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Measurement and Calculation of Liquid−Liquid Equilibria of Ternary and Quaternary Systems Containing Water, Propan-1-ol, and 2,2,4-Trimethylpentane (TMP) with 2,2′-Oxybis(propane) (DIPE) or Dimethyl Carbonate (DMC)

Changwei Wang, Yao Chen,* and Aiping Ying

Department of Chemistry, Jinan University, Guangzhou, 510632, China

ABSTRACT: Liquid−liquid equilibrium data for quaternary systems of water + propan-1-ol + 2,2,4-trimethylpentane (TMP) + 2,2′-oxybis(propane) (DIPE) or dimethyl carbonate and ternary systems of water + propan-1-ol + TMP or DIPE or dimethyl carbonate (DMC) were measured at 298.15 K and ambient pressure. The experimental tie-line results were correlated with the modified and extended universal quasichemical (UNIQUAC) activity coefficient models both with ternary and quaternary parameters in addition to binary ones. Distribution coefficients were calculated to evaluate the solubility of DMC or DIPE in aqueous and organic phases. The phase diagrams for the ternary and quaternary systems measured in this work including both the experimental and the correlated tie lines are presented.

INTRODUCTION

Since the use of 2-methoxy-2-methylpropane (MTBE) as an octane booster in reformulated gasoline causes significant contamination of groundwater, several oxygenated compounds such as alcohols, ethers, and dialkyl carbonates are studied as substitute materials. Some alcohols such as methanol, ethanol, and propan-1-ol, while having higher octane numbers and being less expensive than ethers, have the disadvantage that they have a higher blending Reid vapor pressure and are very soluble in water. 2,2′-Oxybis(propane) (DIPE) has been pointed out as healthier and friendlier antiknock additives for gasoline because of its high octane number and lower vapor pressure, replacing typical leaded compounds.[1] Dimethyl carbonate (DMC) has about three times the oxygen content as MTBE and excellent characteristics as a gasoline additive: high octane number, lower vapor pressure, reduction of automotive CO and NO_x emissions, and a very high density.[2] DIPE and DMC may be ideal fuel additives to replace MTBE. However, the addition of DIPE and DMC to gasoline may affect the mutual hydrocarbon−water solubility, resulting in either greater or less likelihood of an aqueous phase appearing in the gasoline tank or fuel line. The phase equilibrium data are vital to understand phase behavior for the mixtures containing DMC or DIPE. Some studies on the phase equilibria of mixtures containing oxygenated compounds have gained much interest in recent years. The phase equilibria for these oxygenated compounds have been systematically measured to provide accurate solubility data.[3−6]

In this work, we present liquid−liquid equilibria (LLE) for three ternary systems of water + propan-1-ol + 2,2,4-trimethylpentane (TMP) or DMC or DIPE and two quaternary systems of water + propan-1-ol + TMP + DIPE or DMC at 298.15 K and ambient pressure. The measured LLE results are correlated by means of the extended and modified universal quasichemical (UNIQUAC) models.[7,8] The binary parameters of miscible binary subsystem mixtures of ternary and quaternary systems were obtained from vapor−liquid equilibria (VLE) data,[9−14] whereas those of immiscible mixtures were obtained from mutual solubility data.[6,15,16] The ternary parameters, obtained from the ternary systems of water + DIPE + TMP,[4] water + DMC + TMP,[17] and water + propan-1-ol + TMP or DMC or DIPE measured in this work are needed to represent accurately the two quaternary LLE data.

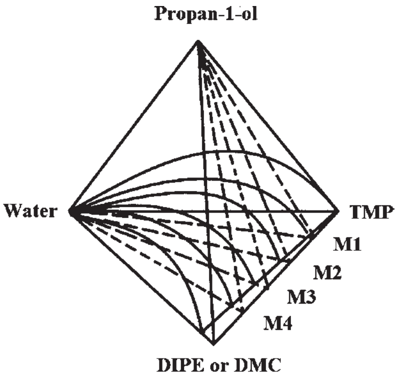

Figure 1. Phase equilibria of (water + propan-1-ol + DIPE + TMP) and (water + propan-1-ol + DMC + TMP). M1, M2, M3, and M4 denote quaternary section planes.

EXPERIMENTAL SECTION

Materials. DMC was obtained from Alfa Aesar Company with a nominal minimum mass fraction of 0.990. TMP was supplied by Guangzhou Chemical Reagent Factory with

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Table 1. Equilibrium Phase Compositions for Ternary Mixtures of Water (1) + Propan-1-ol (2) + TMP (3) at 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}
0.0009	0.0000	0.9991	1.0000	0.0000	0.0000
0.0000	0.0038	0.9962	0.9921	0.0079	0.0000
0.0047	0.0097	0.9856	0.9813	0.0187	0.0000
0.0086	0.0189	0.9725	0.9708	0.0292	0.0000
0.0190	0.0435	0.9375	0.9625	0.0375	0.0000
0.0205	0.0653	0.9142	0.9569	0.0431	0.0000
0.0444	0.1111	0.8445	0.9474	0.0526	0.0000
0.0508	0.1402	0.8090	0.9354	0.0646	0.0000

Table 2. Equilibrium Phase Compositions for Ternary Mixtures of Water (1) + Propan-1-ol (2) + DMC (3) at 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}
0.1300	0.0000	0.8700	0.9834	0.0000	0.0166
0.1851	0.0380	0.7769	0.9575	0.0114	0.0311
0.2619	0.0831	0.6550	0.9547	0.0158	0.0295
0.3020	0.1086	0.5894	0.9386	0.0256	0.0358
0.4263	0.1272	0.4466	0.9161	0.0345	0.0494
0.4899	0.1423	0.3678	0.9124	0.0417	0.0458
0.5731	0.1398	0.2871	0.8918	0.0519	0.0564
0.6574	0.1243	0.2184	0.8555	0.0645	0.0800
0.6864	0.1186	0.1950	0.8625	0.0638	0.0737

Table 3. Equilibrium Phase Compositions for Ternary Mixtures of Water (1) + Propan-1-ol (2) + DIPE (3) at 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}
0.0289	0.0000	0.9711	0.9980	0.0000	0.0020
0.0359	0.0376	0.9265	0.9922	0.0078	0.0000
0.0571	0.0500	0.8929	0.9836	0.0142	0.0022
0.0691	0.0937	0.8372	0.9771	0.0212	0.0016
0.0827	0.1411	0.7762	0.9728	0.0252	0.0020
0.1072	0.2085	0.6843	0.9669	0.0313	0.0019
0.1685	0.2741	0.5574	0.9630	0.0351	0.0019
0.2928	0.3645	0.3428	0.9547	0.0439	0.0014
0.3716	0.4038	0.2246	0.9456	0.0527	0.0017
0.4368	0.3997	0.1635	0.9422	0.0564	0.0014

nominal minimum mass fraction of 0.997. DIPE and propan-1-ol were obtained from the Tianjin Chemical Reagent Institute with nominal minimum mass fractions of 0.995 and 0.998, respectively. Gas chromatography analysis gave mass fractions of 0.9940 for DMC, 0.9960 for TMP, 0.9950 for DIPE, 0.9970 for propan-1-ol, and 0.9990 for water. Redistilled water was used.

Table 4. Equilibrium Phase Compositions for Quaternary Mixtures of Water (1) + Propan-1-ol (2) + DIPE (3) + TMP (4) at 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 Propan-1-ol + x_3 DIPE + $(1 - x_1 - x_2 - x_3)$ TMP$\}^a$					
$x'_4 = 0.20^b$					
0.5474	0.3789	0.0561	0.9135	0.0848	0.0017
0.2150	0.3768	0.3326	0.9615	0.0385	0.0000
0.4267	0.4270	0.1179	0.9343	0.0642	0.0015
0.5067	0.4005	0.0722	0.9216	0.0768	0.0016
0.0901	0.0948	0.6531	0.9817	0.0174	0.0010
0.1767	0.2843	0.4238	0.9618	0.0382	0.0000
$x'_4 = 0.40$					
0.5177	0.3947	0.0492	0.9163	0.0827	0.0010
0.4209	0.4396	0.0837	0.9303	0.0686	0.0011
0.2323	0.3566	0.2414	0.9458	0.0531	0.0011
0.1600	0.2804	0.3308	0.9518	0.0473	0.0009
0.0691	0.1318	0.4666	0.9713	0.0287	0.0000
0.0431	0.0356	0.5375	0.9868	0.0132	0.0000
0.2854	0.4360	0.1644	0.9376	0.0614	0.0010
0.1701	0.2212	0.3557	0.9555	0.0437	0.0009
$x'_4 = 0.60$					
0.0758	0.0644	0.3443	0.9822	0.0178	0.0000
0.1070	0.1199	0.3006	0.9592	0.0408	0.0000
0.1165	0.2367	0.2527	0.9477	0.0523	0.0000
0.4096	0.4403	0.0569	0.9138	0.0862	0.0000
0.5034	0.3953	0.0358	0.8996	0.1004	0.0000
0.1742	0.3570	0.1800	0.9399	0.0601	0.0000
0.3337	0.4626	0.0795	0.9203	0.0797	0.0000
0.1504	0.3223	0.2031	0.9407	0.0593	0.0000
$x'_4 = 0.80$					
0.1180	0.0177	0.1694	0.9839	0.0161	0.0000
0.2685	0.4085	0.0389	0.8727	0.1273	0.0000
0.3171	0.4296	0.0433	0.8843	0.1157	0.0000
0.1509	0.2763	0.1048	0.9179	0.0821	0.0000
0.2057	0.3936	0.0733	0.9053	0.0947	0.0000
0.6328	0.3221	0.0363	0.9036	0.0936	0.0028
0.0836	0.0789	0.1581	0.9562	0.0438	0.0000
0.2666	0.3869	0.2025	0.9438	0.0562	0.0000

[a] Obtained by mixing pure water and propan-1-ol with the binary mixtures of $\{x'_4$ TMP + $(1 - x'_4)$ DIPE$\}$. [b] Mole fraction of TMP in the binary mixtures.

Procedure and Results. Ternary and quaternary LLE measurements were carried out at the temperature 298.15 K. The temperature uncertainty was ± 0.05 K. The quaternary mixtures with a volume of about (70 to 100) mL were prepared by adding water and propan-1-ol into the mixtures TMP + DIPE or TMP + DMC whose compositions are M1, M2, M3, and M4 to cover the two-phase regions. The values of M1, M2, M3, and M4 are 0.20, 0.40, 0.60, and 0.80, respectively, indicating the mole fraction of TMP in the TMP + DIPE or TMP + DMC mixtures. The mixtures loaded in an equilibrium glass cell were

Table 5. Equilibrium Phase Compositions for Quaternary Mixtures of Water (1) + Propan-1-ol (2) + DMC (3) + TMP (4) at 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}
$\{x_1\,\mathrm{Water} + x_2\,\mathrm{Propan\text{-}1\text{-}ol} + x_3\,\mathrm{DMC} + (1 - x_1 - x_2 - x_3)\,\mathrm{TMP}\}^a$					
$x'_4 = 0.20^b$					
0.0751	0.0396	0.6626	0.9618	0.0132	0.0250
0.1136	0.0878	0.5976	0.9530	0.0223	0.0247
0.1845	0.1737	0.4792	0.9217	0.0451	0.0333
0.2869	0.2266	0.3558	0.9068	0.0568	0.0364
0.2523	0.2321	0.3509	0.8995	0.0623	0.0382
0.0789	0.1270	0.2383	0.8789	0.0798	0.0412
0.1328	0.1393	0.3609	0.8805	0.0748	0.0439
$x'_4 = 0.40$					
0.0473	0.1289	0.1810	0.8781	0.0878	0.0342
0.0566	0.1235	0.1528	0.8786	0.0901	0.0313
0.0745	0.0969	0.3978	0.9319	0.0394	0.0287
0.0780	0.1441	0.3241	0.8992	0.0632	0.0376
0.0459	0.0321	0.4543	0.9613	0.0162	0.0225
0.0315	0.0308	0.4612	0.9875	0.0053	0.0072
0.0494	0.1309	0.2113	0.8821	0.0822	0.0357
$x'_4 = 0.60$					
0.0213	0.0182	0.2366	0.9599	0.0198	0.0203
0.0235	0.0443	0.2154	0.9458	0.0341	0.0201
0.0373	0.0854	0.1724	0.9210	0.0566	0.0224
0.0427	0.1118	0.1365	0.8924	0.0827	0.0249
0.0465	0.1190	0.0918	0.8986	0.0847	0.0167
0.0307	0.1202	0.1058	0.8974	0.0834	0.0192
0.0432	0.1742	0.0860	0.8111	0.1600	0.0289
$x'_4 = 0.80$					
0.0161	0.0125	0.0896	0.9711	0.0191	0.0098
0.0242	0.0262	0.0820	0.9546	0.0354	0.0100
0.0272	0.0830	0.0687	0.9260	0.0634	0.0106
0.0297	0.1241	0.0572	0.9013	0.0875	0.0111
0.0333	0.1249	0.0520	0.9050	0.0851	0.0099
0.0336	0.1268	0.0469	0.9045	0.0865	0.0091
0.0392	0.1355	0.0399	0.9039	0.0874	0.0087
0.0458	0.1828	0.0214	0.8783	0.1154	0.0063
0.0700	0.1695	0.0557	0.8709	0.1164	0.0127

[a] Obtained by mixing pure water and propan-1-ol with the binary mixtures of $\{x'_4\,\mathrm{TMP} + (1 - x'_4)\,\mathrm{DMC}\}$. [b] Mole fraction of DMC in the binary mixtures.

Table 6. Structural Parameters for Pure Components

component	r	q	q'^a	q'^b
water	0.92	1.40	1.28	0.96
DMC	3.06	2.82	$q^{0.75}$	$q^{0.20}$
DIPE	4.74	4.09	$q^{0.75}$	$q^{0.20}$
TMP	5.85	4.94	$q^{0.75}$	$q^{0.20}$
propan-1-ol	2.78	2.51	1.32	0.89

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

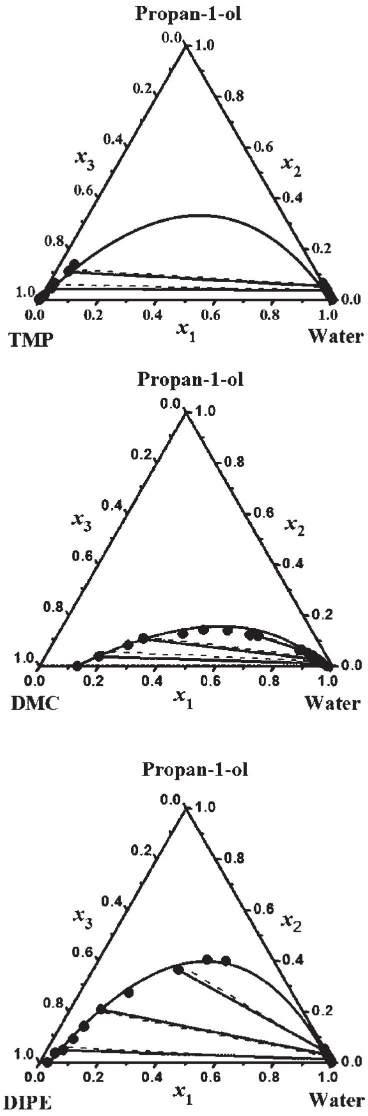

Figure 2. Experimental and calculated LLE for the ternary systems of water + propan-1-ol + TMP, water + propan-1-ol + DMC, and water + propan-1-ol + DIPE at 298.15 K. ●, experimental data point. - - -, predicted by the modified UNIQUAC model with binary parameters. —, correlated by the modified UNIQUAC model with binary and ternary parameters.

stirred vigorously by using a magnetic stirrer for 3 h and settled for 3 h, which was sufficient for separation into two phases. After reaching phase equilibrium, samples of two liquid phases were withdrawn and analyzed by a gas chromatograph (GC-14C) with a thermal conductivity detector. The detector and injection port temperatures were set at 483.15 K. The hydrogen flow rates for both the separation and the reference columns were set at 60 mL·min^{-1}. Each component of the mixtures was separated clearly using a stainless steel column with 2 m in length packed with Porapak QS. The peak areas of the components, detected with a chromatopac (N2000), were calibrated and converted to mole fraction. Three analyses were done for each sample to obtain a mean value. The estimated uncertainty of the mole fraction was about 0.005.

Table 7. Calculated Results of Binary Phase Equilibrium Data Reduction

system (1 + 2)	T/K	a_{12}/K	a_{21}/K	$\delta(P)$/kPa	$\delta(T)$	$10^3\delta(x)$	$10^3\delta(y)$
water + propan-1-ol	360.49 to 372.81	262.46[a]	159.09	1.49	0.1	2.8	6.7
		244.51[b]	138.20	1.52	0.1	2.9	6.8
propan-1-ol + DIPE	303.15	16.12	449.77	1.21	0.0	1.0	3.2
		15.48	437.74	1.19	0.0	1.0	3.2
propan-1-ol + TMP	357.93 to 365.46	70.52	950.09	0.46	0.0	0.5	4.9
		96.26	912.50	0.50	0.0	0.5	4.8
propan-1-ol + DMC	333.15	209.28	213.97	1.05	0.0	0.6	5.8
		231.15	205.06	1.04	0.0	0.6	5.8
DIPE + TMP	397.09 to 342.58	110.01	−37.39	0.73	0.0	0.9	7.6
		129.17	−18.33	0.75	0.0	0.9	7.7
DMC + TMP	333.15	38.58	308.86	1.12	0.0	1.1	3.6
		91.28	343.72	1.02	0.0	1.0	3.2
water + DIPE	298.15	166.68	1590.60				
		158.70	1209.00				
water + DMC	298.15	269.81	702.87				
		272.17	585.84				
water + TMP	298.15	1145.60	3023.30				
		2107.10	2319.30				

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

Table 8. Calculated Results for Ternary Liquid−Liquid Equilibria at 298.15 K

system (1 + 2 + 3)	no.[a]	τ_{231}	τ_{132}	τ_{123}	rms[d,e] (%)	rms[d,f] (%)
water + propan-1-ol + TMP	8	−0.7593[b]	2.5315	2.4305	0.82	0.44
		−0.2072[c]	0.2673	0.1223	0.62	0.41
water + propan-1-ol + DMC	9	−0.9039	0.8407	1.9641	2.36	1.28
		0.1922	0.9601	0.2366	7.50	1.78
water + propan-1-ol + DIPE	10	−0.3579	0.1364	0.8953	1.20	0.50
		−0.0724	0.0308	−1.0672	3.52	2.57
water + DIPE + TMP	9	−0.0022	0.1204	0.1311	0.30	0.29
		−0.0346	0.0153	0.0226	1.03	0.73
water + DMC + TMP	9	0.2342	0.3329	0.0873	2.61	0.53
		0.3765	−2.0460	1.1793	0.92	0.65

[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 7. [f] Correlated results using binary and ternary parameters taken from Tables 7 and 8.

Table 9. Calculated Results for Quaternary Liquid−Liquid Equilibria at 298.15 K

system (1 + 2 + 3 + 4)	no.[a]	τ_{2341}	τ_{1342}	τ_{1243}	τ_{1234}	rms[d,e] (%)	rms[d,f] (%)
water + propan-1-ol + DIPE + TMP	30	7.8863[b]	3.0725	−21.9883	−15.9745	3.38	1.84
		0.9928[c]	0.2212	−0.5752	−1.0955	3.08	2.37
water + propan-1-ol + DMC + TMP	30	−0.4153	0.9621	−0.3872	−5.8993	3.81	2.83
		0.4398	0.4405	0.1005	0.1938	2.77	1.91

[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 7 and 8. [f] Correlated results using binary, ternary, and quaternary parameters taken from Tables 7 to 9.

Figure 1 represents schematically a tetrahedron to show the quaternary LLE surface for the (water + propan-1-ol + DIPE + TMP) and (water + propan-1-ol + DMC + TMP) systems, respectively. Tables 1 to 3 summarize the experimental tie-line compositions for three ternary systems of water + propan-1-ol + DMC, water + propan-1-ol + TMP, and water + propan-1-ol + DIPE at 298.15 K. Tables 4 and 5 list the experimental tie-line compositions for two quaternary systems of water + propan-1-ol + DIPE + TMP and water + propan-1-ol + DMC + TMP at 298.15 K. The sensitivity of the GC for DIPE and TMP are 0.0001 in mole fraction, respectively.

CALCULATION PROCEDURE

The experimental ternary and quaternary LLE data were correlated by using the extended and modified UNIQUAC

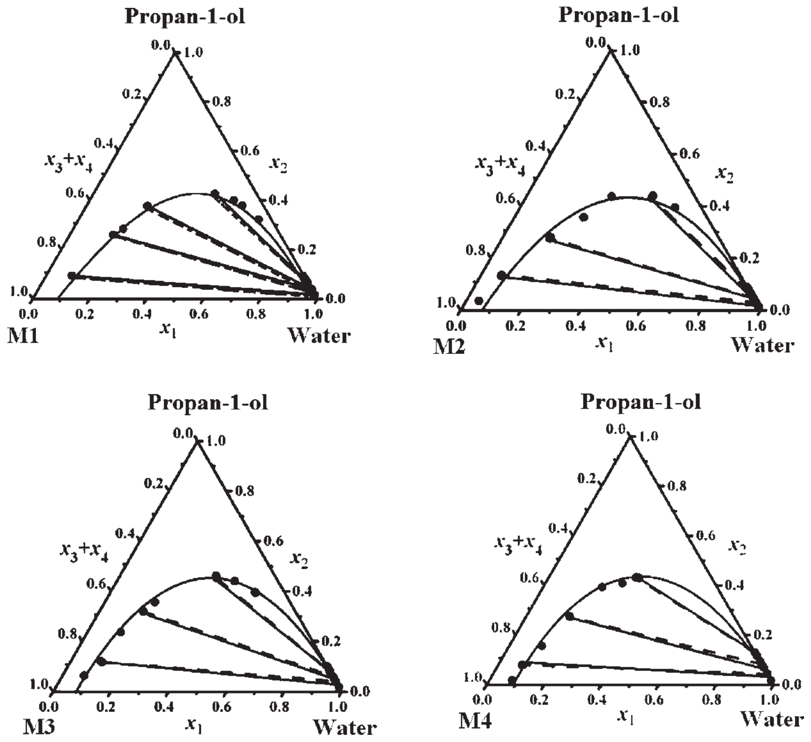

Figure 3. Experimental and calculated LLE composition in mole fraction on the planes M1, M2, M3, and M4 for quaternary mixtures of water + propan-1-ol + DIPE + TMP at 298.15 K. ●, experimental tie-line data. - - -, predicted by modified UNIQUAC. —, correlated by modified UNIQUAC.

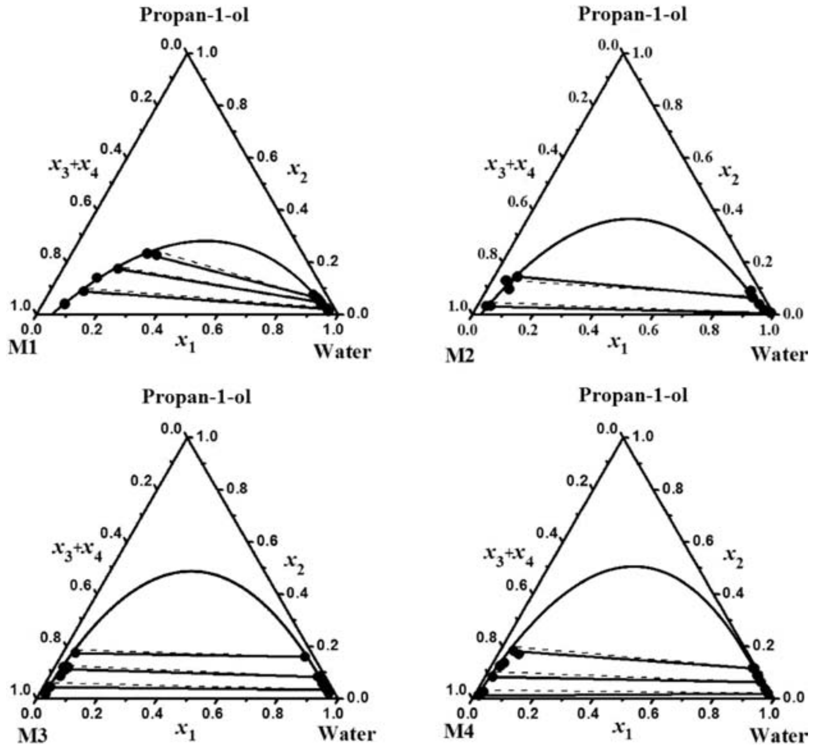

Figure 4. Experimental and calculated LLE composition in mole fraction on the planes M1, M2, M3, and M4 for quaternary mixtures of (water + propan-1-ol + DMC + TMP) at 298.15 K. ●, experimental tie-line data. - - -, predicted by modified UNIQUAC. —, correlated by modified UNIQUAC.

models[7,8] with binary and additional multicomponent interaction parameters. The parameters for completely miscible binary mixtures were obtained from experimental VLE data. The binary data reduction was performed by using a computer program

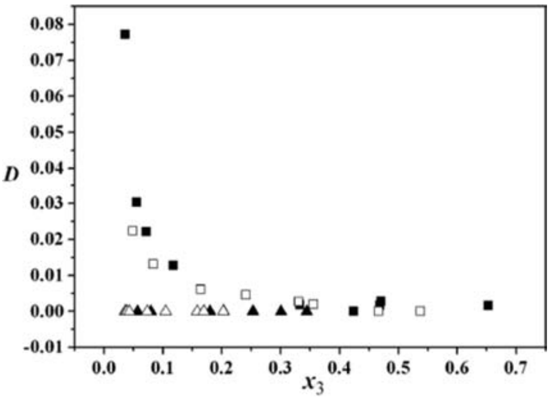

Figure 5. Distribution ratio of DIPE in the quaternary system of water + propan-1-ol + DIPE + TMP, D, as a function of mole fraction of DIPE in the organic-rich phase, x_3. ■, □, ▲, △, X'_4 = 0.2, 0.4, 0.6, and 0.8, respectively.

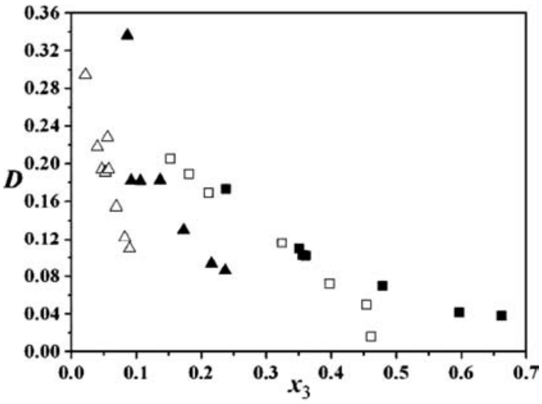

Figure 6. Distribution ratio of DMC in the quaternary system of water + propan-1-ol + DMC + TMP, D, as a function of mole fraction of DMC in organic-rich phase, x_3. ■, □, ▲, △, X'_4 = 0.2, 0.4, 0.6, and 0.8, respectively.

described by Prausnitz et al.[18] according to the following thermodynamic equations

$$Py_i\phi_i = x_i\gamma_i P_i^S\phi_i^S \exp[V_i^L(P - P_i^S)/RT] \tag{1}$$

$$\ln \phi_i = (2\sum_j y_jB_{ij} - \sum_i\sum_j y_iy_jB_{ij})P/RT \tag{2}$$

where P, x, y, and γ are the total pressure, liquid phase mole fraction, vapor phase mole fraction, and activity coefficient, respectively. The pure component vapor pressure P^S was calculated by using the Antoine equation. The liquid molar volume V^L was obtained by a modified Rackett equation.[19] The fugacity coefficient ϕ, calculated by the virial equation of state with the second virial coefficient B, was expressed by eq 2. The superscript S stands for a value at saturation vapor pressure. The pure and cross-second virial coefficients were estimated by the method of Hayden and O'Connell.[20]

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.

$$(x_i\gamma_i)^{\mathrm{I}} = (x_i\gamma_i)^{\mathrm{II}} \tag{3}$$

$$\sum_i x_i^{\mathrm{I}} = 1 \quad \text{and} \quad \sum_i x_i^{\mathrm{II}} = 1 \tag{4}$$

where I and II represent the equilibrium phases, x is the liquid phase mole fraction, and γ is the activity coefficient given by the modified or extended UNIQUAC models. 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 3 and 4. The additional ternary parameters, τ_{231}, τ_{132}, and τ_{123}, are obtained from the experimental ternary LLE results, and the quaternary parameters, τ_{2341}, τ_{1342}, τ_{1243}, and τ_{1234}, are obtained from the correlation of the quaternary LLE results. The ternary and quaternary parameters were determined using a simplex method[21] by minimizing the objective function:

$$F = 10^2[\sum_k \min \sum_i\sum_j (x_{ijk}^{\mathrm{exp}} - x_{ijk}^{\mathrm{cal}})^2/M]^{0.5} \tag{5}$$

where min denotes minimum values, i = 1 to 3 for ternary mixtures or i = 1 to 4 for quaternary mixtures, j = 1, 2 (phases), k = 1, 2, ..., n (no. of tie lines), $M = 2ni$, and x denotes the liquid phase mole fraction.

■ CALCULATED RESULTS AND DISCUSSION

Table 6 shows the molecular structural volume and area parameters, r and q, for DMC calculated by the method of Bondi,[22] while the others were taken from Prausnitz et al.[18] The interaction correction factor q' for self-associating components was taken from the literature,[7,8] 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 7 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 8 presents the ternary parameters, together with the root-mean-square deviations between the experimental and the calculated tie lines for the ternary LLE. The experimental and calculated results for three ternary systems of water + propan-1-ol + TMP, water + propan-1-ol + DMC, and water + propan-1-ol + DIPE agreed well as shown in Figure 2. For the three ternary systems, the average root-mean-square deviations between the measured results and the correlated results by using the extended and modified UNIQUAC models are 1.23 % and 0.61 %, respectively. The correlated results obtained from the both models are better than the predicted ones in representing the ternary LLE measured in this work.

Table 9 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 7 and 8. Figures 3 and 4 compare the experimental and calculated results for the quaternary LLE of the water + propan-1-ol + DIPE + TMP and water + propan-1-ol + DMC + TMP systems, which are plotted on planes M1, M2, M3, and M4 illustrated in Figure 1. Good agreement between experimental LLE results and correlated results of the modified UNIQUAC model is shown in Figures 3 and 4. The correlated results obtained from the both models are better than the predicted ones in representing the quaternary LLE measured in this work.

To observe better the influence of DIPE or DMC addition on aqueous and organic phases, distribution ratio, *D*, for DIPE or DMC, calculated from the experimental quaternary LLE data, was defined by

$$D = \frac{x_i^{\text{aqueous phase}}}{x_i^{\text{organic phase}}} \qquad (6)$$

where *i* denotes component DIPE or DMC and *x* is the liquid phase mole fraction. Figures 5 and 6 show the distribution ratios of DIPE and DMC in the quaternary systems of water + propan-1-ol + DIPE + TMP and water + propan-1-ol + DMC + TMP as a function of its mole fraction in organic-rich phase. For the quaternary systems, the distribution ratios of DIPE and DMC are quite small, and the distribution ratios of DIPE are much smaller than those of DMC. The distribution ratios of DIPE and DMC were almost decreasing as its mole fraction in organic-rich phase increased. This implies that the addition of DIPE and DMC does not increase evidently the solubility of DIPE and DMC in aqueous phase. As gasoline additives, DIPE and DMC are more soluble with hydrocarbon compounds.

CONCLUSIONS

Quaternary LLE results for water + propan-1-ol + TMP + DIPE or DMC and ternary LLE results for water + propan-1-ol + TMP or DMC or DIPE were investigated at 298.15 K and ambient pressure. The extended and modified UNIQUAC models are used to describe the phase equilibria of these systems. The ternary and quaternary adjustable parameters were obtained in fitting the models to the experimental ternary and quaternary LLE systems. Agreement between the calculated and the experimental values is satisfactory for the three ternary and two quaternary systems measured in this work. The average root-mean-square deviations of the two quaternary systems correlations were 2.33 % for the modified UNIQUAC model and 2.14 % for the extended UNIQUAC model, respectively. The phase diagrams show a good agreement between experimental and calculation results.

AUTHOR INFORMATION

Corresponding Author

*Fax: +86-20-85221697. E-mail: tlirq@jnu.edu.cn.

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