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Adsorption of Surface Active Substance at Aqueous Surface Using Tritium Labeled Compounds: Adsorption from Mixed Aqueous Solution of Sodium Dodecylsulfate and Dodecanol

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Adsorbed amount of sodium dodecylsulfate (SDS) and *n*-dodecanol (DOH) at the gas-solution interface of their mixed aqueous solution was directly measured as a function of bulk concentration of DOH by the radiotracer method. For this purpose the surface radioactivity of the mixed solution in which either SDS or DOH was labeled with tritium, was counted by using a 2π windowless gas-flow counter. It was found that the adsorbed amount of DOH rapidly increases with increasing bulk concentration of DOH, while that of SDS gradually decreases. The adsorption of DOH and desorption of SDS are not a simple 1 : 1 replacement. A maximum total adsorption of about 13×10^{-10} mol/cm^2, which exceeds the amount of close-packed monolayer adsorption extends over a wide range of concentration studied. It was suggested that the adsorbed film consists of mixed monolayer or double layers. The latter film is composed of mixed monolyaer of SDS and DOH with adsorbed layer of SDS beneath. The molar ratio of adsorbed amount of DOH to SDS in the surface became unity, when the ratio of the bulk concentration of DOH to SDS was about one hundredth, which shows a stronger adsorption tendency of DOH than that of SDS.

It was reported in a previous paper[1] that the soft β-rays of tritium are very useful for the measurements of the amount of adsorption of a detergent at the surface of an aqueous detergent solution. By using a tritiated SDS it has been confirmed that the amount of saturate adsorption of SDS at the aqueous surface is 5.9×10^{-10} mol/cm^2 at 20°C. In the present paper, the measurements have been extended for studying the competitive adsorption between SDS and DOH at the surface of their mixed solution. It has been reported that the addition of a small amount of alcohol causes marked changes in the surface-chemical properties of a detergent solution, such as foam stability,[2] mechanical strength of adsorbed film,[3,4] and surface tension lowering.[5] These phenomena have been explained by the preferential or mixed adsorption of alcohol for the adsorbed film of the detergent at the aqueous surface.[6] Few papers, however, deal with the direct measurement of adsorption of these components in the mixed film at gas-solution interface under the static condition.

The experiments were carried out to determine the composition of this mixed adsorbed film by the adsorption measurement of the aqueous SDS-DOH system in which either SDS or DOH was labeled with tritium.

Experimental

The tritiated samples were synthesized according to the method reported in the previous papers[1,7] which gave the product of sufficiently high purity both surface-chemically and radiochemically. The solutions were prepared by dissolving in thrice distilled water the solid mixture of the samples, which had been obtained by evaporating to dryness the ethanol solutions of TSDS (tritium-labeled SDS) and DOH or SDS and TDOH (tritium-labeled DOH) of a desired composition. The surface radioactivity was measured by a 2π windowless gas-flow counter (Aloka DC-1001) using a humidified propane gas to prevent the evaporation of solution. The detailed procedures of the adsorption measurement were described.[1] In the present study special precaution was made further for the measurement of TDOH at the surface, since it is slightly volatile even in solution,[8,9]

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[1] M. Muramatsu, K. Tajima and T. Sasaki, This Bulletin, **41**, 1279 (1968).

[2] G. Miles, J. Ross and L. Shedlovsky, *J. Am. Oil Chemists Soc.*, **27**, 286 (1950).

[3] A. G. Brown, W. C. Thuman and J. W. McBain, *J. Colloid Sci.*, **8**, 491 (1953).

[4] K. J. Mysels, M. C. Cox and J. D. Skewis, *J. Phys. Chem.*, **65**, 1107 (1961).

[5] G. Miles and L. Shedlovsky, *ibid.*, **48**, 57 (1944).

[6] K. Shinoda and J. Nakanishi, *ibid.*, **67**, 2547 (1963).

[7] M. Muramatsu and K. Tajima, *J. Labelled Compounds*, **2**, 304 (1966).

[8] J. H. Brooks and A. E. Alexander, Proceedings of the 3rd International Congress of Surface Activity, Vol. II, p. 196 (1960).

[9] G. Nilsson, *J. Phys. Chem.*, **61**, 1635 (1957).

as mentioned in the later section. The pH of the solution was in the range of 5.8—6.2, and the temperature was kept at 20±0.5°C.

Throughout the measurements, the concentration of the detergent was kept at 5.63×10^{-3} mol/1000 g solution. The value corresponds to the minimum concentration for saturate adsorption attained below the CMC (critical micelle concentration). The amounts of adsorption of SDS and DOH were measured for DOH-TSDS and TDOH-SDS systems respectively.

Results and Discussions

Mixed Solution of TSDS and DOH. The time dependence of surface radioactivity due to TSDS in the mixed solution was measured and the result is shown in Fig. 1. It is noted in this figure that the radioactivity first increases rapidly, then slowly and linearly with time after about 30—40 min. This seems to indicate both the rapid increase of adsorption towards the equilibrium and the rapid approach of counting efficiency to its steady state as mentioned previously.1) Therefore, the radioactivity in adsorption equilibrium was evaluated by extrapolating the linear portion of the curve to time zero. The adsorbed amount of SDS in the mixed solution, Γ_{SDS}, was obtained by subtracting the radioactivity due to the bulk of the solution from the counting rate obtained above and multiplying the value obtained by the specific activity.10) The value of Γ_{SDS} thus obtained is shown as a function of DOH concentration by the curve A of Fig. 2. The curve A shows the decrease in Γ_{SDS} with increasing concentration of DOH from the initial value of 5.9×10^{-10} mol/cm^2 (saturate adsorption from the solution containing SDS alone) to 2.9×10^{-10} mol/cm^2 and becomes constant beyond the DOH concentration of 8.4×10^{-4} mol/1000 g solution, where the opalesence evidently appeared in the solution. We can confirm from these facts that the amount of adsorption of SDS decreases with an increasing amount of the addition of DOH. The maximum effect appeared in the region beyond the saturation of DOH where its effective concentration became constant.

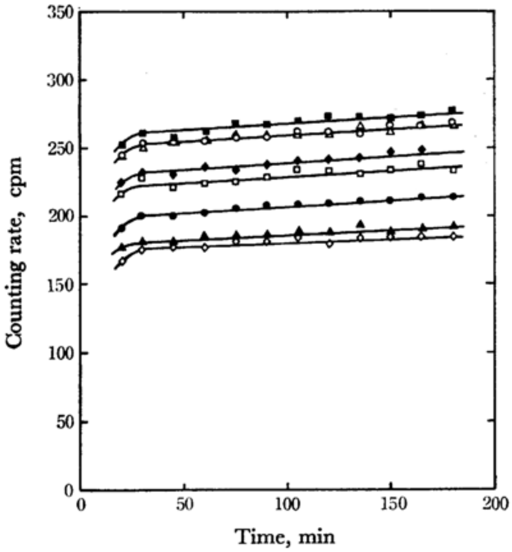

Fig. 1. Time dependence of surface radioactivity of TSDS due to adsorption of SDS from SDS-DOH mixed solution.
Concentration of SDS: 5.63×10^{-3} mol/1000 g solution.
Concentration of DOH (in mol/100 g solution):
■ 0 □ 3.61×10^{-4} △ 6.02×10^{-6}
● 6.02×10^{-4} ○ 6.02×10^{-5} ◇ 8.43×10^{-4}
◆ 2.41×10^{-4} ▲ 1.08×10^{-3}

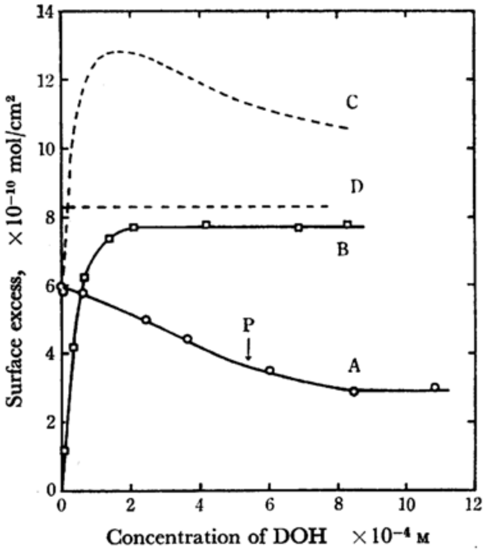

Fig. 2. Adsorbed amounts of SDS (curve A) and DOH (curve B) at aqueous surface for SDS-DOH mixed solution, as a function of DOH concentration at 20°C. Total adsorbed amount (curve C) and monolayer adsorption (curve D).

Mixed Solution of SDS and TDOH. Similar experiments as mentioned above were carried out, except for the use of tritiated DOH instead of SDS. Surface radioactivity due to TDOH in the mixed solution is shown in Fig. 3. It is seen that radioactivity decreases gradually with time over the range of DOH concentration of the mixed solution, approaching a constant value at higher DOH concentration and after sufficient lapse of time (about 90 min). This gradual decrease of radioactivity was considered to be due to the volatile

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10) G. Aniansson and O. Lamm, *Nature*, **165**, 357 (1950); D. J. Salley, A. J Weith, Jr., A. A. Argyle and J. K. Dixon, *Proc. Roy. Soc.*, **A203**, 42 (1950).

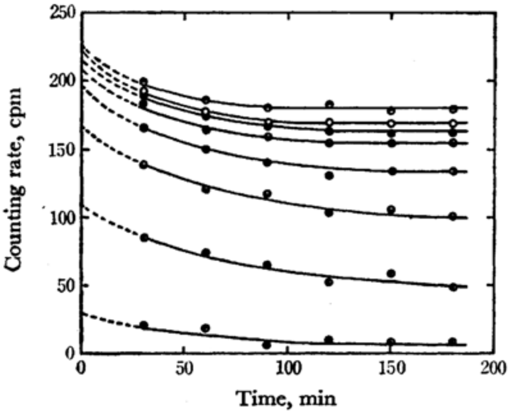

Fig. 3. Time dependence of surface radioactivity of TDOH due to adsorption of DOH from SDS-DOH mixed solution. Dotted lines show extrapolated value to zero time.
Concentration of DOH (in mol/100 g solution):
⊙ 6.86×10^{-6} ⊖ 2.06×10^{-4}
◐ 3.43×10^{-5} ● 4.12×10^{-4}
◒ 6.86×10^{-5} ○ 6.86×10^{-4}
◑ 1.36×10^{-4} ◓ 8.23×10^{-4}

nature of adsorbed DOH film at the surface.[8,11] In this connection the surface radioactivity of saturate TDOH solution without the addition of SDS is shown in Fig. 4. It is seen from Fig. 4 that surface radioactivity exhibited a similar tendency as in the case of Fig. 3. From these facts, it is presumed that the variation of surface radioactivity in Fig. 3 is partly due to the difference in adsorption rate between SDS and DOH, and partly to the evaporation of adsorbed DOH film as is shown in Fig. 4. The plateau appearing in the curve of Fig. 3 for DOH concentration of more than 2.06×10^{-4} mol/1000 g solution may be explained as a result of the dynamic equilibrium between the rate of adsorption of DOH into the surface layer from the bulk of solution and the rate of evaporation of it from the surface.

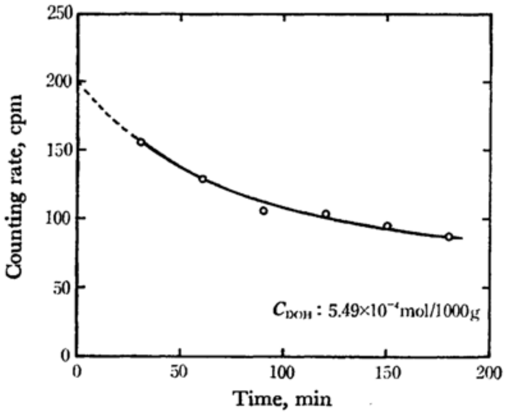

Fig. 4. Time dependence of surface radioactivity of TDOH due to the adsorption of DOH from its aqueous solution.

Thus, the value of counting rate of DOH corresponding to the equilibrium adsorption over the mixed solution was reasonably obtained by the extrapolation of the curve (as shown by the dotted line in Fig. 3). The extrapolation was made assuming an exponential decrease of the surface radioactivity (A) with time (t). The exponential relation was adopted since it was confirmed to hold fairly well for all experimental data of Figs. 3 and 4 as shown in Fig. 5. The adsorbed amount of DOH in mixed solution, Γ_{DOH}, was calculated similarly as in the case of Γ_{SDS}. The results are shown by the curve B in Fig. 2. We can confirm in Fig. 2 that in the mixed adsorbed film Γ_{DOH} steeply increases with the DOH concentration contrary to the gradual decrease of Γ_{SDS} and reaches the saturate adsorption of 7.8×10^{-10} mol/cm^2 in the region of DOH concentration greater than 2.5×10^{-4} mol/1000 g solution. The curves show a strong tendency of DOH adsorption with no marked desorption of SDS.

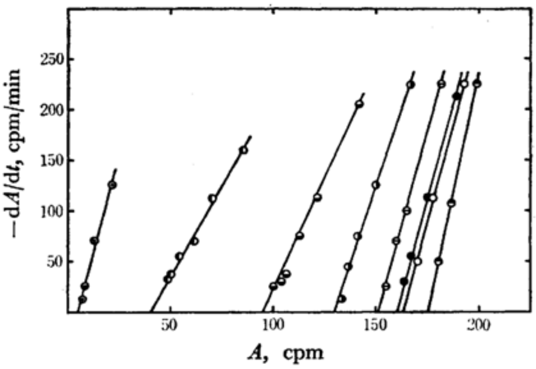

Fig. 5. A *versus* $\mathrm{d}A/\mathrm{d}t$ plot.

Composition of Adsorbed Film. Few studies have been reported on the amount of adsorption at the surface of mixed aqueous solution of SDS and DOH by a direct and reliable method.[6,12] As an instance, we can cite the data of Wilson *et al.* obtained by foaming method. They reported $\Gamma_{SDS}=3.4\times10^{-10}$ mol/cm^2 and $\Gamma_{DOH}=3.9\times10^{-10}$ mol/cm^2 at 25°C for the mixed aqueous solution containing 8.7×10^{-3} mol/1000 g of SDS and 5.3×10^{-4} mol/1000 g of DOH. Corresponding data of the present study are $\Gamma_{SDS}=3.6\times10^{-10}$ mol/cm^2 and $\Gamma_{DOH}=7.7\times10^{-10}$ mol/cm^2 for the aqueous solution containing the same concentration of DOH

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[11] G. L. Gaines, Jr., Ed., "Insoluble Monolayers at Liquid-Gas Interface," Interscience Publishers, New York (1966), p. 208.

[12] A. Wilson, M. B. Epstein and J. Ross, *J. Colloid Sci.*, **12**, 345 (1957).

as that of Wilson and 5.63×10^{-3} mol/1000 g of SDS as estimated from Fig. 2.

It is confirmed from these data that the two values of Γ_{SDS} are nearly equal, but those of Γ_{DOH} are largely different from each other. This discrepancy will be explained by the solubilization of DOH in aqueous SDS beyond CMC and resulting decrease in DOH activity in Wilson's measurement. A similar effect of the decrease in adsorption due to the solubilization has been reported by Aniansson[13] in the case of solubilization of sodium hexadecysulfate by SDS. Also, the effects of fatty alcohol on CMC and on surface tension *vers.* concentration curve of soap and other surface active substances may be closely related to the phenomena mentioned above.[5,14]

In Fig. 6, the fraction of DOH in the adsorbed film, X_{DOH}, is plotted against the logartithm of the ratio, R, of DOH concentration to SDS concentration (constant) in the solution. It is seen in this figure that X_{DOH} shows a high value, although the value of R is still rather small: for instance, at $R=0.01$, $X_{DOH}=0.5$, *i. e.*, Γ_{SDS} is nearly equal to Γ_{DOH}. This means a strong tendency of DOH adsorption already at the small value of X_{DOH}, even in the presence of adsorbed film of SDS. Similar phenomena have been reported by Shinoda.[6] These facts may reasonably explain the remarkable effects of the addition of small amounts of DOH on the surface chemical properties of SDS solution.[2-4]

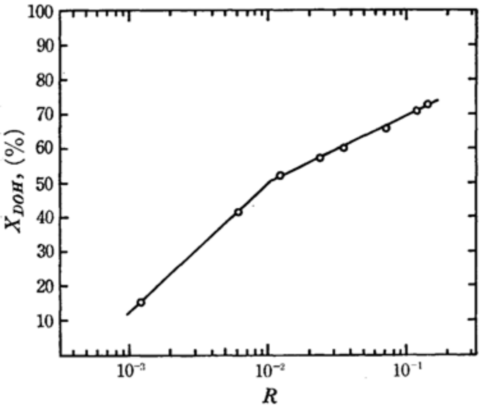

Fig. 6. Relation between X_{DOH} and R.
X_{DOH}: fraction of DOH in adsorbed film,
R: ratio of DOH concentration to SDS concentration in solution.

As for the mixed adsorption layer, the simple replacement of SDS by DOH in the layer cannot be conceivable, since the adsorption of DOH and the desorption of SDS did not occur in a simple ratio. The total amounts of adsorption of Γ_{DOH} and Γ_{SDS} together with the amount of adsorption corresponding to the close-packed monolayer are shown by dotted lines C and D respectively in Fig. 2. This figure shows that it is impossible for such a mixed adsorbed film to form a close-packed monolayer. This suggests that all molecules of SDS and DOH are not in the monomolecular layer at the surface of solution. In this connection it is noticed that the addition of SDS to the sufficiently concentrated solution of DOH (5.49×10^{-4} mol/1000 g solution) hardly affects the amount Γ_{DOH} (comparision of the extrapolated value of $\Gamma_{DOH}=7.4\times10^{-10}$ mol/cm^2 in Fig. 4 with the saturated value of $\Gamma_{DOH}=7.6\times10^{-10}$ mol/cm^2 for the mixed solution P in Fig. 2 containing the same amounts of DOH as in Fig. 4), while the addition of the same amounts of DOH to a solution of SDS markedly decrease the amount of Γ_{SDS} (from 5.9×10^{-10} mol/cm^2 at DOH concentration being zero to 3.6×10^{-10} mol/cm^2 for the mixed solution P in Fig. 2). These facts may suggest that adsorbed SDS molecules in excess of close-packed monolayer go beneath the monolayer at the surface of the solution while all adsorbed DOH appear in the monolayer. As to the structure of such a mixed adsorbed film, Fowkes reported[15] that the transition point is always observed in the pressure—area curve of the insoluble mixed monolayer composed of alkylsulfate and alcohol, when the alcohol content in the film exceeds 50%. He suggested the structure of film from the theory of ideal two-dimensional solution, in which the polar heads of sulfate are considered to be hydrated and placed beneath the surface of water, when the alcohol content of the film is less than 50%, but sulfate ions are dehydrated and occupy the same position as alcohol in the adsorbed film, when the alcohol content is over 50%.

In the present experiments, somewhat different behavior can be observed in the case of soluble adsorbed film composed of surfactant and alcohol. Namely, in the case of DOH composition being less than 50% in film, DOH molecules strongly penetrate into the adsorbed SDS film forming mixed monolayer, without marked desorption of SDS. In case of DOH composition being more than 50%, a mixed monolayer is likely to form, but here the mixed monolayer alone can not explain the total sum of Γ_{SDS} and Γ_{DOH} which exceeds the adsorbed amounts corresponding to the close-packed monolayer indicated by the dotted line D in Fig. 2. In this case a part of adsorbed SDS molecules are considered to form a mixed monolayer with DOH, while the rest of SDS molecules lie beneath the mixed monolayer as mentioned above. Thus, the structure of adsorbed layer is confirmed to be not a monolayer, contrary

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13) G. Aniansson, *J. Phys. and Colloid Chem.*, **55**, 1286 (1951).
14) K. Shinoda, *J. Phys. Chem.*, **58**, 1136 (1954).
15) F. M. Fowkes, *ibid.*, **67**, 1982 (1963).

to the suggestion of Fowkes in the region of sufficiently large concentration of DOH, and the Fowkes' transition phenomena if it appears may be understood as the change from monolayer to double layers formation.

In order to study the composition of adsorbed mixed film further in detail, it is necessary to use a more improved method of measuring radioactivity. The work is being continued along this direction.

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