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Radiotracer Studies of the Adsorption of Surface Active Substances at Aqueous Surfaces. VI. Urea Adsorption on an Adsorbed Monolayer of a Nonionic Surfactant

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The surface tension and adsorption were observed by the Wilhelmy plate and radiotracer methods at the air-solution interface of an aqueous solution of urea and α-dodecyl-ω-hydroxyhexa(oxyethylene) ($D(EO)_6$). The adsorption of $D(EO)_6$ was dependent on the concentration of urea below the CMC values, but above the values it was independent of the concentration. Urea adsorption occurs positively for low-surface packing of the poly(oxyethylene) group of $D(EO)_6$, but negatively for the closest packing of the group and high concentrations of urea. It was confirmed that $D(EO)_6$ adsorption took place at the solution surface according to the Gibbs adsorption isotherm, which was taken into account as an activity coefficient in an empirical equation for the interactions of $D(EO)_6$ and urea in solution. Urea adsorption for the adsorbed monolayer of $D(EO)_6$ above the CMC value was interpreted assuming that urea, as for the nonionic micelle, was non-penetrating, which was examined by gel permeation.

The surface tension of the aqueous urea solution is almost invariant or is slightly increased with increasing urea concentration at the air-solution interface.[1,2] When covered with stearic acid[2] or protein[3] monolayers on the urea solution, urea adsorption occurs at the monolayers due to the dipole-dipole interactions of the urea and film substances, but not at the ionic monolayer of the stearate.[4] However, the micelle formation in the aqueous solution of ionic and nonionic surfactants is markedly affected by urea present in the solution, and the CMC value is shifted to higher surfactant concentrations.[5] Also, urea decreases the surface tension lowering of the surfactant solution, and causes a change in the activity of the surfactant in the solution due not only to a reduction of the dielectric constant of water, but also to a direct interaction with the surfactant.[6]

If the activity for each kinetic unit in the urea–surfactant solution is undeterminable, the Gibbs adsorption of solutes cannot be calculated from only the relationship between the surface tension and the apparent concentration of solutes in the solution,[7] without additional experimental information about the surface adsorption. In a previous paper,[1] the surface adsorption of a nonionic surfactant at constant concentration was measured as a function of the concentration of various additives, but no additive adsorption was obtained. The surface compositions of adsorbed mixed monolayers are not easily determined in comparison with the case of insoluble monolayers.

The present report is concerned with the elucidation of urea adsorption for the adsorbed monolayer by measuring the adsorption of nonionic surfactant at the air–solution interface. Further, the micelle size will be examined by the gel permeation of the urea–surfactant solution in order to check whether or not urea has penetrated into the micelle.

Experimental

Materials. α-Dodecyl-ω-hydroxyhexa(oxyethylene) ($D(EO)_6$), α-dodecyl-2,3-$^3H_2$-ω-hydroxyhexa(oxyethylene), and urea (EP. grade, purified by recrystallization with water) were the same as those used in previous experiments.[1] The water used was distilled three times after refluxing with alkali-permanganate overnight. The experimental temperature was maintained at 30.0±0.5 °C.

Measurements of Surface Tension and Adsorption. The surface tensions of surfactant solutions with and without urea were measured by the Wilhelmy plate method. The surface tension at equilibrium was taken to be those values which no longer changed with time (usually equilibrium was established after several hours). The amount of nonionic surfactant adsorption was measured by the radiotracer method using a tritiated compound. Details of the equipment and of the experimental procedure have been presented previously.[8,9]

Gel Permeation. The apparatus and procedure used for the gel permeation of a urea–nonionic surfactant solution, are almost the same as those used by Suzuki and Sasaki.[10] The gel (Sephadex G75) was embedded in a column (diameter 1.2 cm and gel height 15.0 cm) after swelling in a urea solution of the same concentration as was eluted in the gel permeation. The nonionic surfactant in the each fraction (1 ml) was analyzed by the iodine turbidity method.[11] Constant amounts of iodine (10^{-2} M, 0.3 ml) in excess of the requirement for forming the iodine–nonionic complex, and then hydrochloric acid (1 M, 0.4 mol), were added to each fraction. After shaking the mixture for about 30 min, the turbidity of the solutions was measured at 660 mμ using a Shimadzu spectrophotometer (Spectronic 20).

Results and Discussion

The surface tensions of the $D(EO)_6$ solution with and without urea are shown in Fig. 1. Surface tension lowering is markedly dependent on the urea concentration, but independent above the CMC value to within experimental error. Quite similar observations above the CMC value have been reported by Schwuger,[12] who has measured the surface tension of a urea(3 M)–D(EO)$_6$ solution by the ring method. A weak break point is observed on each curve in Fig. 1 at some solution concentration below the CMC value. This phenomenon appears to give the possibility of a change in the solubility state of the solutes in the solution, as is discussed in detail below.

Figure 2 shows the adsorption isotherms of $D(EO)_6$ at various urea concentrations. These isotherms are

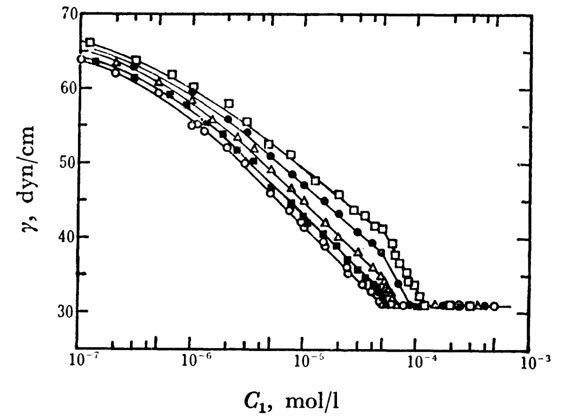

Fig. 1. Surface tension *vs.* concentration curves of $D(EO)_6$ solution at various concentrations of urea. ○: 0 M, ■: 0.04 M, △: 0.40 M, ●: 2.5 M, □: 4.0 M.

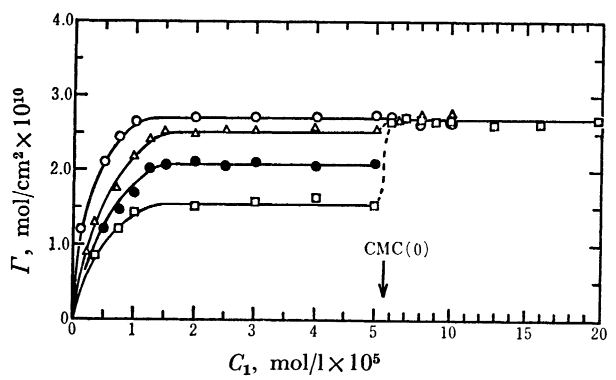

Fig. 2. Adsorption isotherms of $D(EO)_6$ at various concentrations of urea.
○: 0 M, △: 0.04 M, ●: 2.5 M, □: 4.0 M.

characterized by the following two parts above and below about 5.5×10^{-5} mol/l of $D(EO)_6$, which corresponds approximately to the CMC(0) of a $D(EO)_6$ solution without urea. Below the CMC(0) value, adsorption of $D(EO)_6$ obviously decreases with the increasing urea concentration present in the solution as is shown in a previous paper,[1)] and reaches saturation. This suggests that urea may directly interact with the poly(oxyethylene) group of $D(EO)_6$ and probably forms some kind of urea–nonionic aggregations. If urea affects the solution by breaking the water structure, the isotherm should not give such a saturated adsorption as that shown in Fig. 2, but should only increase gradually depending on the change in the activity of $D(EO)_6$ in the urea solution. Above the CMC(0) value, the isotherms at varying urea concentrations coincide with the isotherm of the simple $D(EO)_6$ solution. These phenomena will be discussed in later section.

Adsorption of D(EO)$_6$. An attempt was made to apply the Gibbs adsorption isotherm to the calculation of the surface excess of nonionic in the urea–nonionic solution. The Gibbs isotherm is generatlly written as:[7)]

$$-\mathrm{d}\gamma = RT\sum\Gamma_i\,\mathrm{d}\ln a_i \tag{1}$$

where γ denotes the surface tension, Γ_i and a_i the surface excess and activity of the i-th components of the solution, respectively, and R and T the gas constant and absolute temperature, respectively. The interaction between urea and $D(EO)_6$ in the solution can be expressed implicitly as an activity coefficient (f_i) in Eq. 1. At constant urea concentration, Eq. 1 can be rewritten using the Gibbs-Duhem equation for bulk solutions,

$$-\left(\frac{\partial\gamma}{RT\partial\ln C_1}\right)_{2,3} = \Gamma_1 - \left\{\Gamma_1\frac{C_2}{C_1}-\Gamma_2\right\}\left(\frac{\partial\ln f_2}{\partial\ln C_1}\right)_{2,3} - \Gamma_1\frac{C_3}{C_1}\left(\frac{\partial\ln f_3}{\partial\ln C_1}\right)_{2,3} \tag{2}$$

where C_i is the concentration of the i-th component in the solution, and the subscripts 1, 2 and 3 refer to $D(EO)_6$, urea and water, respectively. The last term on the right-hand side of Eq. 2 can reasonably be neglected, because the activity coefficient of water in the urea–nonionic solution should be constant at concentrations, C_1, less than 5.5×10^{-5} mol/l. If the cross-differentiation relation of Eq. 3 can be adopted for this system as a good approximation,[13)]

$$\left(\frac{\partial\ln f_1}{\partial C_2}\right)_1 = \left(\frac{\partial\ln f_2}{\partial C_1}\right)_2 \tag{3}$$

Eq. 2 is reduced to:

$$-\left(\frac{\partial\gamma}{RT\partial\ln C_1}\right)_2 = \Gamma_1\left\{1-\left(\frac{\partial\ln f_1}{\partial\ln C_2}\right)_1\right\} \tag{4}$$

since $C_1/C_2\ll1$, *e.g.* $C_1\leq5.5\times10^{-5}$ and $C_2\geq4.0\times10^{-2}$ mol/l in this study. Tajima *et al.* have reported the following empirical relation from a study on the salting-in effect of urea upon the adsorption of $D(EO)_6$:[1)]

$$\Gamma_D = -\frac{4.5\times10^{-11}}{\Delta}C_u^{0.15} \tag{5}$$

where Γ_D is the surface excess of $D(EO)_6$, C_u ($=C_2$) the concentration of urea and $\Delta=(\partial\ln f_1/\partial\ln C_2)_1$. Substituting Eq. 5 into Eq. 4, we finally obtain

$$\Gamma_1 = -\left(\frac{\partial\gamma}{RT\partial\ln C_1}\right)_2 - 4.5\times10^{-11}C_2^{0.15} \tag{6}$$

The Γ_1 value in Eq. 6 may be calculated from the data in Fig. 1 at constant concentration, C_2. The calculated and observed values for Γ_1 at various urea concentrations are shown in Table 1, where Γ_1 is compared at 4.0×10^{-5} mol/l for C_1 in the region of saturated adsorption. The values of Γ_1 calculated using Eq. 6 are in good agreement with the observed results. Therefore, it is seen that the adsorption of $D(EO)_6$ in the urea solution takes place according to the relation expressed by Eq. 6, which has a term which is a function of C_2.

Adsorption of Urea. Urea adsorption on the

TABLE 1. COMPARISON OF THE CALCULATED AND OBSERVED VALUES OF $D(EO)_6$ ADSORPTION AT VARIOUS UREA CONCENTRATIONS ($C_1=4.0\times10^{-5}$ mol/l)

C_2 mol/l	δ[a)] mol/cm² $\times10^{10}$	$-\left(\frac{\partial\gamma}{RT\partial\log C_1}\right)_2$ mol/cm² $\times10^{10}$	$\Gamma_1^{\mathrm{calcd}}$ mol/cm² $\times10^{10}$	Γ_1^{obsd} mol/cm² $\times10^{10}$
0	0	2.72	2.72	2.73
0.040	0.277	2.60	2.32	2.41
0.40	0.392	2.48	2.09	2.09
4.0	0.554	2.09	1.54	1.57

a) See Eq. 10′.

nonionic adsorbed monolayer may be expected from the isotherms in Fig. 2. Sears has reported[2)] that urea adsorption for a constant molecular area of a stearic acid monolayer occurs roughly in proportion to the concentration of urea in the solution. In the case of an adsorbed monolayer, the constant molecular area (constant $D(EO)_6$ density on the surface) corresponds to a constant value of Γ_1 in Fig. 2, because of the very dilute solution for C_1. Therefore, urea adsorption in the adsorbed monolayer may be estimated using a relationship between the surface tension and bulk concentrations of urea and $D(EO)_6$ such that a constant value of Γ_1 is maintained. Differentiating Eq. 1 applied to this system with respect to the logarithmic concentration of urea, we have at constant Γ_1,

$$-\left(\frac{\partial\gamma}{RT\partial\ln C_2}\right)_{\Gamma_1}=\left\{\left(\frac{\partial\ln f_1}{\partial\ln C_2}\right)_{\Gamma_1}+\left(\frac{\partial\ln C_1}{\partial\ln C_2}\right)_{\Gamma_1}\right\}\Gamma_1+\left\{1+\left(\frac{\partial\ln f_2}{\partial\ln C_2}\right)_{\Gamma_1}\right\}\Gamma_2. \tag{7}$$

Since $C_1/C_2 \ll 1$, $(\partial \ln f_2/\partial \ln C_2)_{\Gamma_1}$ may be replaced by that for a simple aqueous solution of urea. From the empirical data for the osmotic coefficient of a urea solution[14)] and Bjerrum's equation,[15)] we have

$$\frac{\partial\ln f_2}{\partial\ln C_2}=-0.046C_2.$$

Also, from the Gibbs-Duhem equation for the solutes in the bulk solution and assuming Eq. 3, we have

$$\left(\frac{\partial\ln f_1}{\partial\ln C_2}\right)_{\Gamma_1}=\left\{1-\left(\frac{\partial\ln C_1}{\partial\ln C_2}\right)_{\Gamma_1}\right\}\left(\frac{\partial\ln f_1}{\partial\ln C_2}\right)_1. \tag{9}$$

Combining Eqs. 5, 7, 8 and 9, we have

$$\Gamma_2=\frac{1}{1-0.046C_2}\left[-\left(\frac{\partial\gamma}{RT\partial\ln C_2}\right)_{\Gamma_1}+\delta\left\{1-\left(\frac{\partial\ln C_1}{\partial\ln C_2}\right)_{\Gamma_1}\right\}-\Gamma_1\left(\frac{\partial\ln C_1}{\partial\ln C_2}\right)_{\Gamma_1}\right] \tag{10}$$

where

$$\delta = 4.5\times10^{-11}C_2^{0.15}. \tag{10'}$$

The relations between the surface tension and urea concentration, and C_2 vs. C_1 at constant Γ_1 are shown in a and b of Fig. 3. The amount of urea adsorbed, Γ_2, calculated using Eq. 10 with 1.4×10^{-10} mol/cm² for Γ_1 is shown in Table 2.

The increasing urea concentration in the solution enhances the urea adsorption at the adsorbed monolayer of a nonionic surfactant, the same as in the case of a stearic acid monolayer.[2)] However, there are some essential differences pertinent to urea adsorption in these monolayers. The amount of adsorbed urea for an insoluble monolayer may be the absolute amount, but this is not the case for adsorbed monolayers, as expressed by Eq. 10. Namely, the last term in Eq. 10 represents the amount of urea accompanying the Γ_1 amount in proportion to the composition ratio of solutes in the bulk phase (here $\partial C_1/\partial C_2$ is almost constant), which is similar to the concept for the Gibbs adsorption.[7)] Since urea itself is a surface inactive substance, it is easily deduced that Γ_2 is the difference in amounts of urea accumulated in the poly(oxyethylene) chain of the nonionic surfactant on the surface and in the bulk phases.

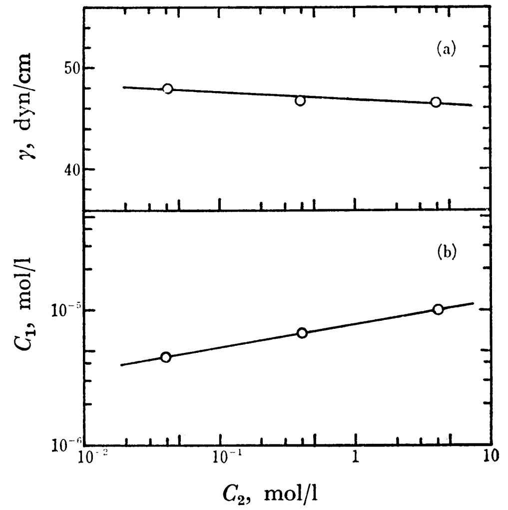

Fig. 3. Surface tension and bulk concentrations of solutes so as to maintain a constant adsorption of $D(EO)_6$ (1.4×10^{-10} mol/cm²).
(a): Surface tension vs. concentration curve of $D(EO)_6$.
(b): Relationship of C_1 and C_2.

Table 2. Adsorption of urea onto the adsorbed $D(EO)_6$ monolayer under various conditions

C_1 mol/l × 10^5	C_2 mol/l	Area of $D(EO)_6$ A²/molecule	Urea adsorption mol/cm² × 10^{10}
0.45	0.040	118.6	0.90
0.70	0.40	118.6	1.01
1.0	4.0	118.6	1.39
4.0	0.040	38.9	0.06
4.0	0.40	79.4	0.06
4.0	4.0	105.7	−0.61

The Γ_2 value at the saturated adsorption region of $D(EO)_6$ (C_1 is maintained constant at 4.0×10^{-5} mol/l) at various urea concentrations is cited in Table 2. The calculation of Γ_2 in this case were performed using Eq. 11, which was derived in the same manner as in a previous paper,[16)] assuming $C_1/C_2 \ll 1$ and $(\partial \ln f_1/\partial \ln C_1)_2 \approx 0$, as

$$\Gamma_2=\left(-\frac{\partial\gamma}{RT\partial\ln C_2}\right)_1-\left(\frac{\partial\ln f_1}{\partial\ln C_2}\right)_1\left(-\frac{\partial\gamma}{RT\partial\ln C_1}\right)_2 \tag{11}$$

where $(\partial \ln f_1/\partial \ln C_2)_1$ was deduced from Eq. 5, and the value of $(\partial\gamma/\partial \log C_2)_1$ was obtained from the curve in Fig. 4. The value of Γ_2 in the saturated adsorption region is almost zero at low urea concentrations, but is negative in 4.0 mol/l urea solutions. This property of urea adsorption can be explained by that at low urea concentrations, the accumulation of urea at the poly(oxyethylene) group of adsorbed nonionic surfactant is almost the same as that in the bulk phase, however, at high urea concentrations, it decreases in comparison with that of urea in the bulk solution owing to a squeezing from the poly(oxyethylene) group with the lateral cohesive force of hydrocarbon chains of adsorbed molecules at the surface. A similar phenomenon, which occurs when the surface density of a surface active material increases at constant urea concentration, is

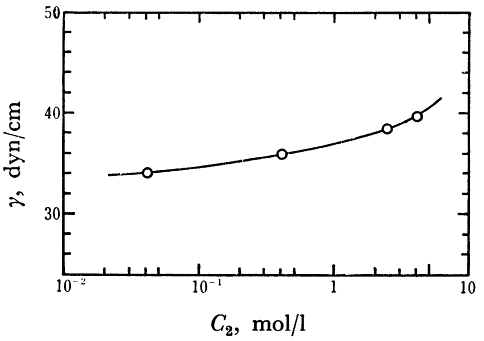

Fig. 4. Surface tension *vs.* concetration curve of urea at constant concentration of $D(EO)_6$ (4.0×10^{-5} mol/l).

observed not only in stearic acid monolayers,[2)] but also in adsorbed monolayers at concentrations above the CMC value as described in the following section.

The Effect of Urea on Micelle. In the preceding section it was stated that urea adsorption occurs at adsorbed monolayers of $D(EO)_6$. However, above the CMC(0) value in the surface phase, urea appears to be forced out from inter-poly(oxyethylene) chains to below the $D(EO)_6$ monolayer as expected from the findings shown in Fig. 2. The micelle in the bulk solution is generally considered to attain the following equilibrium relation with the single species:[17)]

$$\underset{\text{(single)}}{nA} \rightleftharpoons \underset{\text{(micelle)}}{A_n^M},$$

where n is the micelle aggregation number, A the single molecule and the superscript M denotes the micelle. In urea–nonionic solutions, the following processes for micellization are proposed:

$$nA + n \cdot mU \rightleftharpoons n(AUm) \rightleftharpoons [(AUm)_n^M] \rightleftharpoons A_n^M + n \cdot mU,$$

where m is conventionally constant, AUm the single molecule of nonionic surfactant ureanized, and $(AUm)_n^M$ the urea-penetrated micelle. If bound urea is squeezed out from the interior of micelle toward the outside, it may be considered to be almost the same as the $D(EO)_6$ micelle in the absence of urea. The micelle penetrated urea, which would be enclosed in either the hydrocarbon moiety and poly(oxyethylene) group or only the head group, is likely, if present, to be unstable due to the occurence of weak break points on the surface tension *vs.* concentration curves in Fig. 1 and also from the peculiar isotherms in Fig. 2. Schick *et al.*[18)] have observed that the aggregation number of α-(*p*-nonylphenyl) - ω - hydroxypentadeca(oxyethylene) micelle slightly increases with the presence of urea in the solution, and suggested that the marked increments in the CMC values of α-alkyl-ω-hydroxypoly(oxyethylene) solutions are caused by a decrease in the cooperative structure of water.[5)] According to Schik's suggestion, Hammes and Schimmel[6)] predicted, from the results of the ultrasonic attenuation measurements in aqueous urea–poly(oxyethylene) glycol solutions, that the change in local solvent structure could involve a cooperative binding of urea to the poly(oxyethylene) group in solution. To elucidate this possibility of urea behavior in the micelle solution, the elusion volume of micelle, which is closely dependent on the micelle size,[19)] was measured from the gel permeations of the micelle solution with and without urea. The results obtained are cited in Table 3. No large difference in elusion volume was observed at a urea concentration of 2.5 mol/l. Consequently, it is considered that the micelle size is not affected by the presence of urea.

Table 3. Elusion volumes of micelle and single species of $D(EO)_6$ solutions with and without urea

(A) Water			(B) 2.5 M of urea		
C_1 mol/l $\times 10^5$	Micelle ml	Single species ml	C_1 mol/l $\times 10^5$	Micelle ml	Single species ml
4.4	—	17.0	4.4	—	17.0
6.6	—	17.0	6.6	—	16.6
7.7	5.5	17.0	7.7	—	17.5
8.25	5.2	17.5	8.25	—	17.0
9.9	5.5	17.3	11.0	—	16.8
11.0	5.2	17.2	15.4	5.4	17.0
13.2	5.3	17.0	18.7	5.6	17.0
			20.6	5.5	17.2
			22.0	6.0	17.5

Muller *et al.*, who studied the effects of additives on aqueous sodium ω,ω,ω-trifluorododecyl sulfate (F_3-SDS)[20)] and α-(ω,ω,ω-trifluorododecyl)-ω-hydroxyhexa(oxyethylene)[21)] solutions by the fluorine NMR method, have reported that the micelle chemical shifts with the presence and absence of urea in the solutions are about half (the R value in Ref. 20 is about 0.5), in comparison with those for single molecules. Though the aggregation number of nonionic micelle could not be determined and that of F_3SDS micelle was rather reduced with the presence of urea, they maintain that the urea, glycerol and glycine additives should be nonpenetrating in nonionic micelle. These results are in good agreement with the result for gel permeation and support the proposed mechanisms for micellization in urea–nonionic solutions.

The findings of the present studies and FNMR spectra may lead to the conclusion that the micelle of $D(EO)_6$ solutions with urea is almost the same as that of solutions without urea. If no urea entered into the micelle entity, none could be incorporated in the adsorbed monolayer, thermodynamically equilibrated with the micelle in bulk solution.

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