The Effect of the Pressure on the Micellization of the Surfactant in Aqueous Urea Solutions

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The critical micelle concentrations (CMC) of dodecyltrimethylammonium bromide (DTAB) in aqueous urea solutions have been determined over a range of pressures up to 2500 atm at 25 and 35 °C. The partial molal volumes of DTAB in micellar ($\bar{V}_m$) and singly-dispersed states ($\bar{V}_s$) have also been determined in aqueous urea solutions at 25 °C. $\bar{V}_s$ increases with the addition of urea, while $\bar{V}_m$ remains approximately constant. The partial molal entropy change of micellization ($\Delta\bar{S}_m$) in water increases with an increase in the pressure up to about 1500 atm, while $\Delta\bar{S}_m$ in 3-m urea solution remains virtually unaltered in the low-pressure region. The results suggest that the "iceberg" structure of water around the hydrocarbon chain of the monomeric surfactant is effectively broken down by urea.

The effect of urea on the micelle formation has already been studied by many workers,[1-9] and it is well known that the addition of urea raises the critical micelle concentration (CMC) of surfactant solutions. A smaller negative free energy change and a smaller positive entropy change on micellization have been interpreted in terms of the breakdown of the water structure by urea.

The study of the pressure effect as well as the temperature effect on the CMC of a surfactant in aqueous solutions has given very important thermodynamic information on micelle-forming properties.[10-15] Therefore, the effects of the pressure and temperature on the CMC of a surfactant in aqueous urea solutions are expected to give a deeper insight into the surfactant solution than has hitherto been reported. A knowledge of the thermodynamic properties of model compounds such as surfactants in aqueous urea solutions helps to understand the urea denaturation of proteins and the effect of urea on the water structure.

In this study the CMC of dodecyltrimethylammonium bromide (DTAB) in aqueous urea solutions of various concentrations was determined over a range of pressures up to 2500 atm at 25 and 35 °C. Then the partial molal volumes of DTAB in aqueous urea solutions were determined above and below the CMC. The effect of urea on the thermodynamic parameters for micellization was also examined.

Experimental

The DTAB used was synthesized and purified by the method described previously.[16] The CMC of the DTAB solution determined by the conductivity method was 0.01554 in molality (m) at 25 °C. This value is in good agreement with that in the literature. All the solutions were prepared on a molal basis. Urea was recrystallized from an ethanol-water (95 : 5) mixture. The urea concentrations of 3.0 and 6.0 in molality correspond to the values in 2.64 and 4.75 in molarity (M) at 25 °C respectively.

The high-pressure apparatus used is the same as has been described previously.[17] The CMC of DTAB in aqueous urea solutions under high pressures was determined by the conductivity method in a way similar to that used under atmospheric pressures.

The densities of a series of solutions were simultaneously measured by using ten pycnometers with a capacity of about 20 ml; the error of measurements was within $\pm 5\times 10^{-5}$ g/cm^3. The thermostated bath was controlled to 25 ($\pm$0.005) °C. The volume of solution per 1000 g of solvent (water+urea) was plotted against the molality of DTAB, resulting in a straight line below and above the CMC. The partial molal volume of DTAB in aqueous urea solutions was taken as the slope of the line; it was determined by the least-squares method. Since the partial molal volume is almost independent of the surfactant concentration over the concentration ranges studied here,[18,19] the experimental values thus obtained have been assumed to be identical with those corresponding to an infinite dilution.

Results and Discussion

The CMC of DTAB in several urea solutions is shown in Fig. 1 as a function of the pressure. The

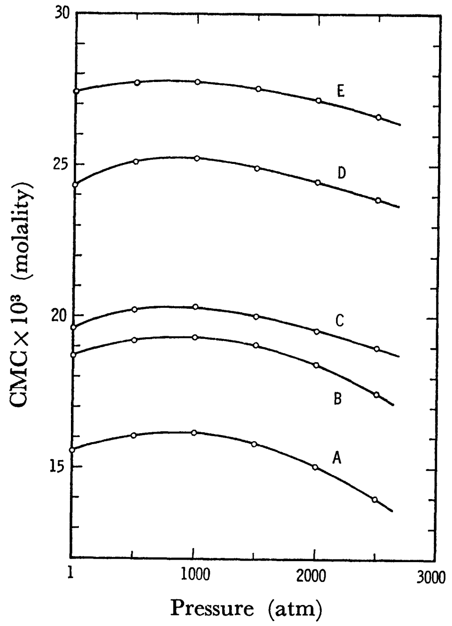

Fig. 1. Effect of pressure on the CMC in some urea solutions at 25 °C. Urea concentration; A: 0, B: 1.99, C: 2.94, D: 4.49, and E: 6.08 (mole/kg-H_2O).

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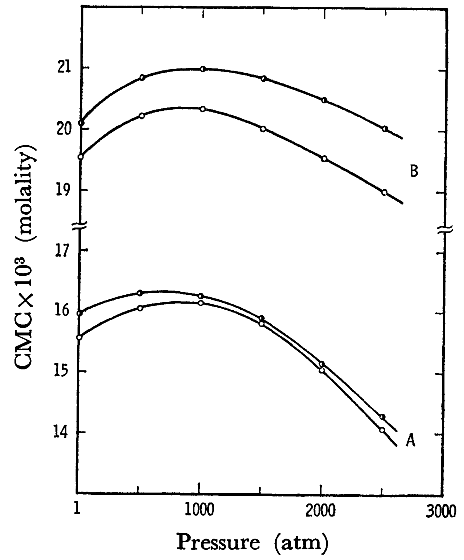

Fig. 2. Effect of pressure on the CMC in water and 3 m (2.94 molality) urea solution at two temperatures, 25 °C (○) and 35 °C (◑). A: in water, B: in 3 m urea solution.

CMC *vs.* pressure curve in water is in fair agreement with that of Tuddenham and Alexander.[11] At about 800 atm, the CMC *vs.* pressure curve has a maximum which remains even in a 6-m urea solution. The CMC of DTAB increases with the addition of urea in the whole pressure region studied. This increase in the CMC by urea at 1 atm is comparable with the results reported by other workers.[2,5,9] In Fig. 2, the effects of the temperature and pressure on the CMC of DTAB in water and a 3-m urea solution are compared. It is known that the CMC *vs.* temperature curve for DTAB reaches a minimum at about 25 °C in water[5,17] and at 15—20 °C in the 3-M urea solution.[5,9] As may be seen from Fig. 2, in water the increase in the CMC by the elevation of the temperature is reduced upon the application of pressure, while in the 3-m urea solution it becomes progressively greater as the pressure increases.

There remain some factors to be considered in the interpretation of the effect of urea on the micelle formation; the change in the dielectric constant of the solution, the solubilization of urea into the micelle, the change in the structured water around the hydrocarbon chain of the monomeric surfactant, and so on. It is known that the dielectric constant of a solution increases with the urea concentration up at least to 3 M;[20] this increase of the dielectric constant of urea solution is most likely responsible for the dissociation of the ionic micelle.[9] In the methanol–water mixture, however, the effective micellar charge increases with the methanol content to a 0.3 mole fraction of methanol[21] in spite of the decrease in the dielectric constant with the increase in the methanol content.[20] The CMC increases in both solutions. The micellar weight decreases not only in a methanol solution,[21,22] but also in an urea solution.[23] Thus, the change in the dielectric constant which is due to the change in the composition of solvent seems not to affect the micelle formation very much. Secondly, it is known that in general the addition of solubilizates lowers the CMC.[24] The solubilization effect of urea on the micellization is very little, if any, because the CMC increases with the addition of urea.

The change in the partial molal volume on micellization, $\Delta\bar{V}_m$, was calculated from the pressure dependence of the CMC through the following equation which has previously been discussed:[14,15]

$$\Delta\bar{V}_m = (1+\beta)RT\left(\frac{\partial \ln \mathrm{CMC}}{\partial P}\right)_{T,\Delta\bar{G}_m} \qquad (1)$$

where β is a constant which indicates the ratio of the number of the gegenion to that of the surfactant ion in a micelle. The values of $\Delta\bar{V}_m$ in water and aqueous urea solutions are calculated from Eq. (1) using the results shown in Fig. 1; they are given in Table 1. The value of β used was taken from the literature[9,25] except for that in a 6-m urea solution, which was assumed to be 0.76 by an extrapolation of the available data.

Table 1. Partial molal volumes of micellar and singly dispersed surfactant, and the changes of partial molal volume on micellization

Urea concn. (mol/kg)	β	From CMC $\Delta\bar{V}_m$	From density measurement $\bar{V}_m$	$\bar{V}_s$	$\bar{V}_m-\bar{V}_s$
0	0.744	4.1	295.5	287.0	8.5
2.94	0.756	4.2	295.4	290.2	5.2
6.08	(0.76)	1.5	294.7	291.0	3.7

The values of the partial molal volumes in the micellar ($\bar{V}_m$) and singly dispersed ($\bar{V}_s$) states and their difference ($\bar{V}_m—\bar{V}_s$) are also shown in Table 1. The values of $\Delta\bar{V}_m$ calculated from the pressure dependence of the CMC are somewhat smaller not only in water, as has been described previously,[14] but also in urea solutions than the $\bar{V}_m—\bar{V}_s$ determined from the density measurement. It is obvious from Table 1 that the partial molal volume change on micellization is reduced by the addition of urea. This reduction may be attributed to the increase in $\bar{V}_s$ with the addition of urea, as $\bar{V}_m$ is kept approximately constant.

The change in the partial molal volume for the transfer of the solute molecule, which has a hydrophobic tail, from water to urea solutions has been studied by several authors.[26,27] This volume change is positive, and it tends to increase as the length of the hydrocarbon chain increases. It is known that the transfer of hydrocarbons from a nonpolar environment to water results in a negative volume change;[28] this is considered to reflect the ordering of water molecules around the hydrocarbon chains, or the "iceberg" formation.[29] Therefore, the positive volume changes for the transfer of a monomeric surfactant from water to urea solutions are consistent with a structure-breaking role of urea in aqueous solutions. On the other hand, $\bar{V}_m$ is quite insensitive to the presence of urea. This constancy of $\bar{V}_m$ can be attributed to the loss of hydrocarbon-water contact due to the formation of micelles.

The change in the partial molal entropy on micelliza-

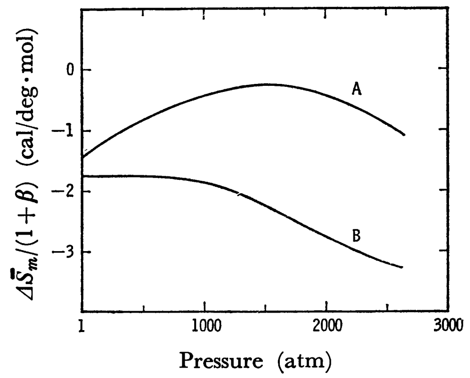

Fig. 3. Partial molal entropy change of micelle formation in the range of temperature, 25—35 °C, as a function of pressure. A: in water, B: in 3 m urea solution.

tion is given by the following equation, as has been described previously:[15)]

$$\Delta\bar{S}_m = -(1+\beta)RT\left(\frac{\partial \ln \mathrm{CMC}}{\partial T}\right)_{P,\Delta\bar{G}_m} \tag{2}$$

On the basis of the data shown in Fig. 2, the partial molal entropy change on micellization was calculated at the mean temperature, 30 °C. Of course, the value of the CMC has no minimum or maximum in the range of temperature of 25—35 °C.[5,9,17)] Values of β under high pressures are not available at present. Thus, the $\Delta\bar{S}_m/(1+\beta)$ value calculated from the CMC's at two temperatures is shown in Fig. 3 as a function of the pressure. As β probably changes with the pressure,[15)] the form of the pressure dependence of $\Delta\bar{S}_m$ may be slightly transformed from that shown in Fig. 3. It may be noted from Fig. 3, however, that the $\Delta\bar{S}_m$ in water increases initially with an increase in the pressure and then decreases with the pressure via a maximum at about 1500 atm, while the $\Delta\bar{S}_m$ in the 3-m urea solution remains virtually unaltered at low pressures and then decreases gradually with the pressure.

The pressure dependence of $\Delta\bar{S}_m$ is related to the temperature dependence of $\Delta\bar{V}_m$ as follows:

$$\left(\frac{\partial\Delta\bar{S}_m}{\partial P}\right)_T = -\left(\frac{\partial\Delta\bar{V}_m}{\partial T}\right)_P \tag{3}$$

Regarding micellization in water, it is known that $(\partial\Delta\bar{S}_m/\partial P)_T>0$ in the region of lower pressures; *i.e.*, $(\partial\Delta\bar{V}_m/\partial T)_P<0$.[15,18)] The effect of the temperature on the partial molal volume for singly dispersed and micellar states leads to $(\partial\bar{V}_s/\partial T)_P>(\partial\bar{V}_m/\partial T)_P>0$.[18)] The positive larger value for $(\partial\bar{V}_s/\partial T)_P$ than for $(\partial\bar{V}_m/\partial T)_P$ is attributable to the thermal expansion as well as to the breakdown of the "iceberg" structure around the hydrocarbon chain as a results of thermal motion. Thus, we can regard $(\partial\bar{S}_s/\partial P)_T<(\partial\bar{S}_m/\partial P)_T<0$ as true at low pressures. That is, the entropy decrease with the compression for the singly dispersed state outweighs that for the micellar state. According to Le Chatelier's principle, the compression leads to a decrease in volume and is more favorable to a structure-making of water around hydrocarbon. Therefore, it may be concluded that the compression causes the promotion of the "iceberg" formation around the hydrocarbon chain. In the micelle formation in the 3-m urea solution, on the other hand, $(\partial\Delta\bar{S}_m/\partial P)_T\simeq0$ at lower pressures, judging from Fig. 3. Consequently, $(\partial\bar{S}_s/\partial P)_T\simeq(\partial\bar{S}_m/\partial P)_T<0$ and/or $(\partial\bar{V}_s/\partial T)_P\simeq(\partial\bar{V}_m/\partial T)_P>0$, which means that the "iceberg" structure of water around the hydrocarbon chain is effectively broken down by the urea added.

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