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Adsorption of Sodium and Calcium Dodecyl Sulfates at the Surface of Their Aqueous Solutions

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Adsorption of sodium dodecyl sulfate (NaDS) and calcium dodecyl sulfate ($Ca(DS)_2$) at the aqueous surface was measured by a radiotracer method using tritium labelled compounds at constant ionic strength of 1×10^{-2} and 7.5×10^{-3} adjusted by the addition of NaCl and $CaCl_2$, respectively. The adsorbed amounts increased with increasing concentration of dodecyl sulfates in both cases, and approached saturation values of 3.65×10^{-10} mol/cm² at 25°C for NaDS and 3.8×10^{-10} mol/cm² at 55°C for $Ca(DS)_2$. The amounts calculated from surface tension data by applying the Gibbs adsorption isotherm were confirmed to be in good agreement with the values directly measured. The adsorbed amounts of chloride ion, generally assumed to be zero, were confirmed to be negligible in the concentration region from zero up to critical micelle concentration.

Numerous investigations have been reported on the study of surface active substance at air-solution interface with the purpose of examining the applicability of the Gibbs adsorption isotherm under various conditions.[1–5] However, there are only a few discussions based on the direct measurement of surface excess, especially for well defined plane aqueous surface.[5–8]

In the previous studies,[6,8] the Gibbs adsorption isotherm $-d\gamma=nRT\Gamma d\ln a$ was confirmed to hold for the adsorption from aqueous solution of NaDS with $n=2$ for salt free solution, and with $n=1$ for the solution containing excess salt. Several workers have studied the adsorption of ionic surfactant solution at constant ionic strength[2,4,9,10] and eliminated activity coefficients from the Gibbs adsorption isotherm.

In the present study, we have carried out direct measurements of adsorbed amounts of tritiated NaDS and $Ca(DS)_2$ at aqueous interface, and at constant ionic strength by a radiotracer method. Measurements of surface tension were also carried out under the same conditions. From the results the validity of the Gibbs adsorption isotherm at constant ionic strength was checked.

Experimental

Materials. Sodium dodecyl-2,3-t_2 sulfate (TNaDS) was prepared as previously reported.[11] Dodecan-2,3-t_2-1-ol used for the preparation was confirmed to be chemically and radiochemically pure by radiogaschromatography. Calcium dodecyl-2,3-t_2 sulfate ($TCa(DS)_2$) was also synthesized in the same manner as TNaDS from dodecan-2,3-t_2-1-ol, except for the neutralization of dodecyl sulfuric acid by $Ca(OH)_2$. Both surfactants were carefully recrystallized from ethanol and subjected to Soxhlet extraction using ethyl ether for 48 hr to remove unreacted tritiated dodecanol and other surface active impurities. Specific activity of the substances obtained was 16 Ci/mol. Both surfactants were further confirmed to be free from surface active impurities as judged from the absence of minimum in surface tension *vs.* concentration curves. Triply distilled water was used.

Procedure. Ionic strengths of TNaDS and $TCa(DS)_2$ solutions used were kept constant at 1.0×10^{-2} and 7.5×10^{-3} respectively, by diluting 1.0×10^{-2} mol/*l* TNaDS with NaCl solution of the same concentration and 2.5×10^{-3} mol/*l* $TCa(DS)_2$ with $CaCl_2$ solution of the same concentration. Radioactivity of tritiated dedecyl sulfate solution was meas-

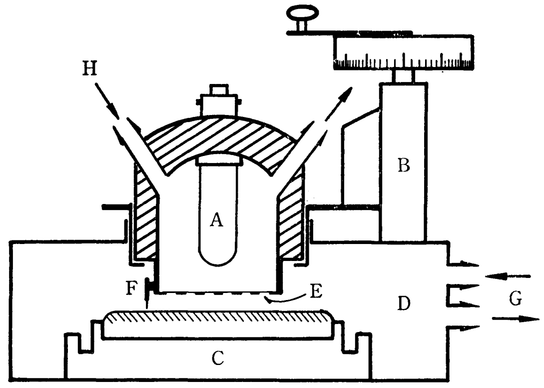

Fig. 1. Thin-window gas-flow GM counter for adsorption measurement.
A: GM counter
B: elevator
C: cell
E: polycarbonate thin film window
F: needle point
G: N_2 gas
H: counting gas (Q-gas)

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[12] K. Tajima, This Bulletin, **44**, 1767 (1971).

ured by using a gas-flow GM counter[13] equipped with a thin film (polycarbonate) window as shown in Fig. 1. A counter tube A can be raised or lowered by the rack and pinion device B. Surfactant solution was contained in a polyethylene cell C, 70 mm in diameter. The distance constant to 0.70±0.02 mm by means of electrical contact of the aqueous surface with the point of a needle F fixed to the GM tube. To avoid the effect of carbon dioxide from the surrounding atmosphere, nitrogen gas, well humidified by passing through a glass tube of 6 m in length packed with wet glass wool was slowly introduced and allowed to leak from the chamber D. During the course of measurement, gas flowing was stopped in order not to disturb the solution surface. The whole apparatus was placed in a thermostated glove box filled with humidified nitrogen gas.

After standing both the cell and dodecyl sulfate solution for about 30 min in the glove box, 25 m*l* of the solution was poured into the cell. Radioactivity of the aqueous solutions of TNaDS and $TCa(DS)_2$ was measured at 25±1°C and 55±1°C, respectively. The temperature was chosen several degrees above each Krafft point. Measurements were continued until equilibrium steady counting was obtained. Radioactivity due to the bulk of solution was measured over the surface of tritiated dodecanol dissolved in non-radioactive dodecanol as in the preceeding method[6] and was subtracted from the total radioactivity to give the radioactivity due to adsorption. To convert the radioactivity thus obtained to the amount of adsorbed surfactant, known amount of tritiated stearic acid of 9.0 Ci/mol in specific activity was spread on aqueous solution of 0.1 N H_2SO_4 using the same cell, and the surface count was measured at 25°C and 55°C for TNaDS and $TCa(DS)_2$, respectively. From the inclination of the straight line of count rate *vs.* spread amount multiplied by the ratio of specific activity of tritiated stearic acid to that of tritiated dodecyl sulfate, a conversion factor (mol cm^{-2} cpm^{-1}) was obtained. The surface count rate obtained by subtracting bulk count rate from the count rate over the aqueous solution was converted to surface excess Γ_{D^-} by multiplying it with the conversion factor. Surface tension was measured by the drop volume method applying the Harkins and Brown correction, and by the Wilhelmy plate method, both under the same conditions as in the case of the adsorption measurement.

Results and Discussion

Adsorption. The observed amounts of adsorption Γ_{D^-} were plotted against concentration C for TNaDS and $TCa(DS)_2$ as shown by open circles in Figs. 2 and 3, respectively, The value of Γ_{D^-} for TNaDS rapidly increased with increasing concentration of TNaDS and approched a saturation value of $\Gamma_{D^-}=3.65\times10^{-10}$ mol/cm^2 at the concentration of 2.5×10^{-3} mol/*l*. However, above critical micelle concentration (CMC), it gradually decreased with increasing TNaDS concentration. At the concentration of 1×10^{-2} mol/*l*, where the concentration of NaCl became zero, Γ_{D^-} decreased to 3.09×10^{-10} mol/cm^2, which is in good agreement with the former Γ_{D^-} value of the saturation amount of adsorption for the same system measured by the sheet scintillation counter[6] as shown in Fig. 2. Coincidence of both results obtained by two different methods of measurement for the same solution shows sufficient reliability of both methods and the absolute value of adsorbed amount obtained. The decrease of Γ_{D^-} above CMC is a direct indication of the effect of decrease of ionic strength or the decrease of NaCl concentration with nearly constant concentration of single dodecyl sulfate ions.[8] Thus, the increase of adsorption of dodecyl sulfate ion due to the addition of NaCl is distinct in a wide range of concentration as shown in Fig. 2. Adsorbed amount from aqueous solution of $TCa(DS)_2$ was also measured for the whole range of concentration up to CMC. It also increased rapidly with increasing concentration and arrived at a saturation value of $\Gamma_{D^-}=3.8\pm0.7\times10^{-10}$ mol/cm^2 at the concentration of 5×10^{-4} mol/*l*, which was roughly equal to the saturation value for TNaDS. Adsorption isotherm for $TCa(DS)_2$ showed fluctuation which might be due to the fluctuations of the count rate. This is inevitable since the absorption coefficient of air space between surface of the solution and window of the GM counter becomes unsteady owing to the incomplete saturation of the space with water vapor at elevated temperature. Gradual contamination of the thin film of the GM counter by radioactive substance, presumably dodecanol produced by hydrolysis of $TCa(DS)_2$ at high temperature, was also observed during the measurement. Radioactivity due to this

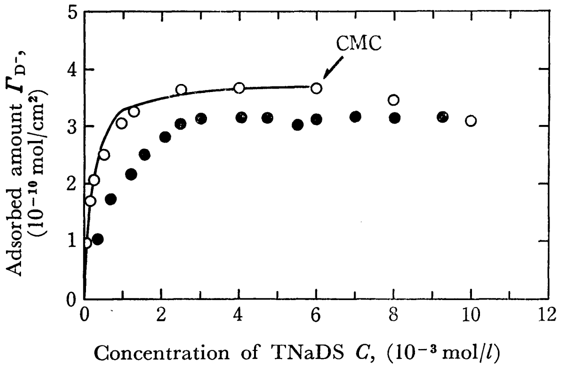

Fig. 2. Adsorption isotherm of TNaDS at constant ionic strength (25°C).
○: present study (TNaDS+NaCl$=1\times10^{-2}$ mol/*l*)
●: previous study (without added salt)
—: calculated value

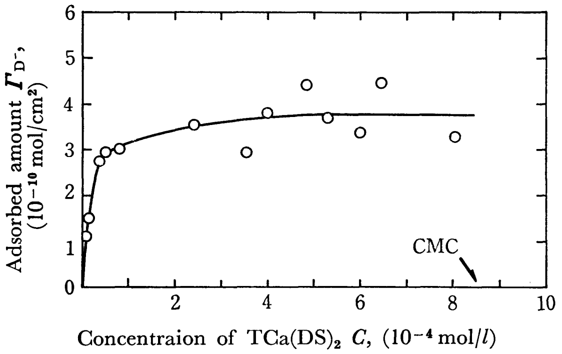

Fig. 3. Adsorption isotherm of $TCa(DS)_2$ at constant ionic strength (55°C).
○: observed value ($TCa(DS)_2+CaCl_2=2.5\times10^{-2}$ mol/*l*)
—: calculated value

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[13] T. Seimiya, K. Sekine, and T. Sasaki, *J. Sci. Instr.*, **42**, 906 (1956).

contamination was subtracted as background count rate. The water vapor absorbed and permeating through the thin film might have some influence upon the count rate observed. However, it turned out to be negligible in the present experiment.

Surface Tension. Figure 4 shows the surface tension *vs.* concentration curve for the aqueous solution of TNaDS measured by the drop volume and Wilhelmy plate methods. The surface tension obtained by the drop volume method is seen to agree with that obtained by the self-recording Wilhelmy plate method. This differs from the general tendency of the former being somewhat larger. This is due to the rapid attainment of steady surface tension exhibited by the surfactant solution in the presence of added neutral salt. The surface tension of aqueous solution of TCa(DS)$_2$ measured by the Wilhelmy plate method is shown in Fig. 5. In this case, 2 — 3 hr was required to attain equilibrium even in the presence of neutral salt, presumably due to the low concentration of both the surfactant and added salt.

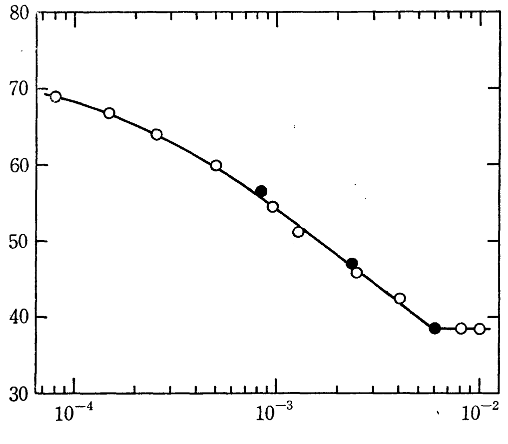

Fig. 4. Surface tension *vs.* concentration of TNaDS solution (25°C).
○: drop volume method
●: Wilhelmy plate method

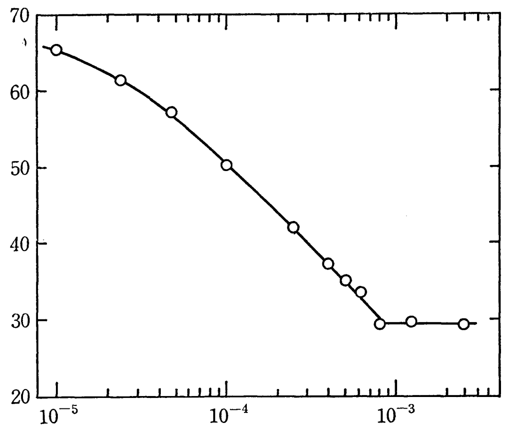

Fig. 5. Surface tension *vs.* concentration of TCa(DS)$_2$ solution (55°C).

Gibbs Adsorption Isotherm. In the present system, where the concentration of hydrogen ion is taken as constant, the Gibbs adsorption isotherm is given by

$$-\frac{\mathrm{d}\gamma}{RT} = \Gamma_{\mathrm{D}^-}\mathrm{dln}C_{\mathrm{D}^-}f_{\mathrm{D}^-} + \Gamma_{\mathrm{M}^{n+}}\mathrm{dln}C_{\mathrm{M}^{n+}}f_{\mathrm{M}^{n+}} + \Gamma_{\mathrm{Cl}^-}\mathrm{dln}C_{\mathrm{Cl}^-}f_{\mathrm{Cl}^-}, \tag{1}$$

where f's express activity coefficients, and subscripts D^-, M^{n+}, and Cl^- denote dodecyl sulfate ion, n-valent counter ion and chloride ion, respectively. Activity coefficients of the ions in aqueous solution drop for constant ionic strength and Eq. (1) is reduced to

$$-\frac{1}{RT}\left(\frac{\mathrm{d}\gamma}{\mathrm{dln}C_{\mathrm{D}^-}}\right)_{\mathrm{I}} = \Gamma_{\mathrm{D}^-} - \Gamma_{\mathrm{Cl}^-}\frac{C_{\mathrm{D}^-}}{C_{\mathrm{Cl}^-}}, \tag{2}$$

where subscript I indicates the constancy of ionic strength. The value of $\Gamma_{\mathrm{D}^-}-\Gamma_{\mathrm{Cl}^-}(C_{\mathrm{D}^-}/C_{\mathrm{Cl}^-})$ was calculated with this equation by graphically evaluating $\mathrm{d}\gamma/\mathrm{dln}C_{\mathrm{D}^-}$ from γ *vs.* $\ln C_{\mathrm{D}^-}$ plot shown in Fig. 4. The results for TNaDS are shown by a solid line in Fig. 2. Satisfactory agreement of calculated value with independently observed Γ_{D^-} might give the experimental evidence that $\Gamma_{\mathrm{D}^-}-\Gamma_{\mathrm{Cl}^-}(C_{\mathrm{D}^-}/C_{\mathrm{Cl}^-})$ is essentially equal to Γ_{D^-}, and $\Gamma_{\mathrm{Cl}^-}=0$.[12] This confirms the view that the Gibbs adsorption isotherm can be applied in the form

$$-\frac{1}{RT}\left(\frac{\mathrm{d}\gamma}{\mathrm{dln}C_{\mathrm{MD}_n}}\right)_{\mathrm{I}} = \Gamma_{\mathrm{D}^-} \tag{3}$$

in the concentration region from zero up to CMC for the TNaDS solutions containing a neutral salt with common counter ion at constant ionic strength. Thus it might be concluded that the counter ion of added neutral salt is not adsorbed regardless of the amount added in the solution as is actually indicated, and Eq. (1) is valid without the term $\Gamma_{\mathrm{Cl}^-}\mathrm{dln}C_{\mathrm{Cl}^-}f_{\mathrm{Cl}^-}$. It is worth noting that although $\Gamma_{\mathrm{Cl}^-}=0$ can readily be anticipated from a theoretical viewpoint and this assumption has been adopted by many investigators,[1,4,14] experimental confirmation is not satisfactory. So, the conclusion obtained is significant. Schwuger,[9] in his study of adsorption of divalent metal tetradecyl sulfate at constant ionic strength, neglected the term $\Gamma_{\mathrm{Cl}^-}(C_{\mathrm{D}^-}/C_{\mathrm{Cl}^-})\mathrm{dln}C_{\mathrm{Cl}^-}$ assuming that salt is added in excess. Actually, however, neither was the salt in excess nor the ratio $C_{\mathrm{D}^-}/C_{\mathrm{Cl}^-}$ small at CMC. It is because of the term Γ_{Cl^-} being zero at any concentration of added salt that the above calculation is justified. Schwuger insisted that at CMC the addition of salt under constant ionic strength has no effect on surfactant adsorption. However, the enhancing effect of salt on the adsorption amount of surfactant is evident as shown in Fig. 2. On close inspection, a small but distinct increase can be observed also in his Γ_{D^-}'s caused by the addition of salt at constant ionic strength, in accordance with our results.

Adsorption of TCa(DS)$_2$ was calculated from Eq.

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[14] E. J. W. Verwey and T. Th. G. Overbeek, "Theory of the Stability of Lyophobic Colloids," Elsevier, Amsterdam (1948), p. 22.

(3) by applying the data of the surface tension curve shown in Fig. 5. The values of Γ_{D^-} were plotted against the concentration of $\mathrm{TCa(DS)_2}$ with a solid line in Fig. 3. Allowing for the experimental error mentioned above, Eq. (3) can also be applied to the adsorption at aqueous surface of $\mathrm{TCa(DS)_2}$ solution. The results of the present study also confirmed experimentally the applicability of the Gibbs adsorption isotherm in the form of Eq. (3) for divalent metal dodecyl sulfate from zero concentration up to CMC. It is inferred also in this case that non-adsorption of co-ion in deriving Eq. (3) is not an assumption but the experimental fact, and Eq. (2) without the Γ_{Cl^-} term is safely applicable as is generally believed.