長崎大学学術研究成果リポジトリ

NAOSITE

Nagasaki university's Academic Output SITE

Title	Sorption of Surface Active Agents onto Nylon
Author(s)	ayashi, Makoto
Citation	Acta medica Nagasakiensia. 1961, 5(4), p.197-205
Issue Date	1961-03-25
URL	http://hdl.handle.net/10069/15449
Right	

This document is downloaded at: 2019-03-19T19:32:22Z

Sorption of Surface Active Agents onto Nylon

Makoto HAYASHI*

Department of Pharmacology,
Nagasaki University School of Medicine,
Nagasaki, Japan

The equilibrium sorption amounts of the surface active agents onto nylon film and their desorption rates from the nylon which sorbed the solutes into various liquids were measured by using the radioactive sodium hexadecyl sulfate and sodium tetradecyl sulfate tagged with S^{35}. In the sorption isotherms of these detergents, the abrupt increases of the sorption amount were clearly observed near the respective cmc. The desorption rate into pure water rised abruptly at the concentration corresponding to cmc as it was plotted against the equilibrium concentrations of the detergent solution in the sorption test. In 0.1 N sodium chloride solution, the difference of the desorption rates between the both sides of cmc was small and in radioinactive detergent solution there was no appriciable difference. These facts were considered to show the difference of the state of sorption between the both sides of cmc. The formation of a surface micelle was predicted in the concentrations higher than cmc, while the chemical adsorption was assumed below cmc.

One of the general features in the adsorption of surface active agents on solid surfaces is that the adsorption amount increases abruptly near the cmc of the respective agent, which has been reported by many workers. However, we have not yet known any satisfactory interpretation about this point up to the present. In the previous paper[6], the studies on sorption of some surface active agents by nylon plates and their diffusion in them were reported, in which it was seen that the diffusion of these agents in nylon was very important in their sorption process. It is, however, impossible for such a thick plate (ca. 2 mm) that the sorption equilibrium is reached completely up to the center of the plate in the ordinary experimental condition, so that the thin films (ca. 25μ) were used to measure the sorption in this study. This method is also available to see the diffusion coefficients of these agents in nylon which are obtained by using an appropriate diffusion equation from measuring the desorption or the sorption rate. In this paper, the abrupt increase of the sorption amount at cmc was mainly discussed from the consideration of the desorption rates under the various conditions.

---

* 林 誠 人

EXPERIMENTAL AND RESULTS

Nylon films used in this study, which were supplied from Toyo Rayon Co., were non-drawing pure 6-nylon of about 25 μ thickness, and were used to test after the following pretreatment. They were immersed in 50 % ethyl alchol aqueons solution for a day to purify after the adhered fatty substances were removed by ether and acetone, then were washed by water for several hours. The surface active agents used here were radioactive sodium hexadecyl sulfate (SHS) and sodium tetradecyl sulfate (STS), which were synthesized from the respective purified alcohol and radioactive sulfuric acid (S^{35}) by the same method as that in other papers[7,8] and the purity of them was confirmed surface-chemically.

Sorption test was accomplished as follows. Nylon film treated as described above was cut in a square size of 20×20 mm², and it was fitted in a test tube with a ground stopper containing the respective radioactive surface active agent solution which was set in a thermostat. After a sorption equilbrium was reached, the specimen was taken out and washed in water for several seconds, and blotted by filter paper to remove an adhered water. The time required to reach the sorption equilbrium was determined experimentally for the condition in this measurement by the concentration change of the solution by using 35 pieces of specimens in a test tube. The result is shown in Fig. 1.
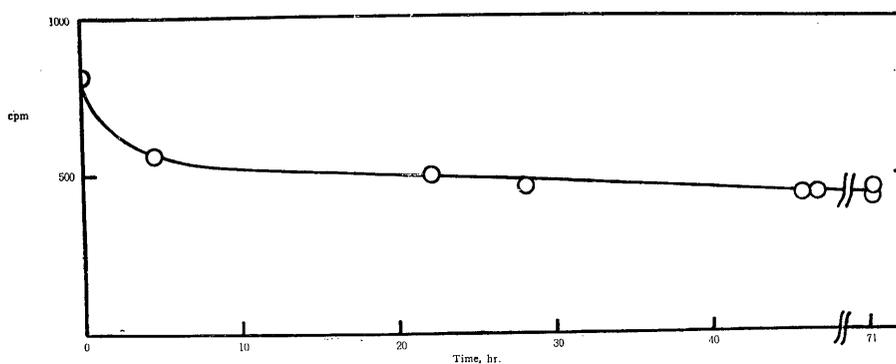

FIG. 1. Sorption rate of SHS onto nylon films at 35°C in non-stirred solution.
The films used are 35 pieces and the total weight is 330 mg. The
initial concentration of the solution is 2.49×10^{-4} mol./l and the final
one is 1.46×10^{-4} mol./l, and the weight of the solution is 117 g.
The ordinate denotes the solution concentration expressed by cpm of
solute in 0.1 ml. of the solution.

The amount of solutes sorbed by the film was determined by the following method. Radiation from the surface of the specimen was counted by using the method shown in Fig. 2 (a). Then, an extent of absorption by this film of radiation from S^{35} source which was set at a

fixed position under the film was measured as shown in Fig. 2 (b). From this value and the absorption curve for this radiation source, which was decided by the standard film of known thickness, the thickness of each film specimen was obtained. As shown in Fig. 3 (a), the apparent amount sorbed per unit area of film had a trend to increase as increasing thickness. When these values were simply divided by the respective thickness, the reverse trend appeared (Fig. 3,b), which was considered to be due to the self-absorption of radiation of solutes in nylon film. Therefore, if the calibration with respect to self-absorption was added to the above calculation, these trends disappeared and the values were obtained with a standard deviation of 5.5 % as shown in the same figure (c). The amount (A) of solutes sorbed per unit
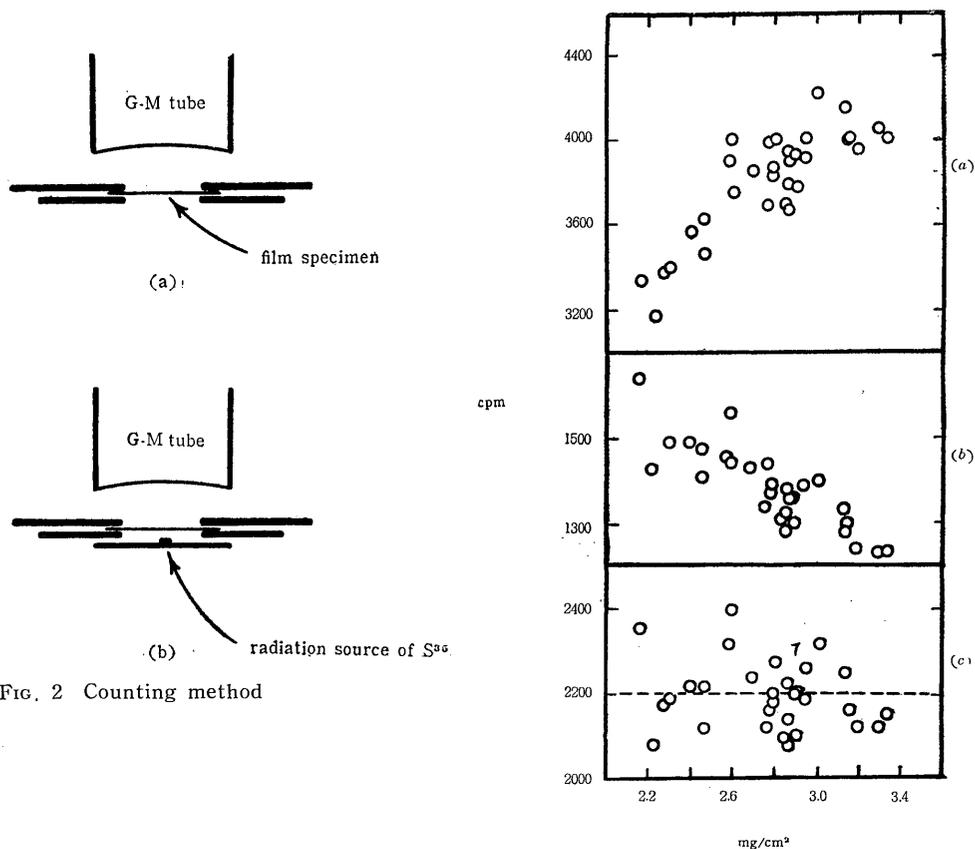

Fig. 2 Counting method

Fig. 3 Effect of thickness of film specimen on counting in measurement of sorption amount. (a) Values without any calibration. (b) Values divided by the thickness. (c) Values further treated with the calibration factors for self-absorption in films. The broken line shows the mean value.

weight of nylon was calculated from the following equation, using the thickness of film (l) and the calibration factor for self-absorption (fs).

$$A = (c \cdot s)/(f_s \cdot l \cdot a \cdot \eta) \quad ----(1)$$

where a, c, η and s are the counting area of the film, the counts observed, the counting efficiency and the specific radioactivity of solutes, respectively.   Calibration factor f_s is defined as follows.

$$f_s = I/I_0 = (1 - e^{-alox})/\alpha l_0 x \quad ----(2)$$
$$x = l/l_0$$

where α and l_0 are the absorption coefficient and the maximum range, they are 0.36 cm^2 /mg and 31.7 mg/cm^2 in the present experiment. Counting efficiency η is expressed by the relation, $\eta = \int_0^R 2\pi r \eta_r dr / \int_0^R 2\pi r dr$ where R is the radius of the counting area and η_r is the relative counting efficiency which is a function of the distance r from the center. The sorption isotherms obtained are shown in Figs. 4 and 5.
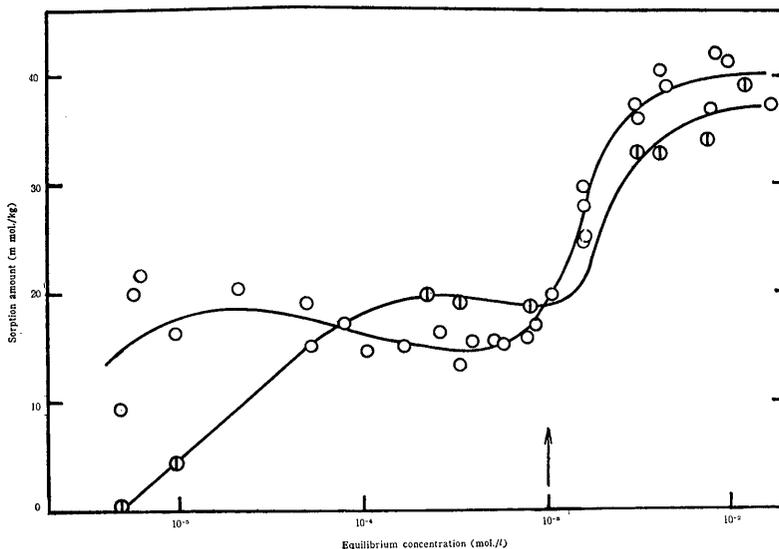

FIG. 4.   Sorption isotherms of STS at 35°C (○) and 49°C (◐).
The arrow shows cmc.

Desorption test was accomplished as follows.   Film specimen which had sorbed the radioactive agent from the solution of the respective concentration was rinsed for a definite time in a sufficiently large volume of solution which was thoroughly stirred in a thermostat.   The rinsing liquids used here were pure water, 0.1 N sodium chloride solution and the radio-inactive detergent solution of the same concentration as that at the adsorption equilibrium.   After the appropriate time (50 min. for 35°C, 20 min. for 50°C), the film was taken ont and instantly blotted. From a difference of counts between before and after the test, the desorption amount was determined.   In this case, it is a problem whether a penetrating velocity of water into the film affects the desorption rate in

<figure>
<div style="text-align:center">

Sorption amount (m mol./kg)

40

30

20

10

0

10⁻⁶   10⁻⁵   10⁻⁴   10⁻³

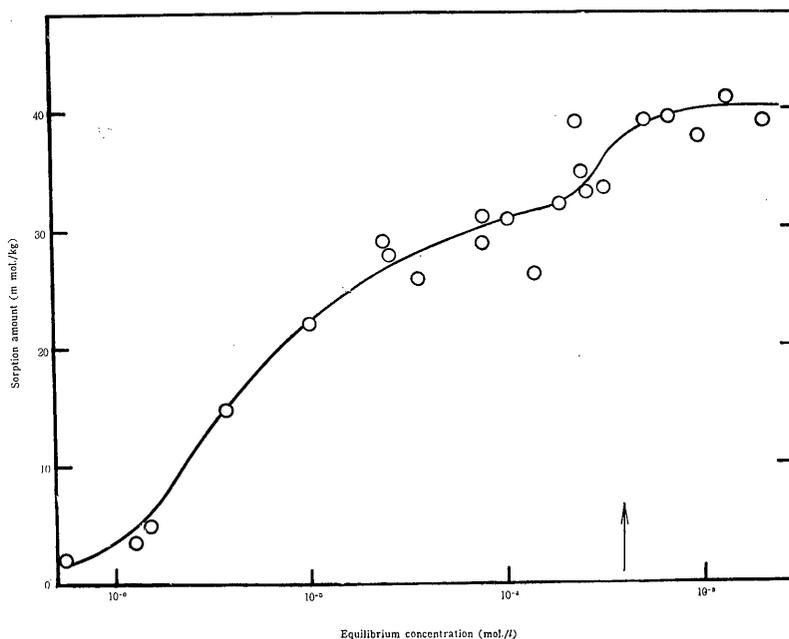Equilibrium concentration (mol./l)

</div>

FIG. 5. Sorption isotherm of SHS at 35°C. The arrow shows cmc.
</figure>

this experimental condition. So a stretching velocity of a film due to the swelling was measured. One of the results of this swelling experiment is shown in Fig. 6, from which it is seen that the swelling velocity is so fast as compared with the desorption rate of the solutes that it is negligible. The results in the desorption measurement are shown in Figs. 7,8 and 9.

<figure>
<div style="text-align:center">

Swelling (arbitrary unit)

0   1   2   3   4
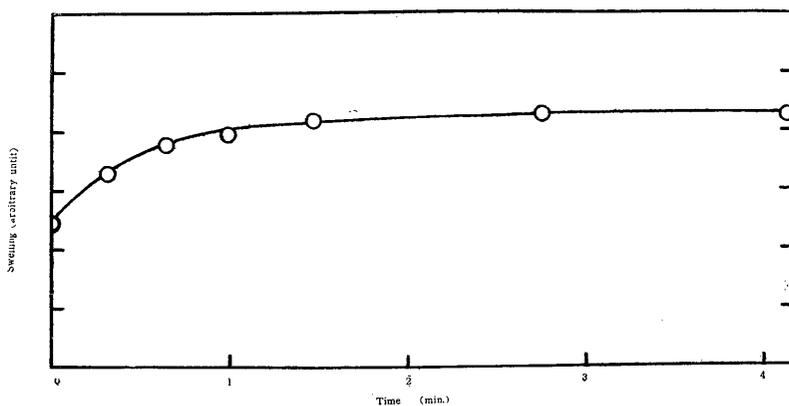
Time   (min.)

</div>
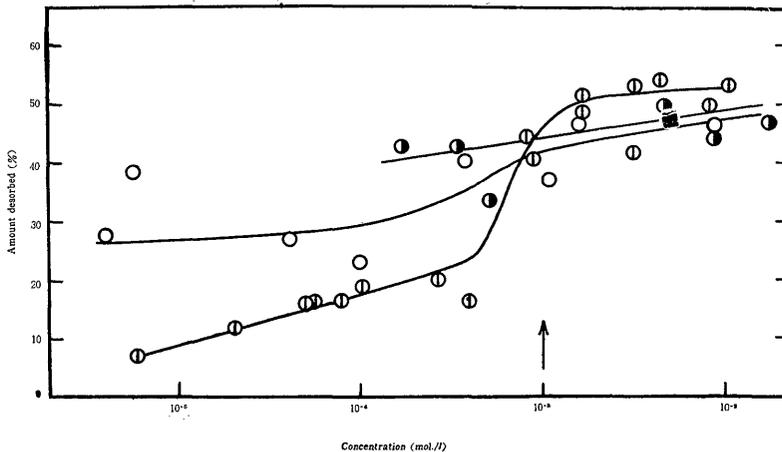
FIG. 6. Swelling rate in water
</figure>

FIG. 7. Desorption rates of STS at 35°C. The ordinate is the amount of solute desorbed from nylon film by rinsing in solutions or water for 50 minutes. Desorbing liquids: ◐ pure water, ○ 0.1 N sodium chloride solution, ◐ respective radio-inactive STS solution. The arrow shows cmc.
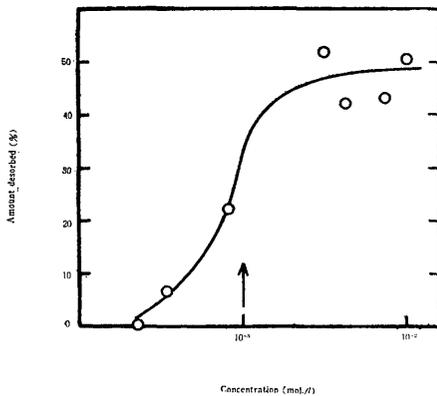

FIG. 8. Desorption rate of STS in water at 49°C. Rinsing time is 20 minutes. The arrow shows cmc.
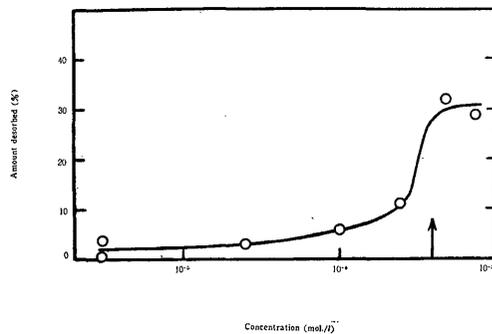

FIG. 9. Desorption rate of SHS in water at 35°C. Rinsing time is 50 minutes. The arrow shows cmc.

DISCUSSION

In the adsorptions of surface active agents onto various solids, it has been generally observed that the adsorption amount increases abrupty near cmc, though it was not always attended. A maximum in the adsorption amount at a higher concentration above cmc is also a common feature. These two phenomena have been mainly discussed up to the present, with respect to which the following two points have been considered, (a) the change in the state of the solute in

solution, (b) the change in the nature of the adsorbent.

With respect to the latter, a swelling of adsorbent was adopted by EVANS[3] to interpret the maximum in the isotherms for the adsorption of the surface active agents on cotton, nylon and others. This is, however, not only insufficient for interpreting an abrupt increase at cmc, but also untenable excepting polymer substances.

CORRIN et al[2] observed the clear discontinuity at cmc in the adsorption isotherms of dodecyl sulfate and potassium myristate on graphite, but they did not interpret the mechanism. MEADER AND FRIES[12] observed the similar behavior in the adsorption of various detergents on cotton and considered an adsorption of usual micelles for this phenomenon. FAVA AND EYRING[5] rejected this consideration and assumed a presence of adsorbable small aggregates to interpret the abrupt rise of the adsorption amount near cmc. They considered that these aggregates turned into usual micelles at the concentration corresponding to the maximum. According to this argument, however, the desorption rates of solutes should be different between the both sides of this increasing point (cmc), but they did not observe such a difference. To overcome this difficulty, they further assumed that whole adsorbates were probably distributed in the same way on the surface of the adsorbent irrespective of the adsorbing process.

In the present experimental results any maximum in the adsorption isotherms was not observed, which was also confirmed by some measurements[7,11]. On the other hand, the abrupt increase at cmc was clearly observed as shown in Figs. 4 and 5, especially it was pronounced in the case of STS. As shown in Fig. 7, the desorbing rates into pure water increases abruptly at the increasing point of the sorption amount (cmc), when they are plotted against the concentration of the detergent solution to which the sorption has been equilibrated. In the desorption into 0.1 N sodium chloride solution, the difference of the desorption rates between the both sides of cmc is comparatively small and in the case of radio-inactive STS solution, in which the self-diffusion rate of STS in nylon is the rate determining step, it is further small. And in the region of the concentrations above cmc, the difference is not evident among the desorbing liquids used.

SHEPARD ET al.[13,14] studied the adsorption and the desorption of fluorocarbon compounds on various solid surfaces and observed that the desorption rate by an exchanging process which was accomplished by using the solution of radio-inactive compounds as the desorbing liquid was always larger than that by pure solvent. They also observed that the desorption of the physically adsorbed layer is faster than the chemically adsorbed one. UNDERWOOD ET al.[15] observed the similar effect between water and solution as desorbing liquid in the desorption of sodium sulfate absorbed on hair. The behavior below cmc in the

present results is similar to these results, but above cmc the situation is quite different, that is, little difference in the desorption rate is observed in this region among the desorbing liquids. This is considered to show that an exchanging process does not contribute to the desorption of the adsorbates above cmc and the fraction of the chemisorption is small. Therefore, it is probable that some extent of solutes is adsorbed by van der Waals force to the hydrocarbon portion of nylon molecule or the formation of the surface micelle. On the contrary, the behavior in the region below cmc shows that the adsorption is mainly introduced by chemisorption which is probably an attachment at the amine end groups. The difference between water and 0.1 N sodium chloride solution in this region strengthens this idea and that between sodium chloride and STS solutions shows the difference in affinity for nylon of these solutes.

CHIPALKATTI ET al.[1] showed that some non-ionic substances were adsorbed on nylon by hydrogen bond. It has been considered that ionic compounds such as dyes are attached at the amine and amide groups, but TACHIBANA ET al.[5] showed in their study on monolayer of nylon the physical adsorption of some dyes for hydrocarbon chain of nylon molecule. VOLD ET al.[16] predicted the formation of surface micelle in their study of the adsorption of SDS on carbon black and used this consideration to interpret the maximum which appeared in the higher concentration above cmc. The results in the present report suggest that the surface micelle is probably formed near cmc.

REFERENCES

1) CHIPALKATTI, H.R. GILES, C.H. AND VALLANCE, D.G.M.: *J. Chem. Soc.*, 4375 (1954).
2) CORIN, M.L. LIND, E.L. ROGINSKY, A. and HARKINS, W.D.: *J. Colloid Sci.*, 4: 485 (1949).
3) EVANS, H.C. *ibid.*, 13: 537 (1958).
4) FAVA, A. AND EYRING, H.: *J. Phys. Chem.*, 60: 890 (1956).
5) HAYASHI, M. TACHIBANA, T. and YABE, M.: *J. Chem. Soc. Japan, Ind. Chem. Sec.*, (*Kogyo Kagaku Zasshi*), 63: 1545 (1960).
6) HAYASHI, M.: *Bull. Chem. Soc. Japan*, 33: 1184 (1960).
7) HAYASHI, M. AND NAKAZAWA, Y.: *Radioisotopes*, 8: 149 (1959).
8) HENRIQUES, F.C. KISTIAKWAKY, C.B. MARGUETTI, C. AND SCHNEIDER, W.G.: *Ind. Eng. Chem. Anal. Ed.*, 18: 349 (1946).
9) LIBBY, W.F.: *Anal. Chem.*, 19: 2 (1947).
10) MATUURA, R. KIMIZUKA, H. MIYAMOTO, S. AND SHIMOZAWA, R.: *Bull. Chem. Soc. Japan*, 31: 532 (1958).
11) MATUURA, R. AND SHIMOZAWA, R., unpublished

12) MEADER, A.L.Jr. AND FRIES, B.A.: *Ind. Eng. Chem.*, **44**: 1636 (1952).
13) RYAN, J.P. KUNZ R.J. AND SHEPARD, J.W.: *J. Phys. Chem.*, **64**: 525 (1960).
14) SHEPARD, J.W. AND RYAN, J.P.: *ibid.*, **63**: 1729 (1959).
15) UNDERWOOD, D.L. AND WHITE, H.J.: *Discussion Faraday Soc.*, **54**: 66 (1954).
16) VOLD, R.D. AND SIVARAMAKRISHNAN, N.H.: *J. Phys. Chem.*, **62**: 984 (1958)
17) YANKWICH, P.E. NORRIS, T.H. AND HUSTON, J.: *Anal. Chem.*, **19**: 439 (1947).