The Effect of Pressure on the Mutual Solubility of a Nonionic Surfactant-Water System

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Synopsis. The cloud-point temperature (T) of an aqueous hexa(oxyethylene) dodecyl ether solution was determined as a function of the pressure (P) and the composition (x_2). The volume (ΔV) and entropy (ΔS) changes for the separation of the surfactant phase from the water phase were estimated from the T-P-x_2 relation. Both ΔV and ΔS were positive.

An aqueous solution of nonionic surfactants suddenly becomes turbid on being heated to a critical temperature, known as the cloud point, and the solution separates into two phases. This peculiar dissolution phenomenon has been explained especially by an acceptable model based on the thermodynamic properties of a nonionic surfactant–water system,[1,2] since accurate thermodynamic data have been determined for pure nonionics in water. Although the pressure is necessarily an important thermodynamic variable, as well as the temperature and the concentration, defining the state of solution, few studies have been made on the effect of pressure on the solution behavior of nonionic surfactants in water.[3–5] In this paper, the cloud-point temperature of an aqueous hexa(oxyethylene) dodecyl ether solution has been determined as a function of both the pressure and the composition. From the relation of the cloud-point-temperature-pressure-composition, the thermodynamic quantities (volume ΔV and entropy ΔS) accompanied by the separation of the surfactant phase from the water phase were estimated.

Experimental

Homogeneous hexa(oxyethylene) dodecyl ether ($C_{12}E_6$) was obtained from Nikko Chemicals. Its purity was checked by gas chromatography, and it was found to show a single peak. The cloud-point temperature of a 1.0% (w/w) solution was 48.8 °C. The cloud points under a high pressure were determined by a method described previously.[4]

Results and Discussion

The cloud-point temperatures of aqueous $C_{12}E_6$ solutions were determined in the pressure range of 0.1—150 MPa and the composition range of 0.1—10% (w/w). The cloud-point temperatures for all the surfactant solutions increase monotonously with an increase in the pressure up to 150 MPa (Fig. 1). Since the cloud point of a surfactant solution is generally taken to be the temperature where the separation of the liquid-surfactant phase containing dissolved water is caused by the dehydration of ether oxygens of the poly(oxyethylene) group,[1] a pressure of up to 150 MPa seems to favorable for the dissolution of surfactant molecules in water. An increase in the pressure enhances the formation of hydrogen bonds between water and ether oxygens of the poly(oxyethylene) group.[6]

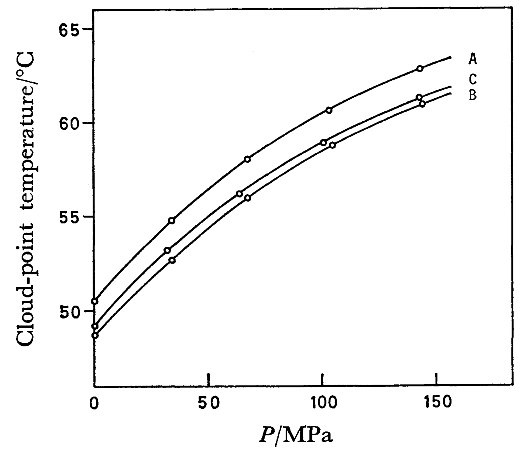

Fig. 1. Cloud-point temperature *vs.* pressure curves for some aqueous hexa(oxyethylene) dodecyl ether solutions. Concentration; A: 0.124, B: 2.06, and C: 5.02 %(w/w).

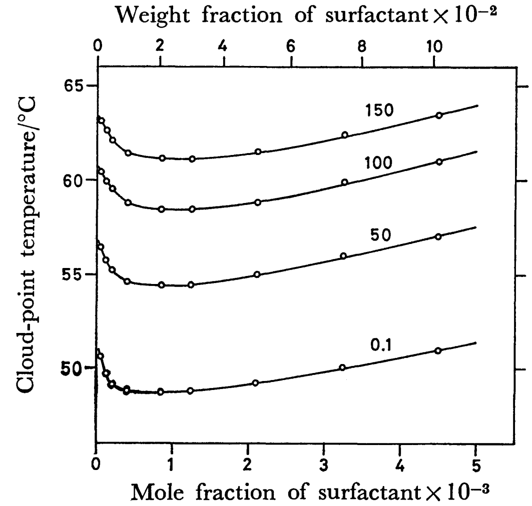

Fig. 2. Cloud-point temperature of aqueous hexa(oxyethylene) dodecyl ether solutions as a function of surfactant concentration at various pressures. Numerical values refer to the pressure in MPa.

In Fig. 2, the cloud points are shown as a function of the concentration of $C_{12}E_6$ at various pressures. Note that each curve in Fig. 2 is a part of the phase diagram representing the liquid-liquid mutual solubility, which has a lower critical solution temperature (LCST). As may be seen from Fig. 2, the LCST can be elevated by increasing the pressure.

At the cloud point, the two phases (an aqueous phase containing a small amount of a singly dispersed surfactant and a liquid surfactant phase containing dissolved water) are in equilibrium.[1,2] In the two-component, two-phase system, the curves of the coexistence of pairs of phases are described by these equations:[7]

$$\left(\frac{\partial T}{\partial x_2}\right)_P = g_{22}\left(\frac{RT}{y_1\Delta\bar{s}_1+y_2\Delta\bar{s}_2}\right)\left(\frac{x_2-y_2}{x_1x_2}\right), \tag{1}$$

$$\left(\frac{\partial P}{\partial x_2}\right)_T = -g_{22}\left(\frac{RT}{y_1\Delta\bar{v}_1+y_2\Delta\bar{v}_2}\right)\left(\frac{x_2-y_2}{x_1x_2}\right), \tag{2}$$

and:

$$\left(\frac{\partial T}{\partial P}\right)_{x_2} = \frac{y_1\Delta\bar{v}_1+y_2\Delta\bar{v}_2}{y_1\Delta\bar{s}_1+y_2\Delta\bar{s}_2}, \tag{3}$$

where x and y refer to the mole fraction in an aqueous phase and a surfactant phase respectively. $\Delta\bar{s}_1$ and $\Delta\bar{s}_2$ are the partial molal entropy changes in the water and surfactant respectively transferred from the aqueous into the surfactant phase, and $\Delta\bar{v}_1$ and $\Delta\bar{v}_2$ are the partial molal volume changes in the water and surfactant respectively transferred from the aqueous into the surfactant phase. The expression for g_{22} can be written:

$$g_{22} = \left(\frac{\partial \ln a_2}{\partial \ln x_2}\right)_{T,P}. \tag{4}$$

In a dilute solution, the activity is usually proportional to the concentration, and Eq. 4 becomes $g_{22}=1$.

The entropy change on the phase separation of a surfactant solution, ΔS ($\equiv y_1\Delta\bar{s}_1+y_2\Delta\bar{s}_2$), can be estimated by applying Eq. 1 to Fig. 2 (T-x_2 diagram). The volume change on the phase separation of a surfactant solution, ΔV ($\equiv y_1\Delta\bar{v}_1+y_2\Delta\bar{v}_2$), can be estimated by using Eq. 3, the value of ΔS, and the slope of Fig. 1 (T-P diagram).

The values of ΔV and ΔS, which were calculated at the surfactant concentration of $x_2=5.0\times10^{-5}$, are listed in Table 1. Both ΔV and ΔS are positive. These positive changes in volume and entropy are attributable partly to the dehydration of the poly(oxyethylene) chain and partly to the hydrophobic bonding of alkyl chain. The value of ΔV, 2.1 cm^3 is in good agreement with the volume change of 2.2 cm^3, which was determined from the density measurements above and below the cloud point.[8]

The volume change for the transfer of the poly(oxyethylene) chain from the aqueous solution into the pure liquid state amounts to about 2.0 cm^3 per oxyethylene unit.[6] Therefore, the volume change of 12 cm^3 may be expected for the complete dehydration of the hexa(oxyethylene) group. On the other hand, the volume change for the transfer of the hydrocarbon part from the aqueous to the nonpolar environment amounts to 1.2—1.5 cm^3 per methylene group.[9—11] Despite the large volume change to be expected for both the dehydration and the hydrophobic bonding, the volume change calculated thermodynamically or measured directly is appreciably small. Since the liquid-surfactant phase contains a considerable amount of water, the partial dehydration of the poly(oxyethylene) chain and the incomplete transfer of the alkyl chain are considered to be responsible for the small volume change on the separation of the liquid-surfactant phase from the aqueous phase.

TABLE 1. THERMODYNAMIC PARAMETERS ON THE CLOUD POINT OF AN AQUEOUS HEXA(OXYETHYLENE) DODECYL ETHER SOLUTION AT THE CONCENTRATION OF $x_2=5.0\times10^{-5}$

P / MPa	T / K	ΔS / J K^{-1} mol^{-1}	ΔV / cm^3 mol^{-1}
0.1	323.6	16	2.1
50	329.4	20	1.9
100	333.4	26	1.7
150	336.1	31	1.4

As is shown in Table 1, the value of ΔV decreases with the increase in the pressure, while the value of ΔS increases with the pressure. The large compressibility of the dehydrated system compared with the hydrogen-bonded system is considered to be responsible for the decrease in the ΔV with the pressure. The increased in ΔS with the pressure may be ascribed to the increased numbers of the hydrogen bonds between the poly(oxyethylene) chain and water molecules. In other words, the hydrogen-bonded water, which should be released at the cloud point, is likely to be increased by applying pressure. The hydrophobic bonding may also be responsible for the increase in ΔS with the pressure; the value of ΔS for the hydrophobic bonding (*i.e.*, micelle formation) increases initially with an increase in the pressure and then decreases with the pressure *via* the maximum at about 100 MPa.[11]

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