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Measurement of Adsorbed Amount of Sodium Dodecylsulfate at Gas-Solution Interface by Radiotracer Method Using Tritium-Labeled Compounds

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Sodium dodecyl-2,3-^3H,^3Hsulfate (SDS) was synthesized from non-radioactive dodecanol, and the adsorbed amount of SDS at the gas-water interface, Γ, was directly measured by the radiotracer method with the use of 2π gas-flow windowless counter and humidified propane as a flow-gas. Because of a very soft nature of tritium β-rays, surface radioactivity is exclusively due to the solute adsorption compared with the large contribution from the bulk of the solution as in the case of ^{14}C or ^{35}S labeled detergents. Therefore the use of ^3H labeled compounds enables the determination of the amount of adsorption in high accuracy, even in the region of high concentration beyond the critical micelle concentration (CMC) of SDS solution. However, no reliable reports have appeared as yet on the studies of adsorption of surfactant at gas-solution interface using ^3H labeled compounds. Our measurement was carried out under exactly specified conditions, namely using chemically and radiochemically pure sample and under the condition free from evaporation. It was confirmed that Γ increased with the increase of SDS concentration and approached the saturation value of 5.9×10^{-10} mol/cm^2 or 28.2 Å^2/molecule at the concentration higher than 6×10^{-3} mol/1000 g solution and beyond CMC. Furthermore, Γ proved to be independent of the acidity of solution above pH 4, while it increased with increasing acidity below pH 4. The phenomenon is explained by the presence of hydrolytically formed dodecylsulfuric acid whose surface activity is higher than that of SDS.

Recently, much experiment has been carried out in an effort of determining the adsorbed amounts of surface-active substances at gas-solution interfaces by the radiotracer technique using soft β-emitters, such as ^{35}S[1-3] or ^{14}C.[3,4] Though these isotopes enable us to make a direct and hitherto difficult measurement of adsorption for compact aqueous surfaces, the results obtained are not satisfactory in the accuracy especially in the region of concentrated solution and in the case of weak adsorption. In this connection, it is particularly recommended to use a compound labeled with tritium which emits an extremely soft β-radiation. This is best explained by the following equation:

$$\frac{A_1-A_2}{A_1}=\frac{1}{1+C/(1000\Gamma\mu)}, \qquad (1)$$

where A_1 denotes the total radioactivity in cpm measured over the solution surface and A_2 that due to the bulk of the solution, C the concentration (mol/1000 g solution), Γ the adsorbed amount (mol/cm^2) and μ the mass-absorption coefficient (cm^2/g) for β-rays in the solution. The higher accuracy can thus be expected either for small value of C/Γ, or for large μ value. The value for C/Γ, however, is inherent to the surfactant chosen as a sample. Therefore, in order to obtain a high accuracy for a relatively large value of C/Γ as in the case of SDS, a radioisotope of sufficiently small μ is required to use as a tracer. For this reason, ^{14}C or ^{35}S is not satisfactory, and the use of ^3H is recommended since μ value of ^3H is about 50 times as large as that of ^{14}C or ^{35}S. Also, the use of ^3H is favorable because hydrogen is a common constituent of organic compounds.

However, no reliable reports have appeared as yet on the studies of adsorption of surfactant at gas-solution interface using ^3H labeled compounds. It appears that the tentative experiments by Nilsson[5] on adsorption of tritiated sodium dodecylsulfate (TSDS) have involved some uncertainty as to his synthetic processes leading to the tritiated sample, as pointed out previously.[6]

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[1] 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); *etc.*

[2] R. Matuura, H. Kimizuka, S. Miyamoto and D. Shimozawa, This Bulletin, **31**, 532 (1958).

[3] K. Shinoda and K. Mashio, *J. Phys. Chem.*, **64**, 54 (1960); K. Shinoda and K. Kinoshita, *J. Colloid Sci.*, **18**, 174 (1963).

[4] C. P. Roe and P. D. Brass, *J. Am. Chem. Soc.*, **76**, 4703 (1954); S. N. Flengas and E. Rideal, *Trans. Faraday Soc.*, **55**, 306 (1959); *etc.*

[5] G. Nilsson, *J. Phys. Chem.*, **61**, 1135 (1957).

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

We have obtained the radiochemically and surface-chemically pure surfactants,[6,7] and developed the 2π windowless gas-flow counting for determining tritium radioactivity over solution surfaces.[8] In the present paper an attempt is made to determine the adsorbed amount of TSDS at gas-solution interface by means of 2π windowless counter under the flow of humidified propane.

Experimental

Reagents. TSDS was prepared by the method formerly reported,[6] the process of which is shown as follows:

$C_{12}H_{25}OH$ (I) → $C_{11}H_{23}COOH$ (II) →
$C_{10}H_{21}CHBrCOOH$ (III) →
$C_9H_{19}CH{=}CHCOOH$ (IV) →
$C_9H_{19}CH^3HCH^3HCOOH$ (V) →
$C_9H_{19}CH^3HCH^3HCH_2OH$ (TDOH) →
$C_9H_{19}CH^3HCH^3HCH_2OSO_3Na$ (TSDS).

Normal-dodecanol-1 (I) purified by fractional distillation (bp 141—142°C/11 mmHg) was oxidized by sulfuric acid and potassium dichromate mixture to II. For the bromination of the compound II it was mixed with phosphorus trichloride and bromine was added to the mixture gradually at 85—90°C. The compound III thus obtained was dehydrogenated by potassium iodide and potassium hydroxide. A resulting compound IV was tritiated to V with tritium gas using Urushibara nickel (U-N-A)[9] as a catalyst. The reduction of V to TDOH was carried out using lithium aluminum hydride with good yield. TDOH thus obtained was carefully purified by means of preparative gas chromatography to remove homologue impurities. TDOH thus purified was treated with chlorosulfonic acid to obtain TSDS. Purification of TSDS was performed in a usual manner.[10] In addition to the usual chemical purification, a radiochemical purification was worked out to remove radioactive TDOH by the isotopic dilution method, that is, by repeating the addition of non-radioactive dodecanol to the alcoholic solution of TSDS and subsequent precipitation of TSDS from the solution. TSDS was finally purified by the Soxhlet extraction using ether followed by a recrystallization from ethanol. The TSDS thus obtained was sufficiently pure both chemically and radiochemically showing neither minimum in surface tension *versus* concentration curve nor the trace of volatile radioactive impurities presumably due to TDOH. Specific activity was 720 mCi/mol both for TDOH and TSDS.

Other reagents used in the present experiment were purified thoroughly by pertinent procedures. Samples of propane (98—99% pure) and methane (99.6%) used as flow gases were kindly supplied from Toa Nenryo Kogyo K. K.

Apparatus. Figure 1 illustrates schematically the apparatus which consists of the flow-gas preheater C, humidifier D, and the counting probe F of 2π windowless gas-flow counter (Aloka DC-1001). A solution of TSDS or TDOH for counting was contained in the planchette G, covered with the concentric mask H, which eliminates radioactivity from the periphery of G. The planchette and the mask made of stainless steel were polished and cleaned electrolytically with 1.2 A/cm^2 d. c. current in a solution of phosphoric acid prior to the experiments. The whole system was thermostatted to 20±0.5°C.

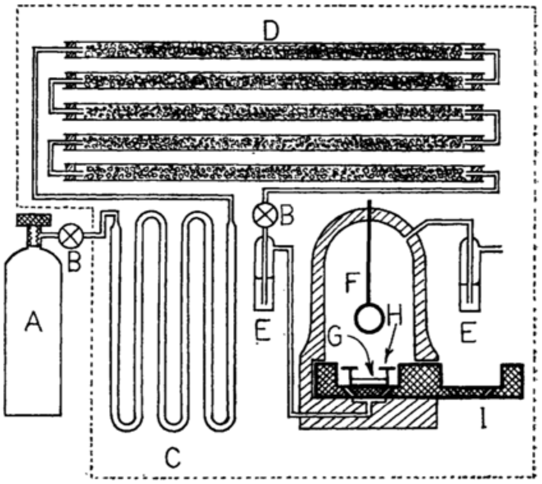

Fig. 1. Experimental apparatus.

A	Propane gas tank	B	Control valve
C	Preheater tube	D	Humidifying tubes
E	Bubbler	F	Counting probe
G	Planchette	H	Cover mask
I	Turn table		

It has been pointed out in the previous paper[8] that the flow gas for counting the radioactivity over a solution surface should be moistened moderately to keep humidity neither so high as to permit multiple discharge, nor so low to enhance evaporation, since evaporation sometimes causes the concentration of solute at gas-solution interface. The optimum conditions for the least evaporation without multiple discharge were examined by changing the type of flow gas, its humidity and flow rate. The humidity was controlled by changing the length of preheater C, and the number of humidifier tubes D (2.0 cm diameter and 55 cm length each), which were packed with pieces of filter paper soaked with distilled water. The best condition was found to use propane of 82.6% humidity and 9.7 m*l*/min gas flow rate, and a voltage from 4600 to 4900 V applied to the counter. Under this condition, the rate of water evaporation from SDS solution in the planchette G, was less than 0.10 mg/cm^2/hr. This amount corresponds approximately to a surface deposition of SDS of 6×10^{-10} mol/cm^2/hr at the surface of 6×10^{-3} mol/1000 g solution, if we assume the deposit to remain undisturbed. However, the surface cooling involved in the actual system causes a convection current which results in a retardation of surface enrichment

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[7] M. Muramatsu, O. Fujii and T. Sasaki, *Radioisotopes*, **10**, 100 (1961).

[8] M. Muramatsu and T. Sasaki, "Proc. 3rd Japan Conference on Radioisotopes," Japan Atomic Energy Ind. Forum, Tokyo (1959), p. 453.

[9] K. Hata, S. Taira and I. Motoyama, This Bulletin, **31**, 776 (1958); *ibid.*, **34**, 261 (1961); *etc.*

[10] E. E. Dreger, C. L. Keim, G. D. Miles, L. Shedlovsky and J. Ross, *Ind. Eng. Chem.*, **36**, 610 (1944).

of solute.[11] Therefore, it seems possible that the surface enrichment of the actual system is much less than the above value, as has been suggested in the experiments using $^{35}SO_4^{2-}$ in aqueous solution under the flow of dry nitrogen.[12]

Procedures. A portion of 0.80 m*l* of TSDS solution which had been aged in the thermostat for more than 15 min was brought by a syringe into the planchette G. The turn table, I, was revolved to get it into the counting chamber, in which humidified propane had been flowed previously for 5 hr to make its humidity and temperature constant. Surface radioactivity, A_1, of the solution was then determined as a function of time which elapsed from the revolving of the table.

The bulk radioactivity, A_2, of aqueous TSDS solution was estimated by converting the radioactivity (bulk) A_2', obtained with TDOH solution of the same radioactive concentration in non-radioactive dodecanol under the same geometrical conditions in the flow counter. For the same radioactive concentration C_r (dpm/g solution), these quantities are expressed by

$$A_2 = G\eta C_r \frac{f}{\mu}(1 - e^{-\mu R}), \tag{2}$$

$$A_2' = G\eta C_r \frac{f'}{\mu'}(1 - e^{-\mu' R'}), \tag{3}$$

where G is the geometrical factor, η the counting efficiency, f the back- and self-scattering factor, and R the maximum range (g/cm^2) of medium for β-particles. The prime denotes the TDOH-dodecanol system. Combining the Eqs. (2) and (3), we have

$$A_2 = \frac{f}{f'}\,\frac{\mu'}{\mu}\,\frac{1 - e^{-\mu R}}{1 - e^{-\mu' R'}}\,A_2' = kA_2'. \tag{4}$$

The proportionality factor, k, was determined by evaluating the individual terms in Eq. (4).

The adsorption amount of surfactant Γ (mol/cm^2) was calculated by the following equation,

$$\Gamma = \frac{A_1 - A_2}{S\sigma D}, \tag{5}$$

where S denotes the surface area (cm^2), σ the specific activity of the radioisotope used (dpm/mol) and D the detection coefficient (cpm/dpm). The term $S\sigma D$ was determined separately by the method to be described in the following section.

Radioactivity was measured under the condition that the counting rate lies within a 1—1.5% standard deviation. The background radioactivity was about 30 cpm throughout the experiments.

Results and Discussion

Determination of A_1 and A_2. In Fig. 2 are shown the values of surface radioactivity of TSDS solutions as a function of time elapsed from revolving the turn table. Neither acid nor alkali was added to these solutions. Therefore pH values were in a range of 5.8 to 6.1, depending on concentration. It can be seen in this figure that the radioactivity increases with time and reaches a constant value in 30—40 min, depending on concentration. The initial increase with rather steep slope seems to indicate the dynamic processes of adsorption and the removal from flow gas of air which has been mixed by revolving the turn table. In fact, *ca.* 15 min was required for obtaining the stationary value of counting rate for a sample of stearic-9,10-^{3}H,^{3}H acid[7] spread over the same planchette. Thus, in Fig. 2, the linear portion of the curve after at least 40 min was extrapolated to time zero and the corresponding surface radioactivity was taken as A_1, for each solution.

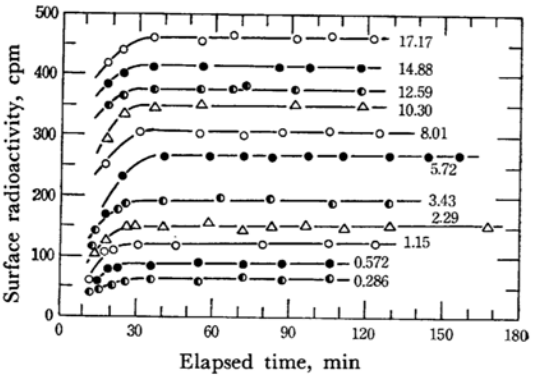

Fig. 2. Surface radioactivity for various TSDS solutions as a function of elapsed time. The figures by the curves indicate concentration of the solutions in 10^{-3} mol/1000 g.

Similar experiments were carried out for determining the radioactivity, A_2', over the surfaces of TDOH solutions in non-radioactive dodecanol-1 at 30—60 min after the initial revolving. To convert A_2' into A_2, reasonable approximations have been made for the propotionality factors in Eq. (4). First, the ratio, f/f' is estimated to be approximately unity, because the scattering power of aqueous TSDS solution is not much different from that of dodecanol-1. It is well known[13] that the scattering power for β-rays can be expressed as a function of the average atomic number

$$Z_{av} = \sum x_i m_i Z_i / \sum x_i m_i\,, \tag{6}$$

where x_i is fractional number of ith constituent atom of mass number m_i and atomic number Z_i. In the second line of Table 1 are shown the Z_{av} values calculated for the solutions of SDS in water and of TDOH in dodecanol-1. Putting these values into the empirical relationship between Z_{av} and the scattering factor[14] gives f/f'. Secondly, the mass-absorption coefficient, μ or μ', of a medium for given β-particles is determined by the

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[11] N. L. Jarvis and R. R. Kagarise, *J. Colloid Sci.*, **17**, 501 (1962); N. L. Jarvis, *ibid.*, **17**, 512 (1962).

[12] T. Seimita and T. Sasaki, *J. Colloid Interface Sci.*, **21**, 229 (1966).

[13] H. A. Bethe and J. Ashkin, "Experimental Nuclear Physics," Vol. 1, ed. by E. Segré, John Wiley and Sons, Inc., New York (1953), p. 166.

[14] For example, K. Siegbahn, "Beta and Gamma Ray Spectroscopy," North-Holland Publ. Co., Amsterdam (1955), p. 7.

TABLE 1. FACTORS INVOLVED IN THE PROPORTIONALITY CONSTANT IN EQS. (5)—(8)

Medium	$(0-2)\times10^{-2}$ mol/1000 g SDS solution	Dodecanol-1
Z_{av}	7.2	5.5
$(Z/m)_{av}$	0.833	0.833
Mass absorption coefficient, μ or μ'	19.4 cm²/mg	19.0 cm²/mg

average ratio of atomic number to mass number,

$$(Z/m)_{av} = \sum x_i Z_i/m_i\,. \tag{7}$$

As a first approximation,

$$\mu = \alpha (Z/m)_{av}, \tag{8}$$

where α denotes the proportionality constant, which depends only on the energy of β-particles. Equation (8) which has been verified with rather hard β-rays[15] seems to be applicable to the tritium β-rays, as shown in Table 2 from which one obtains 23.3 cm²/mg for average α value. Combining the value with individual $(Z/m)_{av}$ values, which are given in the third line of Table 1, one can estimate the mass-absorption coefficient, values of which are shown in fourth line of Table 1. Thirdly, $R=R'=0.55$ mg/cm² was obtained by interpolation of the energy-range relationship for various β-particles.[18] Putting these values into Eq. (4), we have

$$\begin{aligned} A_2 &= \frac{19.4}{19.4}\cdot\frac{1-\exp(-19.4\times0.55)}{1-\exp(-19.0\times0.55)}A_2' \\ &= 1.00\,A_2'\,. \end{aligned} \tag{9}$$

The amounts of A_1, A_2 and A_1-A_2 thus obtained are plotted in Fig. 3 against the radioactive concentration, C_r, for each solution.

TABLE 2. μ, $(Z/m)_{av}$, AND α FOR TRITIUM β-RAYS IN GASEOUS ABSORBER

Absorber	μ cm²/mg	$(Z/m)_{av}$	α cm²/mg	Observer
Hydrogen	22	1.008	22	Dorfman[16]
Helium	11.4	0.500	22.8	Dorfman[16]
Air	12.5	0.500	25.0	Muramatsu *et al.*[17]
			Av. 23.3	

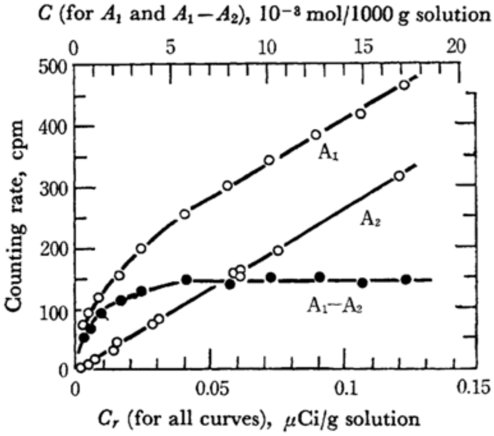

Fig. 3. A_1, A_2 and A_1-A_2 as a function of C_r or C (for A_1 and A_1-A_2).

Determination of $S\sigma D$. The value of $S\sigma D$ in Eq. (5) was determined by counting the surface radioactivity for known amounts of TSDS film spread over the nearly saturated solution of ammonium sulfate. A mixture of ethanol and benzene (1 : 40 in volume) containing TSDS was applied to the surface of 0.80 *ml* of the solution in planchette G in Fig. 1 and, after evaporating the solvent, turn table I was revolved to count the surface radioactivity. Exactly same conditions on S, σ and D were employed in the experiments as in determination of A_1 for aqueous TSDS solution. Also, it has been assumed tacitly in the experiments that the value of D and so the back- and self-scattering factor of nearly saturated solution (75.4 g/100 g solvent) of ammonium sulfate is the same as that of TSDS solutions. The assumption seems to be valied, as Z_{av} values are 7.4 for the former and 7.2 for the latter throughout the concentration range from 0 to 2×10^{-2} mol/1000 g solution. The difference in back- and self-scattering factor between the above two solutions could thus be much less than 1%.[14] Consequently, the value of $S\sigma D$ measured on saturated solution of ammonium sulfate can be used for the calculation of Γ using Eq. (5).

Figure 4 shows the dependence of surface radioactivity upon the amount of TSDS, assuming

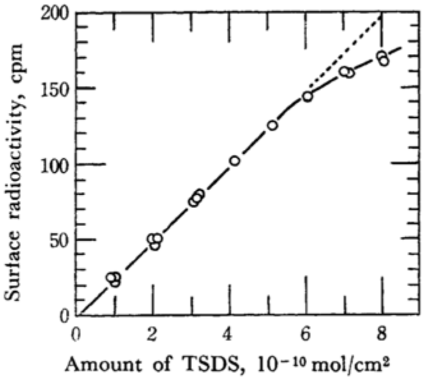

Fig. 4. Surface radioactivity as a function of TSDS applied to the surface of saturated solution of ammonium sulfate.

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[15] G. Friedlander and J. W. Kennedy, "Nuclear and Radiochemistry," John Wiley and Sons, Inc., New York (1955), p. 198; C. Feldman, *Phys. Rev.*, **117**, 455 (1960).

[16] L. M. Dorfman, *Phys. Rev.*, **95**, 393 (1954).

[17] M. Muramatsu, N. Tokunaga and A. Koyano, *Nucl. Instr. Methods*, **52**, 148 (1967).

[18] G. Friedlander and J. W. Kennedy, *loc. cit.*, p. 202.

that the molecules are all retained in the surface under the present experimental condition.[19] It can be seen in Fig. 4 that the radioactivity increases proportionally to the amount of TSDS up to *ca.* 5.5×10^{-10} mol/cm^2 or 30 Å^2/molecule; the value agreeing approximately with the limiting area of docosanylsulfate in insoluble monolayer at air-water interface.[20] Beyond this value, the curve tends to decrease in its slope, showing possible dissolution of the surfactant molecules into subphase. Similar phenomenon was observed by Brady[21] who employed surface tension and microtome methods for determining the nature of SDS films spread on various salt solutions. Therefore, the inclination of the linear portion in Fig. 4 is considered to give the value of $S\sigma D$ and we have empirically

$$\Gamma = 4.03\times10^{-12}(A_1-A_2) \tag{10}$$

with A_1 and A_2 in cpm and Γ in mol/cm^2.

Adsorption Isotherm of SDS at about pH 6. Inserting the A_1-A_2 values shown in Fig. 3 into Eq. (10), we obtain Γ values as a function of TSDS concentration. The results are shown as the open circles in Fig. 5. The adsorbed amount increases with the increase of C and gives the saturation value of 5.9×10^{-10} mol/cm^2 or 28.2 Å^2/molecule beyond the concentration of 6×10^{-3} mol/1000 g solution, the value being in good accord with the value for alkylsulfates in the state of insoluble monolayers at air-water interfaces.[20,21]

In Fig. 5 the semi-closed and closed circles are those reproduced from the papers by Matuura *et al.*[2] and Nilsson,[5] respectively. These data are not in accord with our results. The former investigators used SDS-^{35}S which suffers from an inevitable errors, especially in large concentration; while in the study of the latter author, tritiated SDS contains surface-active impurities whose specific activity might be much high in comparison with that of the main component, as has been pointed out previously.[6] In fact, Nilsson's synthetic product, according to experience, was much complicated in its chemical and radiochemical composition, since he paid no attention to the separation of undesirable impurities in the intermediate and final products formed in his synthetic procedure.

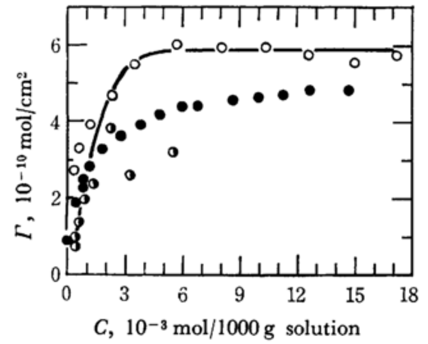

Fig. 5. Adsorption isotherm of SDS solution.
-○-, our results using ^{3}H as a tracer, pH 5.8—6.1;
●, by Nilsson,[5] using ^{3}H as a tracer;
◑, Matuura *et al.*,[2] ^{35}S as a tracer.

pH Dependence of Γ. Similar experiments were carried out with TSDS solutions below and above CMC at various pH values. It can be seen in Fig. 6 that Γ is almost constant throughout the range of pH beyond 4, while it increases markedly with decreasing pH below 4. This suggests at least the enhanced formation of dodecylsulfuric acid which might correspond with the lowering of surface tension at pH lower than 4.[22] The total increase of dodecylsulfate radicals as shown in Fig. 6 may be explained by taking account of the decrease in electrostatic repulsion between charged radicals in adsorbed layer, caused by introduction of free acid.

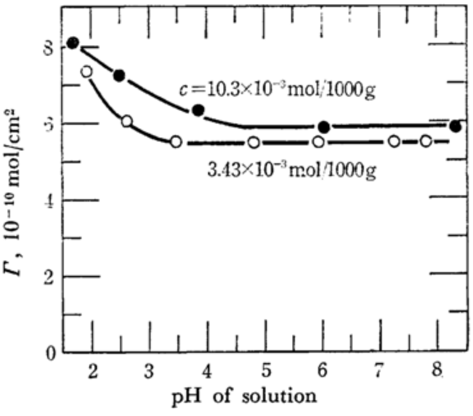

Fig. 6. Effect of solution pH upon the adsorbed amounts of SDS solution below (○) and above (●) CMC.

It might seem evident that the measured value of Γ, especially in acid region, is mainly attributable to TDOH formed by the hydrolytic reaction,

$$C_9H_{19}CH^3H\cdot CH^3H\cdot CH_2O\cdot SO_3^- + H_2O \rightarrow$$
$$C_9H_{19}CH^3H\cdot CH^3H\cdot CH_2OH + HSO_4^-,$$

which is more enhanced in acidic medium. However, a recent radiotracer study on the reaction rate[23] suggests that the dodecanol formation is too small to explain the enhanced adsorption. For 3.43×10^{-3} mol/1000 g SDS solution at 20°C,

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[19] B. A. Pethica, *Trans. Faraday Soc.*, **50**, 413 (1954).
[20] E. Stenhagen, *ibid.*, **36**, 496 (1940).
[21] A. P. Brady, *J. Colloid Sci.*, **4**, 417 (1949).
[22] J. W. James and B. A. Pethica, "Proc. 3rd Int. Congr. Surface Activity," Vol. 1, Butterworths, London (1961), p. 227.
[23] M. Muramatsu, M. Inoue and T. Sasaki, "Proc. 7th Japan Conf. on Radioisotopes," Japan Atomic Energy Ind. Forum, Tokyo (1966), p. 240.

as an example, the reaction rate was estimated to be 3.7×10^{-6} and 1.5×10^{-8} mol dodecanol/1000 g solution/day at pH 1 and 5, respectively. The figures correspond to at most 6.1×10^{-11} and 2.5×10^{-13} mol dodecanol/cm^2 respectively, for the "surface density" of dodecanol, even though we assume the exhaustive adsorption of dodecanol molecules from the bulk phase of 0.8 *ml* solution which has been contained in the planchette of 2.5 cm in diameter for 2 hr. Therefore, it is considered that the pH dependence observed may be mainly explained by the bulk and surface hydrolysis resulting in dodecylsulfuric acid which is more surface active than dodecylsulfate ion. Further studies along this line are desired.

Remarks on the Present Method. In general, 2π windowless gas-flow counting is one of the easiest, simplest and inexpensive methods for determining the radioactivity of tritiated specimen. It has been pointed out previously[8] that the method involves the advantage that the counting rate is not much influenced by the geometric position of the specimen, so far as it is contained in the metallic planchette. Thus, the method seems to be suited for counting the surface radioactivity of relatively small amount of solution containing tritiated specimen.

On the other hand, the windowless gas-flow counting inevitably encounters difficulties arising from the fact that the solution surface is always exposed to flowing gas, which should be humidified moderately so as to minimize the surface enrichment of solute due to the evaporation of the solvent, as mentioned in the former section. In the present experiment, the above mentioned rate and humidity of flowing gas proved to be sufficient to eliminate such a disturbance, since we could hardly detect the additional surface enrichment due to the evaporation. This results can reasonably be expected from the result of a similar evaporation experiment for $^{35}SO_4^{2-}$ solution in which even a flowing of dried nitrogen did not cause a measurable amount of a change in surface concentration.[8]

It must be noted that the results hereby obtained are concerned with the adsorption at the interface between "*humidified propane*" and SDS solution saturated with propane. Such an interface might be different in its nature from SDS solution-air interface, which would best be studied by an end-window counter specially designed for tritium radioactivity measurements.

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