Liquid–liquid equilibria for the ternary system water + diethylene glycol monohexyl ether + 2-methyl-2-butanol

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Abstract

Liquid–liquid equilibrium compositions of the ternary system water + diethylene glycol monohexyl ether + 2-methyl-2-butanol were measured at 293.15, 303.15, and 313.15 K under atmospheric pressure. The experimental equilibrium data were successfully correlated with the UNIQUAC model.
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1. Introduction

Non-ionic surfactants poly(oxyethylene glycol) monoethers $CH_3(CH_2)_{i-1}O(CH_2CH_2O)_jH$ (symbolized by C_iE_j hereafter) are widely used in the industrial processes as liquid–liquid extraction emulsifying agents [1], tertiary oil recovery detergents [2], and herbicides. Hence the thermodynamic liquid–liquid equilibrium data for such systems are therefore essential. Recently, liquid–liquid equilibrium data of systems containing C_iE_j have been measured for binary and ternary mixtures in our laboratory [3–9]. There are, to the best of our knowledge, no liquid–liquid equilibrium experimental data for the ternary systems water + diethylene glycol monohexyl ether + 2-methyl-2-butanol available in the literature. In this study, liquid–liquid equilibrium measurements were performed for two binary systems water + diethylene glycol monohexyl ether and water + 2-methyl-2-butanol, and a ternary system, water + diethylene glycol monohexyl ether + 2-methyl-2-butanol, at 293.15, 303.15, and 313.15 K under atmospheric pressure. The experimental data were then correlated with the UNIQUAC model of Abrams and Prausnitz [10]. The phase behavior of the system was successfully described by the UNIQUAC model.

2. Experimental

2-Methyl-2-butanol was obtained from Merck with a purity of 99% and was used as received. The non-ionic surfactant diethylene glycol monohexyl ether (C_6E_2) was an Aldrich chemical product with a purity of 98% and was fractionally distilled under reduced pressure until a purity of >99% was obtained, as determined by gas chromatography. Water was purified by Millipore Milli-RO PLUS 10 followed by Milli-Q system with the resistivity better than 18.2 MΩ cm.

To analyze the composition of the samples, a gas chromatograph (China Chromatography 9800) equipped with thermal conductivity detector was used. An 1 m long by 3.175×10^{-3} m diameter stainless steel column stuffed with Poropak P 80/100 mesh was used. The signal was transferred to an integrator (Shimadzu, Chromatopac C-R6A) to accomplish data recording. The temperatures of the injection port and of the detector were held at 553.15 and 573.15 K, respectively. The oven temperature was initially held at 398.15 K. Five minutes after injection, the oven temperature was raised to a final temperature of 518.15 K at a speed of 37 K min^{-1}. Helium was the carrier gas with a flow rate of 60 ml min^{-1}. Each analysis took about 18 min.

Single phase binary mixtures of C_6E_2 + 2-methyl-2-butanol and water + 2-methyl-2-butanol with known compositions were used to calibrate the instrument in the composition range of interest. For the calibration of gas

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Table 1

The calibration composition ranges and the corresponding errors of gas chromatograph

	Water + 2-methyl-2-butanol		C_6E_2 + 2-methyl-2-butanol
Mass fraction range of 2-methyl-2-butanol	0.00496–0.0858	0.203–0.955	0.0475–0.995
Average errors[a]	0.000176	0.000751	0.000284

[a] Average errors $= \frac{1}{n_p} \sum_{j=1}^{n_p} |w_{exp} - w_{calb}|_j$, where n_p is the number of calibration points and w is the mass fraction of 2-methyl-2-butanol. The subscript "exp" and "calb" represent the prescribed experimental values and calibrated values, respectively.

chromatography, each prescribed composition was analyzed at least three times. The calibration results were further fitted to a third order polynomial function. The deviations of the calibration curves from the actual values are tabulated in Table 1. These two polynomial functions of calibration curves are combined to simultaneously solve the compositions of the ternary system water + C_6E_2 + 2-methyl-2-butanol. For each tie-line, the water + C_6E_2 + 2-methyl-2-butanol mixtures were prepared in three test tubes with the same total composition. These samples were vigorously shaken and then put into a water-thermostat, whose temperature stability was controlled uncertainty in temperature within ±0.05 K, for at least 24 h to reach equilibrium. During the equilibration process, these samples were shaken several times to ensure thorough mixing. After equilibrium was reached, both liquid phases of each sample were analyzed at least three times by gas chromatography to determine the compositions. The compositions for each tie-line were determined by averaging over three samples. The experimental uncertainty among three samples was within ±0.0009 mass fraction.

3. Results and discussion

The experimental results of liquid–liquid equilibrium of two binary systems water + C_6E_2 and water + 2-methyl-2-butanol at 293.15, 303.15, and 313.15 K are listed in Table 2, also compare with the literature [3,4,6,11]. The data are expressed in units of mass fraction and the superscripts u and l stand for upper and lower liquid phases, respectively. The experimental compositions of tie-lines for the ternary system water + C_6E_2 + 2-methyl-2-butanol at 293.15, 303.15, and 313.15 K are given in Tables 3–5. Figs. 1–3 show the corresponding triangular phase dia-

grams of the system water + C_6E_2 + 2-methyl-2-butanol at 293.15, 303.15, and 313.15 K. Note that in the temperature range of our experiments, the two-phase region is belt-like and it enlarges with increasing temperature. Total compositions of samples prepared for tie-line measurements are also given in Figs. 1–3 by filled diamonds. The fit of a linear expression to each tie-line and its corresponding total composition data point is always better than 0.999.

The UNIQUAC model was used to correlate the experimental data. In this work, the relative van der Waals volume r_i and surface area q_i were adopted from the UNIFAC group contribution of Hansen et al. [12], listed in Table 6. The effective binary interaction parameter a_{ij}, is defined by $a_{ij} = (u_{ij} - u_{ji})/R$, where u_{ij} is the UNIQUAC interaction parameter between molecules i and j and R is the gas constant.

The effective binary interaction parameters a_{ij} and a_{ji} of the binary systems water (1) + C_6E_2 (2) and water (1) + 2-methyl-2-butanol (3) can be numerically solved for each temperature by using experimental binary compositions as input data according to the iso-activity criterion:

$$x_i^l \gamma_i^l = x_i^u \gamma_i^u, \quad i = 1\text{–}3 \tag{1}$$

where x_i is the mole fraction of component i, γ_i is the activity coefficient of component i.

For a ternary system, there are six group-interaction parameters, a_{ij}. In this work, four effective binary interaction parameters, a_{12}, a_{21}, a_{13}, and a_{31} can be directly determined from the experimental data of the binary systems. Therefore, there are two parameters a_{23} and a_{32} left to be determined by a numerical method.

First, we defined an objective function [13]:

$$F_a = \sum_{j=1}^{m} \sum_{i=1}^{3} (x_{ij}^l \gamma_{ij}^l - x_{ij}^u \gamma_{ij}^u)^2 \tag{2}$$

Table 2

Experimental and literature mass fraction of water of equilibrium liquid phases for the binary systems water (1) + C_6E_2 (2) and water (1) + 2-methyl-2-butanol (3)

T (K)	Water (1) + C_6E_2 (2)						Water (1) + 2-methyl-2-butanol (3)					
	This study		Literature [4]		Literature [6]		This study		Literature [3]		Literature [11]	
	w_1^l	w_1^u	w_1^l	w_1^u	w_1^l	w_1^u	w_1^l	w_1^u	w_1^l	w_1^u	w_1^l	w_1^u
293.15	0.981	0.569	0.976	0.566	0.981	0.558	0.884	0.246	0.894	0.238	0.879	0.243
303.15	0.986	0.432	0.980	0.429	0.980	0.430	0.906	0.228	0.907	0.226	0.899	0.227
313.15	0.988	0.348	0.981	0.341	0.982	0.341	0.921	0.207	0.921	0.218	–	–

Table 3
Experimental and calculated mass fractions of equilibrium liquid phases for the ternary system water (1) + C_6E_2 (2) + 2-methyl-2-butanol (3) at 293.15 K

Experimental results				Calculated results			
w_1^u	w_2^u	w_1^l	w_2^l	w_1^u	w_2^u	w_1^l	w_2^l
0.242	0.078	0.884	0.002	0.246	0.073	0.910	0.004
0.246	0.155	0.890	0.004	0.253	0.144	0.928	0.007
0.267	0.236	0.900	0.006	0.268	0.220	0.942	0.009
0.277	0.278	0.911	0.007	0.279	0.262	0.949	0.010
0.289	0.328	0.911	0.009	0.294	0.308	0.956	0.011
0.308	0.366	0.921	0.010	0.311	0.346	0.960	0.012
0.337	0.401	0.930	0.011	0.334	0.387	0.965	0.014
0.380	0.426	0.943	0.012	0.360	0.420	0.969	0.015
0.425	0.451	0.952	0.015	0.404	0.452	0.973	0.016
0.497	0.450	0.965	0.018	0.472	0.462	0.977	0.018
Average absolute deviation[a]				0.009	0.012	0.032	0.002

[a] Average absolute deviation $= \sum_{i=1}^{N} \frac{|w_i^{exp} - w_i^{calc}|}{N}$, where N is the number of tie-lines.

Table 4
Experimental and calculated mass fractions of equilibrium liquid phases for the ternary system water (1) + C_6E_2 (2) + 2-methyl-2-butanol (3) at 303.15 K

Experimental results				Calculated results			
w_1^u	w_2^u	w_1^l	w_2^l	w_1^u	w_2^u	w_1^l	w_2^l
0.224	0.096	0.902	0.001	0.224	0.090	0.931	0.003
0.230	0.198	0.910	0.003	0.230	0.187	0.949	0.005
0.240	0.278	0.922	0.005	0.239	0.260	0.959	0.006
0.251	0.314	0.934	0.006	0.249	0.309	0.965	0.007
0.258	0.362	0.938	0.006	0.258	0.349	0.968	0.008
0.269	0.405	0.942	0.007	0.270	0.389	0.972	0.009
0.290	0.457	0.949	0.009	0.289	0.441	0.976	0.010
0.311	0.499	0.955	0.011	0.310	0.483	0.979	0.011
0.339	0.534	0.965	0.012	0.338	0.522	0.982	0.012
0.392	0.555	0.975	0.014	0.382	0.557	0.984	0.013
Average absolute deviation[a]				0.002	0.011	0.027	0.001

[a] Average absolute deviation $= \sum_{i=1}^{N} \frac{|w_i^{exp} - w_i^{calc}|}{N}$, where N is the number of tie-lines.

where x_{ij}^l and x_{ij}^u stand for the experimental mole fraction of component i of lower and upper phase, respectively, 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. Then the effective binary interaction parameters a_{23} and a_{32} of the UNIQUAC model were determined numerically by minimizing the objective function F_a.

Table 5
Experimental and calculated mass fractions of equilibrium liquid phases for the ternary system water (1) + C_6E_2 (2) + 2-methyl-2-butanol (3) at 313.15 K

Experimental results				Calculated results			
w_1^u	w_2^u	w_1^l	w_2^l	w_1^u	w_2^u	w_1^l	w_2^l
0.212	0.093	0.922	0.001	0.203	0.093	0.940	0.002
0.213	0.201	0.925	0.002	0.207	0.193	0.955	0.004
0.216	0.299	0.933	0.005	0.215	0.285	0.966	0.005
0.227	0.353	0.943	0.005	0.222	0.338	0.970	0.006
0.234	0.435	0.947	0.007	0.236	0.415	0.976	0.007
0.256	0.489	0.960	0.008	0.251	0.478	0.980	0.008
0.275	0.531	0.968	0.008	0.265	0.524	0.982	0.009
0.287	0.572	0.969	0.010	0.282	0.565	0.984	0.010
0.296	0.595	0.973	0.011	0.293	0.587	0.985	0.010
0.324	0.626	0.980	0.012	0.318	0.625	0.987	0.011
Average absolute deviation[a]				0.005	0.009	0.021	0.001

[a] Average absolute deviation $= \sum_{i=1}^{N} \frac{|w_i^{exp} - w_i^{calc}|}{N}$, where N is the number of tie-lines.
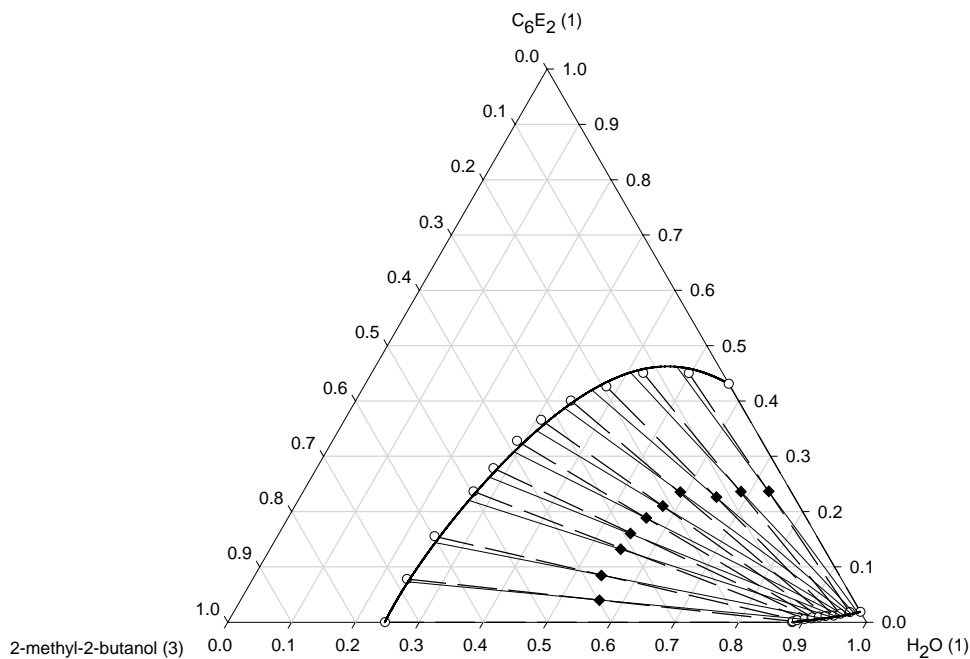
Fig. 1. Ternary liquid–liquid equilibria (mass fraction) for the system water (1) + C_6E_2 (2) + 2-methyl-2-butanol (3) at 293.15 K: experimental tie-lines ($\bigcirc$, dashed line); calculated tie-lines (solid line); calculated binodal curve (solid curve); and experimental total compositions ($\blacklozenge$).

Next, we used the effective binary interaction parameters obtained above as the initial guesses of the following objective function [14]:

$$F_x = \sum_k \sum_j \sum_i \left(\frac{x_{ijk}^{\mathrm{expl}} - x_{ijk}^{\mathrm{calc}}}{x_{ijk}^{\mathrm{expl}}} \right)^2, \qquad (3)$$

Table 6
The relative van der Waals volume r and van der Waals surface area q

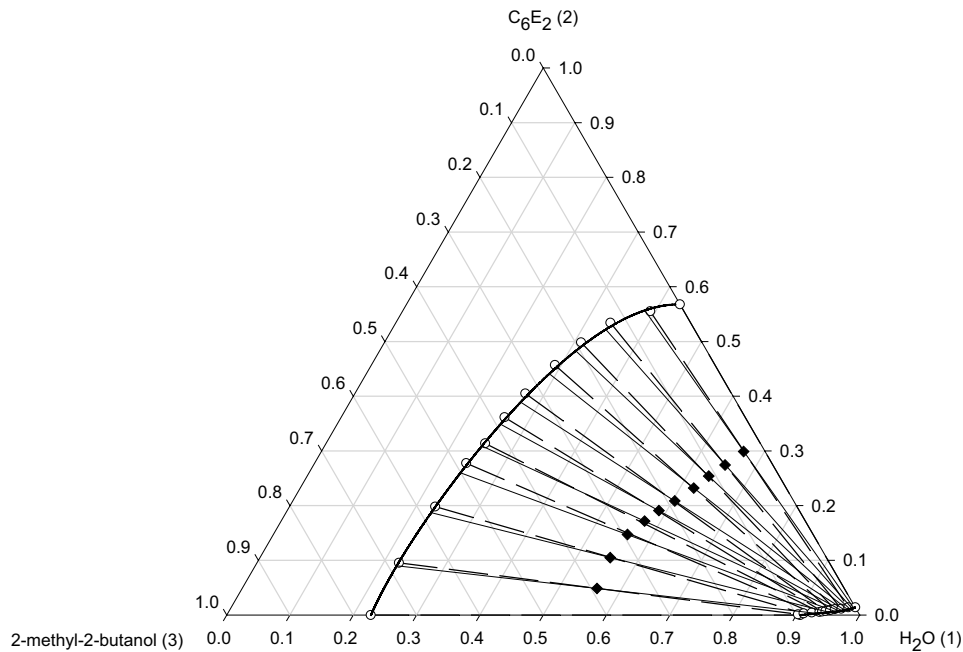| Compound	r	q
Water	0.9200	1.4000
C_6E_2	7.9900	6.7700
2-Methyl-2-butanol	4.5972	4.2840

Fig. 2. Ternary liquid–liquid equilibria (mass fraction) for the system water (1) + C_6E_2 (2) + 2-methyl-2-butanol (3) at 303.15 K: experimental tie-lines ($\bigcirc$, dashed line), calculated tie-lines (solid line); calculated binodal curve (solid curve); and experimental total compositions ($\blacklozenge$).

Fig. 3. Ternary liquid–liquid equilibria (mass fraction) for the system water (1) + C_6E_2 (2) + 2-methyl-2-butanol (3) at 313.15 K: experimental tie-lines (○, dashed line); calculated tie-lines (solid line); calculated binodal curve (solid curve); and experimental total compositions (◆).
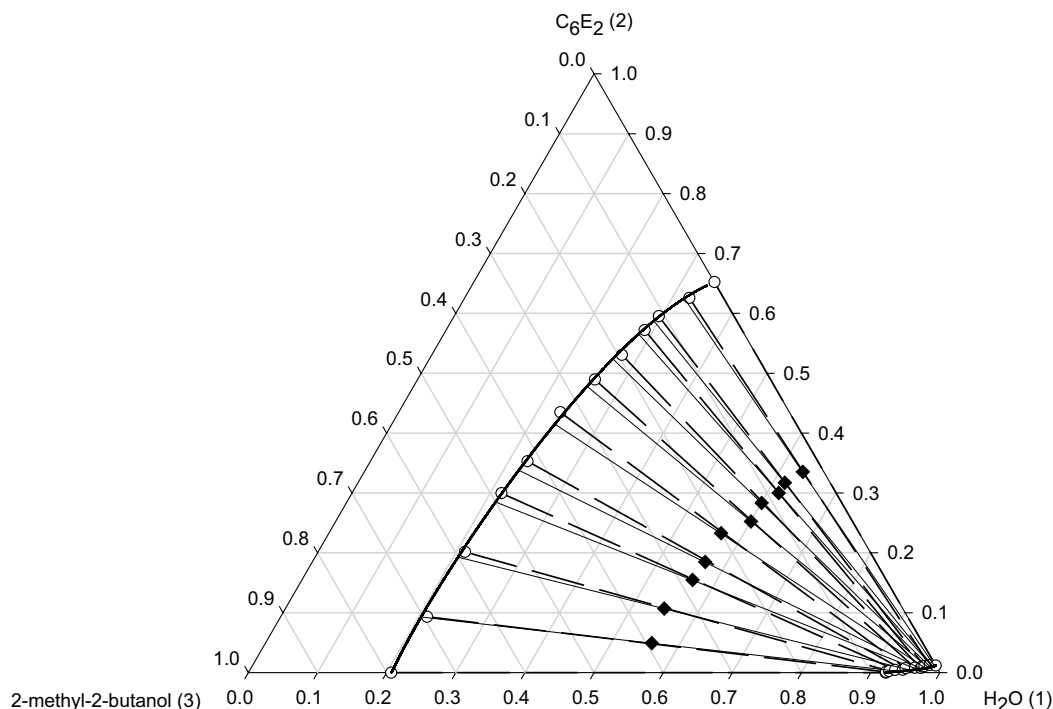
Table 7
UNIQUAC binary interaction parameters for the system water (1) + C_6E_2 (2) + 2-methyl-2-butanol (3)

ij	a_{ij} (K)					
	293.15 K		303.15 K		313.15 K	
12	599.58	−298.27	558.67	−270.26	519.77	−244.13
13	111.51	112.19	132.80	106.81	145.47	114.73
23	−419.83	701.25	−441.24	785.60	−452.68	791.99

where x_{ijk}^{expl} and x_{ijk}^{calc} are the experimental and calculated composition of component i in phase j along a tie-line k, respectively. The minimization of the objective function F_x was accomplished by using the subroutine DUMPOL of IMSL library. Then the regressed binary interaction parameters were applied to the liquid–liquid equilibrium flash calculation [15] to evaluate the calculated tie-lines, listed in

Tables 3–5, by using the experimental total compositions as input data.

The regression results of the UNIQUAC interaction parameters are shown in Table 7 and note that these parameters are temperature-dependent. Table 8 compares the UNIQUAC effective binary interaction parameters of this work and literatures, and there is a good agreement. The calculated results for each tie-line are given in Tables 3–5 to make a comparison with experimental data. The average absolute deviation between experimental data and calculated results are also listed in the bottom of Tables 3–5. As one can see, the phase behavior of the system water + C_6E_2 + 2-methyl-2-butanol is successfully described by the UNIQUAC model.

List of symbols

a group-interaction parameters of the UNIQUAC model (K)

Table 8
Comparison of UNIQUAC binary interaction parameters for this work and literatures

T (K)	Water (1) + C_6E_2 (2)				Water (1) + 2-methyl-2-butanol (3)			
	This work		Literature [4]		This work		Literature [3]	
	a_{12} (K)	a_{21} (K)	a_{12} (K)	a_{21} (K)	a_{13} (K)	a_{31} (K)	a_{13} (K)	a_{31} (K)
293.15	599.58	−298.27	569.45	−290.05	111.51	112.19	118.78	108.28
303.15	558.67	−270.26	518.70	−257.23	132.80	106.81	132.25	108.44
313.15	519.77	−244.13	464.23	−223.50	145.47	114.73	155.50	99.95

F_a first objective function
F_x second objective function
m the total number of tie-lines
q the relative van der Waals surface area
r the relative van der Waals volume
R the gas constant
T temperature
w   water
x mole fraction
x_{ij} the experimental mole fraction of component i along a tie-line j
x_{ijk} composition of component i in phase j along a tie-line k

Greek letters
γ_{ij} activity coefficient of component i along a tie-line j

Subscripts
1   water
2   C_6E_2
3   2-methyl-2-butanol
i component i
ij interactions of i–j pair
ji interactions of j–i pair

Superscripts
calc   calculated values
expl   experimental values

l   lower liquid phase
u   upper liquid phase

Acknowledgements

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