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# Measurement of the Adsorption of Tritium Labelled Sodium Stearate at Air/Water Interface using Thin Windowed Geiger-Müller Counter Tube

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The adsorption of tritium labelled sodium stearate at various pH values and temperatures was directly measured by using a thin end-windowed Geiger-Müller counter. The disturbances due to the application of high electrical potential and the introduction of counting gas were avoided, which are inevitably encountered in an ordinary windowless $2\pi$ counter. Precautions were taken to avoid both surface evaporation effect and contamination of solution due to the absorption of carbon dioxide from the air. The results show that free stearic acid is considered to be the main surface active species in an aqueous sodium stearate.

The radiotracer technique using tritium is particularly suited for the accurate measurement of adsorption because of extreme softness of its beta radiation. But for this same reason the counting of tritium radiation suffers from errors which should not be overlooked. For tritium beta-counting, a windowless gas flow $2\pi$ counter is often used because of its high detection efficiency,[1] and the adsorption of tritium labelled detergent at air-water interface has been measured by this method.[2] However, this counter introduces several difficulties in the measurement of the radioactivity from aqueous surface. They arise chiefly from the high electrical potential applied between the solution surface and the anode placed over it for the counting of radioactivity, and from the contamination of the aqueous surface by a counting gas such as propane, though a good counting stability is shown against moisture. These disturbances can be shown by the following.

In the first experiment, the surface tension of water and that of aqueous solution of sodium dodecyl sulfate (SDS) were measured at 20°C by the Wilhelmy method in atmosphere with and without propane gas. No surface tension depression was observed when the water surface was brought to contact with propane gas, whereas for $5\times10^{-3}$ mol/$l$ aqueous SDS solution the surface tension depression of about 2.3 dyne/cm was produced by contact of propane gas with the aqueous surface. This evidently shows the influence of propane gas, presumably producing a change in adsorption of SDS and/or propane due to its contact. Such a change was demonstrated in a separate experiment.

In the second experiment, the effect of applied electric field upon the surface tension of aqueous solution was checked at the same temperature. Using the electrode assemblies which simulate the conditions of the counting chamber of a windowless $2\pi$ counter usually employed in such a measurement, the surface tension of aqueous SDS solution was measured with and without an applied electric field of 4000 V in the propane gas atmosphere. In this experiment precaution was taken to avoid the influence of direct electrical interaction, if any, between the anode and the glass plate for the surface tension measurement. The results show a surface tension drop of 3.1 dyne/cm for an aqueous surface of SDS solution ($5\times10^{-3}$ mol/$l$) in propane gas by the application of 4000 V external field, while in the case of water surface only 0.1 dyne/cm drop was observed for the surface tension under the same condition. We can observe the streaming of the solution at the surface caused by applied electrical potential from the motion of talc scattered over the surface. These experiments also show the possibility of undesirable effect of high electrical potential upon the establishment of the true adsorption equilibrium. Therefore measurements free from such disturbances are desired.

In our preceding paper,[4] we stated that soft tritium radioactivity could be measured effectively by using a thin polycarbonate end-windowed Geiger-Müller counter tube without the difficulties which an ordinary windowless flow-counter encounters. It also enables measurements free from the above electrical and surface chemical disturbances. In the present investigation, we employed this method for the measurement of the adsorption of tritium labelled sodium stearate on aqueous surface. Here, precautions were further taken to avoid both

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[1] G. W. Eulitz, *Rev. Sci. Instrum.*, **34**, 1010 (1963).

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

[4] T. Seimiya, K. Sekine and T. Sasaki, *J. Sci. Insturm.*, **42**, 906 (1965).

the surface evaporation affecting the surface concentration of the solute,[5] and the absorption of carbon dioxide into the solution from atmosphere, which proved to have great effect on the results.[6]

It may be mentioned in this connection that Flengas and Rideal also studied the adsorption of $^{14}$C-labelled sodium stearate solutions[7] and obtained results somewhat different from ours as will be described later. Their results, however, involve some uncertainty as to the solubilities of soap,[8] evaporation effect, the constancy of pH and the effect of carbon dioxide[3,6] since no distinct statements concerning them could be found. The present paper described the apparatus and measurement of adsorption of sodium stearate, free of these uncertainties and the errors due to the applied electrical field and contact with gas.

## Experimental

**Apparatus.** The surface concentration was measured by a gas flow GM-counter (FC-16, Japan Radiation and Medical Electronics Inc.), the counter tube being equipped with an end-window of a thin polycarbonate film[4] of 34 mm effective aperture. The tritium-labelled sodium stearate was dissolved in distilled water and the solution was contained in a 120×61 mm rectangular Teflon trough of 5.6 mm depth. The distance between the window of the counting tube and the aqueous surface was kept to 0.5 mm by means of a platinum needle fixed to the window. A movable barrier was placed on the trough and was operated from outside the thermostatted box to sweep the aqueous surface.

Special care was taken to avoid a change of geometry due to the difference in pressure across the thin window, by supporting the film with a perforated thin brass sheet (0.15 mm thick and 50% perforation in area). In order to avoid surface evaporation and absorption of carbon dioxide from the surrounding atmosphere, nitrogen gas which was passed through charcoal and saturated with water, was let to flow gently over the liquid surface. The whole apparatus was put in an air thermostat of 30, 40 and 50°C during the experiment.

**Materials.** Sodium stearate was prepared by dissolving tritium-labelled stearic acid (specific activity 7 Ci/mol)[9] in absolute alcohol freshly distilled over sodium hydroxide, and a smaller amount of sodium hydroxide than that required for neutralization of the acid was added. The soap solution thus prepared was evaporated to dryness *in vacuo*, and the residue was washed with benzene to remove excess stearic acid using a Soxhlet extractor. The water used in this experiment was obtained by refluxing ordinary distilled water in an acid permanganate solution for 24 hr, then adding excess alkali and distilling. Water thus obtained was further distilled twice from Hysil flasks connected in series.

**Procedures.** The calibration curve used for calculating the amount of adsorption from the observed counting rate was made by measuring the counting rate of a known amount of radioactive stearic acid monolayer spread on water surface. For this purpose the trough was filled with water of pH controlled to 5.5 by adding distilled hydrochloric acid, and tritium-

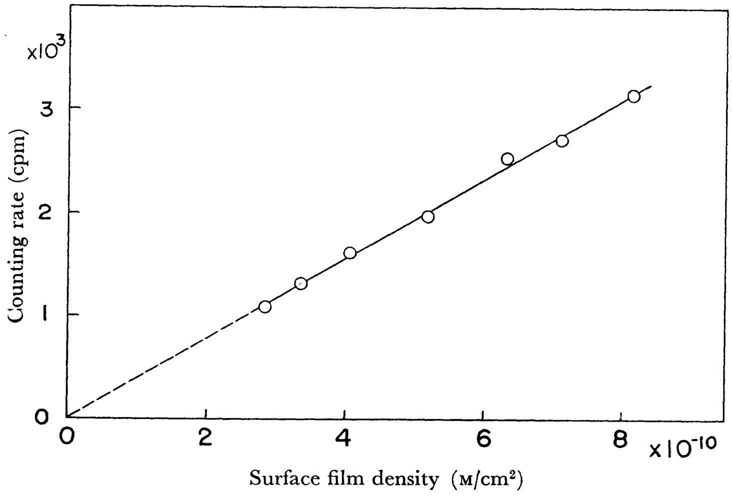

Fig. 1. Surface counting rate against film density for stearic acid monolayer.
Substrate : distilled water, pH 5.5
temperature, 20°C

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[5] T. Seimiya and T. Sasaki, *J. Colloid Interfac. Sci.*, **21**, 229 (1966).

[6] J. Bagg, M. D. Haber and H. P. Gregor, *ibid.*, **22**, 138 (1966).

[7] S. N. Flengas and Sir E. Rideal, *Trans. Faraday Soc.*, **55**, 339 (1959).

[8] J. W. McBain and W. C. Sierichs, *J. Amer. Oil Chem. Soc.*, **25**, 221 (1948).

[3] To be published in the near future.

[9] M. Muramatsu, O. Fuji and T. Sasaki, *Radioisotopes* (in Japanese), **10**, 100 (1961).

labelled stearic acid having the same sprecific activity as that of the tritium-labelled sodium stearate was spread on water surface from $2.40 \times 10^{-4}$ mol/*l* benzene solution by means of a microsyringe. The plots of the counting rate *versus* surface concentration were obtained from the radioactivity measurements made at various surface concentrations by compressing and expanding the monolayer. The result is shown in Fig. 1.

At low surface concentration, surface heterogeneity and its time dependence were observed for this monolayer by the radioactivity measurement (Fig. 2a). Usually, however, by standing the surface film at 20°C for at least several hours the film became homogeneous and the time dependence practically vanished when detected by means of radioactivity. As the surface concentration increased, the surface film became more homogeneous and time effect also disappeared (Fig. 2b).

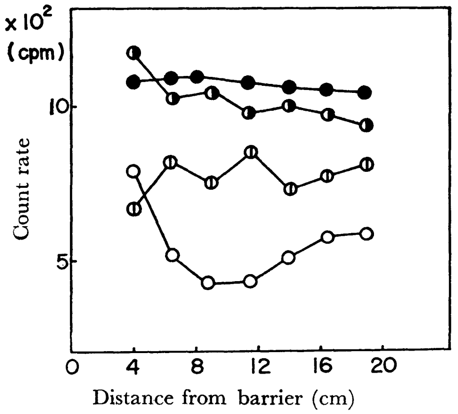

Fig. 2a. Change in homogeneity of monolayer with time.
Substrate : distilled water, pH 5.5
temperature, 20°C
Film density : 55.7 Å$^2$/mol
Age : ○, 0 hr
⦶, 1 hr
◑, 2 hr
●, 3 hr

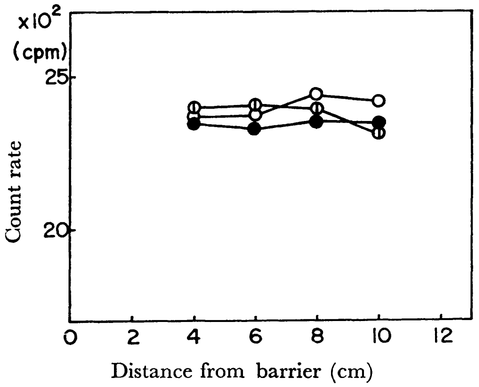

Fig. 2b. Change in homogeneity of monolayer with time.
Substrate : same as Fig. 2a
Film density : 28.0 Å$^2$/mol
Age : ○, 0 min
⦶, 30 min
●, 60 min

To measure the adsorption of sodium stearate at solution-air interface the radioactive sodium stearate solution of $2.5 \times 10^{-5}$ mol/*l* concentration was put in the same Teflon trough as used in the monolayer measurement, and the counting of surface radioactivity was started immediately after the sweeping of surface by the barrier. The geometry of the whole arrangement including the GM-tube was kept constant.

The counting rate obtained by subtracting the one due to the bulk of the solution[2] from the observed surface counting rate gives the amount of sodium stearate adsorbed at the solution/air interface. In this experiment, the bulk counting rate turns out to be a very small fraction of the total counting rate, being comparable to the back ground counting rate when the monolayer adsorption is established. This fact may be expected from an extremely low concentration of the solution ($2.5 \times 10^{-5}$ mol/*l*) and the softness of beta-ray. This can also be confirmed by the fact that for some solutions the surface counting rate at the initial stage of measurement is comparable to that of the back ground. Therefore the bulk counting rate can be neglected within the limit of the counting error. The pH of the solution was controlled by hydrochloric acid and sodium hydroxide free from carbon dioxide, and was kept constant throughout the experiment within ±0.1 by keeping the trough in a humidified nitrogen atomsphere. Measurements were made at 30, 40 and 50°C, and the concentration of sodium stearate was kept at $2.5 \times 10^{-5}$ mol/*l* throughout the experiment.

## Results and Discussion

The equilibrium amount of adsorption $\Gamma$ was measured and plotted against the pH of the solution at each temperature as shown in Fig. 3. The curves for 30 and 40°C show plateaux in the pH region proper for each system and the $\Gamma$ values of these plateaux nearly agree with that of monolayer

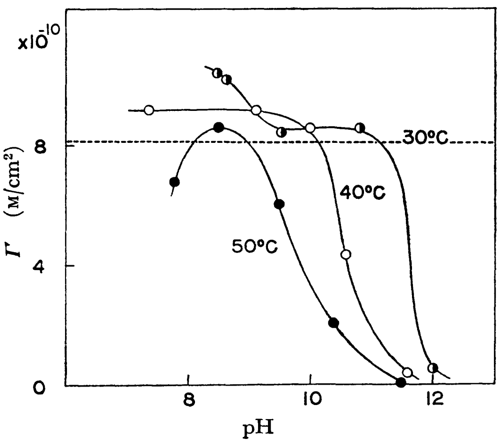

Fig. 3. pH dependence of stearate adsorption at air/solution interface.
Concentration of sodium stearate : $2.5 \times 10^{-5}$ mol/*l*

adsorption (dotted line in Fig. 3) calculated by using the value of 20.5 A$^2$/mol known as the area occupied by a stearic acid molecule on water. In a less alkaline region $\Gamma$ exceeds the monolayer value at 30°C, while $\Gamma$ is smaller than the monolayer value at 50°C.

Apart from some irregularities, the agreement of $\Gamma$ value of the plateaux with that of monomolecular area of stearic acid suggests the possibility that the adsorption layer actually consists of stearic acid instead of stearate ion. We have some evidence to support this view. Lucassen$^{10)}$ pointed out that the major species of the aqueous solution prepared by dissolving sodium stearate in distilled water is changed to free stearic acid. Harkins$^{11)}$ also observed a relatively high surface tension for an aqueous sodium laurate solution in an alkaline region, and low surface tension for a neutral solution and gave a similar explanation. Our study on the surface pressure-area curve for sodium stearate by means of the simultaneous measurements of the amount of adsorption and surface tension of the solution suggests that the adsorbed species is stearic acid.$^{3)}$ Figure 3 shows that at pH higher than 12, the amount of adsorption of the solution is almost reduced to zero. This sudden decrease of adsorption is ascribed to salting out of the soap due to the high concentration of sodium hydroxide added, causing decrease of concentration of stearate ion. To assure the concentration decrease of soap solution at high pH, soap solutions at pH 10.7 and 12.3 were centrifuged, and the concentration of the supernatant solution was determined by radioactivity measurement. The results show a marked decrease of soap concentration in the solution for pH 12.3 while no tendency of decrease is observed for 10.7. Flengas and Rideal$^{7)}$ reported a higher value of stearate adsorption than ours in this pH region. However, their results do not seem to confirm the presence of carbon dioxide in an atmosphere which influence the amount of adsorption (possibly resulting in an overestimation), since it can be confirmed$^{6)}$ that the amount of adsorption is quite sensitive to the presence of carbonate ions in solution even in the pH of the solution is kept unchanged.

We note the decrease of adsorption below pH 8 at 50°C. This may be explained by the formation of free stearic acid precipitate$^{10)}$ as recognized by the turbidity of the solution. However, the increase of adsorption beyond the monolayer at 30°C remains unexplained at present.

An overall trend of decrease of adsorption with temperature is also seen. The adsorption may be affected by temperature in two ways. One, by enhanced degree of bulk hydrolysis at high temperatures, and the other, by the increased solubility of stearic acid at higher temperature. Adsorption is expected to increase in the former case and decrease in the latter case. The result suggests that the latter tendency is dominant as far as the present experimental conditions of temperature and time ranges are concerned.

We are of the opinion that in an aqueous sodium stearate solution the surface active species is exclusively free stearic acid, while stearate ion is less surface active. The adsorption of stearic acid is unexpected although suggestions have been made as to the hydrolysis in bulk of the solution by other investigators. It should be emphasized that the present conclusion is mainly based upon the results of direct adsorption measurements in comparison with the conclusions or predictions obtained more or less theoretically and indirectly.

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10) J. Lucassen, *J. Phys. Chem.*, **70**, 1824 (1966).
11) F. A. Long, G. C. Nutting and W. D. Harkins, *J. Amer. Chem. Soc.*, **59**, 2197 (1937).