the ternary and quaternary LLE data in addition to binary ones from binary phase equilibria. For a reliable representation of the quaternary LLE systems, the constituent ternary systems of (water + ethanol + DIPE),[3] (water + ethanol + TMP),[7] (water + DIPE + TMP),[4] (water + 2-propanol + DIPE),[1] and (water + 2-propanol + TMP) are necessary to obtain the ternary parameters. To obtain suitable ternary parameters, experimental LLE data of (water + 2-propanol + TMP) were measured in this work. Furthermore, the experimental and calculated results are compared with those from the literature.[8] (Vapor + liquid) equilibrium (VLE) data and mutual solubilities of the constituent binary mixtures have been published.[3,9−16]

Experimental Section

Materials. TMP was supplied by the Tianjin Damao Chemical Reagents Factory with nominal minimum mass fraction of 99.0 %. DIPE was provided by the Tianjin Kermel Chemical Reagents Development Center, with a mass fraction purity of 99.5 %. Ethanol and 2-propanol were obtained from the Tianjin Chemical Reagents Institute, both with nominal minimum mass fractions of 99.7 %. The GC analysis gave mass fractions of 99.1 % for TMP, 99.7 % for DIPE, and 99.7 % for ethanol and 2-propanol. Water was distilled twice and had a mass fraction of 99.9 %.

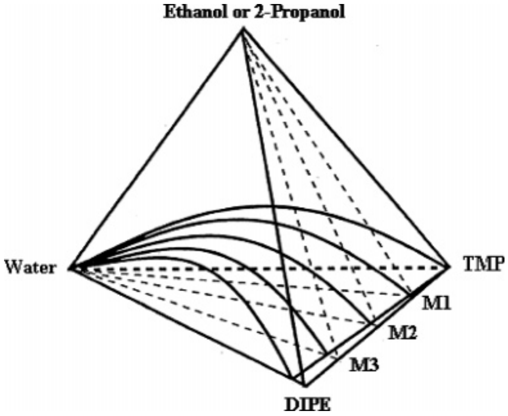

Figure 1. Phase equilibria of (water + ethanol + DIPE + TMP) and (water + 2-propanol + DIPE + TMP). M1, M2, and M3 denote quaternary section planes.

Apparatus and Procedure. The apparatus has been described in a previous paper.[2] Quaternary LLE measurements were carried out at $T = (298.15 \pm 0.01)$ K. The quaternary mixtures were prepared by mixing stepwise (DIPE + TMP) whose compositions are M1, M2, and M3 with water and then ethanol or 2-propanol to cover the two-phase region shown in Figure 1. The values of M1, M2, and M3 are approximate 0.25, 0.50, and 0.75, respectively, indicating the mole fraction of DIPE in (DIPE + TMP). About 70 cm^3 of each mixture was loaded into the equilibrium glass cell and placed in a thermostated water bath. The mixture was then stirred vigorously with a magnetic stirrer for 3 h and allowed to equilibriate for a further 3 h, which was sufficient to separate into two liquid phases. Dry nitrogen gas was used to prevent contamination with moisture in the headspace of the equilibrium cell. Samples were withdrawn from

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Table 1. Equilibrium Phase Compositions in Mole Fraction (x) for Ternary Mixtures of Water (1) + 2-Propanol (2) + 2,2,4-Trimethylpentane (3) at T = 298.15 K

organic phase			aqueous phase		
x_1	x_2	x_3	x_1	x_2	x_3
0.0049	0.0023	0.9928	0.9847	0.0153	0.0000
0.0049	0.0077	0.9874	0.9674	0.0326	0.0000
0.0086	0.0202	0.9712	0.9482	0.0518	0.0000
0.0073	0.0383	0.9544	0.9336	0.0664	0.0000
0.0101	0.0605	0.9294	0.9205	0.0795	0.0000
0.0140	0.0805	0.9055	0.9063	0.0937	0.0000
0.0219	0.1010	0.8771	0.8916	0.1084	0.0000
0.0287	0.1067	0.8646	0.8794	0.1206	0.0000
0.0495	0.1294	0.8211	0.8609	0.1391	0.0000
0.0479	0.1433	0.8088	0.8481	0.1519	0.0000
0.0497	0.1530	0.7973	0.8383	0.1617	0.0000

Table 2. Equilibrium Phase Compositions in Mole Fraction (x) for Quaternary Mixtures of Water (1) + Ethanol (2) + Diisopropyl Ether (3) + 2,2,4-Trimethylpentane (4) Mixtures at T = 298.15 K

organic phase			aqueous phase		
x_1	x_2	x_3	x_1	x_2	x_3
{(x_1) Water + (x_2) Ethanol + (x_3) Diisopropyl Ether + (1 − x_1 − x_2 − x_3) 2,2,4-Trimethylpentane}					
M1 = 0.25					
0.0004	0.0065	0.2350	0.9596	0.0404	0.0000
0.0017	0.0178	0.2314	0.9203	0.0797	0.0000
0.0045	0.0405	0.2126	0.8493	0.1492	0.0015
0.0065	0.0449	0.2020	0.8299	0.1681	0.0020
0.0177	0.0582	0.1850	0.7887	0.2088	0.0025
0.0058	0.0630	0.1775	0.7621	0.2345	0.0034
0.0120	0.0668	0.1594	0.7323	0.2633	0.0044
0.0335	0.0803	0.1445	0.7102	0.2850	0.0048
0.0037	0.0616	0.1361	0.6950	0.2999	0.0051
M2 = 0.50					
0.0028	0.0079	0.4808	0.9802	0.0189	0.0009
0.0111	0.0195	0.4702	0.9560	0.0427	0.0013
0.0108	0.0315	0.4692	0.9385	0.0602	0.0013
0.0218	0.0445	0.4513	0.9150	0.0834	0.0016
0.0038	0.0630	0.4464	0.8783	0.1195	0.0022
0.0224	0.0942	0.4318	0.8514	0.1457	0.0029
0.0187	0.1161	0.4082	0.8227	0.1739	0.0034
0.0347	0.1362	0.3186	0.7220	0.2679	0.0101
0.0288	0.1344	0.3001	0.7023	0.2863	0.0114
0.0290	0.1290	0.2831	0.6884	0.2998	0.0118
M3 = 0.75					
0.0165	0.0154	0.7102	0.9650	0.0322	0.0028
0.0202	0.0472	0.6878	0.9402	0.0584	0.0014
0.0262	0.0676	0.6610	0.9212	0.0759	0.0029
0.0403	0.1108	0.6184	0.8885	0.1089	0.0026
0.0802	0.1590	0.5514	0.8552	0.1405	0.0043
0.0850	0.2051	0.5073	0.8214	0.1716	0.0070
0.1191	0.2545	0.4173	0.7638	0.2205	0.0157
0.1285	0.2620	0.3732	0.7892	0.1995	0.0113
0.1176	0.2425	0.3637	0.6764	0.2971	0.0220

Table 3. Equilibrium Phase Compositions in Mole Fraction (x) for Quaternary Mixtures of Water (1) + 2-Propanol (2) + Diisopropyl Ether (3) + 2,2,4-Trimethylpentane (4) Mixtures at T = 298.15 K

organic phase			aqueous phase		
x_1	x_2	x_3	x_1	x_2	x_3
{(x_1) Water + (x_2) 2-Propanol + (x_3) Diisopropyl Ether + (1 − x_1 − x_2 − x_3) 2,2,4-Trimethylpentane}					
M1 = 0.25					
0.0198	0.0105	0.2522	0.9815	0.0181	0.0004
0.0138	0.0543	0.2379	0.9464	0.0531	0.0005
0.0433	0.0273	0.2462	0.9608	0.0389	0.0004
0.0439	0.0937	0.2218	0.9319	0.0675	0.0006
0.0487	0.1780	0.1972	0.9038	0.0949	0.0013
0.1129	0.2370	0.1626	0.8756	0.1224	0.0020
0.1002	0.2687	0.1513	0.8570	0.1403	0.0028
M2 = 0.50					
0.0139	0.0184	0.4992	0.9816	0.0177	0.0007
0.0779	0.0457	0.4510	0.9640	0.0352	0.0007
0.0648	0.0868	0.4364	0.9496	0.0496	0.0008
0.1019	0.2379	0.3380	0.9202	0.0784	0.0014
0.1855	0.3059	0.2595	0.9020	0.0958	0.0021
0.2818	0.3767	0.1733	0.8675	0.1282	0.0043
0.3365	0.3841	0.1407	0.8451	0.1487	0.0061
0.3589	0.3936	0.1234	0.8259	0.1652	0.0079
0.4226	0.3832	0.0966	0.7899	0.1949	0.0123
0.4511	0.3804	0.0842	0.7613	0.2190	0.0151
M3 = 0.75					
0.0584	0.0227	0.6932	0.9838	0.0150	0.0011
0.0930	0.0633	0.6371	0.9670	0.0318	0.0012
0.0684	0.1193	0.6126	0.9531	0.0456	0.0013
0.1121	0.1722	0.5401	0.9451	0.0535	0.0014
0.1364	0.2152	0.4893	0.9380	0.0603	0.0017
0.2354	0.3220	0.3336	0.9218	0.0760	0.0022
0.3020	0.3510	0.2614	0.9093	0.0881	0.0026
0.3643	0.3598	0.2080	0.9003	0.0966	0.0031
0.4121	0.3628	0.1696	0.8874	0.1076	0.0050
0.4523	0.3611	0.1404	0.8767	0.1171	0.0062
0.5688	0.3237	0.0819	0.8378	0.1504	0.0109

both upper and lower phases in the cell with a microsyringe and each was analyzed by gas chromatograph equipped with a thermal conductivity detector. Each component of the ternary and quaternary mixtures was separated with a stainless steel column (2 m long, 3 mm i.d.) packed with Porapak QS. The temperatures of the injection and detector were set at (498.15 and 518.15) K, respectively. The initial temperature and final temperature of the oven was 468.15 K. The hydrogen flow rates for both the separation and reference columns were 1.1 $\text{cm}^3\cdot\text{s}^{-1}$. The peak areas of the components, detected with a chromatopac, were calibrated with gravimetrically prepared mixtures. The mass of each component determined from the GC was determined from the calibration and converted to mole fraction. At least three analyses were performed 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.

Figure 1 shows the LLE for (water + ethanol + DIPE + TMP) and (water + 2-propanol + DIPE + TMP). Table 1 lists the experimental ternary tie line results for (water + 2-propanol + TMP) at T = 298.15 K. Tables 2 and 3 list the results for (water + ethanol + DIPE + TMP) and (water + 2-propanol + DIPE + TMP) at the same temperature.

Analysis of Experimental Data

Calculation Procedure. To represent the experimental quaternary LLE data as well as the binary VLE and ternary LLE data, we have recently proposed the modified UNIQUAC model[6] with binary and additional ternary and quaternary parameters. The excess molar Gibbs free energy (G^E) for quaternary systems is expressed by two contributions of the combinatorial and residual term; G^E_{comb} and G^E_{res}:

$$G^E = G^E_{\text{comb}} + G^E_{\text{res}} \tag{1}$$

The combinatorial term is given by a modified form of Gmehling et al.:[17]

$$\frac{G^E_{\text{comb}}}{RT} = \sum_i^4 x_i \ln\frac{\phi_i'}{x_i} - \frac{Z}{2}\sum_i^4 q_i x_i \ln\frac{\phi_i}{\theta_i} \tag{2}$$

where the coordination number Z is set to 10. The segment fraction (ϕ), the corrected segment fraction (ϕ'), and the surface fraction (θ) are given by

$$\phi_i = \frac{x_i r_i}{\sum_j^4 x_j r_j} \qquad \phi'_i = \frac{x_i r_i^{3/4}}{\sum_j^4 x_j r_j^{3/4}} \qquad \theta_i = \frac{x_i q_i}{\sum_j^4 x_j q_j} \tag{3}$$

and the residual term is modified by introducing the third parameter C to the residual term of the extended UNIQUAC model[18] and by including additional ternary and quaternary parameters, τ_{jki} and τ_{jkli}:

$$\frac{G^{\mathrm{E}}_{\mathrm{res}}}{RT} = -C \sum_i^4 q'_i x_i \ln\left(\sum_j^4 \theta_j \tau_{ji} + \frac{1}{2} \sum_{\substack{j,\\ j\neq i}}^4 \sum_{\substack{k,\\ k\neq i,\\ k\neq j}}^4 \theta_j \theta_k \tau_{jki} + \frac{1}{6} \sum_{\substack{j,\\ j\neq i}}^4 \sum_{\substack{k,\\ k\neq i,\\ k\neq j}}^4 \sum_{\substack{l,\\ l\neq i,\\ l\neq j,\\ l\neq k}}^4 \theta_j \theta_k \theta_l \tau_{jkli} \right) \tag{4}$$

The adjustable binary parameter τ_{ji} of modified UNIQUAC model is given as following equation:

$$\tau_{ji} = \exp\left(-\frac{a_{ji}}{CT}\right) \tag{5}$$

where a_{ji} is obtained from binary experimental phase equilibrium data, and T is the Kelvin temperature. The third parameter C is set equal to 0.65 in the modified UNIQUAC model. The binary energy parameters a_{ji} 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.:[19]

$$P y_i \varphi_i = x_i \gamma_i P_i^{\mathrm{s}} \varphi_i^{\mathrm{s}} \exp\left\{ \frac{V_i^{\mathrm{L}}(P - x_i \gamma_i P_i^{\mathrm{s}})}{RT} \right\} \tag{6}$$

$$\ln \varphi_i = \frac{(2 \sum_j y_j B_{ij} - \sum_i \sum_j y_i y_j B_{ij}) P}{RT} \tag{7}$$

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.[20,21] The liquid molar volume (V^{L}) was obtained by a modified Rackett equation.[22] The fugacity coefficient φ was calculated from eq 7. The pure and cross second virial coefficients B were estimated by the method of Hayden and O'Connell.[23] An optimum set of binary energy parameters for the miscible mixtures was obtained by minimizing the following objective function:

$$F = \sum_i \left[\frac{(P_i^{\mathrm{cal}} - P_i^{\mathrm{exp}})^2}{\sigma_P^2} + \frac{(T_i^{\mathrm{cal}} - T_i^{\mathrm{exp}})^2}{\sigma_T^2} + \frac{(x_i^{\mathrm{cal}} - x_i^{\mathrm{exp}})^2}{\sigma_x^2} + \frac{(y_i^{\mathrm{cal}} - y_i^{\mathrm{exp}})^2}{\sigma_y^2} \right] \tag{8}$$

where the superscripts cal and exp indicate, respectively, the most probable calculated value corresponding to each measured point and the experimental value. The standard deviations in the experimental values[19] used in eq 8 were taken as $\sigma_P = 1$ mmHg for pressure, $\sigma_T = 0.05$ K for temperature, $\sigma_x = 0.001$ for liquid-phase mole fraction, and $\sigma_y = 0.003$ for vapor-phase mole fraction.

Table 4. Structural Parameters for Pure Components

component	r	q	q'
water	0.92	1.40	1.28
ethanol	2.11	1.97	1.40
2-propanol	2.78	2.51	1.32
DIPE	4.74	4.09	$q^{0.75}$
TMP	5.85	4.94	$q^{0.75}$

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

$$(x_i \gamma_i)^{\mathrm{I}} = (x_i \gamma_i)^{\mathrm{II}} \tag{9}$$

$$\sum_i x_i^{\mathrm{I}} = 1 \text{ and } \sum_i x_i^{\mathrm{II}} = 1 \quad (\mathrm{I, II} = \text{two liquid phases}) \tag{10}$$

For the ternary systems of type 1 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 accurately correlate ternary and quaternary LLE using ternary and quaternary parameters in addition to binary ones. Ternary and quaternary LLE calculations were also carried out using eqs 9 and 10. The additional ternary parameters τ_{231}, τ_{312}, and τ_{123} were obtained by fitting the two models to the ternary 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.[24] The root-mean-square deviation between the experimental and calculated values was evaluated by

$$\beta = 10^2 \left\{ \frac{\sum_k \sum_i \sum_j (x_{ijk}^{\mathrm{exp}} - x_{ijk}^{\mathrm{cal}})^2}{M} \right\}^{0.5} \tag{11}$$

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

Calculated Results. Table 4 shows the molecular structural volume and area parameters, r and q. The value for DIPE is taken from Arce et al.,[1] and the others are from Prausnitz et al.[19] The interaction correction factor q' was fixed to obtain a good representation for all binary VLE systems and mutual solubilities. The value of q' for self-associating components was taken from the literature,[6] while that for nonassociating components was set to $q' = q^{0.75}$ in the modified UNIQUAC model. The third parameter C of eqs 4 and 5 was obtained to reproduce the binary VLE and ternary LLE results as well as possible, fixed empirically as 0.65 in previous work.[6] Once q and C were set, an optimum set of the binary energy parameters was obtained using eqs 6 to 10 by the method of maximum likelihood principle.[19] Table 5 lists the binary energy parameters of the modified UNIQUAC model for the constituent binary mixtures along with the root-mean-square deviations between experimental and calculated values: σ_P for pressure, σ_T for temperature, σ_x for liquid-phase mole fraction, and σ_y for vapor-phase mole fraction. The standard deviations between experimental results and those calculated by the model are less than 0.002 for liquid-phase mole fraction and less than 0.009 for vapor-phase mole fraction. Good agreement between experimental results and those calculated by the model was obtained.

Table 5. Calculated Results of Binary Phase Equilibrium Data Reduction

system (1 + 2)	T/K	no.[a]	a_{12}/K	a_{21}/K	$\sigma(P)$/kPa	$\sigma(T)$/K	$10^3\sigma(x)10^3$	$\sigma(y)$	lit.
ethanol + water	298.14	10	212.17	−46.98	0.6	0.0	1.5	6.0	9
ethanol + DIPE	344.17	9	−24.30	701.41	0.8	0.0	1.6	2.9	10
ethanol + TMP	298.15	10	75.50	1215.25	0.4	0.0	1.0	4.3	11
DIPE + 2-propanol	313.15	24	537.51	6.39	0.1	0.0	0.1	0.3	12
DIPE + TMP	340.85−364.55	10	110.01	−37.39	0.7	0.0	0.9	7.6	13
TMP + 2-propanol	348.15	19	903.01	57.38	1.8	0.0	2.0	8.4	14
water + 2-propanol	303.15	16	−44.88	330.21	1.7	0.0	1.3	8.0	15
DIPE + water	298.15	MS[b]	1590.60	166.68					3
TMP + water	298.15	MS	3023.30	1145.60					16

[a] Number of data points. [b] Mutual solubilities.

Table 6. Calculated Results for Ternary (Liquid + Liquid) Equilibria at T = 298.15 K

			ternary parameters			deviations		
type[a]	system (1 + 2 + 3)	no.[b]	τ_{231}	τ_{132}	τ_{123}	I[c]	II[d]	lit.
I	water + ethanol + DIPE	8	−0.4224	1.4848	−1.7460	1.62[e] 1.30[f]	1.78 1.42	3
I	water + ethanol + TMP	6	−0.2118	−0.2565	0.1161	3.90 0.98	4.28 1.00	7
II	water + TMP + DIPE	13	−0.0022	0.1311	0.1204	0.22 0.22	0.30 0.29	4
I	water + 2-propanol + DIPE	14	−0.4803	0.5168	0.4119	1.70 0.65	1.90 0.70	1
I	water + 2-propanol + TMP	11	−0.2554	−0.0890	1.8992	1.99 0.97	2.53 1.03	this work
I	water + 2-propanol + TMP	7	−0.0376	−2.5336	0.1653	5.85 2.23	7.61 2.37	8

[a] I, only one binary system shows phase separation; II, two binary systems show phase separation. [b] Number of tie lines. [c] Absolute arithmetic mean deviation (mol %). [d] Root-mean-square deviation (mol %). [e] Predicted results using binary parameters alone. [f] Correlated results using binary and ternary parameters.

Table 7. Calculated Results for Quaternary (Liquid + Liquid) Equilibria at T = 298.15 K

		quaternary parameters				deviations	
system (1 + 2 + 3 + 4)	no.[a]	τ_{2341}	τ_{1342}	τ_{1243}	τ_{1234}	I[b]	II[c]
water + ethanol + DIPE + TMP	28	0.8009	−6.3613	63.0301	−29.4679	0.56[d] 0.49[e]	0.89 0.74
water + 2-propanol + DIPE + TMP	28	0.8332	10.5604	−3.9815	−3.8407	1.45 1.44	2.00 1.95

[a] Number of tie lines. [b] Absolute arithmetic mean deviation (mol %). [c] Root-mean-square deviation (mol %). [d] Predicted results using binary and ternary parameters alone. [e] Correlated results using binary, ternary and quaternary parameters.

Table 6 presents the ternary parameters obtained in fitting the modified UNIQUAC model to the experimental ternary LLE systems constituting the quaternary LLEs, together with the absolute arithmetic mean deviation and root-mean-square deviation between the experimental and calculated tie lines for the ternary LLE systems. The calculated results of the (water + 2-propanol + TMP) system measured in this work are much better than those from the literature. The root-mean-square deviation between the experimental and correlated results with binary and ternary parameters is 1.03 %, and the root-mean-square deviation between the literature and correlated results with binary and ternary parameters is 2.37 % for the (water + 2-propanol + TMP) system. To represent accurately the experimental quaternary LLEs, we employed the ternary parameters obtaining by fitting the UNIQUAC model to the experimental LLEs of the (water + 2-propanol + TMP) system measured in this work. The correlated results obtained with the model by using binary and ternary parameters are better than the predicted ones with binary parameters alone. The model can give an accurate representation for the ternary LLEs by including the ternary parameters in addition to the binary ones.

Figure 1 shows the phase equilibria of (water + ethanol + DIPE + TMP) and (water + 2-propanol + DIPE + TMP). M1, M2, and M3 denote quaternary sectional planes. Figure 2 compares the experimental LLEs of the (water + 2-propanol + TMP) system measured in this work at T = 298.15 K with those taken from ref 8. Figure 3 compares the experimental LLEs of the ternary mixtures making up the quaternary (water + ethanol + DIPE + TMP) system at T = 298.15 K with those correlated by the modified UNIQUAC model. Figure 4 com-

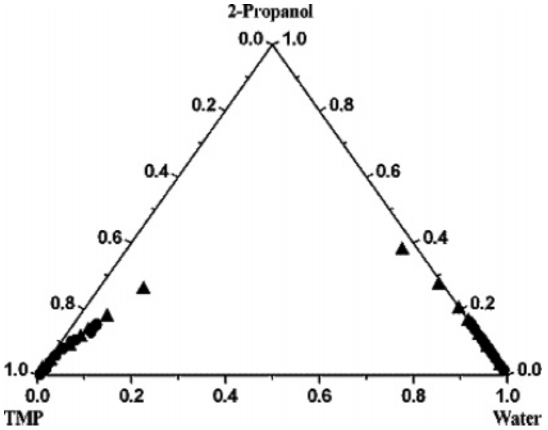

Figure 2. Experimental LLE data of (water + 2-propanol + TMP) at T = 298.15 K: ●, measured in this work; ▲, literature values taken from the ref 8.

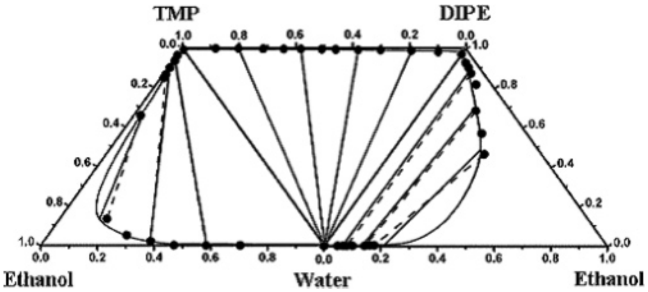

Figure 3. Experimental and calculated LLE data of three ternary mixtures making up (water + ethanol + DIPE + TMP) at $T = 298.15$ K: ● - - ●, experimental tie lines; —, correlated by the modified UNIQUAC model with binary and ternary parameters taken from Tables 5 and 6.

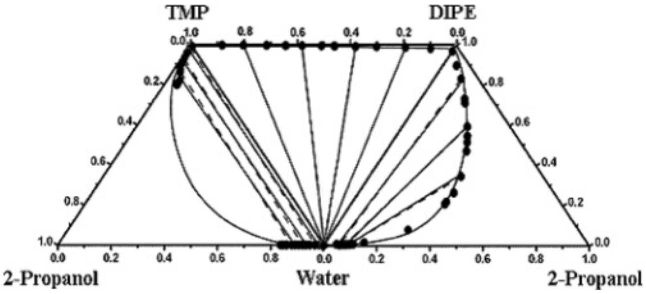

Figure 4. Experimental and calculated LLE data of three ternary mixtures making up (water + 2-propanol + DIPE + TMP) at $T = 298.15$: ● - - ●, experimental tie lines; —, correlated by the modified UNIQUAC model with binary and ternary parameters taken from Tables 5 and 6.

pares the experimental LLEs of the ternary mixtures making up the quaternary (water + 2-propanol + DIPE + TMP) system at $T = 298.15$ K with those correlated by the modified UNIQUAC model. Good agreement between the experimental values and those correlated using the additional ternary parameters was obtained. The two quaternary systems that exhibit type 2 quaternary LLE behavior, which is composed of two ternary LLEs for (water + ethanol + TMP) and (water + ethanol + DIPE) or (water + 2-propanol + TMP) and (water + 2-propanol + DIPE), classified as type 1, and one ternary LLE (water + DIPE + TMP), classified as type 2, are illustrated in Figures 3 and 4, respectively. The figures show good agreement between ternary experiment LLE results and correlated results.

Table 7 summarizes the correlated results obtained in fitting the modified UNIQUAC model with binary, ternary, and quaternary parameters to the experimental quaternary LLE data for the (water + ethanol + DIPE + TMP) and (water + 2-propanol + DIPE + TMP), together with the predicted results by the model with the binary and ternary parameters listed in Tables 5 and 6 and the correlated ones predicted by the model with additional quaternary parameters. The absolute arithmetic mean deviations calculated by the modified UNIQUAC model are slightly small as compared with the root-mean-square deviations. Moreover, the correlated results obtained from the model are better than the predicted ones in representing the quaternary system measured in this work and are in good agreement with the experimental quaternary LLE results. The root-mean-square deviation between the experimental and predicted results with only the binary and ternary parameters is 0.89 % and 2.00 % for (water + ethanol + DIPE +TMP) and (water + 2-propanol + DIPE + TMP) systems, respectively. One between the experimental and correlated results with additional quaternary parameters is 0.74 % and 1.95 % for (water + ethanol + DIPE + TMP) and (water + 2-propanol + DIPE + TMP) systems, respectively.

Conclusions

(Liquid + liquid) equilibrium tie line data were measured for (water + 2-propanol + TMP), (water + ethanol + DIPE +TMP), and (water + 2-propanol + DIPE + TMP) at $T = 298.15$ K. The experimental ternary and quaternary LLE data were successfully represented by the modified UNIQUAC model with binary and ternary parameters as well as quaternary parameters. The quaternary LLE calculated results obtained by the modified UNIQUAC model show a good agreement with experimental results.

Literature Cited

(1) Arce, A.; Arce, A., Jr.; Martínez-Ageitos, J.; Rodil, E.; Rodríguez, O.; Soto, A. Physical and equilibrium properties of diisopropyl ether + isopropyl alcohol + water system. *Fluid Phase Equilib*. **2000**, *170*, 113−126.

(2) Chen, Y.; Pan, Zh.-J.; Dong, Y.-H. Measurement and correlation of liquid−liquid equilibria for quaternary mixtures of water, methyl *tert*-butyl ether and diisopropyl ether with methanol or ethanol. *J. Chem. Eng. Data* **2005**, *50*, 1047−1051.

(3) Arce, A.; Marchiaro, A.; Rodríguez, O.; Soto, A. Liquid−liquid equilibrium of diisopropyl ether + ethanol + water system at different temperatures. *J. Chem. Eng. Data* **2002**, *47*, 529−532.

(4) Dong, Y. H.; Chen, Y.; Pan, Z. J.; Zhang, Y. M. Ternary liquid−liquid equilibria for mixtures of water, diisopropyl ether and *iso*-octane at different temperatures. *J. Jinan Univ. Nat. Sci. Med. Ed. (China)* **2006**, *27*, 87−91.

(5) Tamura, K.; Chen, Y.; Yamada, T. Liquid−liquid equilibria of oxygenate fuel additives with water at 25 °C: ternary and quaternary aqueous systems of methyl *tert*-butyl ether and *tert*-amyl methyl ether with methanol or ethanol. *J. Solution Chem.* **2001**, *30*, 291−305.

(6) 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.

(7) Sørensen, J. M.; Arlt, W. *Liquid−Liquid Equilibrium Data Collection*; DECHEMA: Frankfurt/Main, 1980; Vol. V, Part 2.

(8) Otero, J. J.; Comesana, J. F.; Correa, J. M.; Correa, A. Liquid−liquid equilibria of the system water + 2-propanol + 2,2,4-trimethylpentane at 25 °C. *J. Chem. Eng. Data* **2000**, *45*, 898−901.

(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) Gmehling, J.; Onken, U. *Vapor−Liquid Equilibrium Data Collection, Organic Hydroxy Compounds: Alcohols*; DECHEMA: Frankfurt/Main, 1977; Chemistry Data Series, Vol. 1, Part 2a.

(12) Chamorro, C. R.; Segovia, J. J.; Martín, M. C.; Villamañán, M. A. Isothermal VLE and excess molar Gibbs energy of binary and ternary mixtures containing diisopropyl ether, *n*-heptane and 2-propanol at $T = 313.15$ K. *J. Chem. Thermodyn.* **2002**, *34*, 13−28.

(13) Suresh Reddy, K. V. N.; Prasad, D. H. L.; Krishnaiah, A. Phase equilibria for binary systems of octane boosters with 2,2,4-trimethylpentane. *Fluid Phase Equilib.* **2005**, *230*, 105−108.

(14) Hiaki, T.; Tsuji, T.; Hongo, M. Isothermal vapor−liquid equilibria for 2-propanol + octane and 2-propanol + 2,2,4-trimethylpentane at 348.15 K. *Fluid Phase Equilib.* **1996**, *125*, 79−87.

(15) Gmehling, J.; Onken, U. *Vapor−Liquid Equilibrium Data Collection, Aqueous−Organic Systems*; DECHEMA: Frankfurt/Main, 1977; Chemistry Data Series, Vol. 1, Part 1.

(16) Sørensen, J. M.; Arlt, W. *Liquid−Liquid Equilibrium Data Collection*; DECHEMA: Frankfurt/Main, 1979; Vol. V, Part 1.

(17) Gmehling, J.; Li, J.; Schiller, M. A. Modified UNIFAC model. 2. Present parameter matrix and results for different thermodynamic properties. *Ind. Eng. Chem. Res.* **1993**, *32*, 178−193.

(18) Nagata, I. Modification of the extended UNIQUAC model for correlating quaternary liquid−liquid equilibria data. *Fluid Phase Equilib.* **1990**, *54*, 191−206.

(19) 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.

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

(21) Reddy, S. K. V. N.; Prasad, H. L. D.; Krishnaiah, A. Vapor−liquid equilibria for the binary systems of dimethoxymethane with some fuel oxygenates. *J. Chem. Eng. Data* **2004**, *49*, 1546−1549.

(22) Spencer, C. F.; Danner, R. P. Improved equation for prediction of saturated liquid density. *J. Chem. Eng. Data* **1972**, *17*, 236−241.

(23) 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.

(24) Nelder, J. A.; Mead, R. A simplex method for minimization. *J. Comput.* **1965**, *7*, 308−313.

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