The Study of the Adsorption of Detergents at a Solution-Air Interface by Radiotracer Method. I. Adsorption Isotherm for the Solution of Sodium Alkyl Sulfates

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The surface tension lowering properties of detergent solutions are well known and, of course, associated with the adsorption of the detergent at the solution-air interface. The adsorption isotherm is usually discussed on the basis of the Gibbs adsorption equation. However, the Gibbs equation is an ideal, limited equation and it is a problem whether the equation is actually valid for the adsorption of the surface active electrolytes. In the case of an anionic detergent, RNa, the Gibbs equation may be written as

$$d\gamma = -\boldsymbol{RT}\Gamma_{\mathrm{Na}^+}\,d\ln C_{\mathrm{Na}^+} - \boldsymbol{RT}\Gamma_{\mathrm{R}^-}\,d\ln C_{\mathrm{R}^-} - \boldsymbol{RT}\Gamma_{\mathrm{H}^+}\,d\ln C_{\mathrm{H}^+} \qquad (1)$$

where γ is the surface tension of the solution; Γ_{Na^+}, Γ_{R^-} and Γ_{H^+} are amounts of adsorption of sodium ion, detergent anion and hydrogen ion, respectively; and C_{Na^+}, C_{R^-} and C_{H^+} are concentrations of each specified ion. When the concentration of hydrogen ion is kept constant, the equation may be

$$d\gamma = -\boldsymbol{RT}\Gamma_{\mathrm{Na}^+}\,d\ln C_{\mathrm{Na}^+} - \boldsymbol{RT}\Gamma_{\mathrm{R}^-}\,d\ln C_{\mathrm{R}^-} \qquad (2)$$

Without excessive salts or alkali and with a small concentration of the detergent, assuming that $\Gamma_{\mathrm{Na}^+}=0$, $\Gamma_{\mathrm{H}^+}=\Gamma_{\mathrm{R}^-}=\Gamma_{\mathrm{RH}}$ and $C_{\mathrm{Na}^+}=C_{\mathrm{R}^-}=C_{\mathrm{NaR}}$, the Eq. 2 becomes

$$\Gamma_{\mathrm{RH}} = -\frac{1}{\boldsymbol{RT}}\,\frac{d\gamma}{d\ln C_{\mathrm{RNa}}}. \qquad (3)$$

As the concentration of the detergent becomes higher, hydrogen ion may be replaced by sodium ion in the surface layer; hence, assuming that $\Gamma_{\mathrm{H}^+}=0$, $\Gamma_{\mathrm{Na}^+}=\Gamma_{\mathrm{R}^-}=\Gamma_{\mathrm{NaR}}$ and $C_{\mathrm{Na}^+}=C_{\mathrm{R}^-}=C_{\mathrm{NaR}}$, the Eq. 2 results in

$$\Gamma_{\mathrm{NaR}} = -\frac{1}{2\boldsymbol{RT}}\,\frac{d\gamma}{d\ln C_{\mathrm{NaR}}}. \qquad (4)$$

In discussing on the basis of the Gibbs equation the adsorption of the detergent solution without excess salts or alkali, either Eq. 3 or Eq. 4 should be applied if either of the above assumption is satisfied. The problem is to measure the adsorbed amount directly and to compare the result with that calculated from the surface tension data using Eq. 3 or Eq. 4.

Recently the possibility of using radiotracers for the direct measurement of adsorption of detergents at the solution-air interface was developed by Dixon et al.[1], Aniansson and Lamm[2] and Hutchinson[3]. The method in general consists, though in detail some differences exist among the authors, in measuring the difference between radioactivity of tagged surface active agents in the surface adsorbed layer plus bulk solution and that in bulk solution alone. Since then, the method has actually been applied by some authors to the adsorption of respective detergent from the solutions of di-*n*-octyl sodium sulfosuccinate (Aerosol OTN)[4], potassium palmitate[5] and sodium dodecyl sulfate (abbreviated as SDS)[6-8]. The method has proved very successful for the study of adsorption of a detergent from mixtures, for example, the adsorption of Aerosol OTN from the solution of mixture of Aerosol OTN and Aerosol OT (di-2-ethylhexyl sodium sulfosuccinate) has been measured by Judson et al.[9] by tagging Aerosol OTN. Similar measurements have been made on the adsorption of sodium hexadecyl sulfate (abbreviated as SHS)[10,11] and of sodium tetradecyl sulfate (abbreviated as STS)[12] both in the presence of excess SDS, by tagging the former detergents. Nilsson has measured the adsorption of tritiated SDS and dodecanol in the presence of STS and SDS respectively[8].

The radiotracer method has also been applied to the investigation of gegen-ion adsorption from the detergent solutions, as, for example, the adsorption of the sulfate ion in solutions of some cationic, anionic and non-ionic surface active agents[13,14] and of sodium ion in solutions of SDS[3] and Aerosol OTN[15]. Further, the co-adsorption of metal ions with surface active agents has been studied by Aniansson and Steiger by making use of α-recoil atoms[16,17].

All these works have given us some interesting information which could not have been directly obtained before, as to the nature of the adsorption of detergents at the solution-air interface. Especially the validity of the Gibbs adsorption equation has been checked by a couple of authors. Salley et al.[4], Roe and Brass[5] and Ruyssen[6] obtained in the case of Aerosol OTN, potassium palmitate and SDS, respectively, the results that the adsorption

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[17] N. H. Steiger and G. Aniansson, *J. Phys. Chem.*, **58**, 228 (1954).

of the detergent at the solution-air interface takes place in accordance with the Eq. 3, provided the solution is dilute. However, the problem has not been treated for a series of surface active agents which have a similar structure but different surface activity. The investigation of the adsorption isotherm of various detergents at the solution-air interface in relation to their surface activity is an important problem in elucidating the nature of surface active agents. So we started to study the problem with application of the radiotracer method to the adsorption of a series of sodium alkyl sulfates at the solution-air interface. The present paper describes the results of the study of the adsorption isotherm for the aqueous solutions of SDS, STS and SHS.

Experimental

Materials.—The alkyl sulfates used were synthesized from corresponding fatty alcohols and concentrated sulfuric acid according to the method written in the text of Sisley[18]. The monoester was neutralized with alkali. The sodium alkyl sulfate thus produced was extracted several times with butanol[19]. By heating the butanol extract, water was removed, and the precipitated inorganic salts were separated from the solution by filtration. Then the sodium alkyl sulfate was recrystallized from the filtrate. The crystal was washed with a large amount of ether several times to remove unsulfated alcohol[20]. The result of elementary analysis verified the purity of the sodium alkyl sulfates within an experimental error. The surface tension-concentration curves for three detergents are shown in Fig. 8, which shows no minima and the values of cmc observed are in good agreement with those in literature[21].

Pure fatty alcohols were prepared by fractional distillation of commercial ones in vacuum, followed by redistillation of the fraction with conditions as shown in Table I.

TABLE I

CONDITIONS FOR THE DISTILLATION AND THE MELTING POINT OF ALCOHOLS

Alcohol	Pressure (mmHg)	Distillation temp. (°C)	m. p. (°C)
Dodecyl alcohol	20	149.6～149.8	23.5～24.5
Tetradecyl alcohol	15	167～168	37.5～38.5
Hexadecyl alcohol	17	192～193	48.5～49.5

Butanol and ether used for extraction and recrystallization were purified by redistillation of pure commercial ones, and concentrated sulfuric acid and alkali were extra pure reagents.

The sulfur-35 was obtained from the Radiochemical Center, England, as a carrier-free sodium sulfate solution. It was converted into sulfuric acid by ion-exchange resin and was isotopically diluted by a small amount of sulfuric acid. This was concentrated and used for synthesis of radioactive sodium alkyl sulfates in the manner as stated above. The specific radioactivity of the labeled sodium alkyl sulfates thus prepared was ca. 10 mc. per millimole for SDS and SHS and 2 mc. per millimole for STS.

Method.—The procedure used for measurement of surface excess of a radioactive detergent in aqueous solutions was essentially similar to that described by Anianssonn[10]. The apparatus used in the present experiment is shown in Fig. 1. A lucite cuve A, 5.6 cm. in inner diameter and 0.2 cm. in depth, filled exactly to the brim with the radioactive solution, is fitted exactly to the brass table B, 5.6 cm. in diameter, as shown in the figure. The thickness of the wall of A was all 0.2 cm. The Geiger-Müller tube C (GM-132, an end window type of special use for soft β-ray) is supported by a brass cylinder D with an arm E which is fixed to a universal stand. This enables us to move the Geiger-Müller tube up and down precisely. A brass ring F, 6.0 cm. in inner diameter which is identical with the outer diameter of the cuve A, is fixed to D so that tight fitting of the arrangement and reproducibility of the geometric condition can be realized with ease. The distance between the surface of the solution and the Geiger-Müller tube window is 0.15 cm. This small distance enables us to give a low gas volume over the surface. Since the counting of the radioactive sulfuric acid solution was shown to be constant within an experimental error, 5%, over a period of several hours, the evaporation effect may be ignored during the time interval of the present experiment. The whole arrangement was set in an air thermostat to maintain a constant temperature during the experiment. The fresh

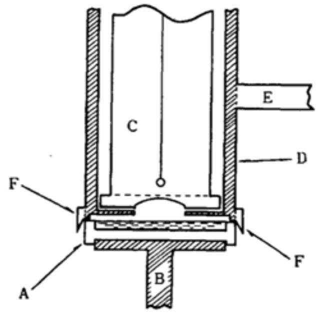

Fig. 1. The measuring apparatus.

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and plane free surface of the solution in the cuve was easily obtained by sweeping away the surface of the solution with a glass plate, about 7 cm. in width and 8 cm. in length. Both the lucite cuve and the glass plate were coated with a thin layer of paraffin to avoid wetting by the solution, and before use they were rinsed with tap water for a few hours, followed by final washing with distilled water. After the plane-free surface was formed, the Geiger-Müller tube was put down into the measuring arrangement and the intensity of radiation from the solution was measured.

The surface excess, Γ (in mole per cm^2), is calculated according to the equation

$$\Gamma=\frac{I_d-I_i}{SA}, \tag{5}$$

where I_d is the intensity (count per min.) of radiation due to the detergent solution; I_i, that (count per min.) due to the sulfuric acid solution which is the same in both specific activity and molar concentration as the detergent solution; S, the specific activity of the detergent in count per min. per mole, and A, the surface area of the solution in cm^2.

Of these quantities, S was obtained by means of the procedure as reported by Aniansson[10]. A solution of sodium alkyl sulfate was used for the determination of S. Evaporating about 2×10^{-3} cc. of a solution of radioactive sodium alkyl sulfate dropped as a point at the center of a polished lucite plate, it was then placed in the same position as the surface of the solution under the Geiger-Müller tube and counted. The volume of the dropped solution was accurately known by using a micropipette. The lucite plate was used for the measurement of S to avoid the error resulting from the difference in back-scattering effect of water and the material of the plate[10]. Sodium alkyl sulfate dropped was 6×10^{-7} g., so that the error due to the self-absorption could be negligible. The plate was placed at the same distance from the window as the solution surface. First the point source was located at the center line of the Geiger-Müller tube and the radiation was counted (S_0). Then the plate was moved horizontally so that the point source would have a distance r from the center line and counted (S_r). The relative counting efficiency η_r may be given by S_r/S_0. In Fig. 2 the $\eta_r\sim r$ curve is plotted. Now the overall counting efficiency, η, relative to that of the center can be computed by the following equation

$$\eta=\frac{\int_0^R 2\pi r\eta_r \mathrm{d}r}{\int_0^R 2\pi r \mathrm{d}r}, \tag{6}$$

where R is the radius of the surface of the solution, 2.8 cm. in the present apparatus. The value of η can be determined by graphical integration using the Fig. 2. It was found that η was 0.2237 in the present experiment. The specific activity S is given by $S_0\eta$. The values of S thus calculated for the three detergents were 7.730×10^{10} counts per min. per mole for SDS, 3.075×10^{10} counts per min. per mole for STS and 10.96×10^{10} counts per min. per mole for SHS at the given geometry in the present experiment. In Fig. 3 I_i is plotted as a function of the concentration of sulfuric acid used for the determination of I_i. This figure shows that over a range of concentration studied I_i can be expressed by an equation

$$I_i=I_0C, \tag{7}$$

where C is the concentration of sulfuric acid and I_0 is the intensity of radiation due to 1 M sulfuric acid. Using the relation I_i of sulfuric acid of any concentration can be obtained.

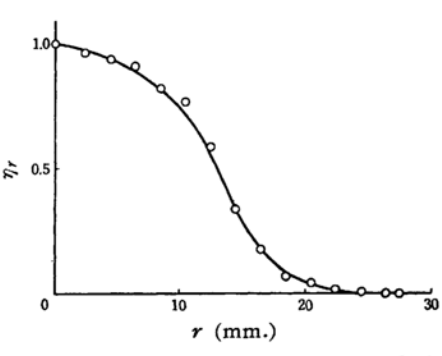

Fig. 2. The counting efficiency relative to that of the center.

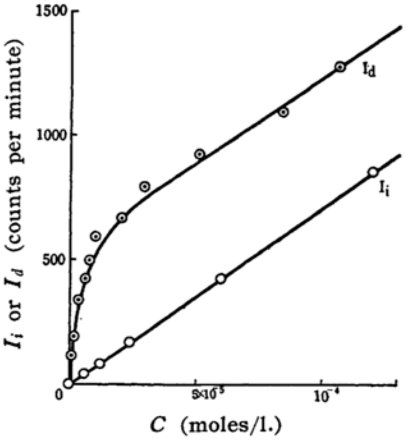

Fig. 3. The surface counts vs. concentration curves. I_i, sulfuric acid solution and, I_d, SHS solution, 28±1°C.

I_d for SHS, as an example, is also shown in Fig. 3, for comparison with I_i, as a function of the concentration of the detergent solution. Since the surface adsorption of the detergent increases with time, I_d is a function of time. I_d plotted in Fig. 3 is the value after the adsorption equilibrium has been attained. Using this figure, I_d-I_i for the same concentration is read off easily and then, knowing S as stated above, the surface excess Γ can be calculated by the Eq. 5. The

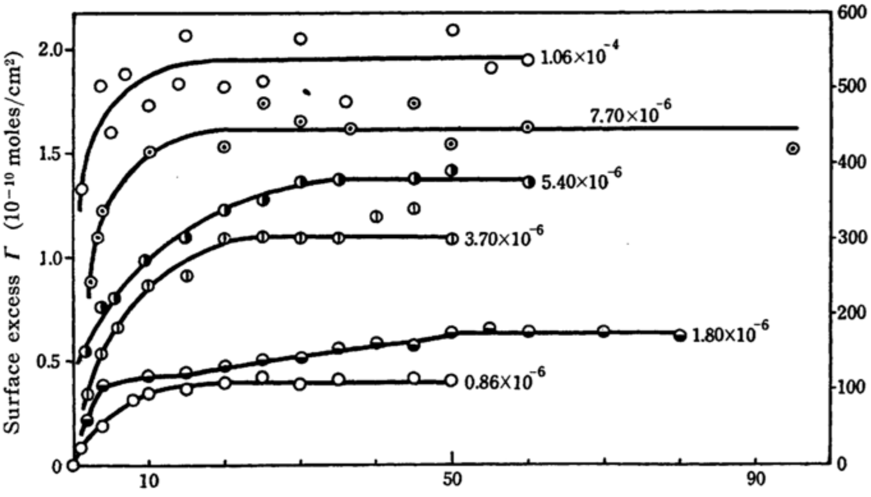

Fig. 4. Surface excess vs. time curves of SHS solution, 28±1°C. Numericals in this figure show the concentration (moles/l.) of the detergent.

same treatment can be done for the other detergents. In this case $I_d - I_i$ should be considerably greater than the statistical error of the value of I_i or I_d; otherwise the reliable value of the surface excess could not be obtained. As the concentration of the detergent solution becomes higher, the ambiguity of this source is introduced and the measurement of an accurate value of the surface excess becomes increasingly difficult. Actually in the case of SDS solution this was the case, and no data of sufficient accuracy could be obtained for this detergent at higher concentrations.

The surface tension of the detergent solution was measured by the Wilhelmy plate method. The plate was of a thin glass and mounted on a Langmuir trough assembly.

Results and Discussion

The surface adsorption of the sodium alkyl sulfates studied in the present experiment reached the equilibrium within about an hour in every case. As an example, the surface excess of SHS is plotted against time in Fig. 4. The equilibrium is reached faster, as the concentration of the solution is higher.

The equilibrium surface excess is plotted against logarithmic concentration for SDS, STS and SHS solutions in Figs. 5, 6 and 7, respectively. The results of the measurement of Γ at different temperatures are also plotted in these figures, which indicate that the effect of temperature is not so appreciable over the range studied in the present experiment. It is seen from these figures that the surface excess has a tendency of taking a saturation value below cmc for every detergent solution.

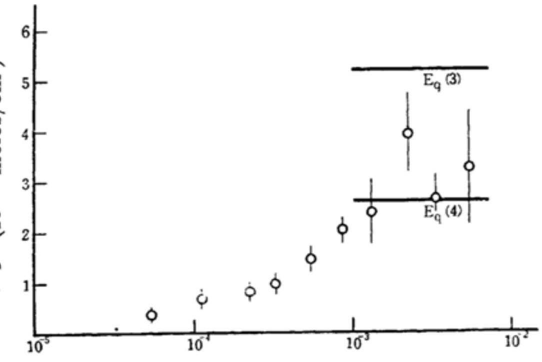

Fig. 5. Surface excess vs. concentration of SDS. 28±1°C. Full lines represent calculated relations from $\gamma \sim \log C$ curves by using Eq. 3 and Eq. 4 at 28°C.

The surface tension *vs.* logarithmic concentration data on aqueous solutions of sodium alkyl sulfates are represented graphically in Fig. 8, in which surface tension observed are those of the surface of the solution aged for an hour. It is shown that an approximately linear relation exists between γ and $\log C$ below cmc for each detergent solution. The linear portion of the $\gamma \sim \log C$ relation corresponds, although approximately, to the saturation of the surface excess obtained in the present experiment. The values of Γ calculated for this region by using Eq. 3 and Eq. 4 are shown in Figs. 5—7 for the three detergents studied. It is seen that the experimental data lie between

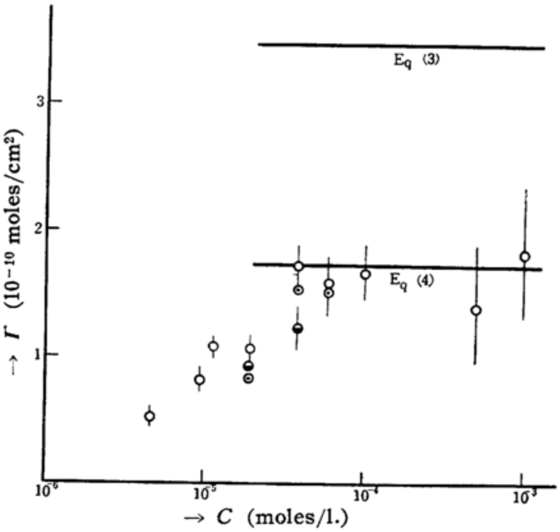

Fig. 6. Surface excess vs. concentration of STS. ○ 28±1°C; ⊙ 40±1°C; ◒ 22±1°C. Full lines represent calculated relations from $\gamma \sim \log C$ curves by using Eq. 3 and Eq. 4 at 28°C.

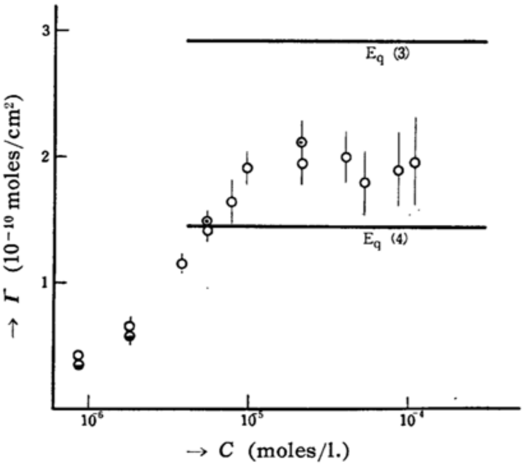

Fig. 7. Surface excess vs. concentration of SHS. ○ 28±1°C; ⊙ 40±1°C; ◒ 22±1°C. Full lines represent calculated relations from $\gamma \sim \log C$ curves by using Eq. (3) and Eq. (4) at 28°C.

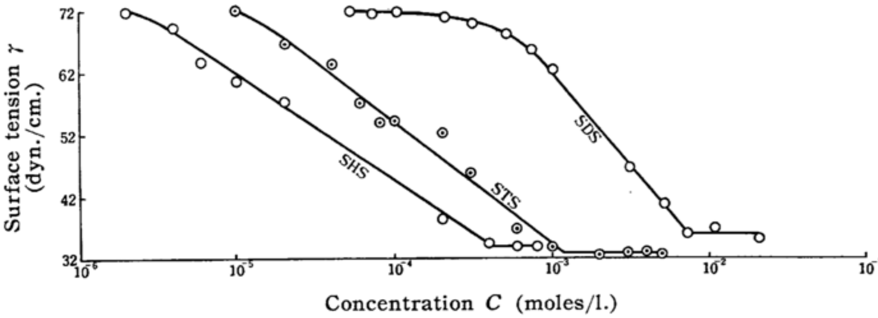

Fig. 8. Surface tension vs. concentration curves, 28±1°C.

the values of Eq. 3 and those of Eq. 4. It is to be noticed that Eq. 3 and Eq. 4 are ideal equations which are valid only if the conditions assumed in the derivation of each equation are perfectly fulfilled. The present results may show that the conditions are not so complete as to permit strict application of Eq. 3 or Eq. 4. It could be said, however, that, as a whole, the experimental points are near the values of Eq. 4 rather than those of Eq. 3 over the concentration range near cmc. Further discussion and the definite conclusion will be postponed until the accuracy of the measurements of both adsorption and surface tension at higher concentration region is improved much more.

By comparing the data of adsorption of three detergents, it is evident that the bulk concentration corresponding to the same surface excess, below the saturation of the adsorption, is lowered as the chain length of the detergent molecule increases. This is what should be expected from the surface tension lowering properties of the three detergents as shown in Fig. 8.

Summary

The adsorption of the three alkyl sulfates, SDS, STS and SHS, at the solution-air interface has been measured directly by means of the radiotracer method. It has been proved that the surface adsorption increases with increase in the concentration and has a tendency to be saturated

at concentrations near cmc for each detergent solution. The results have shown that the adsorption increases with increasing chain length. The Gibbs adsorption equation has been cheked and discussed.

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