J. Chem. Eng. Data **2010,** *55,* 2133–2139

Measurements and Correlation of Liquid−Liquid Equilibria Containing Dimethyl Carbonate and Diethyl Carbonate at $T = 298.15$ K

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(Liquid + liquid) equilibria and tie lines for the quaternary systems of (water + ethanol + dimethyl carbonate + diethyl carbonate) and (water + dimethyl carbonate + diethyl carbonate + heptane) and the ternary system of (water + dimethyl carbonate + diethyl carbonate) were measured at $T = 298.15$ K and atmospheric pressure. The experimental ternary and quaternary (liquid + liquid) equilibrium results were correlated with the modified and the extended UNIQUAC models. The average root-mean-square deviations in the two quaternary system correlations obtained by the modified and extended UNIQUAC models were 0.99 % and 1.21 %, respectively.

Introduction

1,1-Dimethylethyl methyl ether (MTBE), a widely used gasoline additive for octane and oxygen enhancement, was found to be polluting the groundwater and was not biodegradable. As a result, the research activity related to dialkyl carbonates has been motivated greatly. Dialkyl carbonates such as dimethyl carbonate (DMC) and diethyl carbonate (DEC) are recognized as environmentally benign chemicals because of their negligible toxicity and low bioaccumulation persistence, and their high oxygen content makes them promising candidates to be used as an oxygenated fuel additive to replace MTBE.[1] Although some studies on (vapor + liquid) equilibria (VLE) for binary systems of DMC or DEC + alcohols or hydrocarbons have gained interest in recent years,[2−6] (liquid + liquid) equilibria (LLE) studies of multicomponent systems containing DMC and DEC are basically rare. In the last years, our laboratory has been involved in the study of LLE of ternary and quaternary mixtures[7−9] containing DMC or DEC.

For these systematic studies, we present here LLE data obtained at the temperature of 298.15 K for the mixtures containing simultaneously DMC and DEC as ternary mixtures of (water + DMC + DEC) and quaternary mixtures of (water + ethanol + DMC + DEC) and (water + DMC + DEC + heptane). The experimental results were correlated by means of the modified UNIQUAC and extended UNIQUAC models[10,11] including both ternary and quaternary parameters coming from multicomponent intermolecular interactions, in addition to binary parameters. The binary VLE, mutual solubility, and ternary LLE relevant to the quaternaries have been available from the literature: (vapor + liquid) equilibria, (ethanol + DMC),[2] (ethanol + DEC),[3] (DMC + DEC),[4] (DMC + heptane),[5] (DEC + heptane),[6] (ethanol + water),[12] mutual solubilities, (water + DMC),[9] (water + DEC),[13] (water + heptane),[14] the constituent ternary (liquid + liquid) equilibria, (water + ethanol + DMC),[9] (water + ethanol + DEC),[13] (water + DMC + heptane),[9] (water + DEC + heptane),[13] and (water + DMC + DEC) measured in this work.

Experimental Section

Materials. The DEC was obtained from Alfa Aesar Company, with a minimum mass fraction of 0.990. DMC was supplied by Tianjin Guangfu Chemical Reagent Factory, with a mass fraction of 0.992. Ethanol was provided from Tianjin Chemical Reagent Factory, with a mass fraction of 0.997. Heptane was supplied by Guangzhou Chemical Reagent Factory, with a mass fraction of 0.997. Bidistilled water was used. Gas chromatography analysis did not detect appreciable impurity peaks and gave mass fractions of 0.9963 for heptane, 0.9940 for DMC, 0.9962 for ethanol, 0.9911 for DEC, and 0.9996 for water.

Apparatus and Procedures. Ternary and quaternary LLE measurements were carried out at $T = 298$ K. The temperature was measured with an electronic thermometer with the probe totally immersed in the thermostatted water bath. The temperature uncertainty was ± 0.05 K. A solution of volume from (60 to 150) cm^3 was loaded into the glass equilibrium cell placed in the thermostatted water bath. The mixture was then stirred vigorously by magnetic a stirrer for 3 h and then allowed to settle for 3 h, which was sufficient to separate into two liquid phases. The aqueous and organic phases were analyzed by a gas chromatograph (GC-14C) equipped with a thermal conductivity detector. Each component of the ternary and quaternary mixtures was separated cleanly, using a stainless steel column (2 m long, 3 mm i.d.) packed with Porapak QS. The temperatures of the injection system and detector were set at 513.15

Table 1. Equilibrium Phase Compositions for Ternary Mixtures of Water (1) + Dimethyl Carbonate (2) + Diethyl Carbonate (3) at $T = 298.15$ K, x_1^{I}, x_2^{I}, x_3^{I}, x_1^{II}, x_2^{II}, and x_3^{II}

aqueous phase			organic phase		
x_1^{I}	x_2^{I}	x_3^{I}	x_1^{II}	x_2^{II}	x_3^{II}
0.1339	0.8661	0.0000	0.9771	0.0229	0.0000
0.0286	0.1203	0.8511	0.9956	0.0020	0.0024
0.0303	0.2370	0.7327	0.9939	0.0042	0.0019
0.0332	0.3543	0.6125	0.9910	0.0070	0.0020
0.0449	0.4455	0.5096	0.9892	0.0089	0.0019
0.0554	0.5174	0.4272	0.9878	0.0104	0.0018
0.0693	0.6082	0.3225	0.9857	0.0126	0.0017
0.0714	0.6781	0.2505	0.9851	0.0137	0.0012
0.0851	0.7336	0.1813	0.9840	0.0150	0.0010
0.0474	0.0000	0.9526	0.9978	0.0000	0.0022

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10.1021/je900740u

Table 2. Equilibrium Phase Compositions for Quaternary Mixtures of Water (1) + Ethanol (2) + Dimethyl Carbonate (3) + Diethyl Carbonate (4) at T = 298.15 K, x_1^{I}, x_2^{I}, x_3^{I}, x_1^{II}, x_2^{II}, and x_3^{II}

aqueous phase			organic phase		
x_1^{I}	x_2^{I}	x_3^{I}	x_1^{II}	x_2^{II}	x_3^{II}
{x_1Water + x_2Ethanol + x_3Dimethyl Carbonate + $(1 - x_1 - x_2 - x_3)$Diethyl Carbonate}[a]					
$x_4' = 0.20$[b]					
0.0684	0.0000	0.7170	0.9826	0.0000	0.0165
0.0818	0.0727	0.6358	0.9490	0.0288	0.0208
0.1196	0.1224	0.5642	0.9142	0.0608	0.0229
0.1574	0.1949	0.4764	0.8878	0.0801	0.0291
0.2122	0.2266	0.4029	0.8504	0.1069	0.0372
0.2881	0.2715	0.3169	0.8065	0.1381	0.0460
$x_4' = 0.40$					
0.0514	0.0000	0.5118	0.9870	0.0000	0.0109
0.0737	0.0640	0.4586	0.9708	0.0160	0.0111
0.1123	0.1363	0.3972	0.9524	0.0328	0.0125
0.1475	0.1893	0.3342	0.9193	0.0606	0.0157
0.1812	0.2404	0.2679	0.8875	0.0918	0.0149
0.2429	0.2748	0.2151	0.8550	0.1110	0.0232
0.3170	0.3011	0.1734	0.8200	0.1409	0.0233
$x_4' = 0.60$					
0.0314	0.0000	0.3259	0.9921	0.0000	0.0059
0.0692	0.0694	0.2766	0.9728	0.0167	0.0076
0.0868	0.1364	0.2327	0.9345	0.0539	0.0079
0.1191	0.1786	0.2039	0.9105	0.0762	0.0082
0.1534	0.2202	0.1784	0.8880	0.0974	0.0084
0.1833	0.2534	0.1577	0.8568	0.1232	0.0111
0.2429	0.2887	0.1287	0.8307	0.1438	0.0119
0.3386	0.3042	0.1002	0.7783	0.1788	0.0183
$x_4' = 0.80$					
0.0329	0.0000	0.1522	0.9949	0.0000	0.0028
0.0713	0.0835	0.1483	0.9549	0.0386	0.0028
0.1151	0.1581	0.1279	0.9196	0.0721	0.0041
0.1407	0.2369	0.1090	0.8921	0.0968	0.0049
0.1881	0.2768	0.0883	0.8623	0.1229	0.0053
0.2333	0.3011	0.0699	0.8434	0.1377	0.0064
0.3304	0.3333	0.0578	0.7971	0.1712	0.0080
0.2741	0.3194	0.0683	0.8199	0.1552	0.0073

[a] Obtained by mixing pure water and ethanol with the binary mixtures of {x_4'diethyl carbonate + $(1 - x_4')$dimethyl carbonate}. [b] Mole fraction of diethyl carbonate in the binary mixtures.

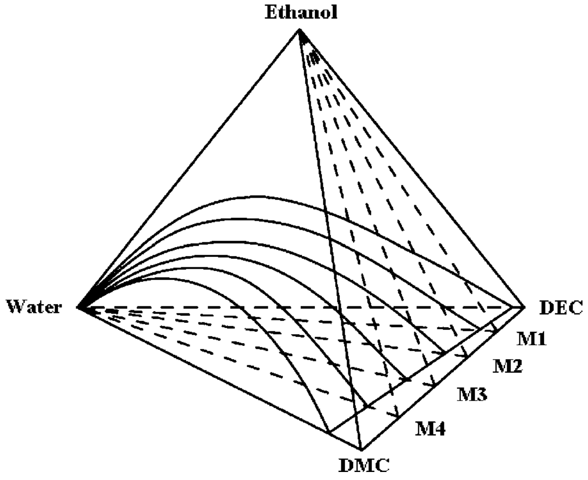

Figure 1. Phase equilibria of (water + ethanol + DMC + DEC). M1, M2, M3, and M4 denote quaternary section planes.

Table 3. Equilibrium Phase Compositions for Quaternary Mixtures of Water (1) + Dimethyl Carbonate (2) + Diethyl Carbonate (3) + Heptane (4) at T = 298.15 K, x_1^{I}, x_2^{I}, x_3^{I}, x_1^{II}, x_2^{II}, and x_3^{II}

aqueous phase			organic phase		
x_1^{I}	x_2^{I}	x_3^{I}	x_1^{II}	x_2^{II}	x_3^{II}
{x_1Water + x_2Dimethyl Carbonate + x_3Diethyl Carbonate + $(1 - x_1 - x_2 - x_3)$Heptane}[a]					
$x_3' = 0.20$[b]					
0.0684	0.7170	0.2146	0.9826	0.0165	0.0009
0.0314	0.6912	0.2119	0.9818	0.0172	0.0010
0.0183	0.6271	0.1899	0.9844	0.0150	0.0006
0.0138	0.5556	0.1644	0.9842	0.0151	0.0007
0.0125	0.4797	0.1443	0.9840	0.0154	0.0006
0.0088	0.3983	0.1218	0.9875	0.0119	0.0006
0.0102	0.3274	0.1026	0.9861	0.0133	0.0005
0.0067	0.2439	0.0818	0.9851	0.0132	0.0007
$x_3' = 0.40$					
0.0514	0.5118	0.4368	0.9870	0.0109	0.0021
0.0357	0.4587	0.4067	0.9887	0.0098	0.0014
0.0198	0.4492	0.3776	0.9871	0.0117	0.0012
0.0121	0.3876	0.3294	0.9875	0.0113	0.0012
0.0111	0.3344	0.2812	0.9908	0.0082	0.0010
0.0093	0.2662	0.2330	0.9898	0.0092	0.0010
0.0097	0.2182	0.1931	0.9908	0.0083	0.0009
0.0024	0.1725	0.1636	0.9908	0.0082	0.0009
0.0016	0.1376	0.1312	0.9930	0.0062	0.0007
$x_3' = 0.60$					
0.0314	0.3259	0.6427	0.9921	0.0059	0.0020
0.0218	0.3016	0.5954	0.9930	0.0051	0.0018
0.0173	0.2788	0.5523	0.9921	0.0063	0.0015
0.0150	0.2455	0.4693	0.9937	0.0049	0.0014
0.0106	0.2016	0.4026	0.9918	0.0066	0.0016
0.0095	0.1683	0.3459	0.9936	0.0050	0.0014
0.0070	0.1122	0.3096	0.9929	0.0058	0.0012
0.0039	0.1068	0.2462	0.9933	0.0053	0.0013
0.0049	0.0992	0.2025	0.9920	0.0048	0.0017
$x_3' = 0.80$					
0.0329	0.1522	0.8149	0.9949	0.0028	0.0023
0.0289	0.1410	0.7682	0.9950	0.0028	0.0022
0.0289	0.1276	0.6811	0.9958	0.0023	0.0018
0.0138	0.1050	0.5941	0.9954	0.0028	0.0018
0.0103	0.0606	0.5296	0.9963	0.0018	0.0019
0.0087	0.0533	0.4618	0.9964	0.0018	0.0018
0.0058	0.0474	0.3843	0.9963	0.0019	0.0017
0.0051	0.0407	0.3185	0.9963	0.0019	0.0017
0.0044	0.0344	0.2506	0.9964	0.0019	0.0015

[a] Obtained by mixing pure water and heptane with the binary mixtures of {x_3'diethyl carbonate + $(1 - x_3')$dimethyl carbonate}. [b] Mole fraction of diethyl carbonate in the binary mixtures.

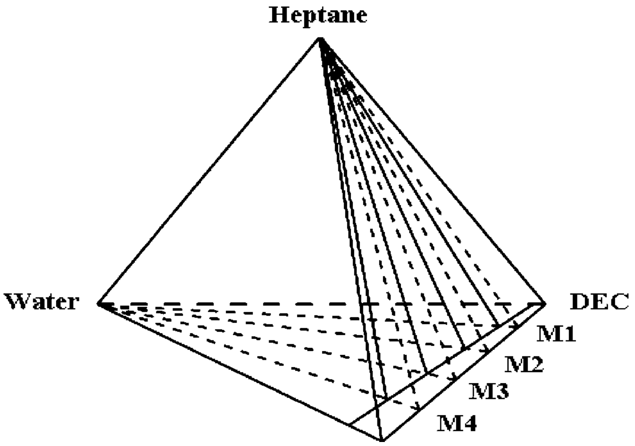

Figure 2. Phase equilibria of (water + DMC + DEC + heptane). M1, M2, M3, and M4 denote quaternary section planes.

K, respectively. The initial and final temperatures of the oven were kept at (423.15 and 493.15) K, respectively. The hydrogen flow rates for both the separation and reference columns were set at 1 $\mathrm{cm^3 \cdot s^{-1}}$. The peak areas of the components, detected with a chromatopac (N2000), were calibrated with known mixtures prepared by mass. The mass of each component of the mixture was determined from the calibration and converted to mole fraction. Three analyses at least for each sample were

Table 4. Structural Parameters for Pure Components

component	r	q	q'^{a}	q'^{b}
water	0.92	1.40	1.28	0.96
ethanol	2.11	1.97	1.40	0.92
DMC	3.06	2.82	$q^{0.75}$	$q^{0.20}$
DEC	4.41	3.90	$q^{0.75}$	$q^{0.20}$
heptane	5.17	4.40	$q^{0.75}$	$q^{0.20}$

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

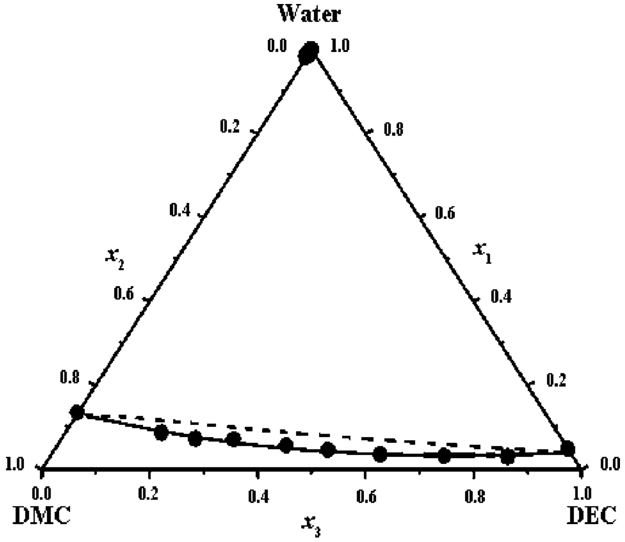

Figure 3. Experimental and calculated LLE of the ternary system (water + DMC + DEC) at $T = 298.15$ K. ●, Experimental tie-line data; - - -, predicted by the modified UNIQUAC with binary parameters taken from Table 5; —, correlated curve by the modified UNIQUAC with binary and ternary parameters taken from Tables 5 and 6.

made to obtain a mean value. The estimated uncertainty of mole fraction was about ± 0.0001.

Tables 1, 2, and 3 list the experimental tie-line compositions for three quaternary systems of (water + ethanol + DMC + DEC) and (water + DMC + DEC + heptane) and one ternary system of (water + DMC + DEC) at $T = 298.15$ K. Figures 1 and 2 represent schematically a tetrahedron to show the quaternary LLE surface for the (water + ethanol + DMC + DEC) and (water + DMC + DEC + heptane) systems, respectively. The quaternary mixtures were prepared by mixing stepwise the binary (DMC + DEC) mixtures whose compositions are M1, M2, M3, and M4 with water and then ethanol or heptane to cover the two-phase regions. The values of M1, M2, M3, and M4 are approximately 0.20, 0.40, 0.60, and 0.80, respectively, indicating the mole fraction of DEC in the binary (DMC + DEC) mixtures.

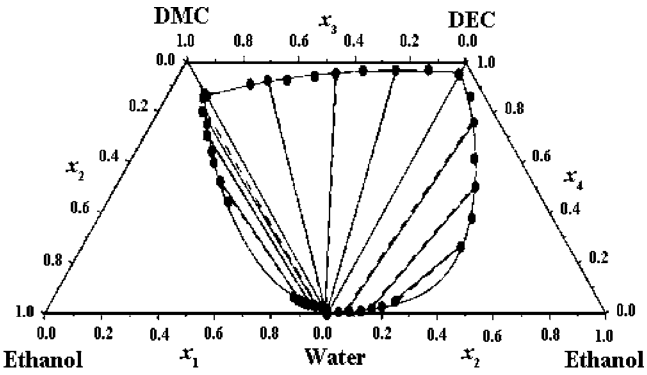

Figure 4. Experimental and calculated LLE composition in mole fraction for three ternary mixtures making up (water + ethanol + DMC + DEC) at $T = 298.15$ K. ●, Experimental tie-line data; - - -, experimental tie lines; —, correlated curve by the modified UNIQUAC model.

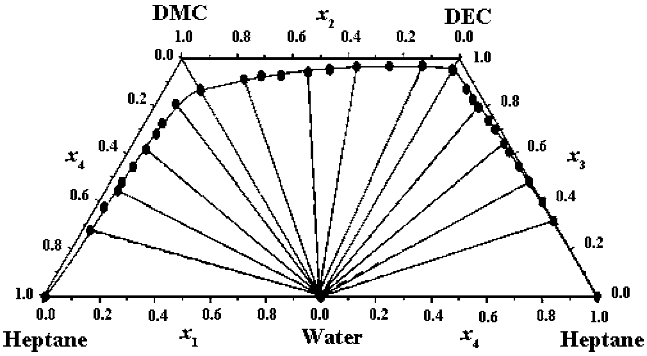

Figure 5. Experimental and calculated LLE compositions in mole fraction for three ternary mixtures making up (water + DMC + DEC + heptane) at $T = 298.15$ K. ●, Experimental tie-line data; - - -, experimental tie lines; —, correlated curve by the modified UNIQUAC model.

Calculated Results and Discussion

The binary energy parameters, a_{ij}, for completely miscible binary mixtures were obtained from experimental VLE data by

Table 5. Calculated Results of Binary Phase Equilibrium Data Reduction

	T		a_{12}	a_{21}	$\delta(P)$				
system (1 + 2)	K	model	K	K	kPa	$\delta(T)$	$10^3\delta(x)$	$10^3\delta(y)$	lit.
ethanol + DMC	313.15	I[a]	162.17	405.48	1.7	0.0	2.0	15.0	2
		II[b]	185.97	408.34	1.7	0.0	1.9	14.9	
ethanol + DEC	351.73 to 396.02	I	39.56	314.63	1.7	0.1	3.0	8.9	3
		II	52.02	314.40	1.7	0.1	3.0	8.9	
ethanol + water	298.15	I	212.17	−46.98	0.1	0.0	1.5	6.0	12
		II	157.12	37.08	0.1	0.0	0.9	4.8	
DMC + DEC	313.15	I	300.44	−133.97	1.5	0.0	0.6	5.1	4
		II	326.89	−105.75	1.5	0.0	0.6	5.1	
DMC + heptane	355.26 to 369.10	I	104.88	237.94	1.6	0.1	1.1	6.6	5
		II	169.86	275.40	1.7	0.1	1.3	6.4	
DEC + heptane	371.49 to 398.17	I	31.52	143.66	1.3	0.1	0.8	8.0	6
		II	69.36	181.24	1.3	0.1	0.8	7.9	
water + DMC	298.15	I	269.81	702.87					9
		II	272.17	585.84					
water + DEC	298.15	I	248.21	1177.60					13
		II	273.66	961.41					
water + heptane	298.15	I	1022.10	1884.20					14
		II	1839.60	2135.50					

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

Table 6. 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,e] (%)	rms[d,f] (%)	lit.
water + ethanol + DMC	9	I[b]	−0.1108	1.3880	1.2213	4.02	0.49	9
		II[c]	0.1994	0.4156	−0.5833	3.05	2.36	
water + ethanol + DEC	7	I	0.1954	−0.0024	0.1186	2.36	1.28	13
		II	−0.6851	1.7185	−1.4540	2.80	1.11	
water + DMC + DEC	10	I	0.0477	−1.3697	−0.8088	1.49	0.98	this work
		II	−0.2400	0.0148	0.0206	2.71	0.97	
water + DMC + heptane	11	I	0.2498	−1.9334	−0.1868	0.75	0.50	9
		II	0.0003	−1.9978	−0.0011	2.58	0.97	
water + DEC + heptane	13	I	−0.0335	0.1110	0.0566	0.48	0.25	13
		II	−0.0374	0.1580	−0.8556	1.31	0.73	

[a] Number of tie lines. [b] Modified UNIQUAC model. [c] Extended UNIQUAC model. [d] Root-mean-square deviation. [e] Predicted results using binary parameters taken from Table 5. [f] Correlated results using binary and ternary parameters.

Table 7. 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,e] (%)	rms[d,f] (%)
water + ethanol + DMC + DEC	29	I[b]	1.1316	4.6115	3.5566	−1.8272	3.89	1.66
		II[c]	4.7587	−13.7194	16.4596	−8.8038	2.61	1.83
water + DMC +DEC + heptane	35	I	−0.1877	−21.6249	−20.9933	2.9290	0.72	0.32
		II	0.3172	−9.5716	−30.2228	6.7846	0.74	0.59

[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 taken from Tables 5 and 6. [f] Correlated results using binary, ternary, and quaternary parameters.

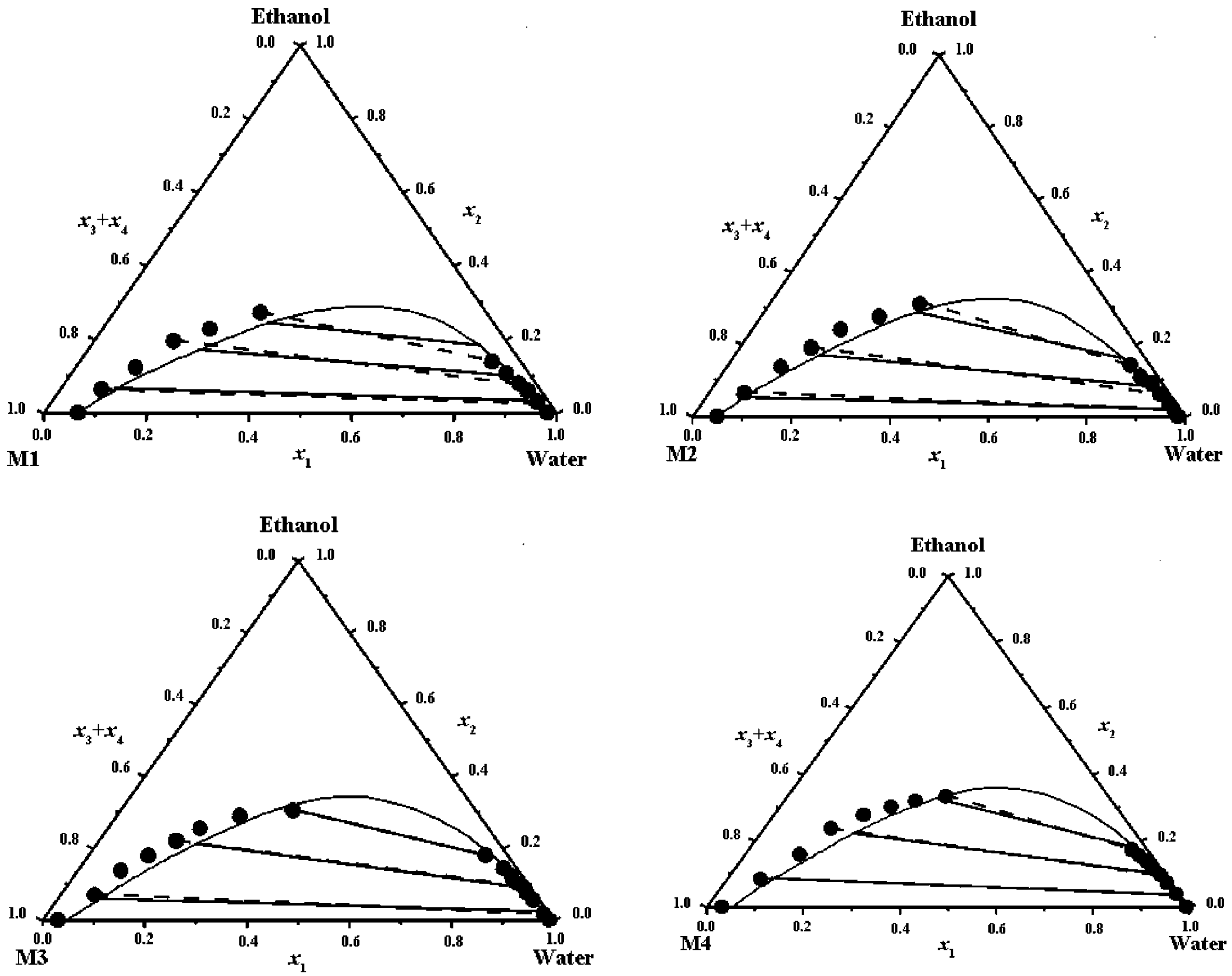

Figure 6. Experimental and calculated LLE compositions in mole fraction on the planes M1, M2, M3, and M4 for quaternary mixtures of (water + ethanol + DMC + DEC) at T = 298.15 K. ●, Experimental tie-line data; - - -, experimental tie lines; −, correlated curve by the modified UNIQUAC model.

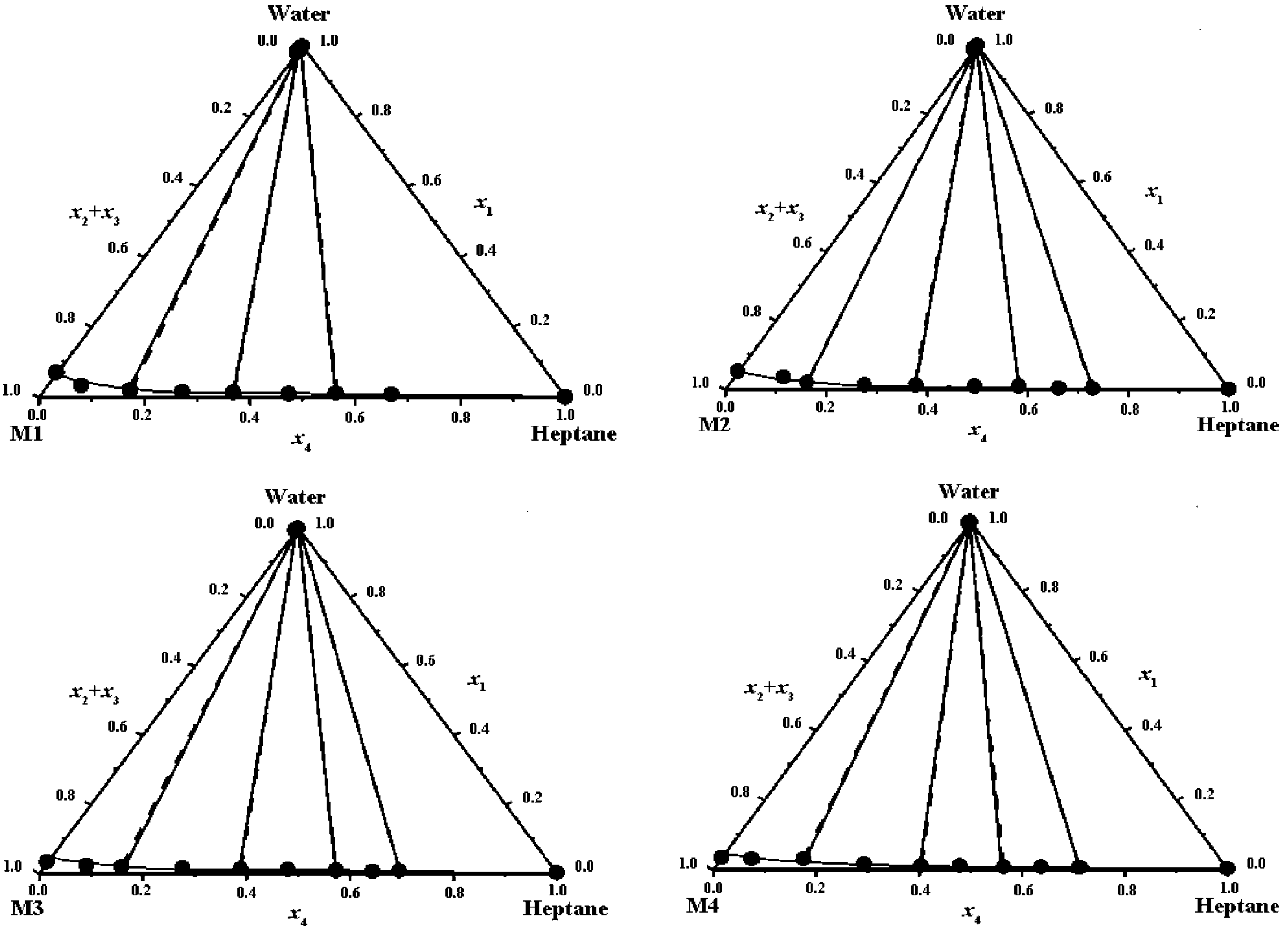

Figure 7. Experimental and calculated LLE composition in mole fraction on the planes M1, M2, M3, and M4 for quaternary mixtures of (water + DMC + DEC + heptane) at T = 298.15 K. ●, Experimental tie-line data; - - -, experimental tie lines; —, correlated curve by the modified UNIQUAC model.

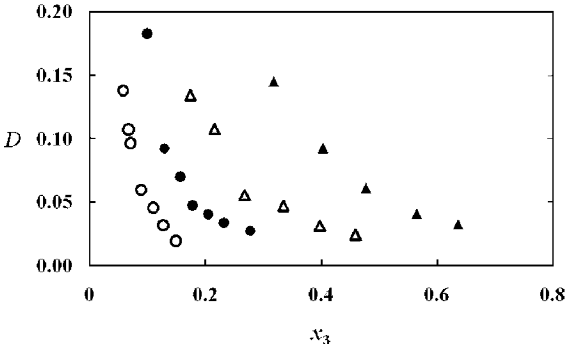

Figure 8. Distribution ratio of DMC in the quaternary system of (water + ethanol + DMC + DEC), D, at 298.15 K as a function of mole fraction of DMC in the organic-rich phase, x_3. ▲, △, ●, ○, x_4' = 0.2, 0.4, 0.6, and 0.8, respectively.

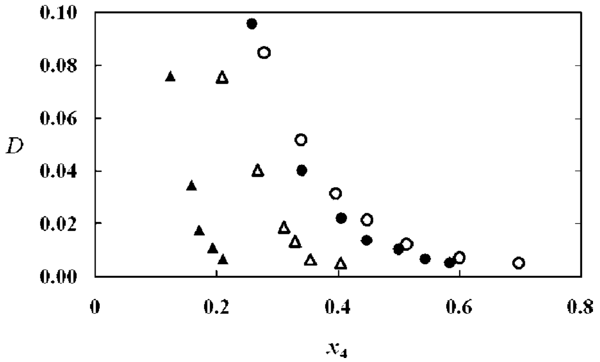

Figure 9. Distribution ratio of DEC in the quaternary system of (water + ethanol + DMC + DEC), D, at 298.15 K as a function of mole fraction of DEC in the organic-rich phase, x_4. ▲, △, ●, ○, x_4' = 0.2, 0.4, 0.6, and 0.8, respectively.

using a computer program described by Prausnitz et al.[15] The binary energy parameters for partially miscible binary mixtures were obtained from the mutual solubility data by solving the thermodynamic criteria and mass balance equation.

$$(x_i\gamma_i)^{\mathrm{I}} = (x_i\gamma_i)^{\mathrm{II}} \tag{1}$$

$$\sum_i x_i^{\mathrm{I}} = 1 \text{ and } \sum_i x_i^{\mathrm{II}} = 1 \tag{2}$$

where I and II represent the equilibrium phases; x is the liquid phase mole fraction; and γ is the activity coefficient. I is the number of components; x is the liquid-phase mole fraction; and γ is the activity coefficient given by the modified UNIQUAC or extended UNIQUAC models described in detail.[10,11] To obtain an accurate description for the ternary LLE, it is necessary to use ternary parameters. Ternary parameters τ_{231}, τ_{312}, and τ_{123} and the quaternary parameters τ_{2341}, τ_{1342}, τ_{1243}, and τ_{1234} were determined from the experimental LLE data using a simplex method[16] by minimizing the objective function

$$F = 10^2[\sum_k \min \sum_i \sum_j (x_{ijk}^{\mathrm{exp}} - x_{ijk}^{\mathrm{cal}})^2/M]^{0.5} \tag{3}$$

where min denotes minimum values; i = 1 to 3 for ternary mixtures or i = 1 to 4 for quaternary mixtures; j = 1, 2 (phases);

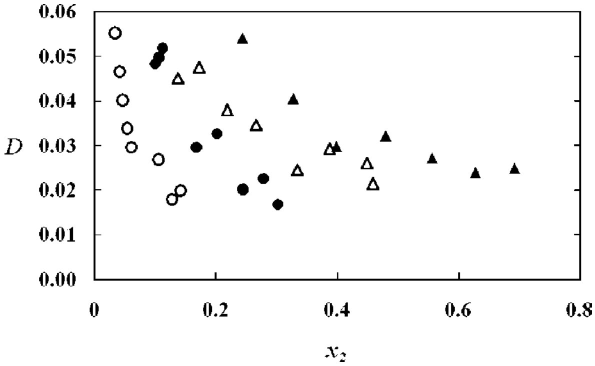

Figure 10. Distribution ratio of DMC in the quaternary system of (water + DMC + DEC + heptane), *D*, at 298.15 K as a function of mole fraction of DMC in the organic-rich phase, x_2. ▲, △, ●, ○, $x_3' = 0.2$, 0.4, 0.6, and 0.8, respectively.

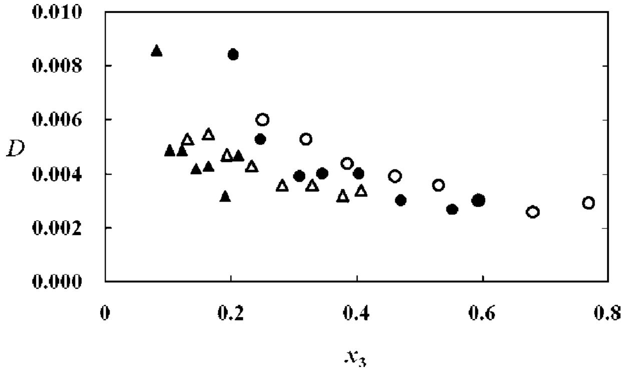

Figure 11. Distribution ratio of DEC in the quaternary system of (water + DMC + DEC + heptane), *D*, at 298.15 K as a function of mole fraction of DEC in the organic-rich phase, x_3. ▲, △, ●, ○, $x_3' = 0.2$, 0.4, 0.6, and 0.8, respectively.

$k = 1, 2, ... n$ (no. of tie lines); $M = 2ni$; and x denotes the liquid phase mole fraction.

Table 4 shows the molecular structural volume and area parameters, *r* and *q*, for DMC and DEC which were calculated by the method of Bondi.[17] The others are taken from Prausnitz et al.,[15] together with the interaction correction factor q', for which the value for self-associating components was taken from the literature,[10,11] 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.

Table 5 lists the binary parameters of the modified UNIQUAC and extended UNIQUAC models for the constituent binary mixtures, along with the root-mean-square deviations between experimental and calculated values: δ_P for pressure, δ_T for temperature, δ_x for liquid phase mole fraction, and δ_y for vapor phase mole fraction. Good agreement between experimental results and those calculated by both models was obtained.

Table 6 presents the ternary parameters, together with the root-mean-square deviation between the experimental and calculated tie-lines for the ternary LLE. The average root-mean-square deviations in the ternary correlations obtained by the modified and extended UNIQUAC models were 0.70 % and 1.23 %, respectively. Figure 3 shows experimental and calculated results for the ternary system (water + DMC + DEC) measured in this work. Figures 4 and 5 show individually the experimental and correlated results for three sets of the ternary systems constituting the quaternary mixtures (water + ethanol + DMC + DEC) and (water + DMC + DEC + heptane) at 298.15 K. Good agreement between the experimental values and those correlated using the additional ternary parameters is shown in Figures 4 and 5.

Table 7 summarizes the correlated results for the quaternary systems obtained in fitting the modified and extended UNIQUAC models with binary, ternary, and quaternary parameters to the experimental quaternary LLE data, together with the predicted results by the models with binary and ternary parameters listed in Tables 5 and 6. The (water + ethanol + DMC + DEC) system exhibits type 1 quaternary LLE behavior,[18] which is composed of two ternary LLE for (water + ethanol + DEC) and (water + ethanol + DMC) that are classified as type 1 and one ternary LLE for (water + DMC + DEC) as type 2, and is illustrated in Figure 1. The (water + DMC + DEC + heptane) system exhibits type 2 quaternary LLE behavior, which is composed of three ternary LLE for (water + DMC + DEC), (water + DMC + heptane), and (water + DEC + heptane) as type 2 and is illustrated in Figure 2. Figures 6 and 7 compare the experimental and calculated results for the quaternary LLE of the (water + ethanol + DMC + DEC) and (water + DMC + DEC + heptane) systems, which are plotted on planes M1, M2, M3, and M4 illustrated in Figures 1 and 2. Good agreement between experimental LLE results and correlated results of the modified UNIQUAC model is shown in Figures 6 and 7. The correlated results obtained from both models are better than the predicted ones in representing the quaternary LLE measured in this work. The average root-mean-square deviations in the quaternary correlations obtained by the modified and extended UNIQUAC models were 0.99 % and 1.21 %, respectively.

Distribution ratio (*D*) is an important parameter in assessing the influence of DMC or DEC addition on aqueous and organic phases. The distribution ratio *D* was defined by

$$D = \frac{x_i^{\mathrm{I}}}{x_i^{\mathrm{II}}} \tag{4}$$

x_i^{I} and x_i^{II} are the mole fraction of DMC or DEC in aqueous and organic phases, respectively. The distribution ratio *D* was calculated from the experimental LLE data. Figures 8, 9, 10, and 11 show the distribution ratios of DMC and DEC in the quaternary systems of (water + ethanol + DMC + DEC) and (water + DMC + DEC + heptane) as a function of its mole fraction in the organic-rich phase. For the quaternary system, the distribution ratios of DMC and DEC are quite small, and the distribution ratios of DMC and DEC decreased as its mole fraction in the organic-rich phase increased. This implies that the addition of DMC and DEC does not increase evidently the solubility of DMC and DEC in the aqueous phase. As gasoline additives, the addition of DMC and DEC does not cause phase separation.

Conclusions

Experimental tie-line compositions for the quaternary systems of (water + ethanol + dimethyl carbonate + diethyl carbonate) and (water + dimethyl carbonate + diethyl carbonate + heptane) and ternary systems of (water + dimethyl carbonate + diethyl carbonate) were measured at $T = 298.15$ K and ambient pressure. The experimental LLE data were successfully correlated by using the modified and extended UNIQUAC models with multicomponent parameters in addition to binary ones. Both of the models involving binary and multicomponent interaction parameters show excellent correlative ability for the experimental quaternary LLE results.

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Received for review September 10, 2009. Accepted November 4, 2009. The authors thank the financial support from National Natural Scientific Research fund of China (20971056) and the Ministry of Education of China (2006-52).

JE900740U