Fluid Phase Equilibria 399 (2015) 16–21

Contents lists available at ScienceDirect

Fluid Phase Equilibria

journal homepage: www.elsevier.com/locate/fluid

Liquid–liquid equilibria for the ternary system water + octane + 2-butyloxy-ethanol

Shin-Hong Chen, Li-Jen Chen *

Department of Chemical Engineering, National Taiwan University, Taipei 10617, Taiwan

ARTICLE INFO

Article history:
Received 2 March 2015
Received in revised form 9 April 2015
Accepted 16 April 2015
Available online 24 April 2015

Keywords:
Liquid–liquid equilibrium
Phase diagram
NRTL model
Ternary system
Gas chromatography

ABSTRACT

Experiment of the fish-shaped phase diagram of the ternary water + octane + 2-butyloxy-ethanol system under atmospheric pressure was performed at constant water/octane mass ratio (1/1) to determine the upper critical solution temperature (UCST = 296.90 ± 0.05 K) and the lower critical solution temperature (LCST = 286.10 ± 0.05 K). The liquid–liquid equilibria of the water + octane + 2-butyloxy-ethanol system at 283.15, 293.15 and 303.15 K were measured under atmospheric pressure. At 283.15 and 303.15 K, there is only one two-liquid-phase-coexisting envelop in the triangle phase diagram. At 293.15 K, in-between the UCST and LCST, the system exhibits three two-liquid-phase-coexisting envelops and one three-liquid-phase-coexisting tie triangle in the triangle phase diagram. The experimental results of liquid–liquid equilibria were further correlated with the nonrandom two-liquid (NRTL) model.

1. Introduction

Mixtures of the type water + oil + surfactant are widely applied in many industrial processes and applications, e.g., pharmaceuticals, liquid–liquid extraction, herbicides, tertiary oil recovery and in the fundamental research of wetting transitions and critical phenomena [1–11]. The homologous series of nonionic surfactant polyoxyethylene alcohol $CH_3(CH_2)_{i-1}(OCH_2CH_2)_jOH$, abbreviated by C_iE_j hereafter, are extensively used as detergents and emulsifying agents and also applied both in industrial and in fundamental research [7–13].

Kilpatrick et al. [14] have studied the phase behavior of water + C_nH_{2n+2} (n = 6, 8, 10, 12, 14) + C_4E_1 at 298.15 and 303.15 K. Precise liquid–liquid equilibrium measurement data of water + decane + C_4E_1 mixture has been investigated by Brandani et al. [15] On the other hand, Lin and Chen [16,17] have reported the phase diagrams of water + dodecane + C_4E_1 and of water + tetradecane + C_4E_1 system at temperatures ranging from 298.15 to 338.15 K. Su et al. [18–23] replaced the ethylene glycol ethers with propylene glycol ethers ($CH_3(CH_2)_{i-1}(OCH_2CHCH_3)_jOH$, abbreviated by C_iP_j), and performed a series of liquid–liquid equilibrium measurements for the water + C_nH_{2n+2} (n = 12, 14, 16) + C_3P_j (j = 1, 2) system at three different temperatures.

In this study, liquid–liquid equilibrium data were measured for the ternary system water + octane + 2-butyloxy-ethanol (C_4E_1) in the temperature range from 283.15 to 303.15 K under atmospheric pressure by gas chromatography. The fish-shaped phase diagram of the system was also performed to search for the lower/upper critical solution temperatures. These experimental liquid–liquid equilibrium data were further correlated with the NRTL model successfully.

2. Experimental

The nonionic surfactant 2-butyloxy-ethanol (C_4E_1) was an Aldrich Chemical product with a purity of >0.990 and was fractionally distilled under reduced pressure. The purity of the distilled C_4E_1 was better than mass fraction 0.995 determined by gas chromatography. Octane (C_8H_{18}) with a purity of 0.990 was purchased from Alfa Aesar Co. and was used as received. Water was purified by double distillation and then followed by a PURELAB Maxima Series (ELGA Labwater) purification system with the resistivity always better than 18.2 MΩ cm. The description of these chemicals used in this study is summarized in Table 1. The comparison of measured densities (DMA 4500 M, Anton-Paar) of C_4E_1 and octane with the literature data are reported in Table 2.

The fish-shaped phase diagram of the water + octane + C_4E_1 was performed by preparing samples of water/octane mass ratio fixed at 1/1 with various mass fractions of C_4E_1. All prepared samples sealed in test tubes were mixed completely and then were put in a homemade computer controlled thermostat with the uncertainty 0.005 K to wait for equilibrium. When the system reached equilibrium, liquid phases were thoroughly transparent and interfaces were very sharp and mirror-like. After reaching

* Corresponding author. Tel.: +886 233663049.
E-mail address: ljchen@ntu.edu.tw (L.-J. Chen).

http://dx.doi.org/10.1016/j.fluid.2015.04.019
0378-3812/

Table 1
Description of chemicals used in this study.

Compound	Source	Initial purity (mass fraction)	Purification method	Final purity	Analysis method
Octane	Alfa Aesar Co.	0.99	–	–	GC
2-Butyloxy-ethanol (C_4E_1)	Aldrich	0.99	Fractional distillation under a reduced pressure	Mass fraction >0.995	GC
Water	–	–	Double-distilled water followed by a PURELAB Maxima Series (ELGA Labwater) purification system	Resistivity >18.2 MΩ cm	–

equilibrium, the number of liquid phases of each sample was recorded. The experiment was performed and systematically scanned at different temperatures ranging from 281 to 304 K to search for the phase boundary separating two-liquid-phase-coexisting (3φ) and three-liquid-phase-coexisting (2φ) region and separating two-liquid-phase-coexisting and one-liquid-phase (1φ) region.

To analyze the equilibrium composition of each liquid phase, we used a gas chromatography (GC-8A, Shimadzu Co., Japan) equipped with a 2 m long steel column packed with Porapak P 80/100 mesh. The temperatures of the injector port, the thermal conductivity detector and the oven were all held at 210 °C. The carrier gas was helium and the flow rate was kept at 30 mL min^{-1}. To calibrate the gas chromatography, single-phase binary mixtures of water + C_4E_1 and octane + C_4E_1 with known compositions were prepared in the concentration range of interest and were analyzed at least three times for each composition.

For each tie line, three samples with the same total composition were prepared in the sealed tubes. These samples were placed in the homemade water thermostat for at least 24 h to reach equilibrium and were vigorously shaken several times to ensure the samples thorough mixing. Following equilibration, all of the liquid phases were carefully sampled by syringe and were injected into gas chromatography to determine the composition. Replicate measurements indicate that the experimental uncertainty was smaller than 0.0008 mass fraction. When the water content in the octane-rich phase was very low, a Karl Fischer moisture titration method was used to determine the water content in the octane-rich phase. The experimental uncertainty of the Karl Fischer moisture measurements was within 0.00002 mass fraction for the water content in the octane-rich phase.

Table 2
Comparison of the experimental results and literature data [24–31] of densities of the pure compounds at T = 293.15 and 313.15 K under atmospheric pressure.[a]

Compound	T (K)	ρ (g cm^{-3})	
		Exptl.	Lit
Octane	293.15	0.70264	0.7025 [24] 0.70267 [25] 0.70259 [26]
	313.15	0.68639	0.6863 [25] 0.6863 [24] 0.68634 [26]
2-Butyloxy-ethanol (C_4E_1)	293.15	0.90064	0.9004 [27] 0.90072 [28] 0.90118 [29] 0.90119 [30]
	313.15	0.88380	0.8835 [27] 0.88421 [29] 0.88359 [30] 0.883775 [31]

[a] Standard uncertainties u are $u(T)$ = 0.01 K, $u(\rho)$ = 0.00005 g cm^{-3}.

3. Results and discussion

Fig. 1 shows the fish-shaped phase diagram of the ternary water + octane + C_4E_1 system. According to Winsor's classification [32], phase equilibria of the water + oil + surfactant system can be classified into four types and all these four types of phase equilibria can be found in the fish-shaped phase diagram of the ternary water + octane + C_4E_1 system, Fig. 1. Inside the fish body, the system exhibits three-liquid-phase-coexisting, identified by 3φ in Fig. 1, that is, the Winsor's type III phase equilibrium. The region of the fish tail, identified by 1φ in Fig. 1, exhibits a single homogeneous liquid phase, classified as the Winsor's type I phase equilibrium. For the region above the fish body, the mixture exhibits two-liquid-phase-coexisting with most of C_4E_1 dissolved in the octane-rich phase, marked by $2\overline{\phi}$ in Fig. 1, i.e., the Winsor's type II phase equilibrium. On the other hand, the Winsor's type I phase equilibrium is also a two-liquid-phase-coexisting with most of C_4E_1 dissolved in aqueous phase instead, that can be observed in the region below the fish body, identified by 2 ϕ in Fig. 1. Note that the UCST and LCST of the system can be determined by,

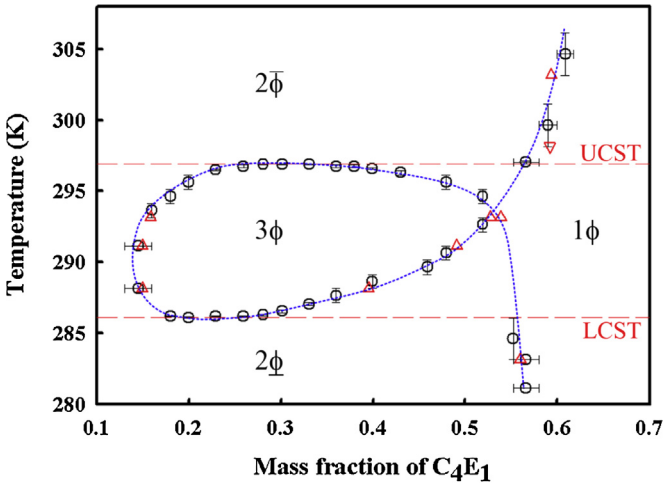

Fig. 1. Fish-shaped phase diagram at constant mass ratio of water: octane = 1:1 as a function of mass fraction of C_4E_1. The symbol circle ○ stands for the phase boundary with error bar. The red long dashed lines indicate the UCST and LCST. The red open triangle (△) and inverted triangle (▽) represent for the experimental phase boundary, obtained by interpolating at a fixed water/octane mass ratio (1/1) in Figs. 2–5 of this study and in Fig. 3(b) of Kilpatrick et al. [14], respectively. The blue dotted curve is a guide for eyes to schematically sketch the fish-shaped phase diagram. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)