Liquid−Liquid Equilibria for the Ternary System Water + *n*-Tetradecane + 2-(2-*n*-Hexyloxyethoxy)ethanol at 293.15 K and 303.15 K

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Compositions of two- and three-phase liquid−liquid equilibria for the ternary system water + tetradecane + 2-(2-hexyloxyethoxy)ethanol at 293.15 K and 303.15 K at atmospheric pressure are presented in this paper. The experimental data were used to correlate the UNIQUAC interaction parameters, and no satisfactory results were obtained.

Introduction

Nonionic surfactants of the homologous series of polyoxyethylene alcohol $CH_3(CH_2)_{i-1}(OCH_2CH_2)_jOH$, abbreviated by C_iE_j hereafter, are widely used as emulsifying agents and detergents. The potential use of C_iE_j compounds for extracting and concentrating organic compounds in aqueous systems has been under active study (Frankewich and Hinze, 1994; Gullickson et al., 1989). Recently, nonionic surfactant C_iE_j has been successfully applied to separate or concentrate proteins and other biological materials using two-phase aqueous micellar systems (Liu et al., 1995 and 1996). Therefore, experimental data of liquid−liquid equilibria are necessary for the design of liquid−liquid extractors and of decanters in distillation systems. Experimental information of such systems is scare. We have investigated the phase behavior of three water + C_iE_j binary systems (Lai and Chen, 1999) and two ternary systems water + 1-pentanol + C_4E_1 and water + 2-methyl-2-butanol + C_4E_1 (Pai and Chen, 1999).

Mixtures of the type water + oil + surfactant are used in several industrial processes, for example, herbicides, the production of drugs, and tertiary oil recovery. The phase information of ternary mixtures of the type water + oil + surfactant is important for the design of experiments and interpretation of data on wetting transitions (Chen and Yan, 1993; Chen et al., 1994; Chen et al., 1996) and phase conductivity (Kahlweit et al., 1993). Kilpatrick et al. (1986) have studied the phase behavior of the ternary mixture water + *n*-alkane + C_6E_2 at 298.15 K for three different *n*-alkanes: hexane, decane, and dodecane. Sassen et al. (1992) have explored the effect of pressure and temperature on the phase behavior of the ternary mixture water + dodecane + C_7E_5. In addition, we have investigated the phase behavior of the ternary mixture water + dodecane + C_6E_2 at 293.15 K and 303.15 K (Hu et al., 1999). In this study, liquid−liquid equilibrium measurements were performed for the ternary system water + tetradecane + C_6E_2 at 293.15 K and 303.15 K under atmospheric pressure.

Experimental Section

Materials. The tetradecane was obtained from Tokyo Kasei Co. with a purity of 99% and was used without further purification. The nonionic surfactant C_6E_2 was a product of Aldrich Chemical Co. and had a purity of 98%. It was fractionally distilled under reduced pressure until a purity of >99.5% was attained, as determined by gas chromatography. Water was purified by reverse osmosis (Millipore, Milli-RO Plus 10) and a Barnstead NANOpure II system with a resistivity >17.8 MΩ·cm.

Procedure. The mixtures of the ternary system were prepared by mass 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 thorough mixing. After equilibrium was reached, both liquid phases were transparent with a sharp, mirror-like interface. Following equilibration, both liquid phases were carefully sampled by syringe and composition was determined by gas chromatography for each liquid phase.

The chemical analysis of water, tetradecane, and C_6E_2 of equilibrium liquid phases was performed using a gas chromatograph (Perkin-Elmer, AutoSystem) equipped with a thermal conductivity detector and connected to an integrator (Perkin-Elmer, model 1020 Plus). The components were isothermally separated along a 2 m by 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 the injection-port temperature was held at 413.15 K. The flow rate of the carrier gas, helium, was kept at 0.167 $cm^3\ s^{-1}$. 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 <1% deviation in mole fractions.

Results and Discussion

The experimental compositions of the equilibrium phases are given in Tables 1 and 2 for the ternary system water + tetradecane + C_6E_2 at 293.15 K and 303.15 K, respectively, at atmospheric pressure. All the data are expressed in mole fractions. All the compositions were reproducible within ±0.0005. For the condition of very low water

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Table 1. Liquid−Liquid Phase Equilibrium Composition of the Ternary System H_2O (1) + Tetradecane (2) + C_6E_2 (3) at 293.15 K and Atmospheric Pressure (x_i: mole fraction of component *i*)

water-rich phase			surfactant-rich phase			oil-rich phase		
x_1	10^4x_2	10^4x_3	x_1	x_2	x_3	x_1	x_2	x_3
0.9984 ± 0.0001	6.35 ± 0.10	9.45 ± 0.10	0.8798 ± 0.0005	0.0196 ± 0.0005	0.1005 ± 0.0005	0.0039 ± 0.0005	0.9292 ± 0.0005	0.0669 ± 0.0005
0.9994 ± 0.0001	5.88 ± 0.05					3.14E−4 ± 0.05E−4	0.9997 ± 0.0001	
0.9989 ± 0.0001	6.05 ± 0.05	5.12 ± 0.05				7.26E−4 ± 0.05E−4	0.9628 ± 0.0005	0.0365 ± 0.0005
0.9986 ± 0.0001	6.19 ± 0.05	7.52 ± 0.05				0.0014 ± 0.0001	0.9443 ± 0.0005	0.0544 ± 0.0005
0.9982 ± 0.0001		18 ± 1	0.9302 ± 0.0003		0.0698 ± 0.0003			
0.9982 ± 0.0001	1.43 ± 0.05	17 ± 1	0.9145 ± 0.0005	0.0046 ± 0.0005	0.0809 ± 0.0005			
0.9982 ± 0.0001	3.56 ± 0.05	15 ± 1	0.8983 ± 0.0005	0.0104 ± 0.0005	0.0913 ± 0.0005			
0.9983 ± 0.0001	5.62 ± 0.05	11 ± 1	0.8844 ± 0.0005	0.0167 ± 0.0005	0.0989 ± 0.0005			
			0.7812 ± 0.0005	0.0442 ± 0.0005	0.1746 ± 0.0005	0.0072 ± 0.0005	0.9136 ± 0.0005	0.0793 ± 0.0005
			0.6847 ± 0.0005	0.0769 ± 0.0005	0.2384 ± 0.0005	0.0141 ± 0.0005	0.8961 ± 0.0005	0.0897 ± 0.0005
			0.6231 ± 0.0005	0.1051 ± 0.0005	0.2718 ± 0.0005	0.0198 ± 0.0005	0.8828 ± 0.0005	0.0974 ± 0.0005
			0.5379 ± 0.0005	0.1723 ± 0.0005	0.2897 ± 0.0005	0.0408 ± 0.0005	0.8497 ± 0.0005	0.1095 ± 0.0005
			0.4409 ± 0.0005	0.2765 ± 0.0005	0.2826 ± 0.0005	0.0711 ± 0.0005	0.8055 ± 0.0005	0.1234 ± 0.0005
			0.3515 ± 0.0005	0.4033 ± 0.0005	0.2452 ± 0.0005	0.1175 ± 0.0005	0.7392 ± 0.0005	0.1433 ± 0.0005

Table 2. Liquid−Liquid Phase Equilibrium Composition of the Ternary System H_2O (1) + Tetradecane (2) + C_6E_2 (3) at 303.15 K and Atmospheric Pressure (x_i: mole fraction of component *i*)

water-rich phase			surfactant-rich phase			oil-rich phase		
x_1	10^4x_2	x_3	x_1	x_2	x_3	x_1	x_2	x_3
0.9931 ± 0.0001	2.62 ± 0.01	0.0066 ± 0.0001	0.8510 ± 0.0005	0.0304 ± 0.0005	0.1186 ± 0.0005	0.0068 ± 0.0001	0.9186 ± 0.0005	0.0746 ± 0.0005
0.9995 ± 0.0001	4.73 ± 0.05					7.30E−4 ± 0.05E−4	0.9993 ± 0.0001	
0.9966 ± 0.0001	3.66 ± 0.05	0.0030 ± 0.0001				0.0013 ± 0.0001	0.9664 ± 0.0005	0.0322 ± 0.0005
0.9948 ± 0.0001	3.09 ± 0.05	0.0049 ± 0.0001				0.0025 ± 0.0001	0.9440 ± 0.0005	0.0535 ± 0.0005
0.9981 ± 0.0001		0.0019 ± 0.0001	0.8885 ± 0.0003		0.1115 ± 0.0003			
0.9974 ± 0.0001	0.565 ± 0.005	0.0025 ± 0.0001	0.8798 ± 0.0005	0.0059 ± 0.0001	0.1143 ± 0.0005			
0.9966 ± 0.0001	1.02 ± 0.05	0.0033 ± 0.0001	0.8721 ± 0.0005	0.0118 ± 0.0005	0.1161 ± 0.0005			
0.9956 ± 0.0001	1.57 ± 0.05	0.0043 ± 0.0001	0.8641 ± 0.0003	0.0182 ± 0.0005	0.1177 ± 0.0005			
0.9941 ± 0.0001	2.26 ± 0.05	0.0056 ± 0.0001	0.8561 ± 0.0005	0.0253 ± 0.0005	0.1186 ± 0.0005			
			0.8295 ± 0.0005	0.0357 ± 0.0005	0.1347 ± 0.0005	0.0114 ± 0.0005	0.9119 ± 0.0005	0.0767 ± 0.0005
			0.7393 ± 0.0005	0.0644 ± 0.0005	0.1964 ± 0.0005	0.0218 ± 0.0005	0.8970 ± 0.0005	0.0812 ± 0.0005
			0.6226 ± 0.0005	0.1264 ± 0.0005	0.2511 ± 0.0005	0.0404 ± 0.0005	0.8705 ± 0.0005	0.0891 ± 0.0005
			0.5406 ± 0.0005	0.1973 ± 0.0005	0.2622 ± 0.0005	0.0596 ± 0.0005	0.8431 ± 0.0005	0.0974 ± 0.0005
			0.4654 ± 0.0005	0.2794 ± 0.0005	0.2552 ± 0.0005	0.0918 ± 0.0005	0.7974 ± 0.0005	0.1109 ± 0.0005
			0.3864 ± 0.0005	0.3769 ± 0.0005	0.2367 ± 0.0005	0.1500 ± 0.0005	0.7141 ± 0.0005	0.1360 ± 0.0005

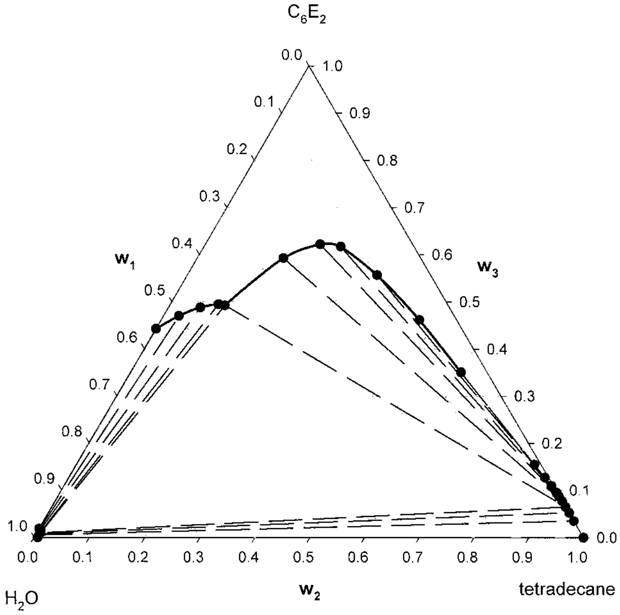

Figure 1. Ternary liquid−liquid equilibria for the system water (1) + tetradecane (2) + C_6E_2 (3) at 20 °C: (●, dotted line) experimental tie line; (solid line) binodal curve.

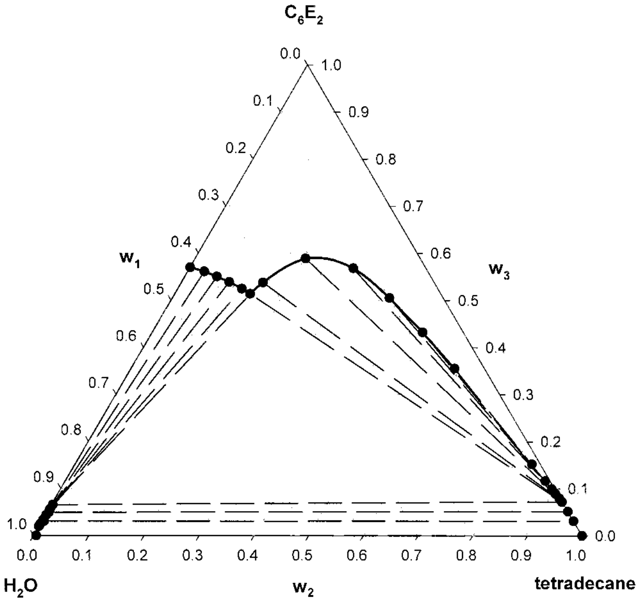

Figure 2. Ternary liquid−liquid equilibria for the system water (1) + tetradecane (2) + C_6E_2 (3) at 30 °C: (●, dotted line) experimental tie line; (solid line) binodal curve.

contents, for example, the oil-rich phase of the two-liquid-phase-coexisting envelope on the water−tetradecane side of the triangle phase diagram, the Karl Fischer titration method (MKC-210, Kyoto Electronics Co., Japan) was used to further confirm the results of gas chromatography. Note that the results of water + C_6E_2 binary systems at 293.15 K and at 303.15 K are in excellent agreement with our previous measurements (Lai and Chen, 1999) resulting from the Karl Fischer titration method.

As shown on the triangle phase diagrams in Figures 1 and 2 (concentrations expressed in mass fractions), this system exhibits one three-liquid-phase-coexisting tie triangle region and three two-liquid-phase-coexisting envelopes. As temperature decreases, the composition of the middle surfactant-rich phase approaches the composition of the lower water-rich phase. If the temperature is further decreased, the surfactant-rich phase and water-rich phase would merge into one phase. That corresponds to a lower critical solution point. On the other hand, if the temperature is further increased, the surfactant-rich phase and oil-rich phase would merge into one phase. That corresponds to an upper critical solution point. The upper and lower critical solution temperatures of the system water + tetradecane + C_6E_2 have been determined by a fish-shaped phase diagram and found to be 307.80 K and 282.30 K, respectively (Chen et al., 1994).

An attempt was made to correlate the experimental data by use of the UNIQUAC model of Abrams and Prausnitz (1975) as well as the algorithm of Negahban et al. (1986 and 1988). There are two UNIQUAC interaction parameters for a binary system and six UNIQUAC interaction parameters for a ternary system. Although we were able to determine the six interaction parameters of the system water + tetradecane + C_6E_2 from regression of only three-liquid-phase-coexisting data, the prediction of two-liquid-phase-coexisting data was very poor. If all the equilibrium data of the system water + tetradecane + C_6E_2 were used to correlate the six interaction parameters, unfortunately, no satisfactory result was obtained. Sassen et al. (1992) pointed out that the UNIQUAC model is unable 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.

Literature Cited

Abrams, D. S.; Prausnitz, J. M. Statistical Thermodynamics of Liquid Mixtures: A New Expression for the Excess Gibbs Energy of Partly or Completely Miscible Systems. *AIChE J.* **1975**, *21* (1), 116−128.

Chen, L.-J.; Yan, W.-J. Novel Interfacial Phenomena at Liquid−Liquid Interfaces of the Three-Component Surfactant System Water + *n*-Tetradecane + C_6E_2. *J. Chem. Phys.* **1993**, *97*, 4830−4837.

Chen, L.-J.; Yan, W.-J.; Hsu, M.-C.; Tyan, D.-L. Wetting Transitions at Liquid−Liquid Interfaces in Three-Component Water + Oil + Nonionic Surfactant Systems. *J. Phys. Chem.* **1994**, *98* (8), 1910−1917.

Chen, Li-Jen; Lin, Shi-Yow; Xyu, Jia-Wen. Wetting/Nonwetting Behaviors in a Ternary Amphiphilic System. *J. Chem. Phys.* **1996**, *104*, 225−232.

Frankewich, R. P.; Hinze, W. L. Evaluation and Optimization of the Factors Affecting Nonionic Surfactant-Mediated Phase Separations. *Anal. Chem.* **1994**, *66*, 944−954.

Gullickson, N. D.; Scamehorn, J. F.; Harwell, J. H. In *Sufactant-Based Separation Processes*; Scamehorn, J. F., Harwell, J. F., Eds.; Surfactant Science Series, vol. 33; Marcel Dekker: New York, 1989; Chapter 6.

Hu, Hohsun; Chiu, Chun-Da; Chen, Li-Jen. Liquid−Liquid Equilibria for the Ternay System Water + *n*-Dodecane + 2-(2-*n*-Hexyloxyethoxy)ethanol. *Fluid Phase Equilib.* **1999**, *164*, 187−194.

Kahlweit, M.; Strey, R. Phase Behavior of Ternary Systems of the Type H_2O−Oil−Nonionic Amphiphile (Microemulsions). *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 654−668.

Kahlweit, M.; Busse, G.; Winkler, J. Electric Conductivity in Microemulsions. *J. Chem. Phys.* **1993**, *99*, 5605−5614.

Kilpatrick, P. K.; Gorman, C. A.; Davis, H. T.; Scriven, L. E.; Miller, W. G. Patterns of Phase Behavior in Ternary Ethoxylated Alcohol−*n*-Alkane−Water Mixtures. *J. Phys. Chem.* **1986**, *90*, 5292−5299.

Lai, Hsuan-Hong; Chen, Li-Jen. Liquid−Liquid Equilibrium Phase Diagram and Density of Three Water + Nonionic Surfactant C_iE_j Binary Systems. *J. Chem. Eng. Data* **1999**, *44*, 251−253.

Liu, C.-L.; Nikas, Y. J.; Blankschtein, D. Partitioning of Proteins Using Two-Phase Aqueous Surfactant Systems. *AIChE J.* **1995**, *41*, 991−995.

Liu, C.-L.; Nikas, Y. J.; Blankschtein, D. Novel Bioseparations Using Two-Phase Aqueous Micellar Systems. *Biotechnol. Bioeng.* **1996**, *52*, 185−192.

Negahban, S.; Willhite, G. P.; Walas, S. M.; Michnick, M. J. Three-Liquid-Phase Equilibria of Ternary and Quaternary Mixtures, Water/*n*-Decane/2-Butyloxyethanol and Water/*n*-Octane/1-Propanol/Sodium Chloride−Experimental Measurements and Their Correlation with the UNIQUAC Model. *Fluid Phase Equilib.* **1986**, *32*, 49−61.

Negahban, S.; Willhite, G. P.; Walas, S. M. Modeling of Three-Phase Liquid/Liquid Equilibria. *SPE Reservior Eng.* **1988**, 1017.

Pai, Yung-Hsiang; Chen, Li-Jen. 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. *Fluid Phase Equilib.* **1999**, *155*, 95−105.

Sassen, C. L.; Gonzalez Casielles, A.; de Loos, Th. W.; de Swaan Arons, J. The Influence of Pressure and Temperature on the Phase Behaviour of the System $H_2O + C_{12} + C_7E_5$ and Relevant Binary Subsystems. *Fluid Phase Equilib.* **1992**, *72*, 173−187.

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