Liquid–liquid equilibria for the ternary system water + tetradecane + 2-butyloxyethanol

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Abstract

Liquid–liquid equilibria of the ternary system water + tetradecane + 2-butyloxyethanol in the temperature range from 298.15 to 338.15 K were investigated at atmospheric pressure. The experimental data correlated well with the UNIQUAC model. For the system with a three-liquid-phase-coexisting region, all the six UNIQUAC interaction parameters can be determined numerically by minimizing the deviation of the compositions of three coexisting liquid phases only.

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1. Introduction

Precise liquid–liquid equilibrium data of mixtures of the type water + oil + surfactant are needed in several industrial applications, for example, herbicides, tertiary oil recovery, and the production of drugs [1,2]. Nonionic surfactants of the homologous series of polyoxyethylene alcohol $\text{CH}_3(\text{CH}_2)_{i-1}(\text{OCH}_2\text{CH}_2)_j\text{OH}$, abbreviated by C_iE_j hereafter, are widely used for emulsifying agents and detergents. In addition, the phase behavior of mixtures of the type water + oil + C_iE_j also plays an important role in the fundamental work of critical phenomena, phase conductivity, and wetting transitions [3–9]. In our laboratory, recently, we have performed liquid–liquid equilibrium measurements on water + C_iE_j binary systems [10] and five ternary systems: water + dodecane + C_4E_1 [11]; water + octane + C_4E_2 [12]; water + decane + C_4E_2 [13]; water + dodecane + C_6E_2 [14]; and water + tetradecane + C_6E_2 [15].

Kilpatrick et al. [16] have studied the phase behavior of the ternary mixture water + alkane + C_4E_1 at 298.15 and 303.15 K for five different alkanes: hexane, octane, nonane, decane, and tetradecane. However, they reported the phase diagram of the ternary system water + tetradecane

+ 2-butyloxyethanol (C_4E_1) only at 298.15 K. In this study, liquid–liquid equilibrium measurements were performed for the ternary system water + tetradecane + C_4E_1 in the temperature range from 298.15 to 338.15 K at atmospheric pressure. The experimental data were further correlated with universal quasi-chemical (UNIQUAC) model [17] to determine the effective binary interaction parameters at different temperatures.

2. Experimental

Tetradecane was obtained from Merck with a purity of 99%. The nonionic surfactant 2-butyloxyethanol was an Aldrich Chemical product with a purity of 99%. These two chemicals were used as received without further purification. Water was purified by a Millipore Milli-RO PLUS 10 and Milli-Q system with a resistivity $>8.2 \text{ M}\Omega \text{ cm}$.

All samples were prepared with known compositions in test tubes sealed with septum and placed in a computer controlled thermostat, whose temperature was controlled within $\pm 0.005 \text{ K}$, and left at least 24 h for equilibration. After equilibrium was reached, each phase was analyzed with a gas chromatograph (China Chromatography 9800, Taiwan) equipped with a thermal conductivity detector. The signal was transferred to an integrator (C-R6A, Chromatopac, Shimadzu Co., Japan) to record area fractions. The tem-

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Table 1
Average deviations of calibration curves of the gas chromatograph

Binary system	Concentration ^a range of C ₄ E ₁	Average error ^b
Water + C ₄ E ₁	0.0238–0.0879	0.0001
	0.04292–0.978	0.0003
Tetradecane + C ₄ E ₁	0–1	0.0002

^a Mass fraction.

^b Average error = $(1/N) \sum_{i=1}^N |W_i^{\text{calc}} - W_i^{\text{act}}|$, where N is the number of calibration points and W is the mass fraction of C₄E₁. The superscript 'calc' stands for the calculated value from the calibration curve and the superscript 'act' refers to the actual value.

peratures of the injector port and the thermal conductivity detector were held at 543.15 and 573.15 K, respectively. The flow rate of the carrier gas, helium, was maintained at 45 ml min⁻¹. The sample was isothermally separated at 508.15 K in a 2 m long × 3.175 mm diameter stainless steel column packed with Poropak P 80/100 mesh. Each analysis took about 8 min. Single-phase binary mixtures, water + C₄E₁ and tetradecane + C₄E₁, with known compositions were used to calibrate the instrument in the composition range of interest. The calibration results were further fitted to a polynomial equation. The average errors of the calibration curves from the actual values are given in Table 1. For each tie line, at least three samples were prepared at the same total composition. After equilibration, at least three gas chromatograph measurements were performed for each phase in every sample. The experimental uncertainty of the gas chromatography was within ±0.0008 mass fraction.

When the water content in the tetradecane-rich phase was low, a Karl Fischer moisture titrator (MKC-210, Kyoto Electronics Co., Japan) was used to determine the water content in these phases. The experimental uncertainty of at

least three Karl Fischer moisture measurements was within ±0.00002 mass fraction for the water content.

3. Results and discussion

The experimental compositions of the equilibrium phases of the ternary system water + dodecane + C₄E₁ at 298.15, 308.15, and 318.15 K are given in Tables 2–4, respectively. According to Kahlweit and Strey [18], the lower critical solution temperature for the ternary system water + tetradecane + C₄E₁ is around 311.15 K and upper critical solution temperature is larger than 373.15 K. There is only one two-liquid-phase-coexisting region in the triangle phase diagram of the system at 298.15 and 308.15 K, as shown in Figs. 1 and 2, respectively. Note that the surfactant C₄E₁ mainly partitions into the lower aqueous phase and the composition of C₄E₁ is relatively small in the upper oil-rich phase. The fitting coefficients (both R and R^2) of a linear expression to each tie line and its corresponding total composition data point are always better than 0.999, as shown in Figs. 1 and 2.

When the temperature is increased above the lower critical solution temperature, 311.15 K, the system should have a three-liquid-phase-coexisting region. As expected, Fig. 3 shows that the system at 318.15 K exhibits one three-liquid-phase-coexisting tie triangle and three two-liquid-phase-coexisting envelopes.

In addition, the temperature effect on the composition of the three-liquid-phase-coexisting region was examined. For the systems higher than 318.15 K, only the compositions of three-liquid-phase-coexisting tie triangles were measured at every 5 K from 318.15 to 338.15 K. The experimental results of the equilibrium compositions of the three-liquid-phase-coexisting tie triangle are

Table 2
Experimental and calculated mass fractions of equilibrium liquid phases for the ternary system water + tetradecane + C₄E₁ at 298.15 K

Experimental data				Calculated results			
Oil-rich phase		Water-rich phase		Oil-rich phase		Water-rich phase	
H ₂ O	C ₄ E ₁	H ₂ O	C ₄ E ₁	H ₂ O	C ₄ E ₁	H ₂ O	C ₄ E ₁
0.0002	0.0216	0.9276	0.0724	0.0016	0.0384	0.9432	0.0568
0.0007	0.0428	0.8678	0.1322	0.0036	0.0674	0.8868	0.1132
0.0008	0.0459	0.7762	0.2238	0.0049	0.0833	0.8005	0.1994
0.0009	0.0464	0.6730	0.3227	0.0043	0.0759	0.6863	0.3133
0.0009	0.0469	0.5523	0.4364	0.0037	0.0674	0.5660	0.4324
0.0009	0.0472	0.4858	0.4987	0.0035	0.0660	0.4985	0.4980
0.0010	0.0484	0.4247	0.5549	0.0036	0.0671	0.4374	0.5554
0.0012	0.0517	0.3636	0.6082	0.0039	0.0714	0.3712	0.6139
0.0014	0.0568	0.2788	0.6765	0.0048	0.0835	0.2845	0.6795
0.0019	0.0667	0.2135	0.7252	0.0061	0.1026	0.2129	0.7156
0.0033	0.1094	0.1301	0.7386	0.0093	0.1532	0.1240	0.7128
0.0125	0.2272	0.0724	0.6438	0.0132	0.2262	0.0709	0.6532
Average error = $\sum_{i=1}^N \frac{ W_i^{\text{expt}} - W_i^{\text{calc}} }{N}$, where N is the number of tie lines.				0.003	0.02	0.01	0.01

Table 3

Experimental and calculated mass fractions of equilibrium liquid phases for the ternary system water + tetradecane + C₄E₁ at 308.15 K

Experimental data				Calculated results			
Oil-rich phase		Water-rich phase		Oil-rich phase		Water-rich phase	
H ₂ O	C ₄ E ₁	H ₂ O	C ₄ E ₁	H ₂ O	C ₄ E ₁	H ₂ O	C ₄ E ₁
0.0007	0.0298	0.9322	0.0678	0.0003	0.0003	0.9075	0.0920
0.0009	0.0598	0.8796	0.1204	0.0003	0.0005	0.8320	0.1671
0.0012	0.0609	0.7923	0.2077	0.0003	0.0008	0.7494	0.2489
0.0012	0.0610	0.6804	0.3136	0.0003	0.0014	0.6500	0.3463
0.0012	0.0615	0.5566	0.4308	0.0003	0.0024	0.5417	0.4501
0.0014	0.0616	0.4880	0.4947	0.0003	0.0036	0.4774	0.5096
0.0015	0.0630	0.4288	0.5493	0.0003	0.0052	0.4195	0.5609
0.0013	0.0645	0.3642	0.6067	0.0003	0.0083	0.3559	0.6138
0.0016	0.0708	0.2801	0.6715	0.0004	0.0170	0.2721	0.6740
0.0022	0.0819	0.2135	0.7131	0.0005	0.0345	0.2028	0.7094
0.0050	0.1353	0.1290	0.7264	0.0012	0.0904	0.1226	0.7138
Average error = $\sum_{i=1}^N \frac{ W_i^{\text{expt}} - W_i^{\text{calc}} }{N}$, where N is the number of tie lines				0.001	0.05	0.002	0.02

Table 4

Experimental and calculated mass fractions of equilibrium liquid phases for the ternary system water + tetradecane + C₄E₁ at 318.15 K

Experimental data						Calculated results					
Oil-rich phase		Surfactant-rich phase		Water-rich phase		Oil-rich phase		Surfactant-rich phase		Water-rich phase	
H ₂ O	C ₄ E ₁	H ₂ O	C ₄ E ₁	H ₂ O	C ₄ E ₁	H ₂ O	C ₄ E ₁	H ₂ O	C ₄ E ₁	H ₂ O	C ₄ E ₁
Three-liquid-phase coexisting											
0.0019	0.0812	0.4250	0.5510	0.8809	0.1191	0.4141	0.5671	0.4204	0.5651	0.8467	0.1531
Two-liquid-phase-coexisting region on the water/tetradecane side											
0.0006	0.0372			0.9419	0.0581	0.0018	0.0350			0.9397	0.0602
0.0020	0.0793			0.8953	0.1047	0.0041	0.0627			0.8777	0.1222
Two-liquid-phase coexisting region on the C ₄ E ₁ /tetradecane side											
0.0025	0.0870	0.3409	0.6222			0.0056	0.0782	0.3379	0.6246		
0.0025	0.0947	0.2525	0.6862			0.0073	0.0971	0.2431	0.6739		
0.0048	0.1264	0.1666	0.7314			0.0112	0.1420	0.1480	0.6759		
0.0136	0.2296	0.1040	0.6770			0.0164	0.2111	0.0883	0.6252		
Two-liquid-phase-coexisting region on the water/C ₄ E ₁ side											
		0.4676	0.5202	0.8717	0.1283			0.4209	0.5630	0.8453	0.1546
Average error = $\sum_{i=1}^N \frac{ W_i^{\text{expt}} - W_i^{\text{calc}} }{N}$, where N is the number of tie lines						0.003	0.01	0.01	0.03	0.02	0.02

Table 5

Experimental mass fractions of equilibrium liquid phases of three-liquid-phase-coexisting tie triangles for the ternary system water + tetradecane + C₄E₁ from 318.15 to 338.15 K

t (°C)	Experimental data						Calculated results					
	Oil-rich phase		C ₄ E ₁ -rich phase		Water-rich phase		Oil-rich phase		C ₄ E ₁ -rich phase		Water-rich phase	
	H ₂ O	C ₄ E ₁	H ₂ O	C ₄ E ₁	H ₂ O	C ₄ E ₁	H ₂ O	C ₄ E ₁	H ₂ O	C ₄ E ₁	H ₂ O	C ₄ E ₁
45	0.0019	0.0812	0.4250	0.5510	0.8809	0.1191	0.0052	0.0652	0.4204	0.5651	0.8600	0.1399
50	0.0024	0.0973	0.3541	0.6084	0.8970	0.1030	0.0060	0.0956	0.3519	0.6112	0.8972	0.1028
55	0.0030	0.1097	0.3241	0.6298	0.9063	0.0937	0.0062	0.1102	0.3089	0.6477	0.9128	0.0872
60	0.0045	0.1300	0.2996	0.6455	0.9135	0.0865	0.0078	0.1296	0.2992	0.6538	0.9102	0.0898
65	0.0052	0.1500	0.2859	0.6520	0.9163	0.0837	0.0086	0.1381	0.2905	0.6575	0.9089	0.0911
Average error = $\sum_{i=1}^N \frac{ W_i^{\text{expt}} - W_i^{\text{calc}} }{N}$, N is the number of data points							0.003	0.005	0.007	0.010	0.010	0.010

Fig. 1. Ternary liquid–liquid equilibria (mass fraction) for the system water + tetradecane + C_4E_1 at 298.15 K: experimental tie lines ((●) solid line); calculated binodal curve (dotted curve) and tie lines ((○) dotted line); total compositions (▲).

Fig. 2. Ternary liquid–liquid equilibria (mass fraction) for the system water + tetradecane + C_4E_1 at 308.15 K: experimental tie lines ((●) solid line); calculated binodal curve (dotted curve) and tie lines ((○) dotted line); total compositions (▲).

Fig. 3. Ternary liquid–liquid equilibria (mass fraction) for the system water + tetradecane + C_4E_1 at 318.15 K: experimental tie lines ((●) solid line); calculated binodal curves (dotted curve) and tie line ((○) dotted line); total compositions (▲); experimental three-liquid-phase-coexisting tie triangle (■, solid line); calculated three-liquid-phase-coexisting tie triangle (□) dotted line).

listed in Table 5. It is obvious that the apex of the three-liquid-phase-coexisting tie triangle, i.e. the C_4E_1 -rich phase, shifts counterclockwise with an increase in temperature, as shown in Fig. 4, consistent with the observation of Kahlweit and Strey [18]. Note that the surfactant moves continuously from the water-rich phase to the oil-rich phase along with increasing temperature, as shown in Table 5.

The UNIQUAC model of Abrams and Prausnitz [17] was used to correlate the experimental data. In this study, the relative van der Waals volume r_i and van der Waals surface area q_i were adopted from the UNIFAC group contribution of Hansen et al. [19], listed in Table 4. 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 .

There are two effective binary interaction parameters for a pair of substances. Therefore, six effective binary interaction parameters are required for a ternary system. For the system at 298.15 and 315.15 K, there is only one two-liquid-phase-coexisting region. These six effective binary interaction parameters were determined by numerically minimizing the following objective

function [20]:

$$F_x = \sum_{k=1}^N \sum_{j=1}^2 \sum_{i=1}^3 \left(\frac{x_{ijk}^{\text{expl}} - x_{ijk}^{\text{calc}}}{x_{ijk}^{\text{expl}}} \right)^2, \quad (2)$$

where x_{ijk}^{expl} and x_{ijk}^{calc} are the experimental and calculated mole fraction, respectively, of component i in phase j along a tie line k . The liquid–liquid equilibrium flash calculation [21] was applied to evaluate the compositions of both liquid phases along each tie line by using the experimental total compositions as input data. As one can see in Figs. 1 and 2, the predicted binodal curve was in a very good agreement with the experimental result. The UNIQUAC model describes the experimental data well except at regions close to the plait point, especially as shown in Fig. 1.

On the other hand, for the systems at 318.15 K and higher temperatures, there are one three-liquid-phase-coexisting tie triangle and three two-liquid-phase-coexisting envelopes in each triangle phase diagram. Sassen et al. [22] pointed out that it is not clear whether the UNIQUAC model is able to predict a three-liquid-phase-coexisting region of the ternary system water + dodecane + C_7E_5 . In our previous study [14,15], we also had the same problem of correlating the experimental data of the three-liquid-phase-coexisting tie triangle to the UNIQUAC model. However, Negahban et al. [23] and Brandani et al. [24] were able to use the

Fig. 4. Variation of the liquid–liquid equilibria (mass fraction) of three-liquid-phase coexisting tie triangle for the system water + tetradecane + C_4E_1 as a function of temperature ranging from 318.15 to 338.15 K: experimental three-liquid-phase-coexisting tie triangle ((●) 318.15 K; (▼) 323.15 K; (■) 328.15 K; (◆) 333.15 K; (▲) 338.15 K; solid symbol and solid line); calculated three-liquid-phase-coexisting tie triangle ((○) 318.15 K; (▽) 323.15 K; (□) 328.15 K; (◇) 333.15 K; (△) 338.15 K, open symbol and dotted line).

UNIQUAC model to describe the ternary system water + decane + C_4E_1 successfully. It should be pointed out that in these studies [23,24], both the van der Waals volume r_i and the van der Waals surface area q_i of C_4E_1 were chosen as adjustable parameters in the regression procedure. It is interesting to note that their regression results ($r_{C_4E_1} = 4.4093$ and $q_{C_4E_1} = 5.8724$) are substantially different from that of Hansen et al. [19] (listed in Table 6, $r_{C_4E_1} = 5.0558$ and $q_{C_4E_1} = 4.3720$). In this study, both the volume parameter and the surface area parameter of C_4E_1 were directly taken from Hansen et al. [19] and fixed as constants in the regression procedure.

As we mentioned above, the systems at 318.15 K and higher temperatures exhibit one three-liquid-phase-coexisting tie triangle and three two-liquid-phase-coexisting envelopes. There are two obvious ways to correlate the experimental data to the UNIQUAC model. The six ef-

fective binary interaction parameters can be determined by the numerical regression of either only three-phase tie triangle or all available data including the three-phase tie triangle and three two-phase envelopes. According to Negahban et al. [25], the effective UNIQUAC binary interaction parameters determined from the correlation of only three-liquid-phase-coexisting data describe the entire phase equilibria satisfactorily. In addition, the deviation of the experimental data and the predicted results based on the interaction parameters determined from the correlation of only three-liquid-phase-coexisting data is slightly worse than that of all available data [25]. Therefore, in this study only the compositions of the three-liquid-phase-coexisting tie triangle were used to determine the six effective binary interaction parameters for the systems at 318.15 K and higher temperatures by numerically minimizing the following objective function [20,23,25]:

$$F_x = \sum_{j=1}^3 \sum_{i=1}^3 \left(\frac{x_{ij}^{\text{expl}} - x_{ij}^{\text{calc}}}{x_{ij}^{\text{expl}}} \right)^2, \quad (3)$$

where x_{ij}^{expl} and x_{ij}^{calc} are the experimental and calculated mole fraction, respectively, of component i in phase j of a three-liquid-phase-coexisting tie triangle. Note that the experimental results of three two-liquid-phase-coexisting

Table 6
The relative van der Waals volume r and van der Waals surface area q [19]

Compound	r	q
Water	0.9200	1.4000
2-Butyloxyethanol	5.0558	4.3720
Tetradecane	9.8948	8.1400

Table 7

The effective UNIQUAC interaction parameters for the system water (1) + C₄E₁ (2) + tetradecane (3)

<i>t</i> (K)	<i>a</i> ₁₂	<i>a</i> ₂₁	<i>a</i> ₁₃	<i>a</i> ₃₁	<i>a</i> ₂₃	<i>a</i> ₃₂
298.15	229.3	−106.2	130.6	1602	−35.67	153.6
308.15	195.0	−68.78	259.2	1916	−111.9	255.2
318.15	356.1	−155.3	370.6	1742	−92.25	216.9
323.15	408.8	−186.3	360.1	1983	−221.4	464.0
328.15	424.0	−195.0	344.2	1984	−227.2	477.6
333.15	418.7	−191.8	348.0	1983	−225.9	472.3
338.15	419.0	−191.6	348.1	1983	−226.5	472.5

regions were not used to correlate the interaction parameters. Once all the six effective binary interaction parameters were determined, the liquid–liquid equilibrium flash calculation [24] was applied to directly predict the compositions of both liquid phases along each tie line in all three two-liquid-phase-coexisting envelopes by using the experimental total compositions as input data. As one can see in Fig. 3, the predicted binodal curves were consistent with the experimental results.

The subroutine DUMPOL of the IMSL library [26] was used to minimize the objective function F_x , Eqs. (2) and (3), and regression results of the UNIQUAC effective binary interaction parameters are shown in Table 7. The calculated results for each tie line are given in Tables 2–5 to make a comparison with experimental data. The calculated binodal curves are also presented by dotted curves in Figs. 1–3. As one can see in Figs. 1–3, the phase behavior of the system water + dodecane + C₄E₁ is successfully described by the UNIQUAC model. Note that variation of the effective UNIQUAC interaction parameters is not a smooth function of temperature. The exact reason for this behavior is not clear. Currently, we are in the process of further examining this problem systematically.

List of symbols

a_{ij}	effective UNIQUAC interaction parameter between species <i>i</i> and <i>j</i>
F_x	objective function
<i>N</i>	number of tie-lines
<i>q</i>	van der Waals surface area parameter
<i>R</i>	gas constant
<i>r</i>	van der Waals volume parameter
<i>u</i>	UNIQUAC interaction parameter
<i>x</i>	mole fraction

Greek symbol

τ_{ij}	UNIQUAC adjustable parameter
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