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Liquid−Liquid Equilibria for Three Quaternary Systems of Water, 2-Propanol, and Dimethyl Carbonate with Isooctane or Toluene or Heptane at 298.15 K

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Experimental tie-line data for three quaternary systems of (water + 2-propanol + dimethyl carbonate + isooctane), (water + 2-propanol + dimethyl carbonate + toluene), and (water + 2-propanol + dimethyl carbonate + heptane) and one ternary system of (water + 2-propanol + dimethyl carbonate) were measured at a temperature of 298.15 K and ambient pressure. The experimental quaternary and its constituent ternary results were compared with those correlated using the modified and extended UNIQUAC models that include multibody interaction parameters in addition to binary ones.

Introduction

Recently, methyl *tert*-butyl ether (MTBE), a widely used motor gasoline additive because of its high octane number and decreasing carbon monoxide emission, was found to pollute groundwater and is not biodegradable. As a result, dimethyl carbonate (DMC) is arousing increasing interest. The most intriguing market opportunities of DMC are use as gasoline additives and as a painting solvent.[1,2] DMC may be an ideal gasoline additive to replace MTBE because of its excellent characteristics as a gasoline additive: high octane, low RVP, reduced CO and NO_x emissions, and a very high density. DMC has about 3 times the oxygen content of MTBE. It has both low toxicity and relatively quick biodegradability,[1,3] and can be considered to be an option for meeting the oxygenate specifications on gasoline and as a means of converting natural gas to a liquid transportation fuel.

There have been a number of studies on (vapor + liquid) equilibria (VLE) for binary systems of DMC + alcohols + aromatic and + naphthenic hydrocarbons.[4−6] (Liquid + liquid) equilibria (LLE) of DMC with other components are basically rare. In modern gasoline-blending operation and refinery process design, it is necessary to assess the advantages of DMC as a fuel additive and the phase behavior of the gasoline mixtures. Experience shows that the commercial gasoline distribution system always contains water because of air humidity or infiltration into storage tanks. Therefore, water was included in this study. The addition of alcohols to the gasoline with DMC significantly affects the hydrocarbon−water solubility. A synthetic gasoline is represented by a mixture of aromatic and naphthenic hydrocarbons, for example, toluene, heptane, and isooctane (TMP). It is therefore necessary to obtain reliable LLE data for these multicomponent mixtures as well as to develop accurate representation of the experimental LLE data for the multicomponent mixtures.

As a continuation of the phase equilibrium study of DMC systems, we report the LLE data for (water + 2-propanol + DMC + TMP), (water + 2-propanol + DMC + toluene), (water + 2-propanol + DMC + heptane), and (water + 2-propanol + DMC) systems at $T = 298.15$ K. The experimental LLE data were correlated by means of the modified UNIQUAC and extended UNIQUAC models[7,8] including ternary and quaternary parameters coming from multicomponent intermolecular interactions in addition to binary parameters. The binary parameters for miscible binary mixtures of constituents of the ternary and quaternary systems were obtained from VLE data,[4−6,9−12] and those of immiscible mixtures were obtained from mutual solubility data.[13−15] For a reliable representation of quaternary LLE systems, the constituent ternary systems of (water + DMC + heptane),[15] (water + DMC + TMP),[15] (water + DMC + toluene),[15] (water + 2-propanol +TMP),[16] (water + 2-propanol + toluene),[17] (water + 2-propanol + heptane),[18] and (water + 2-propanol + DMC) are necessary for obtaining the ternary parameters.

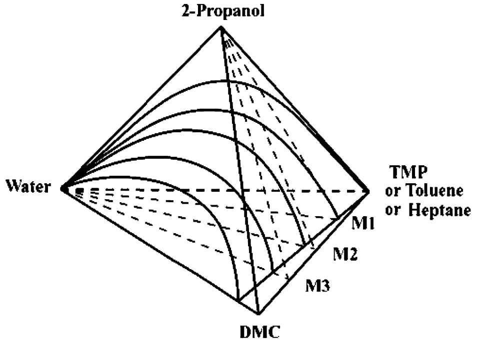

Figure 1. Phase equilibria of (water + 2-propanol + DMC + TMP), (water + 2-propanol + DMC + toluene), and (water + 2-propanol + DMC + heptane). M1, M2, and M3 denote quaternary section planes.

Experimental Section

2-Propanol was provided by Tianjin Chemical Reagent Factory with nominal minimum mass fraction of 99.7 %. Toluene and heptane were supplied by the Guangzhou Chemical Reagent Factory, both with nominal minimum mass fractions of 99.5 % and 99.7 %. The DMC was obtained from Tianjin Guangfu Chemical Reagents Factory with nominal minimum mass fraction of 99.2 %. TMP was supplied by the Tianjin Damao Chemical Reagents Factory with nominal minimum mass fraction of 99.0 %. The gas chromatograghy analysis gave mass fractions of 99.1 % for DMC, 99.5 % for toluene, and

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Table 1. Equilibrium Phase Compositions for Ternary Mixtures of Water (1) + 2-Propanol (2) + Dimethyl 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}

organic phase			aqueous phase		
x_1^{I}	x_2^{I}	x_3^{I}	x_1^{II}	x_2^{II}	x_3^{II}
0.1296	0.0340	0.8364	0.9600	0.0149	0.0251
0.1440	0.0527	0.8033	0.9583	0.0171	0.0246
0.2041	0.0762	0.7197	0.9467	0.0250	0.0283
0.2263	0.0961	0.6776	0.9424	0.0284	0.0292
0.3108	0.1115	0.5777	0.9315	0.0363	0.0322
0.3292	0.1294	0.5414	0.9254	0.0394	0.0352
0.4579	0.1361	0.4060	0.9112	0.0484	0.0404
0.4064	0.1417	0.4519	0.9111	0.0474	0.0415
0.5142	0.1434	0.3424	0.8925	0.0559	0.0516
0.5310	0.1369	0.3321	0.8919	0.0574	0.0507
0.5773	0.1349	0.2878	0.8761	0.0628	0.0611
0.6492	0.1231	0.2277	0.8532	0.0700	0.0768

Table 2. Equilibrium Phase Compositions for Quaternary Mixtures of Water (1) + 2-Propanol (2) + Dimethyl Carbonate (3) + Isooctane (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}

organic phase			aqueous phase		
x_1^{I}	x_2^{I}	x_3^{I}	x_1^{II}	x_2^{II}	x_3^{II}
{x_1 Water + x_2 2-Propanol + x_3 Dimethyl Carbonate + $(1-x_1-x_2-x_3)$ Isooctane}[a]					
$x'_3 = 0.25$[b]					
0.0000	0.0100	0.1361	0.9738	0.0152	0.0111
0.0000	0.0274	0.1263	0.9443	0.0429	0.0128
0.0000	0.0450	0.1125	0.9260	0.0606	0.0135
0.0000	0.0635	0.0997	0.9089	0.0774	0.0137
0.0000	0.0866	0.0833	0.8809	0.1028	0.0163
0.0000	0.1014	0.0712	0.8628	0.1206	0.0165
0.0000	0.1219	0.0631	0.8380	0.1446	0.0170
0.0000	0.1304	0.0569	0.8220	0.1594	0.0186
0.0000	0.1451	0.0512	0.8038	0.1766	0.0179
0.0069	0.1548	0.0461	0.7864	0.1936	0.0179
0.0044	0.1668	0.0410	0.7671	0.2119	0.0176
0.0189	0.1765	0.0393	0.7429	0.2343	0.0185
$x'_3 = 0.50$					
0.0000	0.0220	0.3665	0.9675	0.0154	0.0172
0.0000	0.0474	0.3347	0.9429	0.0372	0.0199
0.0000	0.0788	0.2826	0.9139	0.0604	0.0256
0.0000	0.0941	0.2224	0.8850	0.0831	0.0319
0.0000	0.1028	0.1842	0.8618	0.1031	0.0351
0.0000	0.1120	0.1528	0.8384	0.1240	0.0369
0.0000	0.1231	0.1323	0.8245	0.1425	0.0330
0.0000	0.1303	0.1205	0.7933	0.1651	0.0396
0.0000	0.1427	0.1082	0.7659	0.1902	0.0409
0.0000	0.1509	0.0974	0.7543	0.2021	0.0399
0.0000	0.1587	0.0917	0.7372	0.2182	0.0398
0.0000	0.1707	0.0843	0.7198	0.2353	0.0395
$x'_3 = 0.75$					
0.0000	0.0297	0.6770	0.9661	0.0135	0.0205
0.0153	0.0491	0.6535	0.9612	0.0192	0.0196
0.0201	0.0806	0.6092	0.9480	0.0306	0.0214
0.0355	0.1400	0.5327	0.9157	0.0547	0.0296
0.0620	0.1807	0.4529	0.8821	0.0760	0.0419
0.0610	0.1720	0.4028	0.8543	0.0924	0.0533
0.0317	0.1505	0.3478	0.8282	0.1073	0.0633
0.0246	0.1374	0.3005	0.8089	0.1217	0.0680
0.0202	0.1342	0.1965	0.7578	0.1662	0.0716
0.0342	0.1389	0.1650	0.7408	0.1843	0.0702

[a] Obtained by mixing pure water and 2-propanol with the binary mixtures of {x'_3 dimethyl carbonate + $(1 - x'_3)$isooctane}. [b] Mole fraction of dimethyl carbonate in the binary mixtures.

Table 3. Equilibrium Phase Compositions for Quaternary Mixtures of Water (1) + 2-Propanol (2) + Dimethyl Carbonate (3) + Toluene (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}

organic phase			aqueous phase		
x_1^{I}	x_2^{I}	x_3^{I}	x_1^{II}	x_2^{II}	x_3^{II}
{x_1 Water + x_2 2-Propanol + x_3 Dimethyl Carbonate + $(1-x_1-x_2-x_3)$ Toluene}[a]					
$x'_3 = 0.25$[b]					
0.0371	0.0162	0.2000	0.9749	0.0178	0.0073
0.0443	0.0568	0.1866	0.9561	0.0378	0.0061
0.0373	0.1025	0.1866	0.9402	0.0530	0.0068
0.0556	0.1581	0.1581	0.9241	0.0669	0.0075
0.0844	0.2160	0.1421	0.9137	0.0780	0.0074
0.1072	0.2664	0.1238	0.9027	0.0876	0.0087
0.1405	0.3045	0.1064	0.8947	0.0958	0.0078
0.1903	0.3270	0.0985	0.8927	0.0980	0.0071
0.2228	0.3543	0.0880	0.8792	0.1096	0.0091
0.2425	0.3751	0.0809	0.8759	0.1137	0.0073
0.2995	0.3751	0.0682	0.8642	0.1218	0.0096
0.3414	0.3823	0.0586	0.8538	0.1316	0.0084
$x'_3 = 0.50$					
0.0000	0.0247	0.4406	0.9696	0.0184	0.0120
0.0112	0.0673	0.4140	0.9494	0.0377	0.0129
0.0416	0.1269	0.3640	0.9338	0.0512	0.0147
0.0761	0.1869	0.3213	0.9188	0.0649	0.0153
0.1157	0.2387	0.2761	0.9076	0.0760	0.0157
0.1721	0.2783	0.2357	0.8959	0.0852	0.0174
0.2205	0.3043	0.2037	0.8884	0.0930	0.0174
0.2876	0.2991	0.1746	0.8846	0.0960	0.0174
0.3678	0.3128	0.1364	0.8695	0.1086	0.0190
$x'_3 = 0.75$					
0.1337	0.0408	0.5814	0.9708	0.0163	0.0129
0.1382	0.0792	0.5545	0.9482	0.0344	0.0174
0.1553	0.1247	0.4991	0.9319	0.0469	0.0212
0.2046	0.1818	0.4294	0.9185	0.0582	0.0224
0.2787	0.2257	0.3361	0.9004	0.0702	0.0283
0.3431	0.2751	0.2629	0.8912	0.0794	0.0277
0.4064	0.2964	0.2017	0.8540	0.1032	0.0388
0.4301	0.3039	0.1819	0.8362	0.1120	0.0447

[a] Obtained by mixing pure water and 2-propanol with the binary mixtures of {x'_3 dimethyl carbonate + $(1 - x'_3)$toluene}. [b] Mole fraction of dimethyl carbonate in the binary mixtures.

99.7 % for 2-propanol, TMP, and heptane. Water was distilled twice and had a mass fraction of 99.9 %.

LLE measurements were performed in a water bath in which temperature was keep constant at T = 298 K. The uncertainty of temperature was ± 0.05 K. About 80 cm^3 mixtures were loaded in an equilibrium glass cell, stirred for 3 h, and then left to equilibrate for 3 h before samples of the conjugate phases were withdrawn. Phase compositions were determined by gas chromatograghy equipped with a thermal conductivity detector. The carrier gas was hydrogen with a flow rate of 1.1 cm$^3\cdot$s^{-1} in the column. The injector, detector, and column temperatures were held at (493.15, 513.15, and 460.15) K, respectively. The peak areas of the components were calibrated by gravimetrically weighted mixtures. The mass of each component was determined from the calibration and converted to mole fraction. At least three analyses were performed for each sample to obtain a mean value. The uncertainty of mole fraction was ± 0.001.

Figure 1 schematically shows a tetrahedron to depict three planes of the quaternary systems of (water + 2-propanol + DMC + TMP), (water + 2-propanol + DMC + toluene), and (water + 2-propanol + DMC + heptane). The full range of compositions of the quaternary system was covered using the following procedure. Quaternary mixtures of (water + 2-propanol + DMC + TMP) were prepared from water, 2-propanol, and a preprepared binary mixture of (DMC + TMP). The values of M1, M2, and M3 are approximately 0.25, 0.50, and 0.75, respectively, indicating the mole fraction of DMC in binary mixtures of (DMC + TMP). Table 1 lists the experimental tie-line compositions for one ternary system of (water + 2-propanol + DMC) at T = 298.15 K. Tables 2, 3, and 4 list the experimental tie-line compositions for three quaternary systems of (water + 2-propanol + DMC + TMP), (water + 2-propanol

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

organic phase			aqueous phase		
x_1^{I}	x_2^{I}	x_3^{I}	x_1^{II}	x_2^{II}	x_3^{II}
{x_1 Water + x_2 2-Propanol + x_3 Dimethyl Carbonate + $(1-x_1-x_2-x_3)$ Heptane}[a]					
$x'_3 = 0.25$[b]					
0.0000	0.0088	0.1379	0.9724	0.0155	0.0121
0.0000	0.0241	0.1258	0.9446	0.0417	0.0137
0.0000	0.0460	0.1057	0.9217	0.0639	0.0144
0.0000	0.0678	0.0888	0.8961	0.0879	0.0161
0.0000	0.0875	0.0749	0.8771	0.1066	0.0163
0.0000	0.1013	0.0664	0.8551	0.1268	0.0181
0.0000	0.1171	0.0572	0.8338	0.1465	0.0190
0.0163	0.1407	0.0457	0.7892	0.1881	0.0205
0.0216	0.1513	0.0421	0.7690	0.2068	0.0203
0.0288	0.1682	0.0363	0.7414	0.2325	0.0205
0.0275	0.1815	0.0339	0.7152	0.2567	0.0198
$x'_3 = 0.50$					
0.0000	0.0179	0.3928	0.9650	0.0167	0.0184
0.0000	0.0508	0.3507	0.9401	0.0377	0.0222
0.0000	0.0801	0.2967	0.9124	0.0602	0.0275
0.0000	0.0896	0.2267	0.8816	0.0835	0.0349
0.0000	0.0957	0.1859	0.8632	0.1002	0.0366
0.0000	0.1040	0.1500	0.8358	0.1251	0.0388
0.0000	0.1118	0.1296	0.8136	0.1444	0.0405
0.0116	0.1194	0.1150	0.7877	0.1662	0.0439
0.0170	0.1277	0.1012	0.7733	0.1829	0.0418
0.0197	0.1324	0.0858	0.7412	0.2075	0.0456
0.0207	0.1480	0.0816	0.7310	0.2204	0.0423
0.0227	0.1600	0.0760	0.7098	0.2396	0.0430
$x'_3 = 0.75$					
0.0187	0.0262	0.6703	0.9676	0.0122	0.0202
0.0227	0.0583	0.6242	0.9554	0.0232	0.0214
0.0380	0.0786	0.6089	0.9410	0.0351	0.0239
0.0674	0.1376	0.5315	0.9169	0.0527	0.0304
0.0984	0.1570	0.4747	0.9129	0.0553	0.0317
0.1103	0.1725	0.4541	0.8940	0.0687	0.0373
0.0689	0.1783	0.3853	0.8446	0.0954	0.0587

[a] Obtained by mixing pure water and 2-propanol with the binary mixtures of {x'_3 dimethyl carbonate + $(1 - x'_3)$heptane}. [b] Mole fraction of dimethyl carbonate in the binary mixtures.

+ DMC + toluene), and (water + 2-propanol + DMC + heptane) at T = 298.15 K.

Analysis of Experimental Data

The modified and extended UNIQUAC models[7,8] including the binary and multicomponent interaction parameters were used to represent the experimental tie-line data. We obtained the binary energy parameters, a_{ji}, for the miscible mixtures from the VLE data reduction by using a computer program described by Prausnitz et al.[20] The structural parameters for the modified and extended UNIQUAC models, r and q, were taken from the literature.[20]

At equilibrium, the chemical potentials of each component in the equilibrium phases are equal. This is given in the following eq 1 for every component, i, in the two phases, I and II. x is the mole fraction of liquid phase and γ is the activity coefficient given by the modified UNIQUAC or extended UNIQUAC models previously described in detail.[7,8] We obtained the binary energy parameters for the partially miscible mixtures from the mutual solubility data by solving the following eqs 1and 2 simultaneously

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

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

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 correlate ternary and quaternary LLE accurately using ternary and quaternary parameters in addition to binary ones. Ternary and quaternary LLE calculations were also carried out using eqs 1 and 2. We obtained the additional ternary parameters τ_{231}, τ_{312}, and τ_{123} by fitting the two models to the ternary LLE data, and then we determined the quaternary parameters τ_{2341}, τ_{1342}, τ_{1243}, and τ_{1234}

Table 5. Calculated Results of Binary Phase Equilibrium Data Reduction

system (1 + 2)	T/K	no.[a]	model	a_{12}/K	a_{21}/K	$\delta(P)$/kPa	$\delta(T)$	$10^3\delta(x)$	$10^3\delta(y)$	lit.
2-propanol + DMC	355.05 to 361.68	32	I[b]	230.75	66.87	0.1	0.1	1.0	8.8	4
			II[c]	255.03	81.57	0.1	0.1	1.0	8.9	
DMC + TMP	333.15	22	I	38.25	311.23	0.1	0.0	1.1	3.6	5
			II	91.02	346.33	0.1	0.0	1.0	3.2	
DMC + toluene	333.15	23	I	304.27	−161.30	0.2	0.0	0.9	6.3	5
			II	318.76	−155.85	0.2	0.0	0.9	6.3	
DMC + heptane	355.26 to 369.10	30	I	104.88	237.94	0.2	0.1	1.1	6.6	6
			II	169.86	275.40	0.2	0.1	1.3	6.4	
2-propanol + water	303.15	16	I	330.21	−44.88	0.2	0.0	1.3	8.0	9
			II	308.89	−80.30	0.2	0.0	1.3	8.0	
2-propanol + heptane	353.70 to 362.90	24	I	142.45	711.76	0.4	0.2	2.0	12.2	10
			II	203.82	698.25	0.4	0.2	2.1	12.2	
2-propanol + toluene	298.15	13	I	67.90	812.97	0.0	0.0	1.6	10.3	11
			II	72.12	772.07	0.0	0.0	1.7	10.6	
2-propanol + TMP	348.15	19	I	57.38	903.01	0.2	0.0	2.0	8.4	12
			II	76.69	864.98	0.3	0.0	2.2	8.4	
heptane + water	298.15	MS[d]	I	1884.20	1022.10					13
			II	2135.50	1839.60					
TMP + water	298.15	MS	I	3023.30	1145.60					13
			II	2319.30	2107.10					
toluene + water	298.15	MS	I	1713.30	752.99					14
			II	1540.70	1053.90					
DMC + water	298.15	MS	I	702.87	269.81					15
			II	585.84	272.17					

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

Table 6. 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}	rmsd (%)[e,f]	rmsd (%)[e,g]	lit.
II	water + DMC + heptane	11	I[c]	0.2498	−1.9334	−0.1868	0.75	0.50	15
			II[d]	0.0003	−1.9978	−0.0011	2.58	0.97	
II	water + DMC + TMP	11	I	0.2284	0.0144	0.6101	0.64	0.51	15
			II	0.0513	−0.0246	−0.0284	0.92	0.72	
II	water + DMC + toluene	11	I	−0.0143	−0.6537	−0.1398	0.68	0.41	15
			II	0.0455	−4.3860	0.1331	1.88	0.55	
I	water + 2-propanol + TMP	11	I	−0.2554	−0.0890	1.8992	2.53	1.03	16
			II	−0.0111	−0.8495	−0.0903	1.85	0.58	
I	water + 2-propanol + toluene	12	I	−0.1818	0.4278	0.5175	3.46	1.25	17
			II	0.4544	−0.4546	0.4719	8.39	1.07	
I	water + 2-propanol + heptane	8	I	−0.0462	0.2780	0.0632	4.21	4.17	18
			II	−0.0381	−0.1703	0.1037	4.53	1.30	
I	water + 2-propanol + heptane	8	I	−0.3615	1.5674	−0.7797	4.10	1.82	19
			II	−0.3590	0.1157	0.1982	17.93	6.23	
I	water + 2-propanol + DMC	12	I	−0.4030	−0.2227	2.4593	6.53	0.87	this work
			II	0.9282	−0.5995	0.4197	5.62	2.14	

[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 binary parameters taken from the Table 5. [g] Correlated results using binary and ternary parameters.

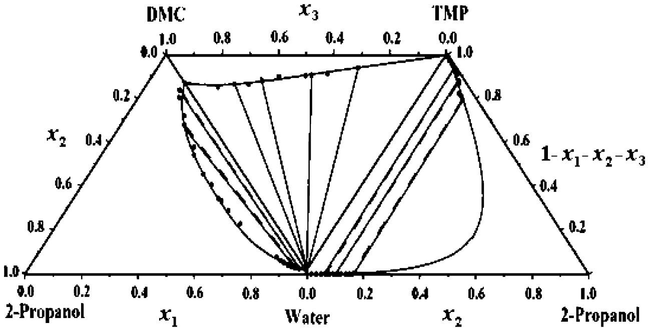

Figure 2. Experimental and calculated LLE composition in mole fraction for three ternary mixtures making up (water + 2-propanol + DMC + TMP) at T = 298.15 K. ●, Experimental tie-line data; —, calculated curve by the modified UNIQUAC model.

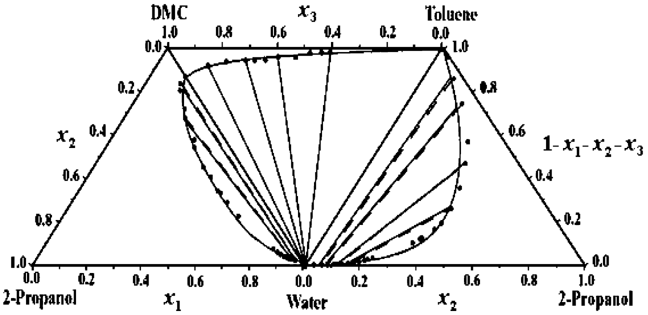

Figure 3. Experimental and calculated LLE composition in mole fraction for three ternary mixtures making up (water + 2-propanol + DMC + toluene) at T = 298.15 K. ●, Experimental tie-line data; —, calculated curve by the modified UNIQUAC model.

from the quaternary experimental LLE data using a simplex method.[21] The root-mean-square deviation between the experimental and calculated values was evaluated by

$$\text{rmsd} = \left\{ \frac{\sum_k \sum_i \sum_j \left(x_{ijk}^{\text{exptl}} - x_{ijk}^{\text{calcd}}\right)^2}{M} \right\}^{0.5} \tag{3}$$

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.

Table 5 lists the binary energy parameters of the modified 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 the models was obtained.

Table 6 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 deviations between the experimental and calculated tie lines. It seems that the correlated results obtained with both the models by using binary and ternary parameters are better than the predicted ones with only binary parameters. Figures 2, 3, and 4 compare, respectively, the experimental tie-line data of the ternary mixtures making up (water + 2-propanol + DMC + TMP), (water + 2-propanol + DMC + toluene), and (water + 2-propanol + DMC + heptane) at T = 298.15 K with those correlated by the modified UNIQUAC model. Better agreement between the experimental values and those correlated using the additional ternary parameters was obtained. Three quaternary systems exhibit type 2 quaternary LLE behavior. These quaternary systems are composed of two ternary LLE classified as type 1 and one ternary LLE classified as type 2. The ternary systems of type 1 are the (water + 2-propanol + DMC), (water + 2-propanol + TMP), (water + 2-propanol + DMC), (water + 2-propanol + toluene), (water + 2-propanol + DMC), and (water + 2-propanol + heptane). The ternary systems of type 2 are the (water + DMC + TMP), (water + DMC + toluene), and (water + DMC + heptane).

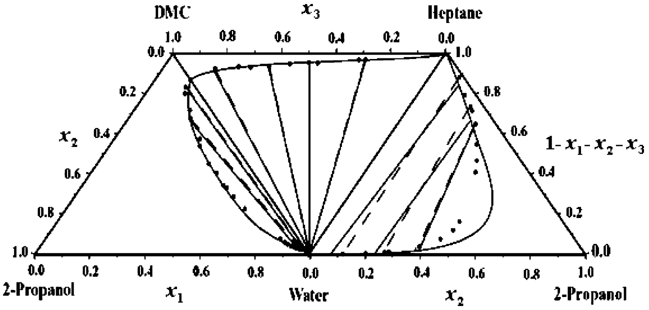

Figure 4. Experimental and calculated LLE composition in mole fraction for three ternary mixtures making up (water + 2-propanol + DMC + heptane) at T = 298.15 K. ●, Experimental tie-line data; —, calculated curve by the modified UNIQUAC model.

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}	rmsd (%)[d,e]	rmsd (%)[d,f]
water + 2-propanol + DMC + TMP	34	I[b]	3.3690	−45.9845	24.1503	−15.0219	3.32	1.93
		II[c]	0.1514	−11.5694	1.1849	−9.8142	3.38	2.92
water + 2-propanol + DMC + toluene	29	I	0.0475	−1.3963	5.8212	2.4930	5.75	1.23
		II	0.0317	17.2503	3.1963	−1.3915	4.70	1.67
water + 2-propanol + DMC + heptane	30	I	5.1630	−30.9059	−28.1120	72.7996	2.33	1.79
		II	0.0727	1.1495	5.2463	2.4337	3.01	1.87

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

In previous work, we investigated LLE for (water + ethanol + DMC + heptane) and (water + ethanol + DMC + TMP) systems.[15] Slopes of the tie lines for the (water + 2-propanol + TMP) and (water + ethanol + TMP) systems are little different, and slopes of the tie lines for the (water + 2-propanol + heptane) and (water + ethanol + heptane) systems are, too. Phase figures show that the areas of the two-phase region of (water + ethanol + TMP) and (water + ethanol + heptane) systems are quite high and are higher than those of (water + 2-propanol + TMP) and (water + 2-propanol + heptane) systems. The solubility of ethanol in heptane or in TMP is relatively larger than that of 2-propanol. It can be seen that ethanol is more soluble in hydrocarbons compared with 2-propanol. DMC is entirely soluble in TMP or heptane or toluene and can be considered to be a good solvent in gasoline.

Table 7 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 the (water + 2-propanol + DMC + TMP), (water + 2-propanol + DMC + toluene), and (water + 2-propanol + DMC + heptane), together with the predicted results by the models with the binary and ternary parameters. The ternary calculated results obtained by using the models with the ref 18 are better than those one obtained by using ref 19 for the system of water + 2-propanol + heptane. To calculate LLE for the quaternary system of water + 2-propanol + DMC + heptane well, it is necessary to use the ternary parameters obtained by using ref 18 in Table 6 for the system of water + 2-propanol + heptane. The correlated results obtained from the models are better than the predicted ones in representing the quaternary systems and are in good agreement with the experimental quaternary LLE data. The root-mean-square deviations between the experimental and correlated results obtained from the modified UNIQUAC model with the binary, ternary, and quaternary parameters are less than 2 % for the three quaternary systems measured in this work. The two models accurately correlated the quaternary experimental LLE data determined in this work.

Conclusions

(Liquid + liquid) equilibrium tie-line data were measured for (water + 2-propanol + dimethyl carbonate + isooctane), (water + 2-propanol + dimethyl carbonate + toluene), (water + 2-propanol + dimethyl carbonate + heptane), and (water + 2-propanol + DMC) at T = 298.15 K and ambient pressure. The experimental quaternary and their constituent ternary results were predicted by both the modified and extended UNIQUAC models. The modified and extended UNIQUAC models were not able to reproduce the quaternary (liquid + liquid) equilibria accurately 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 better agreement with experimental results.

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