Radiotracer Studies on Adsorption of Surface Active Substance at Aqueous Surface. IV.

Direct Measurement of Adsorption of Tritiated Nonionic Surfactant

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The radio- and surface-chemically pure nonionic surfactant, $C_{10}H_{21}(CHT)_2O(C_2H_4O)_6H$, was synthesized, and surface tension and adsorbed amount of its aqueous solution were measured directly at the air-solution interface at 30°C. Surface tension was measured by the drop-volume and Wilhelmy plate methods, while adsorbed amount was measured by the radiotracer method. The adsorption isotherm showed saturation values of 2.73×10^{-10} mol/cm^2 above the concentration of about 1/5 of the critical micelle concentration. The observed amount of adsorption was in good agreement with the values calculated from surface tension data measured by the Wilhelmy plate method by applying the Gibbs adsorption isotherm for a single solute system. The time dependence of surface tension of surfactant solution was further discussed, and the inherent time dependence was shown for pure surfactant solution.

Although the surface and bulk properties of the aqueous solution of nonionic surfactant have been studied by many investigators,[1-3] most of them have referred to surfactants of wide homologous distribution. As has been pointed out in a previous paper on adsorption of ionic surfactant,[4] the exact knowledge of adsorption is very important for understanding various phenomena at the air-solution interface. If the radiotracer method using tritiated nonionic surfactant is adopted, the adsorption on aqueous surface can be measured with high accuracy as in the case of ionic surfactant.[5]

In the present paper, tritiated hexaoxyethylenedodecyl ether (3,6,9,12,15,18-hexaoxa-1-triacontanol-19,20-^3H,^3H; TD(EO)$_6$) was synthesized, and the adsorbed amounts were measured directly at the surface of its aqueous solution by the radiotracer method. The time dependence of the surface tension of this solution was further measured, and the drop-volume and Wilhelmy plate methods were compared with regard to the reliable surface tension value applicable for the Gibbs adsorption isotherm.

Experimental

Materials. TD(EO)$_6$ was synthesized according to the following schema, the details of which will be reported elsewhere.[6] First, tritiated dodecanol (I) was synthesized by the tritiation of dodecenol,[7] and its chemical and radiochemical purities were checked. By the bromination of (I) with hydrogen bromide, tritiated dodecyl bromide was obtained. The product was condensed with trioxyethylene monoalcoholate (II) in the nitrogen atmosphere at about 200°C. The condensation product was extracted with ether and the extract was distilled at 187°C/2 mmHg to give tritiated trioxyethylenedodecyl monoether (III). After chlorination of (III) with thionyl chloride, the product was again reacted with (II) to form TD(EO)$_6$. The crude TD(EO)$_6$ was purified by distillation to remove as completely as possible the lower boiling substances up to about 200°C/2 mmHg. Then the residue was recrystallized repeatedly from absolute hexane at 5—7°C and finally by the chromatography on neutral alumina using mixed solvent of acetone : benzene : methanol in 25 : 24 : 1 volume ratio. Both melting point (25.1°C) and refractive index (n_D^{40} 1.4480) agreed with the published values of 24.9°C and 1.4479, respectively.[8] The surface chemical purity of TD(EO)$_6$ obtained was confirmed by the critical micelle concentration (CMC) determined from a sharp break point of the surface tension *vs.* concentration curve being in agreement with literature value.[9] Water was triply distillated using borosilicate glass apparatus, after being refluxed overnight with the mixture of sulfuric acid and potassium permanganate.

Method and Procedures. The method and apparatus for the measurements of adsorption by a radiotracer technique were previously described in details.[5] The total radioactivity, A_1, on the surface of TD(EO)$_6$ solution which had attained the surface tension equilibrium, and the bulk radioactivity from the interrior of solution, A_2, were measured by a sheet scintillation counter. Radioactivity due to the adsorbed molecules, A_1-A_2, was multiplied by a conversion factor to obtain the amount of adsorption.[5] The surface tension of solution was measured by the drop-volume and Wilhelmy plate methods. In the former method, time required to form each drop was about 5 min. In the latter method, the change of surface tension was automatically recorded up to 24 hr. All measurements were carried out in the atmosphere of saturated humidities in order to prevent the evaporation from the surface of solution. The surface tension of pure water remained constant within the error of ±0.5 dyn/cm for 24 hr. The temperature was maintained at 30±0.2°C.

Results and Discussion

Stability of Aqueous Solution of TD(EO)$_6$. It is well known[10] that the ionic surfactant, for instance

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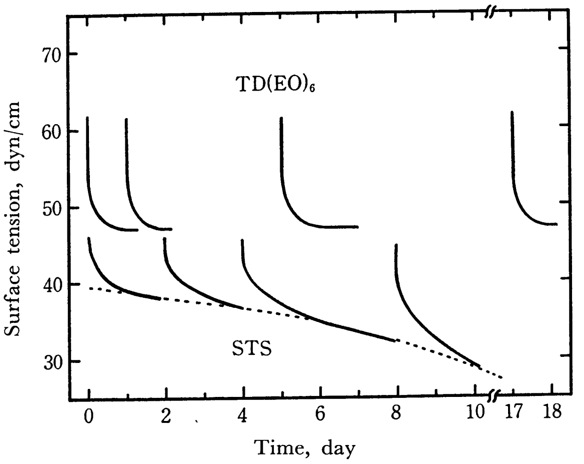

Fig. 1. Time dependence of surface tension for aqueous solution of TD(EO)$_6$ and STS at 30°C.
Upper curves: TD(EO)$_6$, (5.0×10^{-6} M)
Lower curves: STS, (1.0×10^{-3} M)
Broken line: progress of bulk hydrolysis

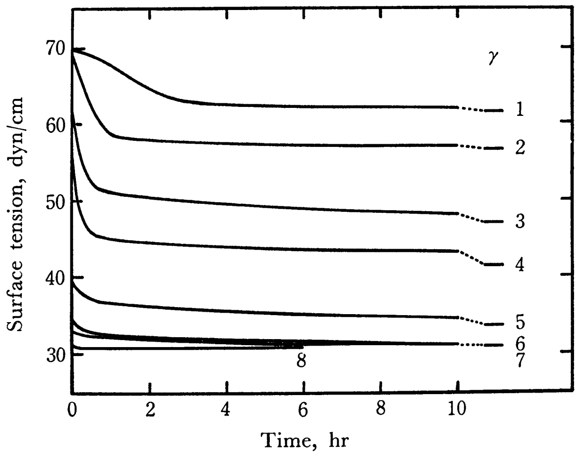

Fig. 2. Time dependence of surface tension of TD(EO)$_6$ solution at 30°C.
γ: equilibrium surface tension.
Concentration of TD(EO)$_6$ (10^{-5} mol/l),
1: 0.020 2: 0.125 3: 0.500 4: 1.00
5: 3.50 6: 5.00 7: 7.50 8: 50.0

sodium tetradecyl sulfate (STS), is readily hydrolyzed in aqueous solution, which has been stocked over 24 hr at room temperature. On the contrary, it is expected that the nonionic surfactants such as polyoxyethylene (EO) alkyl ether consisting of ether bonds, might be more stable in aqueous solution than surfactants having ester bonding like STS. We examined the stability of the aqueous solution of these substances by tracing the time dependence of the surface tension. The results are shown in Fig. 1. The measurements were made for four aqueous solutions of STS and TD(EO)$_6$, successively taken from the respective stock solutions at proper time intervals. In the case of STS, surface tension exhibited a nearly same initial value, and it gradually decreased during the period of 24 hr tending to run along a common broken line, showing no tendency to arrive at equilibrium. The slow decrease of surface tension expressed by the broken line is the indication of hydrolysis taking place in the bulk of the stock solution. On the contrary, surface tension of TD(EO)$_6$ solutions reached to the identical final value after about 24 hr, and the value remained constant even after 17 days. The molecules of TD(EO)$_6$ are chemically stable in aqueous solution which may be stored unchanged for about two weeks at least.

Surface Tension Measurements. Figure 2 shows the typical examples of a time dependence of surface tension for TD(EO)$_6$ solution, where γ shows the equilibrium surface tension. Equilibrium surface tension thus obtained is plotted against the concentration in Fig. 3. The values measured by the drop-volume method are also shown in the same figure for comparison. The surface tension data obtained by the drop-volume method are considerably higher than those by the Wilhelmy plate method. This is due to the slow decrease of surface tension with time, which is pronounced in the dilute solutions. This time dependence also makes the measurement of equilibrium surface tension difficult especially by the drop-volume method. The critical micelle concentration measured by the drop-volume method, CMC′$=8.3\times10^{-5}$ mol/l, is shifted to the higher concentration than that by the Wilhelmy plate method, CMC$=5.2\times10^{-5}$ mol/l. Since the CMC value obtained by the Wilhelmy plate method is more reliable, above discrepancy indicates the fact that the relaxation of surface tension up to about 1 hr is observed even above the CMC up to the concentration of 8.3×10^{-5} mol/l. Since TD(EO)$_6$ exhibits considerable surface activity and considerably lower CMC than STS, a marked time dependence can be expected not only for the solution below the CMC, but also for the solution slightly above the CMC. The latter case may be due to the adsorbing surfactant molecules not being supplied instantaneously from the micelles.

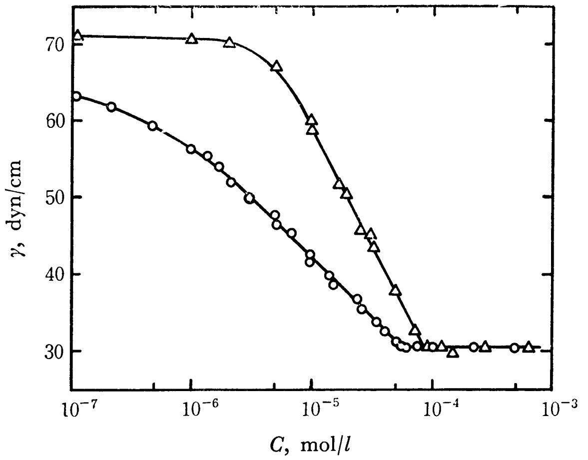

Fig. 3. Surface tension *vs.* concentration of TD(EO)$_6$ solution at 30°C.
○: Wilhelmy plate method
△: drop-volume method

Adsorption Measurement. The adsorption isotherm obtained is shown in Fig. 4. It is found that there is a range of constant adsorption (2.73×10^{-10} mol/cm^2) above the concentration of about 1/5 of the

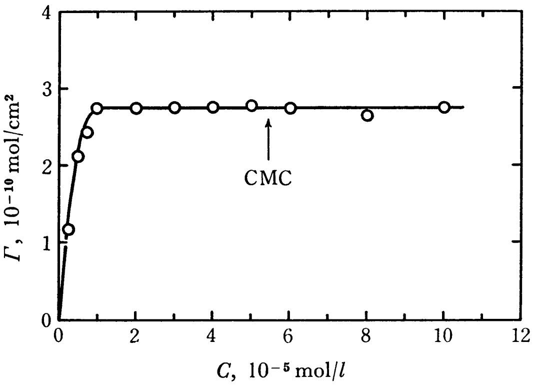

Fig. 4. Adsorption isotherm of TD(EO)$_6$ solution at the air-solution interface at 30°C.

CMC similar to the adsorption isotherm of ionic surfactant with[11] and without[5] salt.

The cross-sectional area per molecule is 60.8 Å^2 in a region of saturated adsorption as shown in Fig. 4. From this value, it is possible to deduce some knowledge concerning the hydrophilic group in the state of adsorption. If the EO groups of the surfactant are in the state of random coil, the relation between the cross-sectional area, S, and the number of EO groups, n, of the molecule is expressed by $S = \pi a^2 n^{2/3}$, where a is a radius of an EO group coil, assumed to be spherical. From the values of $S = 60.8$ Å^2 and $n = 6$, a cross-sectional area, πa^2, of ethylene glycol group of dodecyl ether is calculated as 18.4 Å^2. This value is very close to the limiting area per molecule, 19.5 Å^2, of ethylene glycol monooctadecyl ether spread at the air-water interface.[12] This confirms the view that the hydophilic groups of polyoxyethylenedodecyl ether are practically in the form of random spherical coils in the adsorbed state. From the measurements of hydration for nonionic surfactant possessing long polyoxyethylene groups, Schott[13] also considered them to be in the form of random coils surrounding the hydrocarbon core of the micelle. Thus, it seems that the EO groups are in a similar state of random coil of close mutual contact both in the state of micelle in the solution and in the state of saturated adsorption at the air-solution interface.

Gibbs Adsorption Isotherm. The experimental confirmation of the Gibbs adsorption isotherm has already been made for aqueous solution of ionic surfactant.[4,5,11] However, in applying the Gibbs isotherm to the solution of ionic surfactant, we have made some non-thermodynamical assumptions such as no hydrolysis in the bulk and surface phases, and the electrical neutrality at the surface for adsorbed species. However, since the aqueous solution of nonionic surfactant does not require such non-thermodynamical assumptions, it seems a most favorable system for applying the Gibbs adsorption isotherm.

The Gibbs adsorption isotherm, for a solution of single solute without any bulk hydrolyses, is expressed as follows;

$$-\mathrm{d}\gamma = \Gamma \boldsymbol{R}T\,\mathrm{d}\ \ln C \qquad (1)$$

where γ denotes the equilibrium surface tension, Γ, surface excess and C, concentration of solute. Since the concentration of surfactant used is less than 10^{-4} mol/l, the term of activity coefficient may safely be considered as unity. The adsorbed amounts, calculated from the data of Fig. 3 by applying Eq. (1), are shown by solid lines A and B in Fig. 5. The results calculated from data of surface tension (drop-volume method) *vs.* concentration, measured with the same surfactant by Corkill *et al.*[9] were also shown in the same figure, for comparison. It was seen that the values observed by a radiotracer method are in good agreement with those calculated from the data of the Wilhelmy plate method and not with those from the drop-volume method. Although the values of C and D, which were calculated from the carefully measured data of Corkill *et al.*, are closer to the observed value than that of A, still they are distinctly higher than the observed value. The mean value of C and D, 3.25×10^{-10} mol/cm^2, considered as the value at 30°C, is about 20% higher than the observed value. Therefore, disagreement of the values obtained from the drop-volume method can be ascribed to the application of non-equilibrium surface tension to the Gibbs adsorption isotherm. The deviation of calculated (Wilhelmy) and observed values in concentration below 1×10^{-5} mol/l in Fig. 5, although slight, may be due to the uncertainties for the measurements, of surface tension in extremely low concentration, even for a prolonged measurement of time dependence of surface tension by the Wilhelmy plate method.

A satisfactory agreement between calculated and observed values indicates the validity of the Gibbs adsorption isotherm in the case of ionic surfactant solution.[4,5,11] However, it is important to apply sur-

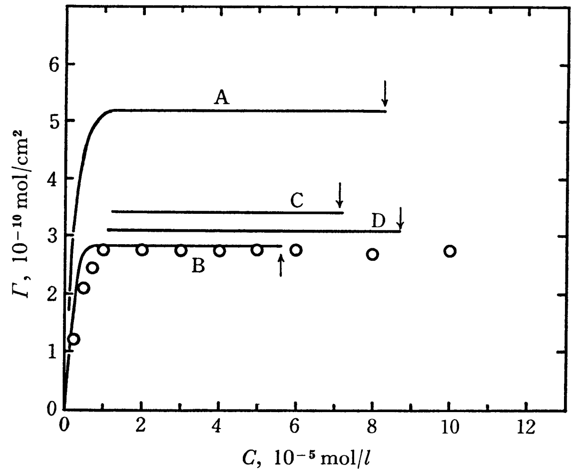

Fig. 5. The test of Eq. (1).
○ : observed value
——: calculated value using data of
(A) drop-volume method (30°C)
(B) Wilhelmy plate method (30°C)
(C) drop-volume method (Corkill, 35°C)
(D) drop-volume method (Corkill, 25°C)
Each arrow shows the CMC.

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face tension values completely in equilibrium, which should be appreciated especially when the time dependence is marked as in the case of polymer surfactant. Also, it should be emphasized that surface tension often deviates largely from the equilibrium value according to the method of measurement as shown in Fig. 3.

Time Dependence of Surface Tension of Surfactant Solution. Corkill *et al.*[9] reported that, with the solution of same surfactant as in the present studies, the equilibrium surface tension is reached almost instantaneously at concentration below the CMC. Razouk and Mysels,[14] in the experiments on film elasticity and surface relaxation, noted reduced increases in the equilibrium surface tension after extensive purification of sodium dodecyl sulfate by foaming, but could not eliminate observed relaxation times of up to 10 min duration. They considered that the relaxation suggested the last traces of impurity not being removed from the system even after the purification by foaming.

In contrast to these statements, slow decrease of the surface tension of pure aqueous surfactant solution has been reported with regard to the solution of hexaoxyethylenedecyl ether,[15] or hexaoxyethylene-hexadecyl ether.[16] Also, in the present study, a remarkable time dependence was observed as shown in Fig. 2. Now, there are many reasons to believe that the surface relaxation or the surface tension aging of surfactant solution appears not only in the surfactant solution containing the surface-active impurity, but also in the solution of pure surfactant.

According to the Gibbs adsorption isotherm applied for the solution containing several independent solutes, Eq. (1) gives the total amounts of adsorption of these solutes.[17] Therefore, the calculated amount of adsorption shown as solid line B in Fig. 5 indicates a sum of the amount of adsorption of TD-$(EO)_6$ and that of impurities if any. Then, the coincidence of these values with the observed amount of adsorption which corresponds exclusively to radiometrically determined tritium labelled species of $TD(EO)_6$ may be taken as the experimental evidence of the absence of the adsorption of any surface-active impurities. The surface tension decrease with time as shown in Fig. 2 cannot be explained merely by the presence of surface-active impurities as Mysels stated.[18] Further, if the surface relaxation is produced only by the presence of impurity, then the equilibrium surface tension of the solution may not be equal to that of pure surfactant. The "true" surface tension, which the solution of pure surfactant might show, can be obtained by adding the surface tension decrease produced by the impurity to the steady value of surface tension attained after long time, provided that the effect of impurity on the surface tension is additive as Mysels postulated.[18] The surface tension value thus obtained which is practically equal to the surface tension extrapolated to time zero in Fig. 2, is applied to Eq. (1), but adsorbed amount obtained deviated even more largely from the observed value than that calculated from the value of drop-volume method. Therefore, additive effect of impurity on the surface tension is not sufficient to elucidate the time effect.

The explanation of relaxation of surface tension by the existance of impurity cannot exclude the possibility of an inherent time effect attributable to the pure aqueous surfactant solution. In fact, we cannot find any report which distinctly shows the surface tension of aqueous surfactant completely independent of time for all concentrations. On the contrary, many investigators rather believe the inherent relaxation in surface tension of aqueous surfactant solutions, and have proposed several empirical formula expressing surface tension *vs.* time relation or giving equilibrium surface tension by the extrapolation of time to infinity.[19]

Thus, it is certain that aging of surface tension does occur even in aqueous surfactant solution of sufficient purity to show a negligible amount of impurity adsorption.

The authors wish to thank the Ministry of Education for the financial support granted for this research.

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