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Liquid−Liquid Equilibria for Triton X-100 + Water as a Function of Pressure

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Liquid−liquid equilibria were measured at pressures of 0.0, 50.0, 100.0, and 150.0 bar for Triton X-100 + water. The lower critical solution temperature of the Triton X-100 + water binary system is about 339 K at all pressures investigated.

Introduction

When the temperature is increased, an aqueous solution containing a nonionic surfactant may become cloudy at some temperature which is called the cloud point (Sjöblom and Stenius, 1989). Above its cloud point, the solution may separate into two phases—a dilute phase and a phase containing the surfactant in high concentration, which is also called the coacervate phase. The concentration of the nonionic surfactant in the coacervate phase is very high; e.g., it is reported to be 20% by mass. However, its concentration in the dilute phase is very low, but generally above the critical micelle concentration (cmc) (Corti et al., 1984). In this case, the system shows a lower critical solution temperature (LCST). At sufficiently high temperature, the multiple phase solution may become one phase; i.e., the system may show an upper critical solution temperature (UCST).

The phase behavior of an aqueous solution containing nonionic surfactants shows several different types, but the cloud point phenomena are observed in a narrow range. Cloud points of many nonionic surfactants in aqueous solutions have been reported in the literature (Sjöblom and Stenius, 1989). For some nonionic surfactant aqueous systems, the cloud point phenomena were observed without phase separation.

The occurrence of a LCST has been attributed to the rapid increase of micelle size or the extensive aggregation of relatively small micelles (Corti and Degiorgio, 1980). However, Sjöblom and Stenius (1989) suggested that very short chain homologues or even pure poly(oxyethylene) also shows a LCST due to the attraction between the poly(oxyethylene) chains irrespective of whether micelles were formed or not. Kjellander (1982) calculated the phase behavior of the LCST system by combining the attraction of the poly(oxyethylene) chain which was the hydrophilic part of the most nonionic surfactant with the Flory−Huggins equation.

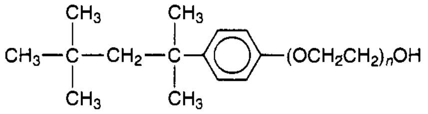
Besides the temperature effects, study of the pressure effects on the phase behavior of a nonionic surfactant aqueous system such as the cloud point has provided thermodynamically valuable information. The high-pressure phase behaviors of the poly(oxyethylene) series (nonionic surfactant) and water mixtures were reported in the literature: ethylene glycol monobutyl ether (C_4E_1) + water (H_2O) by Schneider (1963) and pentaethylene glycol monoheptyl ether (C_7E_5) + *n*-dodecane ($C_{12}H_{26}$) + water (H_2O) and ethylene glycol monobutyl ether (C_4E_1) + *n*-decane ($C_{10}H_{22}$) + water (H_2O) by Sassen et al. (1989a,b, 1991, 1992). C_iE_j is the abbreviation for the *i* alkyl *j* glycol ether, $(H(CH_2)_i(OCH_2CH_2)_jOH)$. The ethylene glycol monobutyl ether (C_4E_1) + *n*-octane (C_8H_{18}) + water (H_2O) system was correlated using the modified Huron−Vidal second-order mixing rule with a two-parameter cubic equation of state (Knudsen et al., 1994).

Triton X-100 has been widely used for studies of cell membrane protein, as it preserves the native conformation of proteins (Tanford and Reynolds, 1976). The phase behavior of Triton X-100 + water in the vicinity of the cloud point has been investigated at normal pressure (Sadaghiania and Khan, 1991), and the cloud point of a dilute Triton X-100 aqueous system was studied by Nakagawa and Shinoda (1963).

In this study, the liquid−liquid equilibrium (LLE) in the vicinity of the cloud point was measured at pressures of 0.0, 50.0, 100.0, and 150.0 bar for a binary Triton X-100 + water system.

Experimental Section

Chemicals. Trixon X-100 (α-[4-(1,1,3,3-tetramethylbutyl)phenyl]-ω-hydroxypoly(oxy-1,2-ethanediyl)), with the structure



$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-\overset{CH_3}{\underset{CH_3}{C}}-C_6H_4-(OCH_2CH_2)_nOH$$

where $n = 9.3$ was supplied by Sigma (manufacturer Union Carbide Chemicals and Plastics Co.). The molar mass of Triton X-100 is 624.9 and critical micelle concentration (cmc) is 0.000 24 M (given by the supplier). From elemental analysis, it contained 0.06 mol % sodium (given by the supplier). Triton X-100 was analyzed by Tiller et al. (1984). They estimate the number of ethoxy groups (*n* in the above structure) to be 9.3 for Triton X-100 by NMR spectroscopy. Glass-distilled water (HPLC grade, evaporation residue <0.0003%) was supplied by Aldrich. Acetonitrile (>99.8 mass %, gradient grade) was supplied by Merck and used as a mobile phase of the HPLC. All chemicals were used directly without further purification.

Apparatus and Procedure. The high-pressure equilibrium apparatus used in this work is shown in Figure 1. The equilibrium cell made of SUS316 has a total capacity of about 200 cm^3. A sapphire window (diameter 5 cm, width 2.5 cm) enabled the visual observation of the phase boundary at high pressure. A movable piston, made of brass, was used to adjust and maintain the pressure in the cell, with water as the pressurizing fluid. An egg-shaped magnetic stirrer in the cell was used to provide rapid mixing. The temperature in the equilibrium cell was

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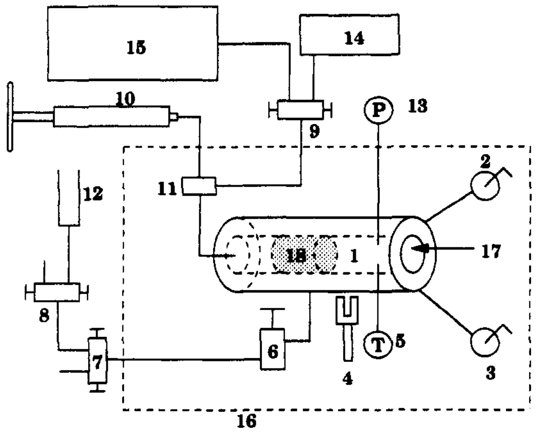

Figure 1. Schematic diagram of the experimental apparatus: (1) equilibrium cell; (2, 3) sampling valve; (4) magnetic stirrer; (5) thermocouple; (6) two-way valve; (7, 8, 9) three-way valve; (10) hand pump; (11) T-connector; (12) sample reservoir; (13) pressure gauge; (14) water reservoir; (15) μ-LC pump; (16) air bath; (17) sapphire window; (18) movable piston.

measured by a K type thermocouple (Cole Parmer, 944-956), and the accuracy was ±0.1 K. The pressure in the equilibrium cell was measured by the pressure gauge (Heise, CMM-104957, 0-600 bar range). The maximum error of this gauge was ±0.1 bar. A micropump (ISCO, μLC-500) with an accuracy of ±2% of full scale (0-700 bar range) was used for the initial adjustment of pressure. A hand pump (HIP, 62-6-10) was used to finely control the pressure. The equilibrium cell, sampling valves, pressure generator, and most of the connection valves were contained in the air bath, the temperature of which was controlled by a PID controller (Cole Parmer, 89700-00) to within ±0.1 K.

The equilibrium cell was evacuated by a vacuum pump (Vacuubrand, RE2) before charging with the sample mixture of a predefined concentration. After the pressure and the temperature of the equilibrium cell were adjusted, the sample was vigorously mixed by the magnetic stirrer for about 10 min. It takes about 24 h for the system to reach equilibrium and give a clear phase boundary. The equilibrium time for 24 h was confirmed by measuring the concentration of each phase as a function of time. Samples of the top and bottom phases were collected using the sampling valves (Rheodyne, 7010) with a loop volume of about 50 μL after 24 h.

Samples were analyzed at 270 nm by a UV spectrophotometer (Varian, Cary13) and HPLC (Waters, 501 pump, 486 detector). The mobile phase of the HPLC was acetonitrile + water (40:60 by volume). A μBondapack C18 125 Å 10 m (Waters) column was used for this analysis. The flow rate of the mobile phase was 0.9 $cm^3 \cdot min^{-1}$. All HPLC signals were integrated by an integrator (HP-3394). Calibration curves were made by measuring the UV and HPLC signals of known composition. The absorbance was measured for UV analysis and the signal area for HPLC. The calibration curves were made for the top phase and bottom phase, respectively, for accurate analysis. These data were correlated by a linear equation, the correlation coefficient of which is 0.999. The photometric noise of the detector is less than 0.0002 × absorbance root mean square, and this instrumental error corresponds to the maximum 0.000 03 mass fraction error. From the correlation coefficient, the maximum experimental errors for the top and bottom phase analyses are 0.000 02 and 0.0005, respectively, which were from sampling and handling of samples etc. not from instrumental noise.

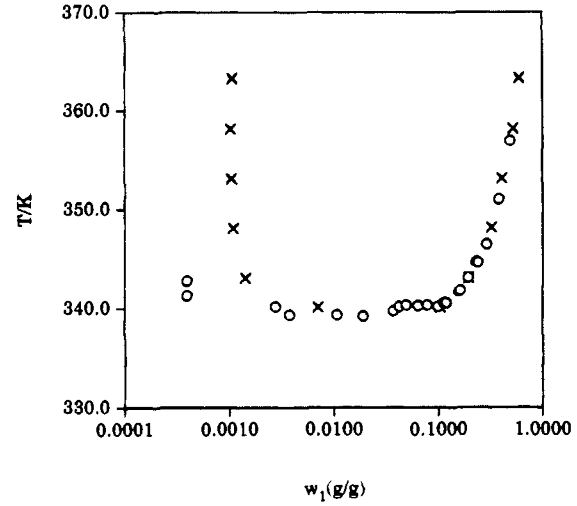

Figure 2. Liquid-liquid equilibria for Triton X-100 (1) + water (2) at 0.0 bar: ○, this work; ×, Sadaghiania et al. (1989).

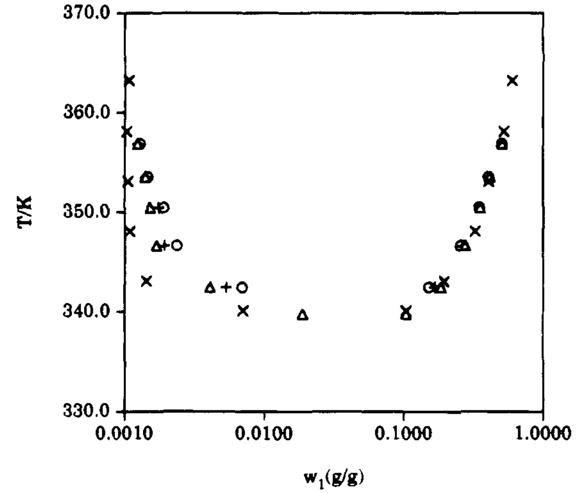

Figure 3. Liquid-liquid equilibria for Triton X-100 (1) + water (2): ×, 0.0 bar; △, 50.0 bar; +, 100.0 bar; ○, 150.0 bar.

Results and Discussion

The liquid-liquid equilibria for Triton X-100 + water at 0.0 bar are compared with the values (Sadaghiania and Khan, 1991) in Figure 2. At a low concentration of Triton X-100 the differences are due to their experimental error because they determined the cloud point visually by noting the temperature at which a solution heated above the clouding temperature lost its turbidity on cooling. The temperature at which the scale of the thermometer was visible in the solution was recorded as the cloud point (Sadaghiania et al., 1991). Their heating and cooling were regulated to about 1 $K \cdot min^{-1}$ around the cloud point. This method can determine the cloud point at large concentration, but makes an error at low concentration. At 343.1 K, the top phase and bottom phase concentrations are 0.0014 and 0.194, respectively, from this study, but 0.0004 at 342.8 K and 0.192 at 343.1 K from the literature. The error at low concentration is 70%, but 1% at high concentration.

The liquid-liquid equilibrium results for Triton X-100 + water at 0, 50, 100, and 150 bar are given in Table 1 and Figure 3. The top and the bottom phases are the dilute and the coacervate phases, respectively. The LCST of the system at 0 bar is about 339 K, and the LCST increases slightly with pressure. The concentration difference of Triton X-100 between the dilute and the coacervate phases increases with temperature and decreases with pressure.

Table 1. Total Pressure (P), Temperature (T), and Mass Fractions of Triton X-100 in the Top (w_T) and Bottom Phases (w_B) for Triton X-100 + Water at 0.0, 50.0, 100.0, and 150.0 bar

P/bar	T/K	dw_T	w_B
0.0	66.9	0.0071	0.104
0.0	69.9	0.0014	0.194
0.0	74.9	0.0011	0.322
0.0	79.9	0.0011	0.408
0.0	85.0	0.0010	0.522
0.0	90.1	0.0011	0.599
50.0	66.6	0.0188	0.104
50.0	69.3	0.0041	0.185
50.0	73.5	0.0017	0.276
50.0	77.3	0.0015	0.351
50.0	80.4	0.0014	0.414
50.0	83.7	0.0012	0.508
100.0	66.6	one phase	
100.0	69.3	0.0053	0.167
100.0	73.5	0.0019	0.265
100.0	77.3	0.0018	0.349
100.0	80.4	0.0014	0.407
100.0	83.7	0.0012	0.504
150.0	66.6	one phase	
150.0	69.3	0.0070	0.152
150.0	73.5	0.0024	0.254
150.0	77.3	0.0019	0.348
150.0	80.4	0.0015	0.405
150.0	83.7	0.0013	0.503

Kjellander (1982) calculated the entropy and enthalpy of the C_iE_j-type surfactant aqueous system and concluded that the increased attraction leading to phase separation was a consequence of a strong entropy dominance. They suggested that the primary reason for this behavior was that water around the poly(oxyethylene) chain was more structured than bulk water; i.e., it had a lower enthalpy and entropy than bulk water. At sufficiently high temperature, the water around the poly(oxyethylene) chain is destructured by overlapping of the chains which is caused by the attraction force of the chains. The entropy change due to the destructuring of the water around the chain overcomes the repulsive enthalpy, which makes the Gibbs free energy negative; i.e., the phase separated is a more favorable state. At high pressure, the water around the chain is more structured than at normal pressure because of the decrease in the free volume around the chain, which makes phase separation less favorable.

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