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Liquid–liquid equilibria for the ternary system water + *n*-dodecane + 2-(2-*n*-hexyloxyethoxy)ethanol

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Abstract

Experiments of the fish-shaped phase diagram for the ternary system water + *n*-dodecane + 2-(2-*n*-hexyloxyethoxy)ethanol (abbreviated by C_6E_2 hereafter) under atmospheric pressure were performed at constant water/*n*-dodecane weight ratio (1/1) to locate the critical end points. The upper and lower critical consolute temperatures for the system of interest are 307.80 K and 282.30 K, respectively. Compositions of two- and three-phase liquid–liquid equilibrium for the ternary system water + *n*-dodecane + C_6E_2 at 293.15 K and 303.15 K under atmospheric pressure are presented in this paper. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Liquid–liquid equilibria; Data; Mixture

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1. Introduction

The homologous series of nonionic surfactant polyoxyethylene alcohol $CH_3(CH_2)_{i-1}(OCH_2CH_2)_jOH$, abbreviated by C_iE_j hereafter, is extensively used both in industrial and in fundamental research applications. However, there is little reliable information on its phase behavior, especially for short chain ($i < 10$) C_iE_js. In our previous study, we have investigated the phase behaviour of three water C_iE_j binary systems [1]. Mixtures of the type water + oil surfactant are applied in several industrial processes, e.g., herbicides, the production of drugs, tertiary oil recovery. The phase behaviors of mixtures of the type water + oil + surfactant are also important for the design

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of experiments and interpretation of data on wetting transitions [2,3] and phase conductivity [4] studies. The phase behavior of the ternary mixture water + *n*-dodecane + C_6E_2 had been studied only at 298.15 K by Kilpatrick et al. [5]. In this study, the fish-shaped phase diagram [6] over the temperature range 273.15–313.15 K was performed to determine the upper and lower critical solution temperature of the system water + *n*-dodecane + C_6E_2 by direct eye observation. In addition, liquid–liquid equilibrium measurements were performed for the ternary system water + *n*-dodecane + C_6E_2 at 293.15 K and 303.15 K under atmospheric pressure by gas chromatography.

2. Experimental

2.1. Materials

The *n*-dodecane was obtained from Merck with a purity of 99%, and used without further purification. The non-ionic surfactant C_6E_2 was a product of Aldrich Chemical, and had a purity of 98%. The surfactant C_6E_2 was fractionally distilled under reduced pressure until a purity of greater than 99.5% was attained as determined by gas chromatography. Water was purified by a Barnstead NANOpure II system with the resistivity better than 17.8 MΩ cm.

2.2. Procedure

2.2.1. Fish-shaped phase diagram

The samples were prepared in a 1-cm-diameter glass test tube at a fixed water/oil weight ratio (1/1), with varying surfactant concentration. The samples were then placed in a water bath, whose temperature stability is better than ±0.004 K, for at least 24 h and sometimes up to 4 days, to allow the system to reach equilibrium. To ensure a thorough mixing, the samples were shaken vigorously several times before and during the equilibrium process. After equilibrium was reached, all the liquid phases were transparent with a sharp, mirror-like interface and the number of liquid phases for each sample was recorded at different temperatures. The phase boundary was systematically searched for each surfactant concentration, by locating the temperature at which the number of liquid phases changed.

2.2.2. Triangle phase diagram

The mixtures of the ternary system were prepared in a 1-cm-diameter test tube, and placed in a computer-controlled water thermostat, whose temperature stability was better than ±0.004 K. These samples were kept in the thermostat for at least 24 h and sometimes up to 3 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 equilibrium was reached, both liquid phases were transparent with a sharp, mirror-like interface. Following equilibration, each of the liquid phases was carefully sampled by syringe for further experiments on the determination of composition by gas chromatography.

The chemical analysis of water, *n*-dodecane and C_6E_2 of equilibrium liquid phases was performed using a Perkin Elmer (AutoSystem) gas chromatograph equipped with thermal conductivity detector and connected to an integrator (Perkin Elmer, model 1020 Plus). The components were isothermally separated along a 2 m × 3.175 mm diameter stainless steel column packed with Poropak P 80/100 mesh. The oven temperature was fixed at 508.15 K. The detector temperature was kept at 593.15 K, while injection-port temperature was held at 413.15 K. The flow rate of carrier gas, helium, was kept at 0.333 ml/s. Each analysis took about 25 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 in mole fractions.

3. Results and discussion

The experimental result of the fish-shaped phase diagram of the system water + *n*-dodecane + C_6E_2 is shown in Fig. 1 at the fixed water/*n*-dodecane weight ratio (1/1). In Fig. 1, the symbols 1ϕ, 2ϕ, and 3ϕ stand for the one-, two-, and three-liquid-phase-coexisting regions, respectively. According to Winsor's classification [7], the various phase equilibria of water + oil + surfactant systems can be grouped into four types.

Type-I phase equilibrium consists of two phases with most of the surfactant dissolved in the aqueous phase and a small amount of oil dispersed in the aqueous phase.

Type-II phase equilibrium consists of two phases with most of the surfactant dissolved in the oil-rich phase and a small amount of water dispersed in the oil-rich phase.

Type-III phase equilibrium consists of three phases with a middle phase containing most of the surfactant and significant amounts of water and oil, which coexists with a water-rich phase and an oil-rich phase.

Type-IV phase equilibrium has only a single homogenous phase in which water, oil and surfactant are mutually solubilized.

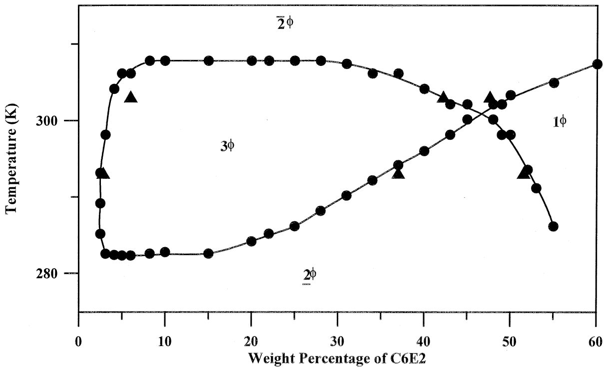

Fig. 1. Fish-shaped phase diagram at constant water/*n*-dodecane weight ratio (1/1) as a function of weight percentage of C_6E_2 in the system water + *n*-dodecane + C_6E_2. The symbol filled triangle (▲) stands for the location of phase boundary obtained by interpolating at a fixed water/*n*-dodecane weight ratio (1/1) in this figure and in Fig. 2.

Table 1
Liquid–liquid phase equilibrium composition of the ternary system $H_2O(1) + n$-dodecane $(2) + C_6E_2(3)$ at 293.15 K

Water-rich phase			Surfactant-rich phase			Oil-rich phase		
X_1	X_2	X_3	X_1	X_2	X_3	X_1	X_2	X_3
0.9990	4.78e − 5	9.17e − 4	0.8541	0.0493	0.0966	0.0071	0.9515	0.0414
< ±0.0001	±0.03e − 5	±0.03e − 4	±0.0003	< ±0.0003	< ±0.0003	< ±0.0003	< ±0.0003	< ±0.0003
0.9987	0.0013					5.29e − 4	0.9995	
< ±0.0001	< ±0.0001					< ±0.03e − 4	< ±0.0001	
0.9989	6.16e − 4	4.49e − 4				0. 0036	0.9769	0.0195
< ±0.0001	< ±0.03e − 4	±0.03e − 4				< ±0.0001	±0.0003	< ±0.0003
0.9982		0.0018	0.9302		0.0698			
< ±0.0001		< ±0.0001	< ±0.0003		< ±0.0003			
0.9988	4.01e − 5	0.0011	0.8692	0.0393	0.0915			
< ±0.0001	< ±0.03e − 5	< ±0.0001	< ±0.0003	±0.0003	±0.0003			
0.9986	3.04e − 5	0.0014	0.8861	0.0279	0.0860			
< ±0.0001	±0.03e − 5	< ±0.0001	< ±0.0003	< ±0.0003	±0.0003			
0.9984	1.97e − 5	0.0015	0.9018	0.0178	0.0804			
< ±0.0001	±0.03e − 5	< ±0.0001	±0.0003	< ±0.0003	±0.0003			
0.9983	7.55e − 6	0.0017	0.9180	0.0077	0.0743			
< ±0.0001	±0.03e − 6	< ±0.0001	< ±0.0003	< ±0.0003	±0.0003			
			0.8145	0.0613	0.1242	0.0093	0.9452	0.0455
			±0.0003	< ±0.0003	±0.0003	< ±0.0003	< ±0.0003	±0.0003
			0.7339	0.0992	0.1669	0.0158	0.9317	0.0524
			±0.0003	< ±0.0003	< ±0.0003	< ±0.0003	< ±0.0003	< ±0.0003
			0.6644	0.1424	0.1932	0.0307	0.9070	0.0622
			±0.0003	±0.0003	±0.0003	±0.0003	±0.0003	< ±0.0003
			0.5598	0.2385	0.2016	0.0716	0.8465	0.0819
			±0.0003	±0.0003	±0.0003	±0.0003	< ±0.0003	< ±0.0003
			0.4577	0.3513	0.1910	0.1519	0.7377	0.1104
			±0.0003	±0.0003	±0.0003	±0.0003	±0.0003	±0.0003
			0.3999	0.4198	0.1804	0.2182	0.6506	0.1312
			±0.0003	±0.0003	±0.0003	±0.0003	±0.0003	±0.0003

Table 2
Liquid–liquid phase equilibrium composition of the ternary system H_2O (1) + *n*-dodecane (2) + C_6E_2 (3) at 303.15 K

Water-rich phase			Surfactant-rich phase			Oil-rich phase		
X_1	X_2	X_3	X_1	X_2	X_3	X_1	X_2	X_3
0.9930 < ±0.0001	3.23e − 4 < ±0.03e − 4	0.0066 < ±0.0001	0.7705 ±0.0003	0.0999 ±0.0003	0.1296 ±0.0003	0.0178 < ±0.0003	0.9167 ±0.0003	0.0656 ±0.0003
0.9985 ±0.0001	0.0015 < ±0.0001					5.93e–4 < ±0.03e − 4	0.9994 < ±0.0001	
0.9964 < ±0.0001	9.26e − 4 ±0.03e − 4	0.0027 < ±0.0001				0.0085 < ±0.0001	0.9430 < ±0.0003	0.0485 < ±0.0003
0.9947 < ±0.0001	4.50e − 4 ±0.03e − 4	0.0048 < ±0.0001				0.0159 < ±0.0003	0.9209 < ±0.0003	0.0632 < ±0.0003
0.9981 < ±0.0001		0.0019 < ±0.0001	0.8885 < ±0.0003		0.1115 < ±0.0003			
0.9968 < ±0.0001	5.16e − 5 ±0.03e − 4	0.0031 < ±0.0001	0.8667 ±0.0003	0.0157 < ±0.0003	0.1176 ±0.0003			
0.9957 < ±0.0001	1.20e–4 < ±0.03e − 4	0.0042 < ±0.0001	0.8369 ±0.0003	0.0377 < ±0.0003	0.1255 ±0.0003			
0.9948 < ±0.0001	1.90e − 4 < ±0.03e − 4	0.0050 < ±0.0001	0.8219 < ±0.0003	0.0505 < ±0.0003	0.1276 < ±0.0003			
0.9944 < ±0.0001	2.31e − 4 < ±0.03e − 4	0.0054 < ±0.0001	0.8017 ±0.0003	0.0688 ±0.0003	0.1295 < ±0.0003			
0.9937 < ±0.0001	2.93e − 4 < ±0.03e − 4	0.0061 < ±0.0001	0.7825 < ±0.0003	0.0871 < ±0.0003	0.1304 < ±0.0003			
			0.7615 ±0.0003	0.1029 ±0.0003	0.1355 ±0.0003	0.0259 < ±0.0003	0.9032 ±0.0003	0.0709 ±0.0003
			0.7226 ±0.0003	1.1248 ±0.0003	0.1526 < ±0.0003	0.0416 < ±0.0003	0.8791 ±0.0003	0.0793 < ±0.0003
			0.6986 ±0.0003	0.1417 ±0.0003	0.1598 ±0.0003	0.0528 < ±0.0003	0.8639 ±0.0003	0.0834 < ±0.0003
			0.6215 ±0.0003	0.2052 ±0.0003	0.1733 ±0.0003	0.1221 < ±0.0003	0.7771 ±0.0003	0.1007 < ±0.0003
			0.5344 ±0.0003	0.2897 ±0.0003	0.1759 ±0.0003	0.3034 ±0.0003	0.5605 ±0.0003	0.1360 ±0.0003
			0.5041 ±0.0003	0.3219 < ±0.0003	0.1740 ±0.0003	0.3962 ±0.0003	0.4503 ±0.0003	0.1536 ±0.0003

Within the temperature range in this study, these four types of phase equilibria can all be observed in the system water + *n*-dodecane + C_6E_2. It is found that Winsor type-I phase equilibria appear at low temperatures ($\underline{2}\phi$) and Winsor type-II phase equilibria at high temperatures ($\overline{2}\phi$). At intermediate temperatures, one finds Winsor type-III phase equilibria (3ϕ). As the temperature rises, the surfactant C_6E_2 transfers continuously from the water-rich phase to the oil-rich phase, i.e., the mutual solubility between surfactant and water decreases and the surfactant becomes more lyotropic. The Winsor type-IV phase equilibria usually occur at high surfactant C_6E_2 concentrations, as shown in Fig. 1 [6]. The highest and the lowest temperatures of the three-liquid-phase-coexisting region (3ϕ) correspond to the upper and lower critical consolute temperatures, which were found to be 307.80 K and 282.30 K, respectively, in Fig. 1.

The experimental compositions of the equilibrium phases obtained for the ternary system water + *n*-dodecane + C_6E_2 at 293.15 K and 303.15 K under atmospheric pressure are reported in Tables 1 and 2, respectively. All the data are expressed in mole fractions. Most of the compositions were reproducible within ±0.0003. For the condition of very low water contents, e.g., the oil-rich phase of the two-liquid-phase-coexisting envelope on the water/*n*-dodecane side of the triangle phase diagram, the Karl–Fischer titration method (MKC-210, Kyoto Electronics, Japan) was applied to further confirm the results of gas chromatography. As shown on a triangle phase diagram in Figs. 2 and 3 (concentrations expressed in weight fractions), this system exhibits one three-liquid-phase-coexisting tie triangle region and three two-liquid-phase-coexisting envelopes. Note that the results of water +

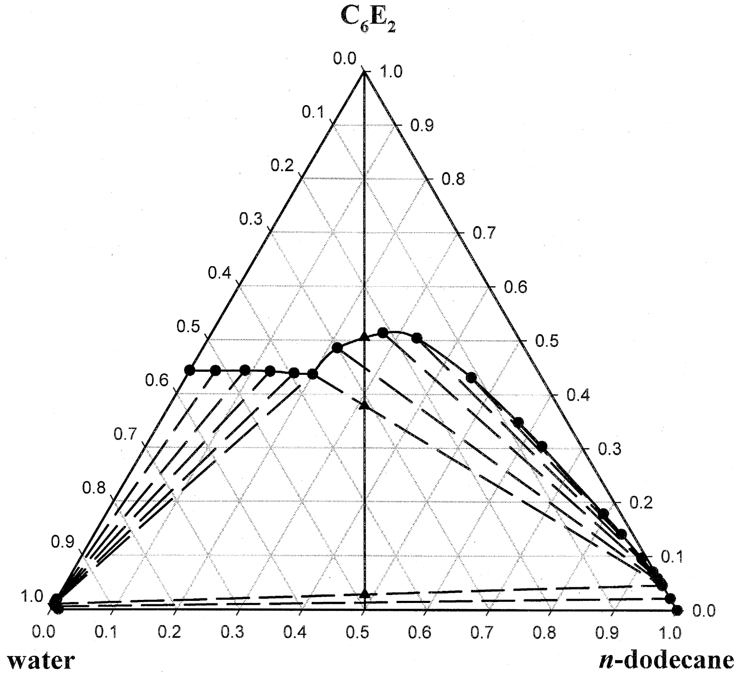

Fig. 2. Ternary liquid–liquid equilibria for the system water + *n*-dodecane + C_6E_2 at 293.15 K: (●, dotted line) experimental tie line, (solid line) binodal curve. The symbol filled triangle (▲) stands for the location of phase boundary obtained by interpolating at a fixed water/*n*-dodecane weight ratio (1/1).

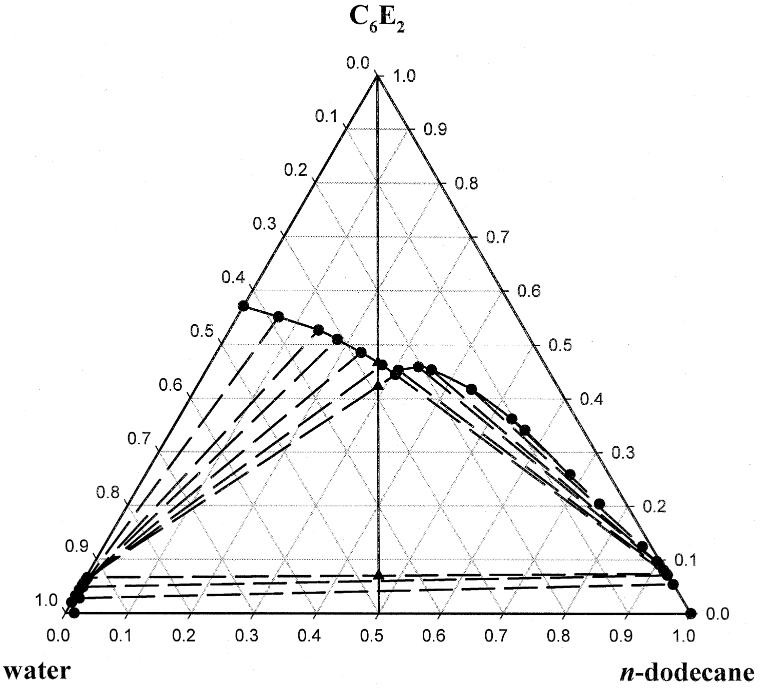

Fig. 3. Ternary liquid–liquid equilibria for the system water + n-dodecane + C_6E_2 at 303.15 K: (●, dotted line) experimental tie line, (solid line) binodal curve. The symbol filled triangle (▲) stands for the location of phase boundary obtained by interpolating at a fixed water/n-dodecane weight ratio (1/1).

C_6E_2 binary systems at 293.15 K and at 303.15 K have an excellent agreement with our previous measurements resulting from Karl–Fischer titration method [1].

We can further check the consistency between the fish-shaped and triangle phase diagrams. A vertical section erected on the center line of the triangle phase diagram is drawn in Figs. 2 and 3, i.e., on the line connecting the point water/n-dodecane = 1/1 on the water/n-dodecane side with the C_6E_2 corner. There are three intercepts across the phase boundaries for each triangle phase diagram, as illustrated by symbol filled triangle (▲) in Figs. 2 and 3. All these three phase boundaries are consistent with the results of direct eye observations, as shown in the fish-shaped phase diagram, Fig. 1.

Compare our results at 293.15 K and 303.15 K with those of Kilpatrick et al.'s at 298.15 K [5] by simply checking the apex of the three-phase tie triangle. The apex of the three-phase tie triangle at 298.15 K [5] consistently falls in between the apexes of the three-phase tie triangles at 293.15 K and at 303.15 K. That is, increasing temperature make the apex of the three-phase tie triangle shift to lower water contents and higher n-dodecane contents, in accord with previously findings [5,6].

An attempt was made to correlate the experimental data by use of the UNIQUAC model of Abrams and Prausnitz [8] as well as the algorithm of Negahban et al. [9,10]. Unfortunately, no satisfactory result was obtained. Sassen et al. [11] also pointed out that the UNIQUAC model can only predict a transition between $\underline{2}\phi$ and $\overline{2}\phi$ in a water + oil + C_iE_j system with increasing temperature and it is not clear whether the UNIQUAC model is able to predict a three-liquid-phase-coexisting region.

Currently, we are in the process of further exploring systematically the possibility of predicting the phase behavior of a water + oil + C_iE_j system by using the UNIQUAC model.

Acknowledgements

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