

Liquid–liquid equilibria of two binary systems: water + 1-pentanol and water + 2-methyl-2-butanol and two ternary systems: water + 1-pentanol + 2-butyloxyethanol and water + 2-methyl-2-butanol + 2-butyloxyethanol

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Abstract

Liquid–liquid equilibrium phase diagrams for two binary systems: water + 1-pentanol and water + 2-methyl-2-butanol and two ternary systems: water + 1-pentanol + 2-butyloxyethanol and water + 2-methyl-2-butanol + 2-butyloxyethanol at 20°C and 30°C are presented in this paper. The experimental results were correlated with the UNIQUAC model by fitting the effective UNIQUAC binary interaction parameters as a function of temperature. Agreement between the calculated and experimental data was very good. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Liquid–liquid equilibria; Data; Mixture; UNIQUAC model

1. Introduction

The experimental data of liquid–liquid equilibrium are necessary for the design of liquid–liquid extractors and of decanters in distillation systems. It is of particular importance in these days of higher energy costs. In this study, liquid–liquid equilibrium measurements were performed for two binary systems: water + 1-pentanol and water + 2-methyl-2-butanol and two ternary systems: water + 1-pentanol + 2-butyloxyethanol and water + 2-methyl-2-butanol + 2-butyloxyethanol at 20°C and 30°C. Although the mutual solubility of the systems water + 1-pentanol and water + 2-methyl-2-butanol had

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Table 1

Comparison of the experimental results and literature data [11] of densities, ρ , refractive index, n_D , and viscosities, η , of the pure compounds at 293.15 K

Compound	$\rho/\text{g cm}^{-3}$		n_D		$\eta/\text{mPa s}$	
	Exptl.	Lit.	Exptl.	Lit.	Exptl.	Lit.
1-Pentanol	0.81453	0.8151	1.4096	1.4100	4.0606	4.0608
2-Methyl-2-butanol	0.80999	0.8096	1.4049	1.4049	4.3817	4.3760
Water	0.99821	0.9982058	1.3330	1.33299	0.9943	1.0020
2-Butyloxyethanol	0.90072		1.4196		3.2861	

been reported previously by several different research groups [1–9], there exists a certain discrepancy among these data. It is our purpose to verify these inconsistent data. On the other hand, there are, to the best of our knowledge, no liquid–liquid equilibrium experimental data for the ternary systems water + 1-pentanol + 2-butyloxyethanol and water + 2-methyl-2-butanol + 2-butyloxyethanol available in the literature.

The experimental data were correlated with the UNIQUAC model of Abrams and Pranusnitz [10]. The effective binary interaction parameters of the UNIQUAC model were determined as a function of temperature. The experimental equilibrium data were successfully described by the UNIQUAC model.

2. Experimentals

Reagent grade 1-pentanol (better than 98.5% purity), 2-methyl-2-butanol (better than 99.5% purity), and 2-butyloxyethanol (better than 99% purity) were obtained from Merck. All the chemicals were used as received without any further purification. Water was purified in a Barnstead NANOpure

Table 2

Experimental mole fraction of water of equilibrium liquid phases for the binary systems: water (1) + 1-pentanol (2) and water (1) + 2-methyl-2-butanol (2) at various temperatures

Temp./°C	Water (1) + 1-pentanol (2)		Water (1) + 2-methyl-2-butanol (2)	
	x_1^l	x_1^u	x_1^l	x_1^u
10	0.9943	0.3391	0.9716	0.6310
20	0.9951	0.3439	0.9764	0.6042
30	0.9955	0.3515	0.9794	0.5883
40	0.9958	0.3591	0.9829	0.5763
50	0.9959	0.3755	0.9853	0.5624
60	0.9959	0.3909	0.9868	0.5514
70	0.9959	0.4040	0.9874	0.5378
80	0.9956	0.4222	0.9880	0.5350

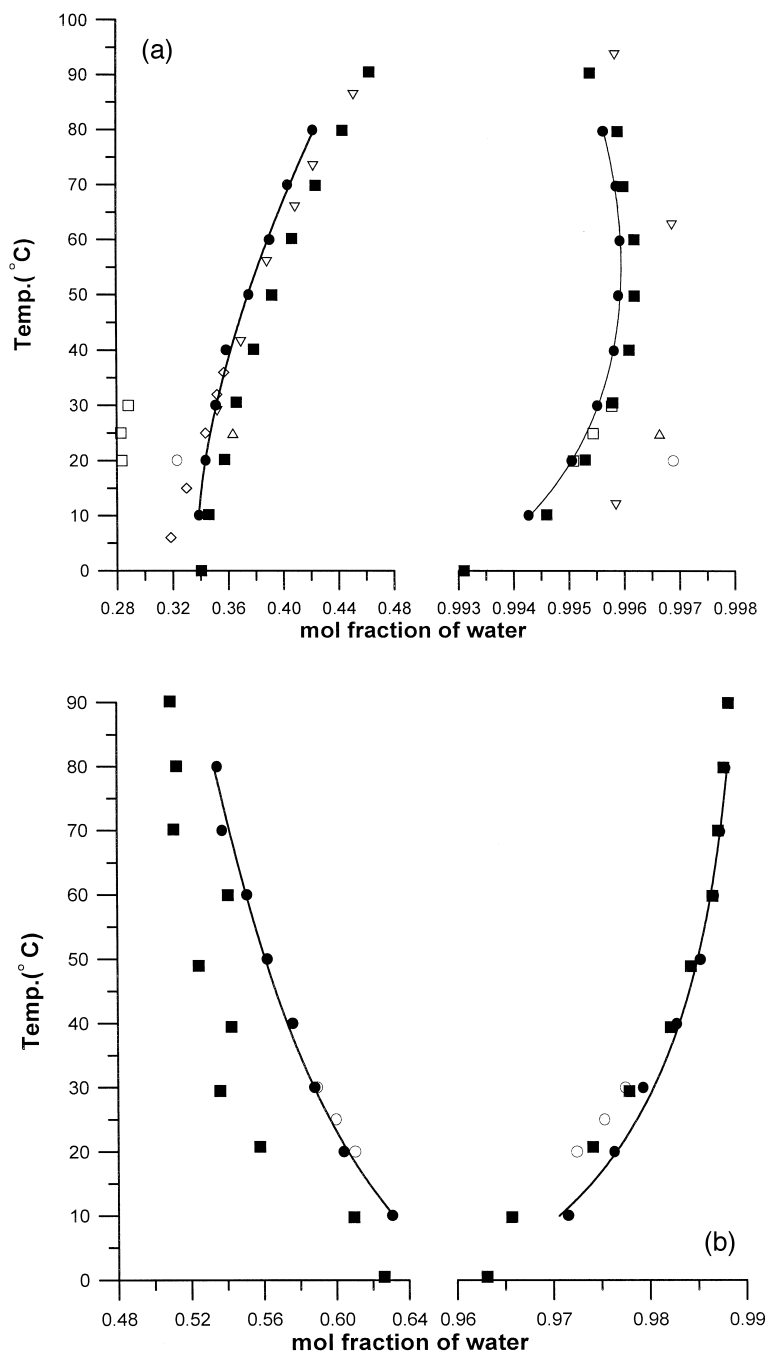


Fig. 1. Coexistence curve for the binary systems: (a) water + 1-pentanol and (b) water + 2-methyl-2-butanol: experimental results of this study (●), of Ginning and Baum (1937) [1] (□), of Krupatkin and Glagoleva (1969) [2] (△), of Laddha and Smith (1948) [3] (○), of Verschaffelt (1894) [4] (◇), of Zhuravleva and Zhuravlev (1970) [5] (▽), of Stephenson et al. (1984) [9] (■), and calculated results by the UNIQUAC model (solid curve).

II system with the resistivity better than $17.8 \text{ M}\Omega \text{ cm}$. The comparison of measured density, refractive index and viscosity of 1-pentanol, 2-methyl-2-butanol, 2-butyloxyethanol and water with literature values [11] at 293.15 K is shown in Table 1. The purity of 1-pentanol was further checked by gas chromatography, confirming the absence of other significant organic components, so no further purification was attempted.

The mixtures of binary and ternary systems were prepared in an 1 cm diameter test tube, and placed in a computer-controlled water-thermostat, whose temperature stability was better than $\pm 0.004^\circ\text{C}$. These samples were kept in the thermostat at least for several hours, sometimes up to two days, to allow the system to reach equilibrium. Before and during the equilibration process, the samples were shaken vigorously several times to ensure a thorough mixing. After the equilibrium was reached, both liquid phases were transparent with a sharp, mirror-like interface. Following equilibration, both liquid phases were carefully sampled by syringe for further experiments on the determinations of composition by gas chromatography for each liquid phase.

A gas chromatograph (Shimadzu, model GC-8A) equipped with thermal conductivity detector and connected to an integrator (Shimadzu, model C-R6A Chromatopac) was used. A 6 ft by 1/8 in. diameter stainless steel column packed with Poropak P 100/200 mesh was used. The oven temperature was held at 200°C for the systems containing 1-pentanol and at 180°C for the systems containing 2-methyl-2-butanol. Both injection-port and detector temperature were held at 230°C . The carrier gas was helium. Each analysis took about 10 min. Samples of single phase with known compositions were used to calibrate the instrument in the composition range of interest. Replicate measurements of a composition analysis indicated a precision of less than 1% deviation.

3. Results and discussion

The experimental compositions of the equilibrium phases obtained for the systems water + 1-pentanol and water + 2-methyl-2-butanol under investigation are reported in Table 2. The data are expressed in units of mole fraction of water. The superscripts u and l stand for the upper and lower phases, respectively. Fig. 1(a) and (b) compare our experimental data to the previous data in the literature [1–9] for the systems water + 1-pentanol and water + 2-methyl-2-butanol, respectively. As one can see in Fig. 1 that our data have a very good agreement with that of Stephenson et al. [9]. It should be pointed out that the experimental uncertainty of Stephenson et al. [9] was claimed to be less than 5%, a relatively large value, which makes most of their data within our experimental uncertainty.

Table 3

The relative van der Waals volume r and van der Waals surface area q [11]

Compound	r	q
1-Pentanol	4.5987	4.208
2-Methyl-2-butanol	4.5972	4.284
Water	0.9200	1.400
2-Butyloxyethanol	5.0469	4.372

Table 4

Estimated coefficients defined in Eqs. (3) and (4) for the systems: water + 1-pentanol and water + 2-methyl-2-butanol

Parameter	Water + 1-pentanol	Water + 2-methyl-2-butanol
a_{12}^o (K)	-1162.18	-1175.73
b_{12}^o	6.90062	6.96258
c_{12}^o (1/K)	-0.00805346	-0.00865876
a_{21}^o (K)	447.452	845.062
b_{21}^o	-0.777057	-4.66108
c_{21}^o (1/K)	-0.000528099	0.00728619

Except the data [9] of the upper phases in the system water + 2-methyl-2-butanol, as shown in Fig. 1(b), are systematically smaller than our result.

The UNIQUAC model of Abrams and Pransnitz [10] was used to correlate experimental data. The relative van der Waals volume, r , and van der Waals surface area, q , of the UNIQUAC model were calculated from the UNIFAC group contribution table of Hansen et al. [12] and are listed for each component in Table 3. The effective binary interaction parameter a_{ij} is defined by

$$a_{ij} = \frac{u_{ij} - u_{jj}}{R} \quad (1)$$

where R is the gas constant and u_{ij} is the UNIQUAC interaction parameter between molecules i and j . The effective binary interaction parameters a_{12} and a_{21} were exactly solved for each temperature by numerical method according to the iso-activity criterion:

$$x_i^l \gamma_i^l = x_i^u \gamma_i^u, \quad i = 1 \text{ and } 2 \quad (2)$$

where x_i is the mole fraction of component i , γ is the activity coefficient, and superscript l and u stand for the lower and upper liquid phases, respectively.

It was found that the effective binary interaction parameters a_{12} and a_{21} are temperature-dependent. Therefore, the effective binary interaction parameters a_{12} and a_{21} were further correlated with temperature T (K) by the following polynomial equation:

$$a_{12} = a_{12}^o + b_{12}^o T + c_{12}^o T^2 \quad (3)$$

Table 5

Average absolute deviation in compositions for the systems: water (1) + 1-pentanol (2) and water (1) + 2-methyl-2-butanol (2)

System	Average absolute deviation	
	$\overline{\Delta x_1^l}$	$\overline{\Delta x_1^u}$
Water + 1-pentanol	0.0010	0.0000
Water + 2-methyl-2-butanol	0.0018	0.0004

Table 6

Experimental and calculated mole fractions of equilibrium liquid phases for the ternary system water (1) + 1-pentanol (2) + 2-butyloxyethanol (3) at 20°C

Experimental results				Calculated results			
x_1^u	x_3^u	x_1^l	x_3^l	x_1^u	x_3^u	x_1^l	x_3^l
0.3887	0.0385	0.9937	0.00094	0.3887	0.0393	0.9947	0.00058
0.4117	0.0654	0.9928	0.0018	0.4117	0.0587	0.9944	0.00099
0.4385	0.0944	0.9928	0.0027	0.4385	0.0800	0.9940	0.0016
0.4879	0.1233	0.9912	0.0042	0.4879	0.1150	0.9930	0.0029
0.5355	0.1463	0.9897	0.0058	0.5355	0.1431	0.9916	0.0046
0.5804	0.1684	0.9892	0.0075	0.5804	0.1640	0.9899	0.0066
0.6397	0.1813	0.9872	0.0098	0.6397	0.1822	0.9868	0.0100
0.7009	0.1833	0.9845	0.0128	0.7009	0.1882	0.9825	0.0148
0.7946	0.1526	0.9792	0.0183	0.7946	0.1682	0.9722	0.0257
0.8694	0.1073	0.9707	0.0260	0.8694	0.1237	0.9566	0.0422
average absolute deviation					0.0076	0.0032	0.0032

and

$$a_{21} = a_{21}^0 + b_{21}^0 T + c_{21}^0 T^2 \quad (4)$$

Table 7

Experimental and calculated mole fractions of equilibrium liquid phases for the ternary system water (1) + 1-pentanol (2) + 2-butyloxyethanol (3) at 30°C

Experimental results				Calculated results			
x_1^u	x_3^u	x_1^l	x_3^l	x_1^u	x_3^u	x_1^l	x_3^l
0.3933	0.0322	0.9952	0.00068	0.3933	0.0390	0.9951	0.00057
0.4123	0.0494	0.9945	0.0011	0.4123	0.0561	0.9949	0.00092
0.4280	0.0693	0.9940	0.0017	0.4280	0.0696	0.9947	0.0013
0.4473	0.0838	0.9936	0.0021	0.4473	0.0852	0.9943	0.0017
0.4725	0.1042	0.9930	0.0028	0.4725	0.1043	0.9937	0.0024
0.5025	0.1228	0.9916	0.0038	0.5025	0.1247	0.9929	0.0035
0.5285	0.1442	0.9908	0.0048	0.5285	0.1404	0.9920	0.0045
0.5574	0.1615	0.9903	0.0058	0.5574	0.1554	0.9908	0.0059
0.5851	0.1725	0.9900	0.0067	0.5851	0.1673	0.9895	0.0073
0.6083	0.1838	0.9888	0.0079	0.6083	0.1754	0.9882	0.0087
0.6517	0.1891	0.9875	0.0095	0.6517	0.1855	0.9853	0.0118
0.6985	0.1912	0.9855	0.0120	0.6985	0.1886	0.9813	0.0160
0.7608	0.1771	0.9817	0.0159	0.7608	0.1791	0.9743	0.0233
0.8261	0.1439	0.9767	0.0211	0.8261	0.1509	0.9632	0.0347
0.8378	0.1365	0.9755	0.0224	0.8378	0.1438	0.9605	0.0375
0.8455	0.1318	0.9739	0.0239	0.8455	0.1389	0.9585	0.0395
0.8628	0.1190	0.9717	0.0260	0.8628	0.1267	0.9534	0.0447
0.9011	0.0883	0.9608	0.0360	0.9011	0.0953	0.9361	0.0621
average absolute deviation					0.0047	0.0060	0.0059

Table 8

Experimental and calculated mole fractions of equilibrium liquid phases for the ternary system water (1) + 2-methyl-2-butanol (2) + 2-butyloxyethanol (3) at 20°C

Experimental results				Calculated results			
x_1^u	x_3^u	x_1^l	x_3^l	x_1^u	x_3^u	x_1^l	x_3^l
0.6381	0.0545	0.9787	0.0023	0.6381	0.0483	0.9780	0.0026
0.6496	0.0703	0.9789	0.0032	0.6496	0.0598	0.9779	0.0038
0.6697	0.0802	0.9785	0.0040	0.6697	0.0763	0.9770	0.0061
0.6910	0.0947	0.9788	0.0053	0.6910	0.0896	0.9751	0.0089
0.7169	0.1061	0.9777	0.0071	0.7169	0.1013	0.9717	0.0130
0.7446	0.1095	0.9770	0.0086	0.7446	0.1089	0.9667	0.0183
0.7812	0.1087	0.9756	0.0111	0.7812	0.1118	0.9576	0.0269
0.8200	0.1018	0.9705	0.0160	0.8200	0.1066	0.9439	0.0388
0.8367	0.0958	0.9652	0.0201	0.8367	0.1019	0.9362	0.0450
0.8886	0.0672	0.9583	0.0243	0.8886	0.0779	0.9040	0.0684
average absolute deviation					0.0056	0.0151	0.0130

The coefficients a_{12}^o , b_{12}^o , c_{12}^o , a_{21}^o , b_{21}^o , and c_{21}^o were estimated by regression of the effective binary interaction parameters a_{ij} s over the whole experimental temperature range. Table 4 lists the values of these coefficients.

Fig. 1(a) and (b) show a comparison between the experimental results and the calculated phase boundaries obtained from the UNIQUAC model with the correlated parameters, Eqs. (3) and (4). The calculated results of phase behavior describe the experimental data very well. Table 5 gives the average absolute deviation of the compositions of water in both lower and upper phases over the experimental temperature range calculated by the UNIQUAC model. The calculated results of the

Table 9

Experimental and calculated mole fractions of equilibrium liquid phases for the ternary system water (1) + 2-methyl-2-butanol (2) + 2-butyloxyethanol (3) at 30°C

Experimental results				Calculated results			
x_1^u	x_3^u	x_1^l	x_3^l	x_1^u	x_3^u	x_1^l	x_3^l
0.6286	0.0555	0.9829	0.0018	0.6286	0.0672	0.9813	0.0033
0.6510	0.0868	0.9819	0.0035	0.6510	0.0881	0.9804	0.0058
0.6673	0.1045	0.9818	0.0047	0.6673	0.0998	0.9791	0.0079
0.6916	0.1165	0.9813	0.0059	0.6916	0.1130	0.9763	0.0115
0.7119	0.1256	0.9809	0.0073	0.7119	0.1207	0.9733	0.0150
0.7476	0.1301	0.9805	0.0091	0.7476	0.1275	0.9661	0.0223
0.7817	0.1261	0.9797	0.0108	0.7817	0.1269	0.9568	0.0311
0.8230	0.1162	0.9779	0.0134	0.8230	0.1174	0.9413	0.0448
0.8449	0.1090	0.9738	0.0177	0.8449	0.1088	0.9303	0.0540
0.8748	0.0924	0.9683	0.0230	0.8748	0.0932	0.9106	0.0693
0.8960	0.0782	0.9634	0.0269	0.8960	0.0795	0.9047	0.0736
average absolute deviation					0.0030	0.0229	0.0195

Table 10

Effective binary interaction parameters of UNIQUAC model for the system water (1) + 1-pentanol (2) + 2-butyloxyethanol (3)

<i>ij</i>	20°C		30°C	
	a_{ij} (K)	a_{ji} (K)	a_{ij} (K)	a_{ji} (K)
12	169.005	173.808	189.532	163.497
13	297.973	−153.181	293.525	−153.693
23	137.816	−157.897	139.104	−168.361

system water + 1-pentanol have a smaller deviation from the experimental data than that of the system water + 2-methyl-2-butanol.

The experimental compositions of tie lines for the ternary systems water + 1-pentanol + 2-butyloxyethanol and water + 2-methyl-2-butanol + 2-butyloxyethanol at 20°C and 30° are given in Tables 6–9.

The experimental data of ternary systems were also correlated by the UNIQUAC model. For the UNIQUAC model, there are six binary interaction parameters for a ternary system. Two binary interaction parameters for the systems water + 1-pentanol and water + 2-methyl-2-butanol can be directly determined from the experimental results of these binary systems. Therefore, there are four binary interaction parameters left for each ternary system under investigation. In this work, the parameter estimation was carried out in a two-step procedure proposed by Negahban et al. [13].

The first step was to minimize the sum of the squared differences between the activities of each component in each phase.

$$F_1 = \sum_{j=1}^m \sum_{i=1}^3 \left(x_{ij}^l \gamma_{ij}^l - x_{ij}^u \gamma_{ij}^u \right)^2 \quad (5)$$

where x_{ij}^l and x_{ij}^u are the experimental mole fraction of component i of, respectively, lower and upper phase along a tie-line j , γ_{ij}^l and γ_{ij}^u are the corresponding activity coefficient calculated from the UNIQUAC model, and m is the total number of tie-lines. The regression results of the effective binary interaction parameters from minimization of Eq. (5) were used as initial guesses for the second step, which was to minimize of the sum of the squared differences between the calculated and experimental mole fractions.

$$F_2 = \sum_{j=1}^m \sum_{i=1}^3 \left\{ \left(x_{ij}^l - \hat{x}_{ij}^l \right)^2 + \left(x_{ij}^u - \hat{x}_{ij}^u \right)^2 \right\} \quad (6)$$

Table 11

Effective binary interaction parameters of UNIQUAC model for the system water (1) + 2-methyl-2-butanol (2) + 2-butyloxyethanol (3)

<i>ij</i>	20°C		30°C	
	a_{ij} (K)	a_{ji} (K)	a_{ij} (K)	a_{ji} (K)
12	118.784	108.277	132.246	108.437
13	159.190	−104.305	144.639	−87.202
23	114.394	−190.425	110.016	−202.564

where \hat{x}_{ij}^l and \hat{x}_{ij}^u are the calculated mole fraction of component i of, respectively, lower and upper phase along the tie-line j .

Tables 10 and 11 summarize the values of the UNIQUAC model parameters obtained from the two-step regression procedure for the systems water + 1-pentanol + 2-butyloxyethanol and water + 2-methyl-2-butanol + 2-butyloxyethanol, respectively. Note that the effective binary interaction parameters are temperature-dependent. The calculated results along each tie-line are also given in Tables 6–9, and have a good agreement with experimental data. The average absolute deviation of the calculated compositions along a tie-line is also given in the bottom of Tables 6–9. Figs. 2 and 3 show a graphical comparison between the experimental and the calculated tie lines for the systems

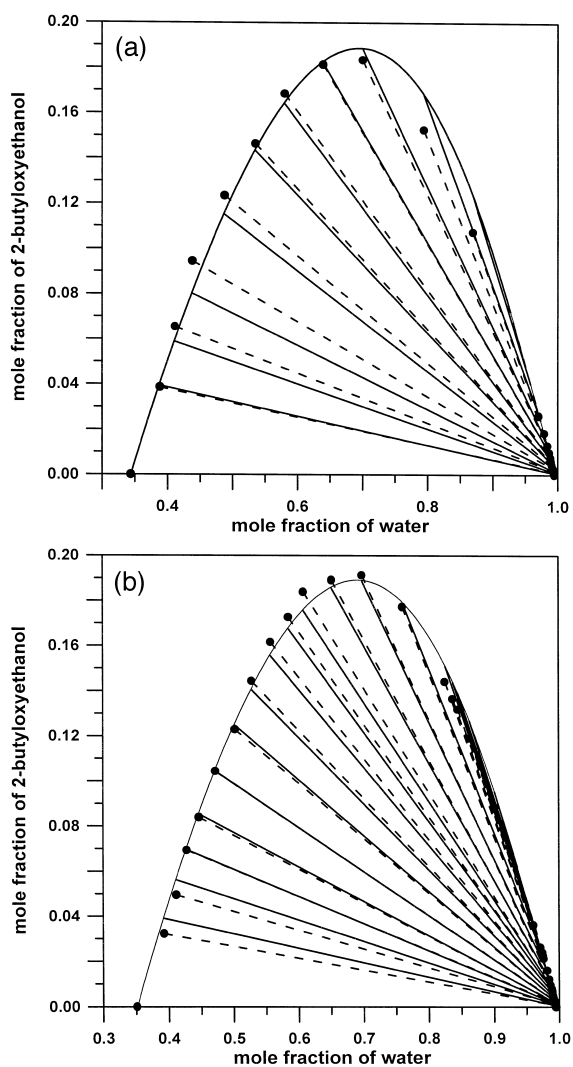


Fig. 2. Ternary liquid–liquid equilibria for the system water+1-pentanol+2-butyloxyethanol (a) at 20°C; (b) at 30°C: experimental tie lines (●, dotted line), calculated tie lines (solid line), and calculated binodal curve (solid curve).

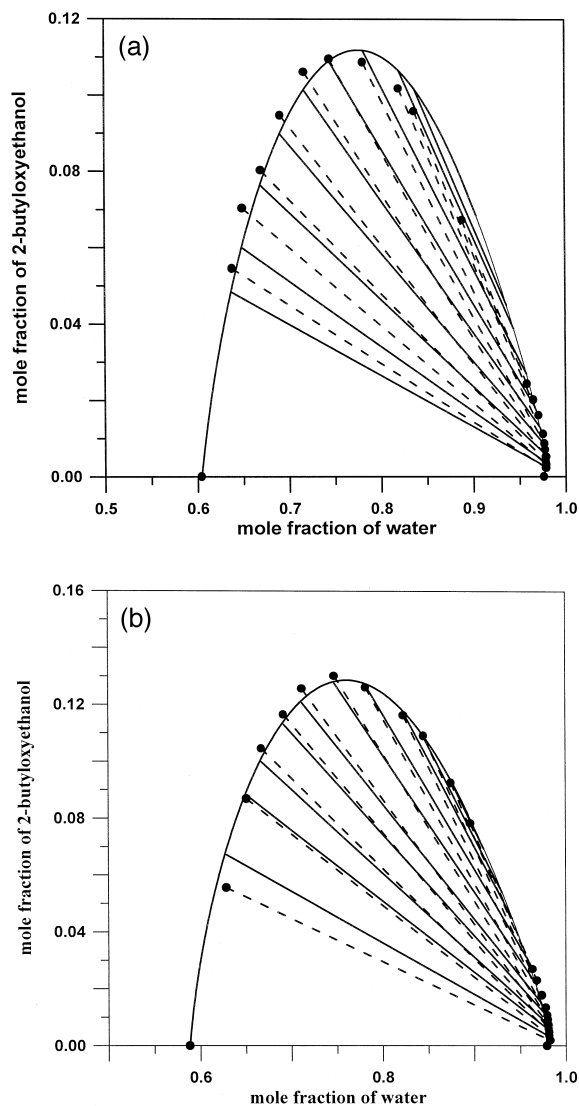


Fig. 3. Ternary liquid–liquid equilibria for the system water + 2-methyl-2-butanol + 2-butyloxyethanol (a) at 20°C; (b) at 30°C: experimental tie lines (●, dotted line), calculated tie lines (solid line), and calculated binodal curve (solid curve).

water + 1-pentanol + 2-butyloxyethanol and water + 2-methyl-2-butanol + 2-butyloxyethanol, respectively. The experimental equilibrium data were successfully correlated by the UNIQUAC model.

List of symbols

a_{ij}	effective binary interaction parameter of UNIQUAC model defined by Eq. (1), (K)
$a_{ij}^{\circ}, b_{ij}^{\circ}, c_{ij}^{\circ}$	coefficients in Eqs. (3) and (4)
F_1	activity objective function
F_2	mole fraction objective function

m	total number of tie-lines in Eqs. (5) and (6)
n_D	refractive index in Table 1
R	gas constant
T	temperature (K)
u_{ij}	the UNIQUAC binary interaction parameter between molecules i and j
x_i	the experimental mole fraction of component i
\hat{x}_i	the calculated mole fraction of component i

Greek letters

η	viscosity (mPa s)
γ_i	activity coefficient of component i
ρ	density (g cm ⁻³)

Subscripts

$i, j, 1, 2, 3$	component identification
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Superscripts

l	lower phase of a two-liquid-phase coexisting system
u	upper phase of a two-liquid-phase coexisting system

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