JOURNAL OF
CHEMICAL &
ENGINEERING
DATA

ARTICLE

pubs.acs.org/jced

Experimental Measurements and Correlations of Liquid−Liquid Equilibria for the Ternary and Quaternary Mixtures Formed by Dialkyl Carbonates at T = 298.15 K

Yao Chen,* Hui Wang, and Changwei Wang

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

ABSTRACT: Tie-line data for two quaternary systems of (water + 1-butanol + diethyl carbonate (DEC) + dimethyl carbonate (DMC)) and (water + 1-butanol + hexane + DMC) and two relevant ternary systems of (water + 1-butanol + DEC) and (water + 1-butanol + DMC) at T = 298.15 K and atmospheric pressure were determined. The experimental ternary and quaternary (liquid + liquid) equilibrium results were correlated by using the modified universal quasichemical activity coefficient (UNIQUAC) model, and the interaction parameters were obtained. The root-mean-square deviations of the two quaternary systems correlations were 0.56 % and 0.75 %, respectively. Distribution coefficients were calculated to evaluate the solubility of DMC in two phases.

INTRODUCTION

Dialkyl carbonates such as dimethyl carbonate (DMC) and diethyl carbonate (DEC) are recognized as environmentally benign chemicals. There has been a considerable interest in using DMC or DEC for meeting the oxygenate specifications on gasoline and as a means of converting natural gas to a liquid transportation fuel.[1] In recent years it has become increasingly important to develop new thermodynamic studies on the (vapor + liquid) equilibria (VLE) of mixtures formed by hydrocarbons and oxygenated additives (DMC or DEC and alkanols) to unleaded gasoline.[2−7] In previous works,[8−10] we reported the (liquid + liquid) equilibria (LLE) results for the quaternary systems containing DMC or DEC.

As these systematic studies we present here LLE data obtained at the temperature of 298.15 K for the mixtures containing DMC and DEC as ternary mixtures of (water + 1-butanol + DEC) and (water + 1-butanol + DMC) and quaternary mixtures of (water + 1-butanol + DEC + DMC) and (water + 1-butanol + hexane + DMC). The experimental results were correlated by means of the modified universal quasichemical activity coefficient (UNIQUAC) model[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: VLE, (1-butanol + DEC),[2] (1-butanol + DMC),[3] (hexane + DMC),[4] (DMC + DEC),[5] (1-butanol + hexane),[12] mutual solubilities, (water + 1-butanol),[13] (water + hexane),[13] (water + DEC),[14] (water + DMC),[10] the constituent ternary LLE, (water + hexane + DMC), (water + 1-butanol + hexane),[15] (water + DMC + DEC),[8] (water + 1-butanol + DEC), and (water + 1-butanol + DMC) measured in this work.

EXPERIMENTAL SECTION

Materials. DEC and DMC were obtained from Shanghai Jingchun Reagent Factory, with mass fractions of 0.992 and 0.990, respectively. Hexane and 1-butanol were supplied by Guangzhou Chemical Reagent Factory, with mass fractions of 0.990, and 0.996, respectively. Bidistilled water was used. Gas chromatography analysis did not detect appreciable impurity peaks and gave mass fractions of 0.9920 for hexane, 0.9940 for DMC, 0.9950 for 1-butanol, 0.9910 for DEC, and 0.9990 for water.

Apparatus and Procedures. LLE measurements for the ternary and quaternary mixtures were carried out at the temperature of 298.15 K. The temperature uncertainty was ± 0.05 K. A solution of volume from (70 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 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. The temperatures of the injection system and detector were set at 513.15 K, respectively. The initial and final temperatures of the oven were kept at (423.15 and 483.15) K, respectively. The hydrogen flow rates for both the separation and the reference columns were set at 1 $cm^3 \cdot s^{-1}$. 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 made to obtain a mean value. The accuracy of the phase composition measurements was estimated to be about ± 0.0001 in mole fraction.

Tables 1 to 5 list the experimental tie-line compositions for two ternary systems of (water + 1-butanol + DEC) and (water + 1-butanol + DMC) and two quaternary systems of (water + 1-butanol + DEC + DMC) and (water + 1-butanol + hexane + DMC) at 298.14 K. Figures 1 and 2 represent schematically a

Special Issue: John M. Prausnitz Festschrift

Received: August 25, 2010
Accepted: October 8, 2010
Published: November 15, 2010

Table 1. Equilibrium Phase Compositions for Ternary Mixtures of Water (1) + 1-Butanol (2) + DEC (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}
0.0474	0.0000	0.9526	0.9978	0.0000	0.0022
0.0502	0.0898	0.8600	0.9886	0.0035	0.0079
0.0833	0.1793	0.7374	0.9876	0.0061	0.0063
0.1281	0.2593	0.6126	0.9764	0.0103	0.0133
0.2132	0.3384	0.4484	0.9822	0.0113	0.0065
0.2892	0.4022	0.3086	0.9813	0.0134	0.0053
0.3444	0.4564	0.1992	0.9813	0.0144	0.0043
0.3956	0.4847	0.1197	0.9809	0.0165	0.0026
0.4266	0.4937	0.0797	0.9810	0.0172	0.0018
0.4608	0.4954	0.0438	0.9769	0.0217	0.0014
0.5120	0.4880	0.0000	0.9808	0.0192	0.0000

Table 2. Equilibrium Phase Compositions for Ternary Mixtures of Water (1) + 1-Butanol (2) + DMC (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}
0.1339	0.0000	0.8661	0.9771	0.0000	0.0229
0.0862	0.1613	0.7525	0.9710	0.0072	0.0218
0.1342	0.2376	0.6282	0.9653	0.0089	0.0258
0.1811	0.2880	0.5309	0.9636	0.0121	0.0243
0.2305	0.3487	0.4208	0.9638	0.0146	0.0216
0.2917	0.4086	0.2997	0.9644	0.0164	0.0192
0.3606	0.4575	0.1819	0.9601	0.0226	0.0173
0.4130	0.4863	0.1007	0.9630	0.0246	0.0124
0.4643	0.4960	0.0397	0.9757	0.0209	0.0034
0.5120	0.4880	0.0000	0.9808	0.0192	0.0000

Table 3. Equilibrium Phase Compositions for Ternary Mixtures of Water (1) + Hexane (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}
0.1339	0.0000	0.8661	0.9771	0.0000	0.0229
0.0396	0.0778	0.8826	0.9784	0.0000	0.0216
0.0314	0.1633	0.8053	0.9809	0.0000	0.0191
0.0248	0.2259	0.7493	0.9810	0.0000	0.0190
0.0140	0.3259	0.6601	0.9815	0.0000	0.0185
0.0107	0.4562	0.5331	0.9811	0.0000	0.0189
0.0000	0.5539	0.4261	0.9830	0.0000	0.0170
0.0000	0.6742	0.3258	0.9849	0.0000	0.0151
0.0000	0.7876	0.2124	0.9898	0.0000	0.0102
0.0000	0.9022	0.0978	0.9951	0.0000	0.0049

Table 4. Equilibrium Phase Compositions for Quaternary Mixtures of Water (1) + 1-Butanol (2) + DEC (3) + DMC (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 1-Butanol + x_3 DEC + $(1 - x_1 - x_2 - x_3)$ DMC$\}^a$					
$x_3' = 0.20^b$					
0.0684	0.0000	0.2146	0.9826	0.0000	0.0009
0.1064	0.1435	0.1590	0.9741	0.0072	0.0008
0.1636	0.2403	0.1349	0.9714	0.0086	0.0022
0.2163	0.3145	0.1180	0.9720	0.0112	0.0018
0.2949	0.3572	0.0868	0.9715	0.0133	0.0015
0.3724	0.4129	0.0597	0.9723	0.0153	0.0011
0.4208	0.4387	0.0418	0.9749	0.0157	0.0009
0.4541	0.4593	0.0248	0.9735	0.0192	0.0007
0.4823	0.4784	0.0097	0.9752	0.0209	0.0005
$x_3' = 0.40$					
0.0514	0.0000	0.4368	0.9870	0.0000	0.0021
0.0961	0.0983	0.3743	0.9805	0.0044	0.0031
0.1462	0.2259	0.2762	0.9785	0.0078	0.0032
0.2104	0.3070	0.2131	0.9732	0.0113	0.0052
0.2910	0.3632	0.1575	0.9751	0.0131	0.0030
0.3647	0.4171	0.1056	0.9751	0.0150	0.0022
0.4123	0.4401	0.0739	0.9756	0.0167	0.0018
0.4518	0.4550	0.0486	0.9723	0.0220	0.0017
0.4765	0.4793	0.0251	0.9729	0.0238	0.0009
$x_3' = 0.60$					
0.0314	0.0000	0.6427	0.9921	0.0000	0.0020
0.0723	0.1101	0.5269	0.9829	0.0052	0.0048
0.1390	0.2227	0.4069	0.9775	0.0085	0.0063
0.2283	0.2965	0.3065	0.9784	0.0103	0.0048
0.3126	0.3628	0.2096	0.9771	0.0128	0.0044
0.3721	0.4006	0.1473	0.9814	0.0125	0.0019
0.4257	0.4346	0.0926	0.9800	0.0151	0.0014
0.4550	0.4545	0.0622	0.9784	0.0179	0.0012
0.4773	0.4686	0.0430	0.9716	0.0254	0.0013
$x_3' = 0.80$					
0.0329	0.0000	0.8149	0.9949	0.0000	0.0023
0.0765	0.1003	0.6846	0.9881	0.0041	0.0046
0.1561	0.2136	0.5100	0.9852	0.0073	0.0046
0.2168	0.3003	0.4005	0.9847	0.0093	0.0034
0.2646	0.3751	0.2961	0.9813	0.0123	0.0041
0.3363	0.4238	0.2005	0.9826	0.0132	0.0025
0.3941	0.4498	0.1337	0.9811	0.0153	0.0022
0.4288	0.4723	0.0869	0.9787	0.0183	0.0020
0.4608	0.4838	0.0516	0.9778	0.0209	0.0013

[a] Obtained by mixing pure water and 1-butanol with the binary mixtures of $\{x_3'$ DEC + $(1 - x_3')$ DMC$\}$. [b] Mole fraction of DEC in the binary mixtures.

tetrahedron to show the quaternary LLE surface for the (water + 1-butanol + DEC + DMC) and (water + 1-butanol + hexane + DMC) systems, respectively. The quaternary mixtures were prepared by mixing stepwise the binary (DEC + DMC) or (hexane + DMC) mixtures whose compositions are M1, M2, M3, and M4 with water and then 1-butanol 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

Table 5. Equilibrium Phase Compositions for Quaternary Mixtures of Water (1) + 1-Butanol (2) + Hexane (3) + DMC (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 1-Butanol + x_3 Hexane + (1 − x_1 − x_2 − x_3) DMC}[a]					
x_3' = 0.20[b]					
0.0427	0.0000	0.2016	0.9792	0.0000	0.0000
0.0535	0.1455	0.1687	0.9733	0.0053	0.0000
0.0782	0.2681	0.1349	0.9706	0.0090	0.0000
0.1166	0.3514	0.1226	0.9697	0.0124	0.0000
0.1766	0.4326	0.0862	0.9761	0.0106	0.0000
0.2703	0.4801	0.0546	0.9699	0.0163	0.0000
0.3483	0.4954	0.0340	0.9724	0.0176	0.0000
0.4154	0.4945	0.0220	0.9693	0.0235	0.0000
0.5120	0.4880	0.0000	0.9808	0.0192	0.0000
x_3' = 0.40					
0.0314	0.0000	0.4195	0.9806	0.0000	0.0000
0.0541	0.1681	0.3369	0.9750	0.0071	0.0000
0.0707	0.2680	0.2945	0.9739	0.0101	0.0000
0.0801	0.3780	0.2356	0.9728	0.0123	0.0000
0.1272	0.4710	0.1843	0.9743	0.0138	0.0000
0.1935	0.5291	0.1329	0.9744	0.0159	0.0000
0.2551	0.5596	0.0861	0.9757	0.0174	0.0000
0.3024	0.5905	0.0514	0.9769	0.0179	0.0000
0.3705	0.5833	0.0249	0.9784	0.0190	0.0000
0.4520	0.5480	0.0000	0.9808	0.0192	0.0000
x_3' = 0.60					
0.0105	0.0000	0.6464	0.9847	0.0000	0.0000
0.0166	0.1277	0.5590	0.9772	0.0082	0.0000
0.0315	0.2595	0.4544	0.9780	0.0096	0.0000
0.0581	0.3783	0.3627	0.9762	0.0126	0.0000
0.1040	0.4742	0.2683	0.9778	0.0135	0.0000
0.1336	0.5535	0.2004	0.9781	0.0148	0.0000
0.2137	0.5879	0.1336	0.9798	0.0152	0.0000
0.2600	0.6188	0.0817	0.9801	0.0171	0.0000
0.3171	0.6335	0.0369	0.9800	0.0185	0.0000
0.3915	0.6085	0.0000	0.9808	0.0192	0.0000
x_3' = 0.80					
0.0123	0.0000	0.7951	0.9905	0.0000	0.0000
0.0201	0.0619	0.7389	0.9823	0.0096	0.0000
0.0248	0.2336	0.6011	0.9822	0.0117	0.0000
0.0474	0.3552	0.4800	0.9808	0.0144	0.0000
0.0845	0.4575	0.3701	0.9815	0.0144	0.0000
0.1294	0.5317	0.2790	0.9817	0.0151	0.0000
0.1705	0.6079	0.1829	0.9821	0.0157	0.0000
0.2494	0.6338	0.0983	0.9819	0.0166	0.0000
0.3104	0.6407	0.0425	0.9818	0.0175	0.0000
0.3820	0.6180	0.0000	0.9808	0.0192	0.0000

[a] Obtained by mixing pure water and 1-butanol with the binary mixtures of {x_3' hexane + (1 − x_3') DMC}. [b] Mole fraction of hexane in the binary mixtures.

fraction of DEC or hexane in the binary (DEC + DMC) or (hexane + DMC) mixtures.

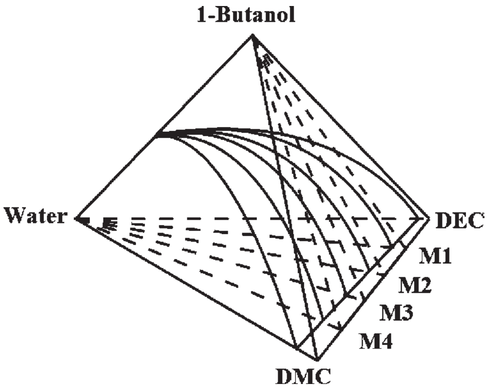

Figure 1. Phase equilibria of (water + 1-butanol + DEC + DMC). M1, M2, M3, and M4 denote quaternary section planes.

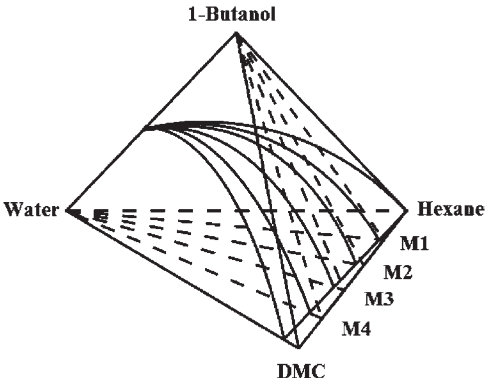

Figure 2. Phase equilibria of (water + 1-butanol + hexane + DMC). M1, M2, M3, and M4 denote quaternary section planes.

■ CALCULATED RESULTS AND DISCUSSION

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.

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

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

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 the liquid-phase mole fraction, and γ the activity coefficient given by the modified UNIQUAC model described in detail.[11] The binary energy parameters, a_{ij}, for completely miscible binary mixtures were obtained from experimental VLE data by using a computer program described by Prausnitz et al.[16] 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[17] by minimizing the objective function:

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

where min denotes the minimum values, i = 1 to 3 for ternary

Table 6. Calculated Results of Binary Phase Equilibrium Data Reduction

system (1 + 2)	T/K	a_{12}/K	a_{21}/K	$\delta(P)$/kPa	$\delta(T)$	$10^3\ \delta(x)$	$10^3\ \delta(y)$	lit.
1-butanol + DEC	390.77 to 398.97	153.13	−13.49	1.2	0.1	0.7	3.6	2
1-butanol + DMC	363.28 to 389.73	102.92	266.34	0.9	0.1	0.5	6.1	3
1-butanol + hexane	341.65 to 380.55	35.05	1015.47	1.9	0.1	3.0	5.4	12
hexane + DMC	338.63 to 359.56	275.20	91.19	2.3	0.1	1.3	6.0	4
DEC + DMC	313.15	−133.97	300.44	1.5	0.0	0.6	5.1	5
water + 1-butanol	298.15	478.79	102.05					13
water + hexane	298.15	1285.90	2890.00					13
water + DEC	298.15	248.21	1177.60					14
water + DMC	298.15	269.81	702.87					10

Table 7. Calculated Results for Ternary LLE at 298.15 K

system (1 + 2 + 3)	no.[a]	τ_{231}	τ_{132}	τ_{123}	rms[b,c] (%)	rms[b,d] (%)	lit.
water + 1-butanol + DEC	11	−0.7974	6.2287	−1.6555	1.76	0.34	this work
water + 1-butanol + DMC	10	−1.2974	1.2312	−0.6898	4.70	1.52	this work
water + hexane + DMC	10	0.4062	0.8864	−14.8690	2.75	0.95	
water + 1-butanol + hexane	9	−0.2725	−0.8656	0.0523	2.44	0.59	15
water + DMC + DEC	10	0.0477	−1.3697	−0.8088	1.49	0.98	8

[a] Number of tie lines. [b] Root-mean-square deviation. [c] Predicted results using binary parameters taken from Table 6. [d] Correlated results using binary and ternary parameters.

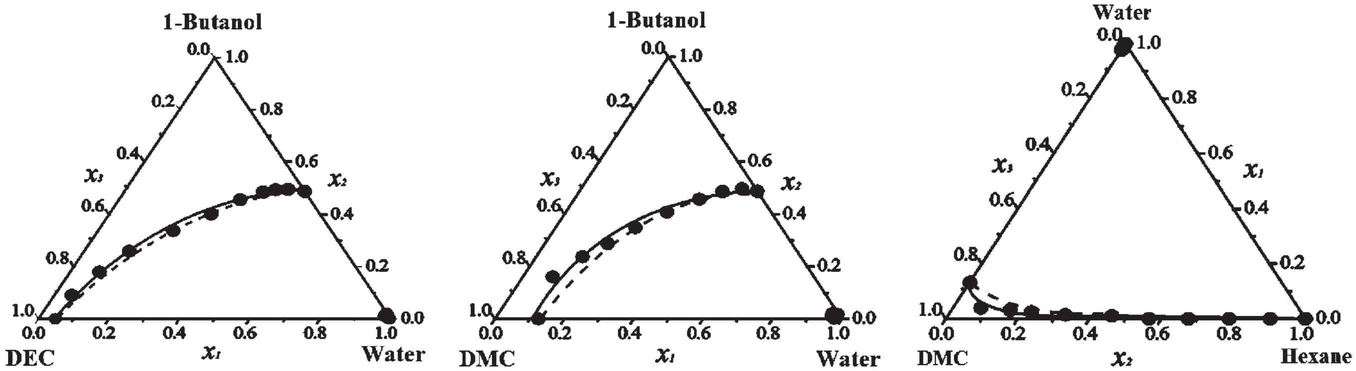

Figure 3. Experimental and calculated LLE of ternary systems (water + 1-butanol + DEC), (water + 1-butanol + DMA), and (water + 1-butanol + DMC) at T = 298.15 K. ●, experimental tie-line data; - - -, predicted results by using binary parameters taken from Table 6. —, correlated results by using binary and ternary parameters taken from Tables 6 and 7.

Table 8. Calculated Results for Quaternary LLE at 298.15 K

system (1 + 2 + 3 + 4)	no.[a]	τ_{2341}	τ_{1342}	τ_{1243}	τ_{1234}	rms[b,c] (%)	rms[b,d] (%)
water + 1-butanol + DEC + DMC	36	0.0171	−0.1721	8.0913	0.7597	3.13	0.56
water + 1-butanol +hexane + DMC	39	5.6988	7.7419	17.6020	3.2992	1.54	0.75

[a] Number of data points. [b] Root-mean-square deviation. [c] Predicted results using binary and ternary parameters taken from Tables 6 and 7. [d] Correlated results using binary, ternary, and quaternary parameters.

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.

Table 6 lists the binary interaction parameters of the modified UNIQUAC model 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 the liquid phase mole fraction, and δ_y for the vapor phase mole fraction. Table 7 presents the ternary parameters, together with the root-mean-square deviations between the experimental and the calculated tie-lines for the ternary LLE. The LLE phase diagrams for these ternary systems of (water + 1-butanol + DEC) and (water + 1-butanol + DMC) were plotted and shown in Figure 3. Because of the introduction of ternary parameters, the root-mean-square deviations of correlation results are less than ones of prediction results for the ternary systems. Table 8 summarizes the correlated results for the quaternary systems obtained in fitting the modified UNIQUAC model with binary,

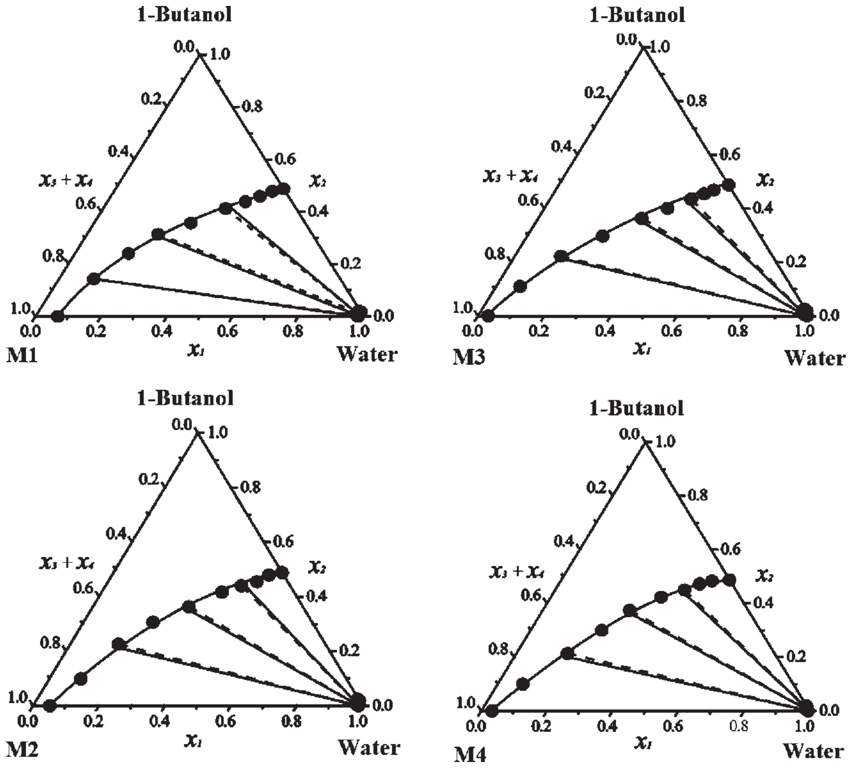

Figure 4. Experimental and calculated LLE composition in mole fraction on the planes M1, M2, M3, and M4 for quaternary mixtures of (water + 1-butanol + DEC + DMC) at T = 298.15 K. ●- - -●, experimental tie lines; —, correlated curve by the modified UNIQUAC model.

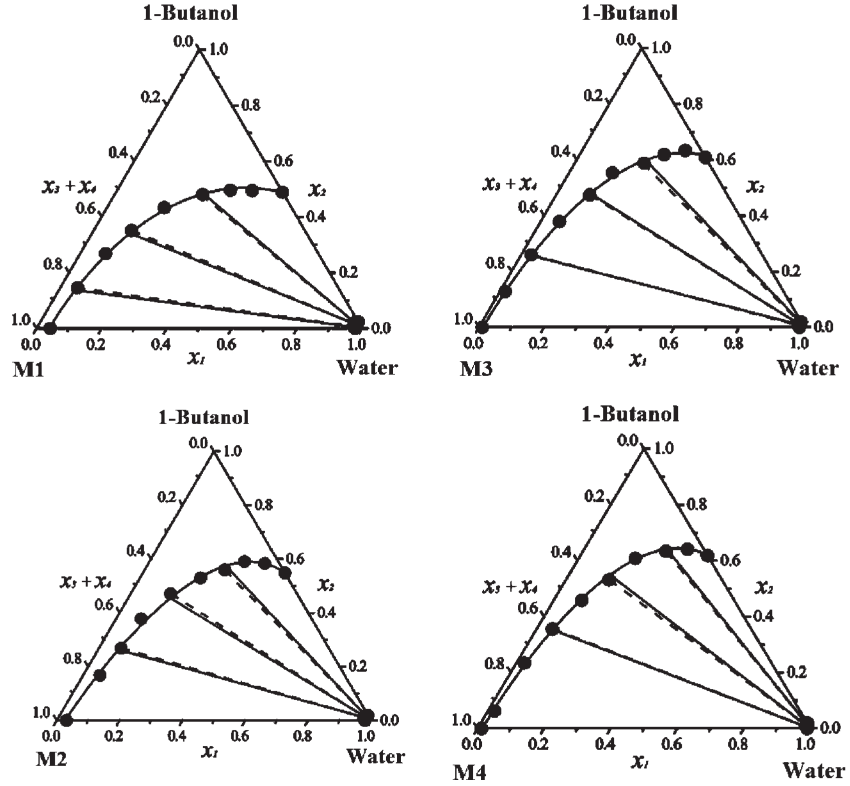

Figure 5. Experimental and calculated LLE composition in mole fraction on the planes M1, M2, M3, and M4 for quaternary mixtures of (water + 1-butanol + hexane + DMC) at T = 298.15 K. ●- - -●, experimental tie lines; —, correlated curve by the modified UNIQUAC model.

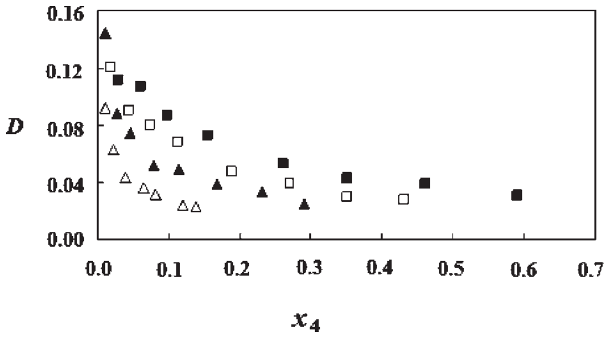

Figure 6. Distribution coefficient of DMC in the quaternary system of (water + 1-butanol + DEC + DMC), D, at 298.15 K as a function of mole fraction of DMC in organic-rich phase, x_4. ■, □, ▲, △, $x_3' = 0.2, 0.4, 0.6, 0.8$, respectively.

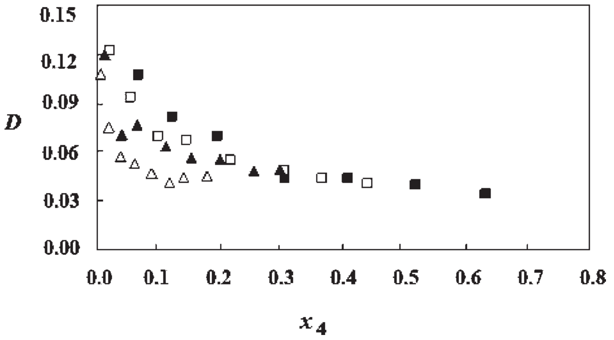

Figure 7. Distribution coefficient of DMC in the quaternary system of (water + 1-butanol + hexane + DMC), D, at 298.15 K as a function of mole fraction of DMC in organic-rich phase, x_4. ■, □, ▲, △, $x_3' = 0.2, 0.4, 0.6, 0.8$, respectively.

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 6 and 7. The correlated results obtained from the model are better than the predicted ones in representing the quaternary LLE measured in this work. The (water + 1-butanol + DEC + DMC) and (water + 1-butanol + hexane + DMC) systems exhibit type 2 quaternary LLE behavior,[18] which are composed of three ternary LLE for the (water + DEC + DMC), (water + 1-butanol + DEC), and (water + 1-butanol + DMC), as type 2 is illustrated in Figure 1, and the (water + hexane + DMC), (water + 1-butanol + DMC) and (water + 1-butanol + hexane), as type 2 is illustrated in Figure 2. Figures 4 and 5 compare the experimental and calculated mole fractions of two phases at equilibrium and the corresponding tie lines for the quaternary systems of (water + 1-butanol + DEC + DMC) and (water + 1-butanol + hexane + DMC), which are plotted on planes M1, M2, M3, and M4 illustrated in Figures 1 and 2. A good agreement between experimental LLE results and correlated results of the modified UNIQUAC model is shown in Figures 4 and 5.

To understand well the solubility of DMC in two phases and assess the influence of DMC addition on aqueous and organic phases, the distribution coefficient 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 in aqueous and organic phases, respectively. The distribution coefficient D was calculated from the experimental LLE data. Figures 6 and 7 show the distribution coefficients of DMC in the quaternary systems of (water + 1-butanol + DEC + DMC) and (water + 1-butanol + hexane + DMC) as a function of its mole fraction in organic-rich phase. Comparing the quaternary systems containing DMC or DEC,[8] since the solubility of DMC in water is small, the distribution coefficients of DMC are quite small, and the distribution ratios of DMC were decreasing as its mole fraction in the organic-rich phase increased.

■ CONCLUSIONS

LLE data of the studied quaternary systems of (water + 1-butanol + DEC + DMC) and (water + 1-butanol + hexane + DMC) and relevant ternary systems of (water + 1-butanol + DEC) and (water + 1-butanol + DMC) at $T = 298.15$ K are presented. The experimental LLE data were correlated using the modified UNIQUAC model. The root-mean-square deviations of (water + 1-butanol + DEC + DMC) and (water + 1-butanol + hexane + DMC) systems calculated by the model were 0.56 mol % and 0.75 mol %, respectively. The modified UNIQUAC model was used to correlate the experimental LLE data, and the parameters of the model are presented. The distribution coefficients of DMC in the quaternary systems of (water + 1-butanol + DEC + DMC) and (water + 1-butanol + hexane + DMC) as a function of its mole fraction in organic-rich phase are plotted.

■ AUTHOR INFORMATION

Corresponding Author

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

Funding Sources

The authors thank the financial support from National Scientific Research Foundation of China (20971056).

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