Measurements and Correlation of Liquid–Liquid Equilibria of (Water + Ethanol + Dimethyl Carbonate + 2,2,4-Trimethylpentane or *n*-Heptane) and (Water + Dimethyl Carbonate + *n*-Heptane + Toluene)

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The experimental equilibrium tie-line compositions for the three quaternary mixtures of (water + ethanol + dimethyl carbonate + 2,2,4-trimethylpentane), (water + ethanol + dimethyl carbonate + *n*-heptane), and (water + dimethyl carbonate + *n*-heptane + toluene) and the five ternary mixtures of (water + ethanol + dimethyl carbonate), (water + dimethyl carbonate + *n*-heptane), (water + dimethyl carbonate + 2,2,4-trimethylpentane), (water + dimethyl carbonate + toluene), (water + *n*-heptane + toluene) have been measured at a temperature of 298.15 K and ambient pressure. The experimental ternary and quaternary (liquid + liquid) equilibrium data were correlated with the modified and extended UNIQUAC models including binary and multicomponent interaction parameters.

1. Introduction

Recently, methyl *tert*-butyl ether (MTBE), a widely used gasoline additive for octane and oxygen enhancement, was found to be polluting the groundwater and was nonbiodegradable. As a result, the research activity related to dimethyl carbonate (DMC) has been motivated greatly. The most intriguing market opportunities of DMC are as a gasoline additive and painting solvent.[1,2] DMC is a strong contender to assist the refining industry in meeting the Clean Air Act specifications for oxygen in gasoline. DMC has about 3 times the oxygen content as MTBE and excellent characteristics as a gasoline additive: high octane, low RVP, reduced CO and NO *x* emissions, and a very high density. DMC may be an ideal gasoline additive to replace MTBE.

Although many studies on (vapor + liquid) equilibria (VLE) for binary systems of DMC + aromatic or naphthenic hydrocarbons have gained interest in recent years, (liquid + liquid) equilibria (LLE) of DMC with other components are basically rare.[3–5] Separation and processes design often relies on thermodynamic data of the mixtures. A synthetic gasoline is represented by a mixture of aromatic and naphthenic hydrocarbons, e.g., toluene and 2,2,4-trimethylpentane (TMP). Therefore, additional studies on the phase behavior of systems that contain hydrocarbons, water, and DMC are necessary to improve our knowledge of these types of systems. Experience shows that the commercial gasoline distribution system always contains water because of air humidity or infiltration into storage tanks. So, water was included in this study.

Here we report LLE measurements at 298.15 K on three quaternary systems, (water + ethanol + DMC + TMP), (water + ethanol + DMC + *n*-heptane), and (water + DMC + *n*-heptane + toluene), and five relevant ternary systems, (water + ethanol + DMC), (water + DMC + *n*-heptane), (water + DMC + TMP), (water + DMC + toluene), and (water + *n*-heptane + toluene). The experimental tie-line data were correlated by means of the modified UNIQUAC and extended UNIQUAC models[6,7] including ternary and quaternary parameters coming from multicomponent intermolecular interactions in addition to binary parameters. The binary parameters of miscible binary mixtures of constituents of the ternary and quaternary systems were obtained from VLE data,[8–14] and those of immiscible mixtures were obtained from mutual solubility data.[15,16] To accurately represent the three quaternary LLE data studied in this work, ternary parameters constituting the quaternary mixtures are necessary and obtained from the ternary systems, (water + ethanol + TMP),[17] (water + ethanol + *n*-heptane),[18] (water + ethanol + DMC), (water + DMC + *n*-heptane), (water + DMC + TMP), (water + DMC + toluene), and (water + *n*-heptane + toluene), which were measured in this work.

2. Experimental Section

Materials. The DMC was obtained from Tianjin Guangfu Chemical Reagents Factory with a nominal minimum mass fraction of 99.2 %. TMP was supplied by the Tianjin Damao Chemical Reagents Factory with a nominal minimum mass fraction of 99.0 %. Ethanol was provided from Tianjin Chemical Reagent Factory with nominal minimum mass fraction of 99.7 %. Toluene and *n*-heptane were supplied by the Guangzhou Chemical Reagent Factory, both with nominal minimum mass fractions of 99.5 % and 99.7 %. The g.c. analysis gave mass fractions of 99.1 % for DMC, 99.5 % for toluene, and 99.7 % for ethanol, TMP, and *n*-heptane. Water was distilled twice and had a mass fraction of 99.9 %.

Apparatus and Procedure. The experimental apparatus was the same as that reported in detail previously.[19] The quaternary (liquid + liquid) measurements were carried out at the temperature (298.15 ± 0.01) K. The experimental procedure in this work was performed as follows. The quaternary mixtures for (water + ethanol + DMC + TMP) and (water + ethanol + DMC + *n*-heptane) were prepared by mixing binary mixtures of (DMC + TMP) or (DMC + *n*-heptane) whose compositions are M1, M2, and M3 with water then ethanol stepwise to cover the two-phase region shown in Figure 1. The quaternary

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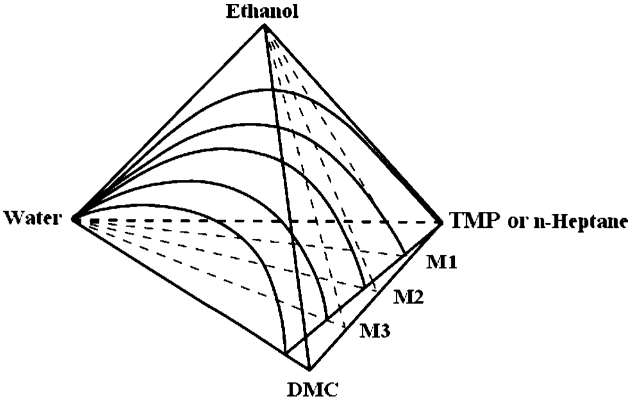

Figure 1. Phase equilibria of (water + ethanol + DMC + TMP) and (water + ethanol + DMC + *n*-heptane). M1, M2, and M3 denote quaternary section planes.

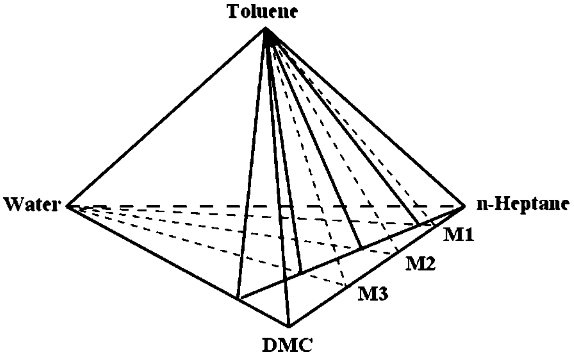

Figure 2. Phase equilibria of (water + DMC + *n*-heptane + toluene). M1, M2, and M3 denote quaternary section planes.

Table 1. Equilibrium Phase Compositions in Mole Fraction (x) for Ternary Mixtures of Water (1) + Ethanol (2) + Dimethyl Carbonate (3) at T = 298.15 K

organic phase			aqueous phase		
x_1	x_2	x_3	x_1	x_2	x_3
0.1326	0.0127	0.8547	0.9641	0.0104	0.0255
0.1562	0.0428	0.8010	0.9413	0.0298	0.0289
0.1998	0.0493	0.7509	0.9348	0.0344	0.0308
0.2204	0.0736	0.7060	0.9142	0.0497	0.0361
0.2697	0.0885	0.6418	0.9044	0.0574	0.0382
0.2999	0.1021	0.5980	0.8873	0.0675	0.0452
0.3600	0.1161	0.5239	0.8700	0.0769	0.0531
0.4285	0.1295	0.4420	0.8492	0.0868	0.0640
0.1300	0.0000	0.8700	0.9834	0.0000	0.0166

Table 2. Equilibrium Phase Compositions in Mole Fraction (x) for Ternary Mixtures of Water (1) + Dimethyl Carbonate (2) + *n*-Heptane (3) at T = 298.15 K

organic phase			aqueous phase		
x_1	x_2	x_3	x_1	x_2	x_3
0.0007	0.0000	0.9993	1.0000	0.0000	0.0000
0.0732	0.8083	0.1185	0.9781	0.0219	0.0000
0.0644	0.7265	0.2091	0.9792	0.0208	0.0000
0.0668	0.6812	0.2520	0.9794	0.0206	0.0000
0.0621	0.6165	0.3214	0.9798	0.0202	0.0000
0.0503	0.5449	0.4048	0.9844	0.0156	0.0000
0.0427	0.4798	0.4775	0.9803	0.0197	0.0000
0.0462	0.4444	0.5094	0.9819	0.0181	0.0000
0.0287	0.2789	0.6924	0.9840	0.0160	0.0000
0.0314	0.3015	0.6671	0.9993	0.0007	0.0000
0.1300	0.8700	0.0000	0.9834	0.0166	0.0000

Table 3. Equilibrium Phase Compositions in Mole Fraction (x) for Ternary Mixtures of Water (1) + Dimethyl Carbonate (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
0.0036	0.0000	0.9964	1.0000	0.0000	0.0000
0.1484	0.7421	0.1095	0.9796	0.0204	0.0000
0.1344	0.6907	0.1749	0.9802	0.0198	0.0000
0.1361	0.6387	0.2252	0.9788	0.0212	0.0000
0.1192	0.5995	0.2813	0.9802	0.0198	0.0000
0.1004	0.5478	0.3518	0.9797	0.0203	0.0000
0.0966	0.4539	0.4495	0.9802	0.0198	0.0000
0.0920	0.4356	0.4724	0.9846	0.0154	0.0000
0.0855	0.3819	0.5326	0.9943	0.0057	0.0000
0.0602	0.2854	0.6544	0.9986	0.0014	0.0000
0.1300	0.8700	0.0000	0.9834	0.0166	0.0000

Table 4. Equilibrium Phase Compositions in Mole Fraction (x) for Ternary Mixtures of Water (1) + *n*-Heptane (2) + Toluene (3) at T = 298.15 K

organic phase			aqueous phase		
x_1	x_2	x_3	x_1	x_2	x_3
0.0007	0.9993	0.0000	1.0000	0.0000	0.0000
0.0000	0.7911	0.2089	1.0000	0.0000	0.0000
0.0000	0.6591	0.3409	1.0000	0.0000	0.0000
0.0000	0.4874	0.5126	1.0000	0.0000	0.0000
0.0000	0.5680	0.4320	1.0000	0.0000	0.0000
0.0000	0.4306	0.5694	1.0000	0.0000	0.0000
0.0000	0.3825	0.6175	1.0000	0.0000	0.0000
0.0000	0.3624	0.6376	1.0000	0.0000	0.0000
0.0000	0.3329	0.6671	1.0000	0.0000	0.0000
0.0000	0.2657	0.7343	1.0000	0.0000	0.0000
0.0000	0.2065	0.7935	1.0000	0.0000	0.0000
0.0023	0.0000	0.9977	1.0000	0.0000	0.0000

mixtures for (water + DMC + *n*-heptane + toluene) were prepared by mixing binary mixtures of (DMC + *n*-heptane) whose compositions are M1, M2, and M3 with water then toluene stepwise to cover the two-phase region shown in Figure 2. The quaternary mixtures whose volume is about 80 cm^3 were loaded in an equilibrium glass cell placed in a thermostatted water bath. The headspace of the equilibrium cell was filled with dry nitrogen gas to prevent contamination of moisture. The mixture was then stirred vigorously with a magnetic stirrer for 4 h and allowed to equilibrate for a further 3 h, which was sufficient to separate into two liquid phases. The liquid samples, about 5 cm^3, withdrawn from both upper and lower phases in the cell by using a milliliter syringe without changing the equilibria between the two layers, were analyzed by a gas chromatograph (Shimadzu, GC-14C) equipped with a thermal conductivity detector. The oven temperatures of the injection port and detector were set at (493.15 and 513.15) K, respectively. The hydrogen flow rates for both the separation and reference columns were 1.1 $cm^3 \cdot s^{-1}$. A stainless steel column (2 m long, 3 mm i.d.) packed with Porapak QS was used for the separation of quaternary components. The peak areas of the components, detected with a chromatopac (Zhejiang, N2000), were calibrated by gravimetrically weighted mixtures. The mass of each component determined from the g.c. 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 schematically a tetrahedron to depict three planes of the quaternary mixtures of (water + ethanol + DMC + TMP) and (water + ethanol + DMC + *n*-heptane). The values of M1, M2, and M3 are approximately 0.25, 0.50, and 0.75, respectively, indicating the mole fraction of DMC in (DMC + TMP) or (DMC + *n*-heptane). Figure 2 shows schematically a tetrahedron to depict three planes of the quaternary mixtures of (water + DMC + *n*-heptane + toluene).

Table 5. Equilibrium Phase Compositions in Mole Fraction (x) for Ternary Mixtures of Water (1) + Dimethyl Carbonate (2) + Toluene (3) at T = 298.15 K

organic phase			aqueous phase		
x_1	x_2	x_3	x_1	x_2	x_3
0.0607	0.7560	0.1833	0.9805	0.0195	0.0000
0.0530	0.6572	0.2898	0.9833	0.0167	0.0000
0.0381	0.5787	0.3832	0.9854	0.0146	0.0000
0.0388	0.5142	0.4470	0.9867	0.0133	0.0000
0.0210	0.4711	0.5079	0.9878	0.0122	0.0000
0.0192	0.4294	0.5514	0.9885	0.0115	0.0000
0.0184	0.3982	0.5834	0.9896	0.0104	0.0000
0.0780	0.8160	0.1060	0.9784	0.0216	0.0000
0.0539	0.6896	0.2565	0.9825	0.0175	0.0000
0.0525	0.6176	0.3299	0.9841	0.0159	0.0000
0.1300	0.8700	0.0000	0.9834	0.0166	0.0000

Table 6. Equilibrium Phase Compositions in Mole Fraction (x) for Quaternary Mixtures of Water (1) + Ethanol (2) + Dimethyl Carbonate (3) + 2,2,4-Trimethylpentane (4) Mixtures at T = 298.15 K

{x_1Water + x_2Ethanol + x_3Dimethyl Carbonate + $(1 - x_1 - x_2 - x_3)$2,2,4-Trimethylpentane}

organic phase			aqueous phase		
x_1	x_2	x_3	x_1	x_2	x_3
		M1 = 0.25			
0.0205	0.0320	0.6490	0.9010	0.0637	0.0353
0.0240	0.0363	0.6545	0.8631	0.0963	0.0406
0.0155	0.0422	0.6559	0.7841	0.1427	0.0732
0.0148	0.0407	0.6605	0.8144	0.1308	0.0548
0.0349	0.0481	0.3186	0.7382	0.1801	0.0817
0.0201	0.0419	0.2567	0.7110	0.2075	0.0815
0.0182	0.0372	0.2026	0.6865	0.2330	0.0805
0.0177	0.0397	0.1795	0.6533	0.2672	0.0795
0.0000	0.0360	0.1628	0.6266	0.2786	0.0948
0.0000	0.0331	0.1315	0.6031	0.3114	0.0855
0.0000	0.0282	0.1161	0.5835	0.3333	0.0832
0.0000	0.0416	0.1013	0.5346	0.3764	0.0822
		M2 = 0.50			
0.0000	0.0105	0.3638	0.9341	0.0409	0.0250
0.0000	0.0173	0.3327	0.8441	0.1153	0.0406
0.0000	0.0264	0.2725	0.8511	0.1093	0.0395
0.0000	0.0217	0.1902	0.7854	0.1670	0.0476
0.0000	0.0273	0.1453	0.7450	0.2028	0.0523
0.0000	0.0274	0.1177	0.7107	0.2386	0.0507
0.0000	0.0294	0.0730	0.6713	0.2770	0.0518
0.0000	0.0351	0.0682	0.6412	0.3064	0.0524
0.0000	0.0351	0.0610	0.6142	0.3336	0.0522
		M3 = 0.75			
0.0000	0.0405	0.2126	0.5831	0.3672	0.0492
0.0000	0.0449	0.2020	0.5708	0.3820	0.0472
0.0000	0.0000	0.1453	0.9357	0.0490	0.0153
0.0000	0.0000	0.1303	0.8820	0.1015	0.0165
0.0000	0.0000	0.1218	0.8710	0.1103	0.0187
0.0000	0.0000	0.0922	0.8376	0.1424	0.0200
0.0000	0.0160	0.0820	0.8096	0.1701	0.0203
0.0000	0.0131	0.0708	0.7699	0.2099	0.0202
0.0000	0.0187	0.0581	0.7508	0.2276	0.0216
0.0000	0.0214	0.0498	0.6682	0.3114	0.0204
0.0000	0.0177	0.0493	0.6954	0.2842	0.0204
0.0000	0.0217	0.0369	0.6681	0.3124	0.0195
0.0000	0.0278	0.0345	0.6231	0.3554	0.0215
0.0000	0.0286	0.0385	0.6382	0.3391	0.0227
0.0000	0.0322	0.0229	0.5689	0.4139	0.0172

The values of M1, M2, and M3 are approximately 0.25, 0.50, and 0.75, respectively, indicating the mole fraction of DMC in (DMC + n-heptane). Tables 1 to 5 list the experimental equilibrium tie-line compositions for the five ternary mixtures of (water + ethanol + DMC), (water + DMC + n-heptane), (water + DMC + TMP), (water + DMC + toluene), and (water + n-heptane + toluene) at T = (298.15 ± 0.01) K.

Table 7. Equilibrium Phase Compositions in Mole Fraction (x) for Quaternary Mixtures of Water (1) + Ethanol (2) + Dimethyl Carbonate (3) + n-Heptane (4) Mixtures at T = 298.15 K

{x_1Water + x_2Ethanol + x_3Dimethyl Carbonate + $(1 - x_1 - x_2 - x_3)n$-Heptane}

organic phase			aqueous phase		
x_1	x_2	x_3	x_1	x_2	x_3
		M1 = 0.25			
0.0000	0.0000	0.1469	0.9214	0.0600	0.0186
0.0000	0.0000	0.1255	0.8606	0.1193	0.0201
0.0000	0.0000	0.0967	0.8007	0.1743	0.0250
0.0000	0.0184	0.0723	0.7759	0.1981	0.0260
0.0000	0.0209	0.0581	0.7266	0.2455	0.0279
0.0000	0.0086	0.0480	0.7053	0.2696	0.0251
0.0000	0.0265	0.0405	0.6400	0.3349	0.0251
0.0000	0.0251	0.0331	0.6064	0.3698	0.0238
0.0000	0.0254	0.0306	0.5784	0.3986	0.0230
0.0000	0.0336	0.0254	0.5578	0.4192	0.0230
0.0000	0.0357	0.0224	0.5178	0.4548	0.0210
0.0000	0.0425	0.0218	0.4582	0.5114	0.0204
		M2 = 0.50			
0.0000	0.0176	0.3966	0.9011	0.0714	0.0275
0.0000	0.0249	0.3518	0.8347	0.1271	0.0382
0.0000	0.0210	0.2799	0.7976	0.1493	0.0531
0.0000	0.0267	0.1815	0.7243	0.2092	0.0665
0.0000	0.0238	0.1341	0.6712	0.2600	0.0688
0.0000	0.0260	0.0972	0.6134	0.3238	0.0628
0.0000	0.0233	0.1127	0.6414	0.2910	0.0676
0.0000	0.0290	0.0843	0.5816	0.3527	0.0657
0.0000	0.0254	0.0865	0.5750	0.3588	0.0662
0.0000	0.0306	0.0719	0.5058	0.4343	0.0599
0.0000	0.0341	0.0633	0.4902	0.4549	0.0549
		M3 = 0.75			
0.0695	0.0129	0.6481	0.9138	0.0554	0.0308
0.1084	0.0384	0.5906	0.8520	0.1109	0.0371
0.0974	0.0584	0.5304	0.7396	0.2009	0.0595
0.0000	0.0314	0.3489	0.6506	0.2527	0.0967
0.0000	0.0357	0.2418	0.6001	0.3006	0.0993
0.0000	0.0332	0.1868	0.5761	0.3279	0.0960
0.0000	0.0350	0.1545	0.5469	0.3618	0.0913
0.0000	0.0287	0.1322	0.4906	0.4262	0.0832
0.0000	0.0397	0.1193	0.4872	0.4298	0.0830
0.0000	0.0401	0.1096	0.4946	0.4111	0.0859
0.0000	0.0485	0.0982	0.4357	0.4760	0.0781

Tables 6 to 8 list the experimental equilibrium tie-line compositions for the three quaternary mixtures of (water + ethanol + DMC + TMP), (water + ethanol + DMC + n-heptane), and (water + DMC + n-heptane + toluene) at T = (298.15 ± 0.01) K. The mole fraction as zero in the tables means that the actual values are below the detectability limit of our gas chromatograph.

3. 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 and extended UNIQUAC models[6,7] 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: $g^{\mathrm{E}}_{\mathrm{comb}}$ and $g^{\mathrm{E}}_{\mathrm{res}}$

$$g^{\mathrm{E}} = g^{\mathrm{E}}_{\mathrm{comb}} + g^{\mathrm{E}}_{\mathrm{res}} \tag{1}$$

The combinatorial term is given by a modified form of Gmehling et al.[20]

$$\frac{g^{\mathrm{E}}_{\mathrm{comb}}}{RT} = \sum_i^4 x_i \ln \frac{\varphi'_i}{x_i} - \frac{Z}{2}\sum_i^4 q_i x_i \ln \frac{\varphi_i}{\theta_i} \tag{2}$$

Table 8. Equilibrium Phase Compositions in Mole Fraction (x) for Quaternary Mixtures of Water (1) + Dimethyl Carbonate (2) + n-Heptane (3) + Toluene (4) Mixtures at T = 298.15 K

{x_1Water + x_2Dimethyl Carbonate + $x_3$$n$-Heptane + (1 − x_1 − x_2 − x_3)Toluene}

organic phase			aqueous phase		
x_1	x_2	x_3	x_1	x_2	x_3
		M1 = 0.25			
0.0578	0.5825	0.2309	1.0000	0.0000	0.0000
0.0501	0.5528	0.2051	1.0000	0.0000	0.0000
0.0466	0.5004	0.1952	1.0000	0.0000	0.0000
0.0471	0.4514	0.1756	1.0000	0.0000	0.0000
0.0415	0.4349	0.1661	1.0000	0.0000	0.0000
0.0362	0.4260	0.1628	1.0000	0.0000	0.0000
0.0285	0.3613	0.1344	1.0000	0.0000	0.0000
0.0276	0.3212	0.1180	1.0000	0.0000	0.0000
0.0263	0.2929	0.1028	1.0000	0.0000	0.0000
0.0179	0.2505	0.0914	1.0000	0.0000	0.0000
0.0171	0.2243	0.0797	1.0000	0.0000	0.0000
0.0154	0.2100	0.0784	1.0000	0.0000	0.0000
		M2 = 0.50			
0.0339	0.3551	0.4954	1.0000	0.0000	0.0000
0.0275	0.3213	0.4366	1.0000	0.0000	0.0000
0.0273	0.3020	0.3913	1.0000	0.0000	0.0000
0.0209	0.2765	0.3545	1.0000	0.0000	0.0000
0.0220	0.2580	0.3173	1.0000	0.0000	0.0000
0.0198	0.2335	0.2788	1.0000	0.0000	0.0000
0.0189	0.2128	0.2514	1.0000	0.0000	0.0000
0.0165	0.1905	0.2193	1.0000	0.0000	0.0000
0.0144	0.1673	0.1898	1.0000	0.0000	0.0000
0.0120	0.1472	0.1681	1.0000	0.0000	0.0000
0.0110	0.1160	0.1377	1.0000	0.0000	0.0000
		M3 = 0.75			
0.0000	0.2601	0.6228	1.0000	0.0000	0.0000
0.0000	0.1311	0.6402	1.0000	0.0000	0.0000
0.0000	0.1206	0.5828	1.0000	0.0000	0.0000
0.0000	0.1118	0.4993	1.0000	0.0000	0.0000
0.0000	0.1073	0.4772	1.0000	0.0000	0.0000
0.0000	0.1116	0.3834	1.0000	0.0000	0.0000
0.0000	0.0981	0.3326	1.0000	0.0000	0.0000
0.0000	0.0885	0.2904	1.0000	0.0000	0.0000
0.0000	0.0787	0.2536	1.0000	0.0000	0.0000
0.0000	0.0678	0.2221	1.0000	0.0000	0.0000
0.0000	0.0596	0.1954	1.0000	0.0000	0.0000

Table 9. Structural Parameters of Pure Components

component	r	q	q'^{a}	q'^{b}
water	0.92	1.40	1.283	0.96
ethanol	2.11	1.97	1.404	0.92
n-heptane	5.17	4.40	$q^{0.75}$	$q^{0.20}$
DMC	3.06	2.82	$q^{0.75}$	$q^{0.20}$
TMP	5.85	4.94	$q^{0.75}$	$q^{0.20}$
toluene	3.92	2.97	$q^{0.75}$	$q^{0.20}$

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

Table 10. Antoine Coefficients of Pure Components

component	A	B	C	lit.
water	8.07131	1730.63	233.426	22
ethanol	8.11220	1592.86	226.184	22
n-heptane	6.89386	1264.37	216.640	22
DMC	6.97807	1201.00	203.116	13
TMP	6.81189	1257.84	220.735	22
toluene	6.95087	1342.31	219.870	22

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

$$\varphi_i = \frac{x_i r_i}{\sum_j^4 x_j r_j},\ \dot{\varphi}_i = \frac{x_i r_i^{3/4}}{\sum_j^4 x_j r_j^{3/4}},\ \theta_i = \frac{x_i q_i}{\sum_j^4 x_j q_j} \tag{3}$$

and the residual term is modified by introducing the third parameter C to the residual term of the extended UNIQUAC model[7] and by including additional ternary and quaternary parameters, τ_{jki} and τ_{jkli}

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

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

$$\tau_{ji} = \exp\left(-\frac{a_{ji}}{T}\right) \tag{6}$$

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.[21]

$$P y_i \varphi_i = x_i \gamma_i P_i^{\mathrm{s}} \varphi_i^{\mathrm{s}} \exp\left\{\frac{V_i^{\mathrm{L}}(P - x_i\gamma_i P_i^{\mathrm{s}})}{RT}\right\} \tag{7}$$

$$\ln \varphi_i = \frac{\left(2\sum_j y_j B_{ij} - \sum_i\sum_j y_i y_j B_{ij}\right)P}{RT} \tag{8}$$

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.[21,22] The liquid molar volume V^{L} was obtained by a modified Rackett equation.[23] The fugacity coefficient φ was calculated from eq 8. The pure and cross second virial coefficients B were estimated by the method of Hayden and O'Connell.[24] An optimum set of binary energy parameters for the miscible mixtures were obtained by minimizing the following objective function

$$\mathrm{F} = \sum_i\left[\frac{(P_i^{\mathrm{calcd}} - P_i^{\mathrm{exptl}})^2}{\sigma_P^2} + \frac{(T_i^{\mathrm{calcd}} - T_i^{\mathrm{exptl}})^2}{\sigma_T^2} + \frac{(x_i^{\mathrm{calcd}} - x_i^{\mathrm{exptl}})^2}{\sigma_x^2} + \frac{(y_i^{\mathrm{calcd}} - y_i^{\mathrm{exptl}})^2}{\sigma_y^2}\right] \tag{9}$$

Table 11. Calculated Results of Binary Phase Equilibrium Data Reduction

system (1 + 2)	T/K	no.[a]	model	a_{12}/K	a_{21}/K	$\sigma(P)$/mmHg	$\sigma(T)$/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	8
			II[c]	157.12	37.08	0.1	0.0	0.9	4.8	
ethanol + *n*-heptane	298.15	19	I	107.23	1327.88	0.1	0.0	0.6	7.0	9
			II	159.99	1325.83	0.1	0.0	0.5	7.5	
ethanol + TMP	298.15	10	I	75.50	1215.25	0.4	0.0	1.0	4.3	10
			II	232.77	1155.98	0.6	0.0	0.5	6.8	
ethanol + DMC	313.15	25	I	162.17	405.48	1.7	0.0	2.0	15.0	11
			II	185.97	408.34	1.7	0.0	1.9	14.9	
DMC + TMP	333.15	22	I	38.25	311.23	1.1	0.0	1.1	3.6	12
			II	91.02	346.33	1.0	0.0	1.0	3.2	
DMC + *n*-heptane	355.26~ 369.1	30	I	104.88	237.94	1.6	0.1	1.1	6.6	13
			II	169.86	275.40	1.7	0.1	1.3	6.4	
DMC + toluene	333.15	23	I	304.27	−161.30	1.2	0.0	0.9	6.3	12
			II	318.76	−155.85	1.2	0.0	0.9	6.3	
n-heptane + toluene	313.15	24	I	163.63	−92.81	1.1	0.0	0.5	4.0	14
			II	188.21	−122.99	1.1	0.0	0.5	3.9	
n-heptane + water	298.15	MS[d]	I	1884.20	1022.10					15
			II	2135.50	1839.60					
TMP + water	298.15	MS	I	3023.30	1145.60					15
			II	2319.30	2107.10					
toluene + water	298.15	MS	I	1713.30	752.99					16
			II	1540.70	1053.90					
DMC + water	298.15	MS	I	702.87	269.81					this work
			II	585.84	272.17					

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

Table 12. Calculated Results for Ternary Liquid–Liquid Equilibria at 298.15 K

type[a]	system (1 + 2 + 3)	no.[b]	model	τ_{231}	τ_{132}	τ_{123}	rms[e]/mol %		lit.
I	water + ethanol + TMP	6	I[c]	−0.2118	−0.2565	0.1161	4.28[f]	1.00[g]	17
			II[d]	−0.4468	−0.0832	0.1709	12.53	0.95	
I	water + ethanol + *n*-heptane	13	I	−0.2730	−0.9130	0.2883	4.78	0.55	18
			II	−0.6339	−0.8177	0.3379	13.61	0.79	
I	water + ethanol + DMC	9	I	−0.0354	1.1024	1.2728	4.02	0.49	this work
			II	−0.7401	4.6015	−1.5553	3.00	2.33	
II	water + DMC + *n*-heptane	11	I	0.2498	−1.9334	−0.1868	0.75	0.50	this work
			II	0.0003	−1.9978	−0.0011	2.58	0.97	
II	water + DMC + TMP	11	I	0.1153	0.9333	−0.0734	0.64	0.53	this work
			II	0.3944	−1.4285	−0.3088	0.92	0.57	
II	water + DMC + toluene	11	I	−0.0143	−0.6537	−0.1398	0.68	0.41	this work
			II	−0.1918	−0.0679	−0.1233	1.88	0.94	
II	water + *n*-heptane + toluene	12	I	−0.0100	−0.0100	−0.0550	0.18	0.05	this work
			II	−0.0106	0.1407	0.1185	0.14	0.04	

[a] I, only one binary system shows phase separation; II, two binary systems show phase separation. [b] Number of tie lines. [c] Modified UNIQUAC model [d] Extended UNIQUAC model. [e] Root-mean-square deviation. [f] Predicted results using only binary parameters. [g] Correlated results using binary and ternary parameters.

where the superscripts calcd and exptl indicate, respectively, the most probable calculated value corresponding to each measured point and the experimental value. The standard deviations in the experimental values[21] used in eq 9 were taken as: $\sigma_P = 0.133$ kPa 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.

The binary energy parameters for the partially miscible mixtures were obtained from the mutual solubility data by solving the following equations simultaneously

$$(x_i\gamma_i)^{\mathrm{I}} = (x_i\gamma_i)^{\mathrm{II}} \tag{10}$$

$$\sum_i x_i^{\mathrm{I}} = 1 \text{ and } \sum_i x_i^{\mathrm{II}} = 1 \quad (\mathrm{I}, \mathrm{II} = \text{two liquid phases}) \tag{11}$$

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 10 and 11. The additional ternary parameters τ_{231}, τ_{312}, and τ_{123} were obtained by fitting the two models to the ternary LLE data, and 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.[25] The root-mean-square deviation between the experimental and calculated values was evaluated by

$$\beta = 10^2 \cdot \left\{ \frac{\sum_k \sum_i \sum_j (x_{ijk}^{\mathrm{exptl}} - x_{ijk}^{\mathrm{calcd}})^2}{M} \right\}^{0.5} \tag{12}$$

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

Calculated Result. Table 9 shows the molecular-structural volume and area parameters, r and q, used in the two different models. The value for DMC is calculated by Bondi's method,[26] and the others are taken from Prausnitz et al.[21] 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

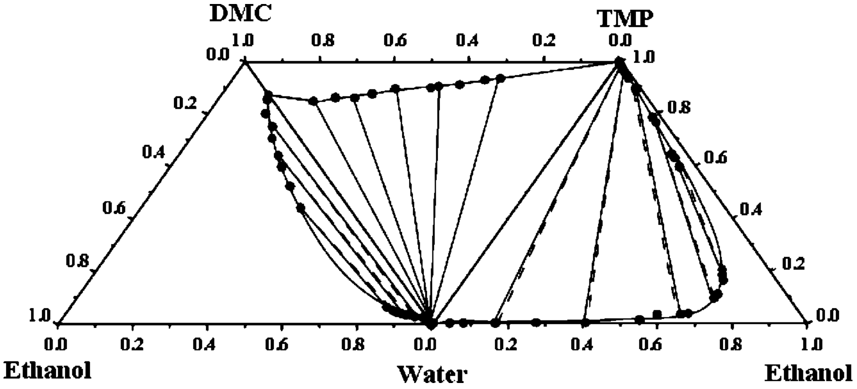

Figure 3. Experimental and calculated LLE data of three ternary mixtures making up (water + ethanol + DMC + TMP) at T = 298.15 K. ●- - -●, experimental tie lines; —, correlated by the modified UNIQUAC model with binary and ternary parameters taken from Tables 11 and 12.

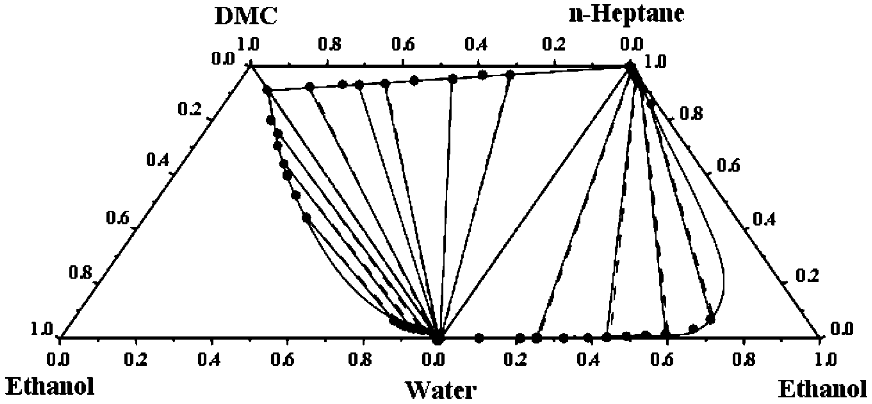

Figure 4. Experimental and calculated LLE data of three ternary mixtures making up (water + ethanol + DMC + n-heptane) at T = 298.15 K. ●- - -●, experimental tie lines; —, correlated by the modified UNIQUAC model with binary and ternary parameters taken from Tables 11 and 12.

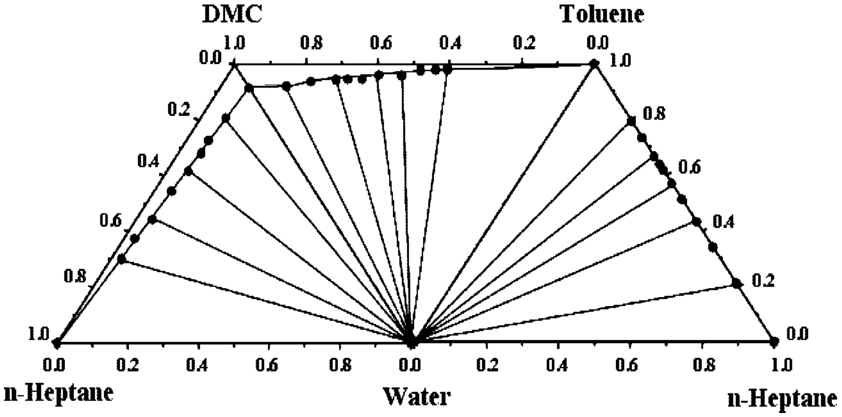

Figure 5. Experimental and calculated LLE data of three ternary mixtures making up (water + DMC + n-heptane + toluene) at T = 298.15. ●- - -●, experimental tie lines; —, correlated by the modified UNIQUAC model with binary and ternary parameters taken from Tables 11 and 12.

Table 13. 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 + ethanol + DMC + TMP	36	I[b]	3.3635	−22.4374	0.7670	−9.0375	3.11[e]	1.80[f]
		II[c]	−4.5406	−26.3120	17.1024	1.8902	4.80	1.95
water + ethanol + DMC + n-heptane	34	I	−0.0551	−0.0023	18.1830	−9.7903	1.66	1.57
		II	−0.0289	−3.7950	7.5171	1.7971	2.40	1.91
water + DMC + n-heptane + toluene	34	I	−0.8959	−43.1065	−24.9222	62.5760	0.43	0.36
		II	−0.0636	−98.4475	164.3643	29.5771	0.68	0.53

[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.

literature,[6,7] 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 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 a previous work.[6] An optimum set of the binary energy parameters a_{ji} was obtained using eqs 7 and 8 by the method of the maximum likelihood principle.[21] Table 10 lists the Antoine coefficients of pure components. Table 11 lists the binary energy parameters of the modified and extended UNI-

QUAC models 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. Good agreement between experimental results and those calculated by the models was obtained.

Table 12 gives the ternary parameters and predicted and correlated results for the ternary mixtures by using the modified and extended UNIQUAC models, along with the root-mean-square deviation between the experimental and calculated tie-lines for the ternary mixtures. The correlated results obtained with the models by using binary and ternary parameters are better than the predicted ones with only binary parameters. The models can give an accurate representation for the ternary LLE by including the ternary parameters in addition to the binary ones.

Figure 1 shows the phase equilibria of (water + ethanol + DMC + TMP) and (water + ethanol + DMC + *n*-heptane). Figure 2 shows phase equilibria of (water + DMC + *n*-heptane + toluene). M1, M2, and M3 denote quaternary sectional planes. Figures 3 to 5 compare, respectively, the experimental (liquid + liquid) equilibrium tie-line data of the ternary mixtures making up (water + ethanol + DMC + TMP), (water + ethanol + DMC + *n*-heptane), and (water + DMC + *n*-heptane + toluene) at $T = (298.15 \pm 0.01)$ 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. Two quaternary systems exhibit type 2 quaternary LLE behavior, which is composed of two ternary LLE for (water + ethanol + DMC) and (water + ethanol + TMP). Or (water + ethanol + DMC) and (water + ethanol + *n*-heptane) are classified as type 1, and one ternary LLE each for the (water + DMC + TMP) or (water + DMC + *n*-heptane) as type 2 is illustrated in Figures 3 and 4. One quaternary system exhibits type 1 quaternary LLE behavior, which is composed of three ternary LLE for the (water + DMC + TMP), (water + DMC + *n*-heptane), and (water + *n*-heptane + toluene) as type 2 which is illustrated in Figure 5. The figures show good agreement between ternary experiment LLE results and correlated results.

Table 13 summarizes the correlated results obtained in fitting the modified and extended UNIQUAC models with binary, ternary, and quaternary parameters to the experimental quaternary LLE data for (water + ethanol + DMC + TMP), (water + ethanol + DMC + *n*-heptane), and (water + DMC + *n*-heptane + toluene), together with the predicted results by the models with the binary and ternary parameters listed in Tables 11 and 12 and correlated ones by the models with additional quaternary parameters. The correlated results obtained from the models are better than the predicted ones in representing the quaternary systems measured in this work and are in good agreement with the experimental quaternary LLE results. The root-mean-square deviations between the experimental and correlated results with the binary, ternary, and quaternary parameters are less than 2 % for (water + ethanol + DMC + TMP) and (water + ethanol + DMC + *n*-heptane) and less than 1 % for (water + DMC + *n*-heptane + toluene). The models can represent accurately the quaternary LLE using binary and ternary as well as quaternary parameters.

4. Conclusions

Quaternary (liquid + liquid) equilibrium results for (water + ethanol + dimethyl carbonate + 2,2,4-trimethylpentane), (water + ethanol + dimethyl carbonate + *n*-heptane), (water + dimethyl carbonate + *n*-heptane + toluene), and ternary (liquid + liquid) equilibrium results for (water + ethanol + DMC), (water + DMC + *n*-heptane), (water + DMC + TMP), (water + DMC + toluene), and (water + *n*-heptane + toluene) were measured at $T = 298.15$ K. The experimental quaternary (liquid + liquid) equilibria as well as their constituent ternary (liquid + liquid) equilibria were predicted by both the modified and extended UNIQUAC models. The modified and extended UNIQUAC models could not always represent accurately the quaternary (liquid + liquid) equilibria in terms of only binary parameters. For an accurate representation of the quaternary (liquid + liquid) equilibria, the models need to include the multicomponent interaction parameters in addition to the binary parameters. The correlated results of quaternary (liquid + liquid) equilibria obtained by the modified and extended UNIQUAC models show a good agreement with experimental results.

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