

Ternary and Quaternary Liquid–Liquid Equilibria for Fuel Additives of the Water + Methanol + Toluene and Water + Methanol + Toluene + Methyl *tert*-Butyl Ether or *tert*-Amyl Methyl Ether Systems at 298.15 K

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Experimental tie-line data of two quaternary mixtures for water + methanol + toluene + methyl *tert*-butyl ether and water + methanol + toluene + *tert*-amyl methyl ether systems and those of one constituent ternary mixture for the water + methanol + toluene system, measured at a temperature of 298.15 K and ambient pressure, are presented. The experimental ternary and quaternary liquid–liquid equilibrium data have been satisfactorily correlated by using a modified form of the UNIQUAC model including multibody interaction parameters in addition to binary ones. The results are further compared with those obtained by the extended UNIQUAC model published previously.

Introduction

Recently benzene-free gasolines used widely, reformulated to contain oxygenate additives such as methyl *tert*-butyl ether (MTBE) and *tert*-amyl methyl ether (TAME), have been demonstrated to reduce automotive exhaust emissions of toxic substances into ambient air. In modern gasoline-blending operation and refinery process design, we need to assess the advantages of these fuel additives, and the physical phase behavior of the gasoline mixtures depends on the compositions of these compounds. The addition of alcohols to the gasolines with MTBE and TAME affects significantly the hydrocarbon–water solubility. It is therefore necessary to obtain reliable liquid–liquid equilibrium (LLE) data for the multicomponent mixtures containing these oxygenate compounds as well as to develop accurate representation of the experimental LLE data for the multicomponent mixtures.

In this paper we report the multicomponent LLE data of oxygenate fuel additives for the ternary water + methanol + toluene mixture and for the quaternary water + methanol + toluene mixtures with MTBE or TAME measured at a temperature of 298.15 K and atmospheric pressure. The experimental results are reproduced by using modified and extended forms of the UNIQUAC models^{1,2} including ternary and quaternary parameters obtained from the ternary and quaternary LLE data in addition to binary ones from binary phase equilibria. The ternary systems relevant to the quaternary mixtures at 298.15 K have been reported for the water + methanol + toluene,³ water + methanol + MTBE^{4,5} or TAME,⁵ and water + toluene + MTBE or TAME⁶ systems. The vapor–liquid equilibrium (VLE) data and mutual solubilities of the constituent binary mixtures are available from the literature.

Experimental Section

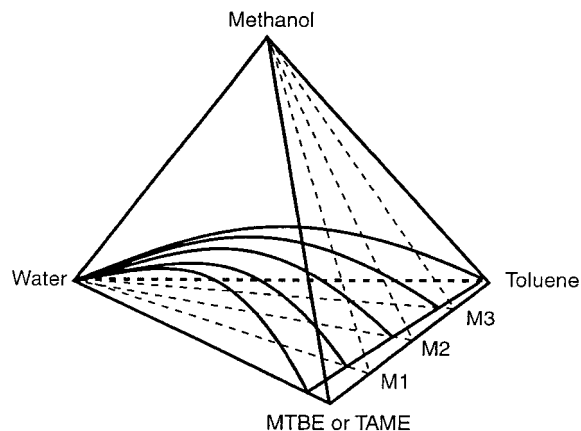
Materials. TAME, MTBE, toluene, and methanol were supplied by Aldrich Chemical with nominal minimum purities of 97, 99.8, 99.8, and 99.8 mass %, respectively. Water was obtained from Wako Pure Chemical with a purity of 99.9 mass %. All chemicals were used without further purification. The purities determined by a GLC analysis were 98.9 mass % for TAME and more than 99.8 mass % for methanol, toluene, and MTBE. The densities of the chemicals measured with a densimeter (Anton Paar, DMA58) at 298.15 K were compared with the literature values^{7,8} in Table 1.

Apparatus and Procedure. Quaternary LLE measurements were carried out at a temperature of (298.15 ± 0.01) K. The experimental apparatus and procedure were described previously.⁹ The quaternary mixtures were prepared by mixing the binary toluene + MTBE or TAME mixtures, whose compositions are M1, M2, and M3, with water and adding methanol into the mixtures stepwise to cover the two-phase region. Figure 1 shows schematically a tetrahedron to depict three planes of the quaternary LLE surface. The quaternary mixture of a volume of $\sim(50\text{--}100)$ cm³ loaded in the equilibrium cell was stirred vigorously by using the magnetic stirrer for 5 h and settled for 1 day, enough to diminish turbidity in the aqueous phase. The headspace of the cell was filled with dry nitrogen gas to reduce the contamination of moisture. The sample mixtures, withdrawn from the upper and lower phases in the cell by using a syringe, were analyzed by a gas chromatograph (Shimadzu, GC-8A) equipped with a thermal conductivity detector. The oven temperatures of the injection port and detector were set at 463.15 K; the initial temperature of the oven was kept at 423 K, and the final temperature of the oven was increased to 493.15 K at a rate of 32 K·min⁻¹. Every component was separated at a helium flow rate of 0.5 cm³·s⁻¹ by means of a 2-m-length stainless steel column packed with Porapak SQ. The peak area of the components was detected at a current of 100 mA to analyze with a Chromatopac (Shimadzu, C-R6A).

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Table 1. Densities, ρ , of Pure Components at 298.15 K

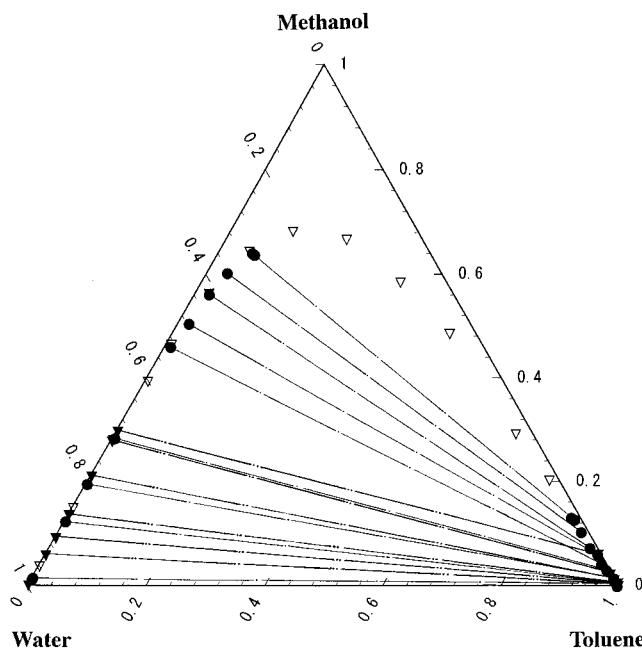
component	$\rho(298.15\text{K})/(\text{g}\cdot\text{cm}^{-3})$	
	exptl	lit.
methanol	0.78652	0.78637 ⁷
MTBE, methyl <i>tert</i> -butyl ether	0.73540	0.73528 ⁸
TAME, <i>tert</i> -amyl methyl ether	0.76587	0.76577 ⁸
toluene	0.86235	0.86219 ⁷
water	0.99692	0.99705 ⁷

**Figure 1.** Phase equilibria of (water + methanol + toluene + methyl *tert*-butyl ether or *tert*-amyl methyl ether). M1, M2, and M3 denote quaternary sectional planes.**Table 2.** Equilibrium Phase Compositions in Mole Fraction x for Ternary Mixtures of Water (1) + Methanol (2) + Toluene (3) at 298.15 K

organic phase			aqueous phase		
x_1	x_2	x_3	x_1	x_2	x_3
0.0047	0.0000	0.9953	0.9859	0.0140	0.0001
0.0043	0.0018	0.9939	0.9835	0.0162	0.0003
0.0040	0.0093	0.9867	0.8748	0.1249	0.0003
0.0032	0.0150	0.9818	0.8026	0.1970	0.0004
0.0070	0.0307	0.9623	0.7122	0.2851	0.0027
0.0092	0.0434	0.9472	0.5302	0.4612	0.0086
0.0070	0.0610	0.9320	0.4768	0.5062	0.0170
0.0141	0.0735	0.9124	0.4145	0.5628	0.0227
0.0133	0.1042	0.8825	0.3635	0.6041	0.0324
0.0124	0.1282	0.8594	0.3002	0.6393	0.0605
0.0162	0.1320	0.8518	0.3020	0.6424	0.0555

The composition of the samples was obtained using a response factor defined by the ratio of the peak area to the mass fraction of the components. The peak area was calibrated by mixtures prepared gravimetrically with experimental uncertainties using the temporary response factors 1.72 for methanol, 1.24 for MTBE, 1.27 for TAME, 1.82 for water, and 1.26 for toluene. Further detailed explanation of the analytical method is given elsewhere.¹⁰ Three analyses at least were made for each sample to obtain a mean value. The accuracy of the measurements was estimated within ± 0.001 in mole fraction.

Experimental Results. Following Sørensen and Arlt,¹¹ the quaternary experimental data exhibit type 2 quaternary LLE behavior as shown in Figure 1 and are composed of two ternary LLE mixtures of type 1 having a plait point, the water + methanol + toluene and water + methanol + MTBE or water + methanol + TAME systems, and one ternary LLE mixture type 2 having two immiscible binary pairs, the water + MTBE + toluene or water + TAME + toluene system. The equilibrium tie-line compositions measured at 298.15 K of the ternary mixtures for the water + methanol + toluene system are shown in Table 2. Our tie-line results for the water + methanol + toluene system were in good agreement with the reported values³ at the

**Figure 2.** Experimental LLE of ternary mixtures for (water + methanol + toluene) at 298.15 K: ●, experimental tie-line, this work; ▼, tie-line data; ▽, solubility data, Mason and Washburn.³

diluted region of methanol as shown in Figure 2. Compared to the literature, we obtained the tie-lines over the methanol-rich region and as close to the plait point as possible, where microemulsion forms in toluene phase were not observed. The tie-line results of the quaternary mixtures for the water + methanol + MTBE + toluene and water + methanol + TAME + toluene systems at 298.15 K are in Tables 3 and 4. As TAME seems to be a hydrophobic component compared with MTBE, water in the organic phase dissolves appropriately into the MTBE mixture rather than the TAME mixture. Meanwhile, the difference of the methyl group between MTBE and TAME hardly influences the solubility concentrations of the ether and toluene in the aqueous phase of the quaternary mixtures.

Data Analysis

Excess Gibbs Free Energy Models. We have used the modified UNIQUAC and extended UNIQUAC models with binary and additional ternary and quaternary parameters for an accurate description of the experimental ternary and quaternary LLE data as well as binary VLE and mutual solubility data. The extended UNIQUAC model including the binary and additional ternary and quaternary parameters was proposed previously, and the expression of the model was described in detail elsewhere.¹ The modified UNIQUAC model² proposed recently is expressed by both the combinatorial contribution given by a modified form of Gmehling et al.¹² and the residual contribution modified by introducing the third parameter C to the residual term of the extended UNIQUAC model. The activity coefficient of the quaternary mixture is expressed in terms of ternary and quaternary parameters from the multibody interactions in addition to binary ones due to the binary interactions. The adjustable binary parameter, τ_{ji} , obtained from the constituent binary phase equilibrium data, is defined by the binary energy parameter a_{ji} :

$$\tau_{ji} = \exp(-a_{ji}/CT) \quad (1)$$

The adjustable ternary parameters, τ_{231} , τ_{132} , and τ_{123} , are determined additionally from the ternary LLE data, and

Table 3. Equilibrium Phase Compositions in Mole Fraction x for Quaternary Mixtures of Water (1) + Methanol (2) + Methyl *tert*-Butyl Ether (3) + Toluene (4) at 298.15 K

organic phase				aqueous phase			
x_1	x_2	x_3	x_4	x_1	x_2	x_3	x_4
M1 ^a							
0.0301	0.0290	0.2356	0.7053	0.9128	0.0856	0.0015	0.0001
0.0350	0.0481	0.2215	0.6954	0.8947	0.1029	0.0020	0.0004
0.0397	0.0592	0.2194	0.6817	0.8667	0.1302	0.0025	0.0006
0.0554	0.0795	0.1989	0.6662	0.8114	0.1850	0.0031	0.0005
0.0612	0.1210	0.1827	0.6351	0.7349	0.2574	0.0059	0.0018
0.0854	0.1550	0.1801	0.5795	0.6507	0.3304	0.0100	0.0089
0.0971	0.1842	0.1694	0.5493	0.6443	0.3337	0.0125	0.0095
M2 ^a							
0.0390	0.0285	0.4257	0.5068	0.9498	0.0480	0.0021	0.0001
0.0456	0.0401	0.4134	0.5009	0.9364	0.0585	0.0047	0.0004
0.0654	0.0701	0.4020	0.4625	0.8783	0.1148	0.0065	0.0004
0.0760	0.0941	0.3830	0.4469	0.8368	0.1542	0.0083	0.0007
0.0945	0.1141	0.3745	0.4169	0.8122	0.1774	0.0096	0.0008
0.0986	0.1456	0.3457	0.4101	0.7589	0.2289	0.0113	0.0009
0.1010	0.1722	0.3376	0.3892	0.7279	0.2555	0.0148	0.0018
0.1190	0.1930	0.3089	0.3791	0.6891	0.2888	0.0188	0.0033
0.1295	0.2171	0.2806	0.3728	0.6495	0.3233	0.0223	0.0049
M3 ^a							
0.0556	0.0287	0.6530	0.2627	0.9595	0.0325	0.0079	0.0001
0.0741	0.0504	0.6242	0.2513	0.9263	0.0651	0.0085	0.0001
0.0864	0.0721	0.6115	0.2300	0.9070	0.0842	0.0087	0.0001
0.1012	0.0876	0.5910	0.2202	0.8860	0.1047	0.0091	0.0002
0.1135	0.1201	0.5445	0.2219	0.8557	0.1301	0.0140	0.0002
0.1277	0.1421	0.5041	0.2261	0.8172	0.1670	0.0151	0.0007
0.1375	0.1698	0.4834	0.2093	0.7853	0.1971	0.0171	0.0005
0.1430	0.1963	0.4551	0.2056	0.7393	0.2367	0.0230	0.0010
0.1510	0.2311	0.4177	0.2002	0.6969	0.2718	0.0295	0.0018

^a Obtained by mixing pure water and methanol with binary mixture (methyl *tert*-butyl ether + toluene).

then the quaternary parameters, τ_{2341} , τ_{1342} , τ_{1243} , and τ_{1234} , are from the quaternary LLE data.

Calculation Procedure. The binary energy parameters for the miscible mixtures were obtained from the VLE data reduction by taking into account the vapor- and liquid-phase imperfections

$$P y_i \Phi_i = x_i \gamma_i P_i^s \Phi_i^s \exp\{V_i^L(P - P_i^s)/RT\} \quad (2)$$

$$\ln \Phi_i = (2 \sum_j y_j B_{ij} - \sum_i \sum_j y_i y_j B_{ij}) P/RT \quad (3)$$

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 fugacity coefficient, Φ , was calculated by the virial equation of state having the second virial coefficient. The pure and cross-second virial coefficients, B , were estimated according to the method of Hayden and O'Connell.¹³ The pure component vapor pressure, P^s , was calculated by using the Antoine equation with coefficients taken from the literatures.^{7,8} The liquid molar volume, V^L , was obtained by using a modified Rackett equation.¹⁴ The binary energy parameters for the partially miscible mixtures were obtained by solving the following thermodynamic equations simultaneously.

$$(x_i \gamma_i)^I = (x_i \gamma_i)^{II} \quad (4)$$

$$\sum_i x_i^I = \sum_i x_i^{II} = 1 \quad (5)$$

Results and Discussion

Table 5 shows the molecular structural parameters of pure components. The values of r and q for MTBE and

Table 4. Equilibrium Phase Compositions in Mole Fraction x for Quaternary Mixtures of Water (1) + Methanol (2) + *tert*-Amyl Methyl Ether (3) + Toluene (4) at 298.15 K

organic phase				aqueous phase			
x_1	x_2	x_3	x_4	x_1	x_2	x_3	x_4
M1 ^a							
0.0138	0.0177	0.2430	0.7255	0.9030	0.0957	0.0012	0.0001
0.0144	0.0230	0.2332	0.7294	0.8749	0.1230	0.0018	0.0003
0.0155	0.0292	0.2335	0.7218	0.8470	0.1503	0.0022	0.0005
0.0166	0.0405	0.2180	0.7249	0.7916	0.2047	0.0029	0.0008
0.0190	0.0597	0.2086	0.7127	0.7050	0.2885	0.0050	0.0015
0.0227	0.0824	0.2154	0.6795	0.6250	0.3594	0.0091	0.0065
0.0234	0.0874	0.2147	0.6745	0.6145	0.3651	0.0113	0.0091
M2 ^a							
0.0190	0.0185	0.4457	0.5168	0.9398	0.0583	0.0018	0.0001
0.0256	0.0201	0.4334	0.5209	0.9269	0.0685	0.0043	0.0003
0.0354	0.0401	0.4320	0.4925	0.8583	0.1354	0.0059	0.0004
0.0460	0.0541	0.4230	0.4769	0.8169	0.1746	0.0079	0.0006
0.0545	0.0741	0.4145	0.4569	0.7922	0.1979	0.0091	0.0008
0.0686	0.0956	0.3857	0.4501	0.7293	0.2589	0.0109	0.0009
0.0710	0.1022	0.3776	0.4492	0.6983	0.2865	0.0138	0.0014
0.0890	0.1330	0.3689	0.4091	0.6702	0.3090	0.0178	0.0030
0.1095	0.1571	0.3406	0.3928	0.6299	0.3427	0.0229	0.0045
M3 ^a							
0.0356	0.0187	0.6785	0.2672	0.9595	0.0365	0.0039	0.0001
0.0441	0.0404	0.6687	0.2468	0.9163	0.0771	0.0065	0.0001
0.0564	0.0521	0.6610	0.2305	0.8970	0.0952	0.0076	0.0002
0.0612	0.0646	0.6505	0.2237	0.8660	0.1247	0.0091	0.0002
0.0735	0.0901	0.6240	0.2124	0.8457	0.1421	0.0118	0.0004
0.0877	0.1121	0.5911	0.2091	0.7972	0.1870	0.0152	0.0006
0.0975	0.1298	0.5686	0.2041	0.7653	0.2171	0.0170	0.0006
0.1030	0.1563	0.5396	0.2011	0.7193	0.2567	0.0232	0.0008
0.1108	0.1911	0.4995	0.1986	0.6869	0.2838	0.0279	0.0014

^a Obtained by mixing pure water and methanol with binary mixture (*tert*-amyl methyl ether + toluene).

Table 5. Structural Parameters for Pure Components

component	$r^{8,15}$	$q^{8,15}$	q'
methanol	1.43	1.43	1.482
MTBE	4.07	3.63	$q^{0.75}$
TAME	4.74	4.17	$q^{0.75}$
toluene	3.92	2.97	$q^{0.75}$
water	0.92	1.40	1.283

TAME were taken from Arce et al.⁵ and the others from Prausnitz et al.¹⁵ The value of q' was fixed to obtain a good representation for all binary VLE systems and mutual solubilities examined in the present work. The third parameter C of eq 1 was obtained to reproduce the binary VLE and ternary LLE results as well as possible, fixed empirically as 0.65 in a previous work.² Once q' and C were set, an optimum set of the binary energy parameters was obtained using eqs 2–5 by the method of maximum likelihood principle,¹⁵ where the standard deviations in the experimental values were taken as 0.133 kPa in pressure, 0.05 K in temperature, 0.001 in liquid phase mole fraction, and 0.003 in vapor phase mole fraction. Table 6 lists the constituent binary energy parameters of the modified UNIQUAC model and those of the extended UNIQUAC model, along with the root-mean-square deviations between the experimental and calculated values for pressure, σ_P , for temperature, σ_T , for liquid phase mole fraction, σ_x , and for vapor phase mole fraction, σ_y .

Prediction of Ternary and Quaternary LLE Using Binary Parameters. The ternary and quaternary LLE calculations were carried out using eqs 4 and 5. For the ternary systems of type 1 having a plait point, two-parameter original UNIQUAC models predict a generally larger solubility envelope than the experimental one. Table 7 compares the ternary LLE results predicted by the

Table 6. Calculated Results of Binary Phase Equilibrium Data Reduction

system (1 + 2)	T/K	no. of data points	model	a_{12}/K	a_{21}/K	$\sigma P/kPa$	$\sigma T/K$	$10^3\sigma_x$	$10^3\sigma_y$	lit.
methanol + water	298.14	13	I ^a	-160.39	158.59	0.080	0.0	0.6	4.0	16
			II ^b	-71.81	70.15	0.080	0.0	0.6	4.1	
methanol + TAME	333.15	20	I	-89.93	657.78	0.200	0.0	1.9	9.2	17
			II	-8.96	626.20	0.227	0.0	1.6	9.4	
methanol + MTBE	313.15	37	I	-107.03	569.52	0.107	0.0	0.1	0.5	17
			II	-63.71	540.64	0.120	0.0	0.6	4.7	
methanol + toluene	318.15	11	I	19.30	906.82	0.120	0.0	0.1	3.0	18
			II	93.98	867.82	0.160	0.0	0.7	3.1	
MTBE + toluene	333.15	10	I	-222.93	334.43	0.187	0.1	1.2	4.7	19
			II	-207.40	337.91	0.187	0.1	1.1	4.7	
MTBE + water	298.15	MS ^c	I	1196.10	173.24					20
			II	1023.70	399.09					
TAME + toluene	293.15	14	I	163.13	-164.05	0.120	0.0	1.0	7.7	8
			II	249.20	-250.59	0.133	0.0	0.6	6.8	
TAME + water	298.15	MS	I	1692.00	171.30					20
			II	1341.90	465.96					
toluene + water	298.15	MS	I	1713.30	752.99					21
			II	1540.70	1053.90					

^a Modified UNIQUAC model. ^b Extended UNIQUAC model. ^c MS, mutual solubilities.

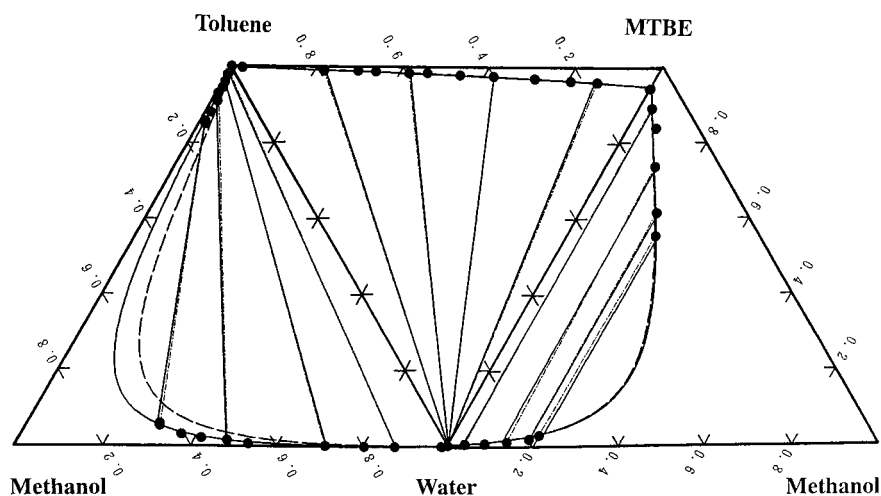


Figure 3. Experimental and calculated LLE of three ternary mixtures making up (water + methanol + toluene + methyl *tert*-butyl ether) at 298.15 K: ●, experimental tie-line; ---, predicted by the modified UNIQUAC model with only binary parameters; —, correlated by the modified UNIQUAC model with binary and ternary parameters.

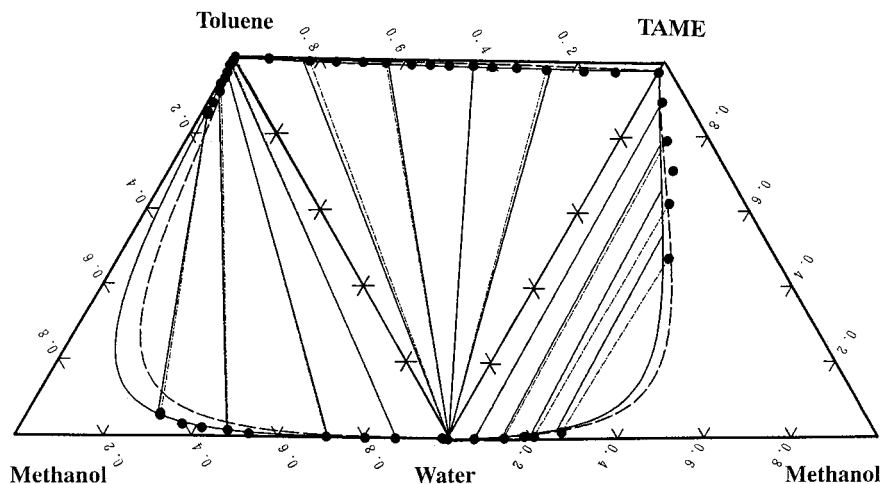


Figure 4. Experimental and calculated LLE of three ternary mixtures making up (water + methanol + toluene + *tert*-amyl methyl ether) at 298.15 K: ●, experimental tie-line; ---, predicted by the modified UNIQUAC model with only binary parameters; —, correlated by the modified UNIQUAC model with binary and ternary parameters.

modified UNIQUAC and extended UNIQUAC models with only the binary parameters. The predicted results were not always good; for example, for the water + methanol + toluene system both models underestimated the experimental tie-lines as shown in Figures 3 and 4.

Correlation of Ternary and Quaternary LLE Using Ternary and Quaternary Parameters in Addition to Binary Ones. The ternary parameters, τ_{231} , τ_{312} , and τ_{123} , were obtained by fitting the model to the ternary experimental LLE data, and the quaternary ones, τ_{2341} , τ_{1342} , τ_{1243} ,

Table 7. Calculated Results for Ternary LLE at 298.15 K

system (1 + 2 + 3)	no. of tie-lines	model	τ_{231}	τ_{132}	τ_{123}	F/mol %		lit.
						pred ^a	corr ^b	
water + MTBE + toluene	13	I ^c	0.00330	0.01133	0.01267	0.17	0.13	6
		II ^d	-0.00160	0.12243	0.12500	0.17	0.14	
water + TAME + toluene	16	I	0.03544	-0.00022	0.01044	0.38	0.15	6
		II	0.03228	-0.00025	0.01153	1.44	0.15	
water + methanol + MTBE	6	I	-0.95210	0.95866	-0.81427	0.64	0.34	5
		II	-0.13910	0.25021	-0.64896	0.83	0.32	
water + methanol + TAME	6	I	0.01919	0.17874	-0.08545	1.73	1.11	5
		II	0.13680	0.16510	-0.19029	2.74	1.16	
water + methanol + toluene	11	I	-0.55290	-1.06040	1.39120	2.80	0.56	this work
		II	-0.61233	-0.49477	0.78602	2.34	0.71	

^a Predicted by using binary parameters alone. ^b Correlated by using binary and ternary parameters. ^c Modified UNIQUAC model. ^d Extended UNIQUAC model.

Table 8. Calculated Results for Quaternary LLE at 298.15 K

system (1 + 2 + 3 + 4)	no. of tie-lines	model	τ_{2341}	τ_{1342}	τ_{1243}	τ_{1234}	F/mol %	
							pred ^a	corr ^b
water + methanol + MTBE + toluene	25	I ^c	2.5759	2.5728	-3.1597	-1.2050	2.20	0.99
		II ^d	7.1938	-1.4942	-4.1899	-5.0962	2.38	0.99
water + methanol + TAME + toluene	25	I	1.3320	0.9116	-0.7020	0.3347	0.94	0.54
		II	1.5424	0.2920	-0.4192	-0.9411	0.97	0.53

^a Predicted by using binary and ternary parameters alone. ^b Correlated by using binary, ternary and quaternary parameters. ^c Modified UNIQUAC model. ^d Extended UNIQUAC model.

and τ_{1234} , were determined from the quaternary experimental LLE data using a simplex method²² by minimizing the objective function:

$$F = 10^2 \left\{ \sum_k \min_i \sum_j (x_{ijk}^{\text{exptl}} - x_{ijk}^{\text{calcd}})^2 / \{M\} \right\}^{0.5} \quad (6)$$

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

Table 7 presents the ternary parameters obtained in fitting the modified UNIQUAC and extended UNIQUAC models to the experimental ternary LLE systems and the root-mean-square deviation of the mole fraction of tie-lines between the experimental and calculated results for the ternary LLE systems. It seems that the modified UNIQUAC model with the only binary parameters predict the ternary LLEs more successfully than the extended UNIQUAC model, and these models can give a much more accurate representation for the ternary LLEs by including the ternary parameters in addition to the binary ones. Figures 3 and 4 compare the experimental tie-lines of the ternary mixtures making up the quaternary water + methanol + MTBE + toluene and water + methanol + TAME + toluene systems at 298.15 K with those calculated by the modified UNIQUAC model; these figures show that good correlation of the ternary LLE systems usually needs not only the binary parameters but the ternary parameters.

Table 8 summarizes the quaternary LLE results predicted by the modified UNIQUAC and extended UNIQUAC models with the binary and ternary parameters without using quaternary parameters, together with those obtained in fitting the modified UNIQUAC model and the extended UNIQUAC model with binary, ternary, and quaternary parameters to the quaternary LLE data. The predicted results using the binary and ternary parameters are slightly large in the deviation F for the water + methanol + MTBE + toluene system, but both models can describe accurately the quaternary experimental LLE data by the correlation involving the additional quaternary parameters.

Conclusions

Quaternary LLE results for the water + methanol + MTBE + toluene and water + methanol + TAME + toluene systems and the constituting ternary LLE data for the methanol + water + toluene system were measured at 298.15 K. Using the modified UNIQUAC model and extended UNIQUAC model including binary and ternary parameters satisfactorily correlated the experimental ternary LLE results. The quaternary LLEs calculated by both the modified UNIQUAC and extended UNIQUAC models having binary, ternary, and quaternary parameters are in good agreement with the experimental results.

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