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Kinetic Studies of Adsorbed Films of Tritium-labelled Sodium Stearate at the Air/Water Interface

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The adsorption of tritium-labelled sodium stearate at the air/water interface was directly measured radiometrically using an ultra-thin-windowed Geiger-Müller tube for varying soap concentrations, pH values, and temperatures. The changes in the amount of adsorption and in the surface tension were simultaneously traced with the lapse of time. The pressure-area curve was then obtained by the successive plotting of the surface pressure against the area at the same aging; the curve at equilibrium was also obtained. Thus, the pressure-area relationship of the adsorbed monolayer was automatically measured during the course of adsorption approaching equilibrium. A close resemblance was observed between the monolayer of stearic acid on neutral water and the adsorbed films on the stearate solution of pH values from 8.85 to 9.30 at 30°C. The amount of adsorption measured for an alkaline solution often exceeds the value to be expected from the saturation value for a completely-ionized stearate monolayer. The pressure-area characteristics suggested a transition from the condensed state of the adsorbed film at a higher surface concentration to an expanded state at a lower concentration. It was also confirmed, by measuring the amount of adsorption in the atmospheres of both nitrogen and air containing carbon dioxide, that the atmospheric carbon dioxide acts to increase the adsorption of stearic acid on the aqueous surface. The diffusion coefficient of the adsorbing solute, calculated from the initial rate of adsorption, showed a smaller value than that obtained by conductometric measurements.

A number of investigations have been presented by many workers into the properties of adsorbed monolayers at both air/water and oil/water interfaces. Efforts have also been made to obtain the pressure-area relationship for the adsorbed monolayers of soluble, surface-active substances. In some of these studies, a monolayer was spread on an aqueous surface,[1,2] and from the observed surface pressure changes against the time, the surface pressure extrapolated to time zero was plotted against the area per molecule, assuming that no molecule was lost by desorption or evaporation.

In other studies the pressure-area relationships were obtained by spreading the film substances on aqueous substrates that contained excess salt, thus preventing the desorption of film molecules by decreasing the solubility of the film substance.[3-8] These methods may be convenient and easy to practise for the study of the soluble monolayer, but at the same time they involve several disadvantages. The major disadvantages exist in using a sufficiently concentrated solution of inorganic salt and/or a solution of a restricted pH as a substrate, especially for a monolayer of an ionizable nature. Another question is an uncertainty arising as to the amount of film substances remaining on the surface. For the theoretical treatment of the adsorbed film, it is also necessary to have exact knowledge regarding the dissolved state of the solute, which may suffer from hydrolysis or association.

In the present report, pressure-area studies were made for the soluble, adsorbed films of tritium-labelled sodium stearate, the amounts being determined directly by the radiotracer method. The pressure-area characteristics at the air/water interface have been investigated under various conditions of the substrate pH, solute concentration, and temperature. The results have then been discussed from both kinetic and equilibrium aspects.

Experimental

The Effect of Evaporation on the Surface Concentration. One of the major troubles encountered

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1) H. L. Rosano and G. Karg, *J. Phys. Chem.*, **63**, 1692 (1959).

2) L. Ter Minassian-Saraga, *J. Colloid Sci.*, **11**, 398 (1956).

3) J. A. Spink, *ibid.*, **18**, 512 (1963).

4) E. D. Goddard, *ibid.*, **18**, 585 (1963).

5) E. D. Goddard, *ibid.*, **21**, 320 (1966).

6) E. D. Goddard, 4 th Int. Congr. Surface Activity (Brussel) B/II. 6.

7) E. D. Goddard, *J. Colloid Sci.*, **24**, 297 (1967).

8) J. T. Davies, *Trans. Faraday Soc.*, **48**, 1052 (1952).

in the study of the properties of the air/water interface is the evaporation of a solute or solvent from the solution surfaces. This evaporation affects the surface properties of liquid in a complicated manner by lowering surface temperature[9] and changing the surface concentration.[10] The first change subsequently changes other surface properties, such as the surface tension, and disturbs the system by promoting the convection current. The change in the concentration of a solute near the surface of the solution depends on a dynamic equilibrium between the rate of evaporation and the convection current occurring near the surface of the liquid. Preliminary radiotracer experiments have proven that only 60 seconds' exposure of the surface of an aqueous solution containing a 1.97×10^{-3} mol/l surface inactive sodium sulfate to an atmosphere of 40% relative humidity at 20°C without any air current produced the accumulation of a solute which is shown in Table 1. The accumulation was detected by the increase in the surface count rate of beta-rays from ^{35}S, with which Na_2SO_4 was labelled. The changed count rate was soon restored to its original value by suppressing the evaporation. Simple calculation shows that the amount of surface-concentration increase is about 50% of the amount of the maximum adsorption of such commonly-used surfactants as sodium dodecyl sulfate. Thus, it can be demonstrated that even a slight evaporation produces a serious error in the measurement of the properties concerning the liquid surface. Great care to prevent evaporation was taken in the present study by placing the trough containing the solution for study in a compact enclosure saturated with water vapor, as will be described later.

Table 1. Effect of evaporation of water on surface concentration of aqueous Na_2SO_4 solution

Surface	Surface count rate (cpm)	Mean
1 Measured after 240 secs' stirring without evaporation	6460 6530 6530 6415 6510 6600	6518±81 ±1.24%
2 After 60 secs' exposure to open air	6760 6590 6600 6710 6740 6690 6860	6707±82 ±1.22%
3 After suppressing the evaporation of the above surface 2	6550 6510 6550 6460	6519±81 ±1.24%

$Na_2{}^{35}SO_4$: 1.97×10^{-3} mol/l
Specific activity: 1.09×10^{-12} mol/cpm. cm^2
Room temperature: 20°C
Humidity of the atmosphere: 40% R.H.

Measurement of Tritium Radioactivity from an Aqueous Surface. The extremely soft beta-radiation is best suited for surface analyses, as has been mentioned above; unfortunately, however, the softness itself renders the detection of tritium very difficult.

Here, a windowless gas-flow 2 π counter is generally used because of its high counting efficiency[11], as in the study of the adsorption of tritium-labelled sodium dodecyl sulfate[12] on an aqueous surface. In this case, however, the aqueous surface was inevitably exposed to hydrocarbon counting gas and to a high electrical field applied for the measurement of radioactivity.[13] To avoid such disturbances, we attempted to measure the tritium beta-radiation using an end-windowed Geiger-Müller counter tube equipped with a thin polycarbonate window. A thin film of polycarbonate was prepared by the following procedure,[14] The polycarbonate was dissolved in an equi-volume mixture of dioxane and ethylene dichloride up to 0.4 % and was then spread on a clean glass plate with an optically-flat surface, using a glass applicator composed of two glass rods tightly bound together with steel wire which determined the thickness of the liquid film. After slowly evaporating the solvent, the deposited film was removed and transferred on the water surface by immersing the plate in water. The thin film, floating on the aqueous surface was scooped up with a steel ring, treated with an aqueous polyvinyl alcohol solution in order to fill up the pinholes inevitably formed in the film, and dried at 100°C. After the vacuum deposition of gold on one side of the film, the film was fixed to an attachment grid with a 75% opening. The thin film thus prepared and attached to the end-windowed Geiger-Müller tube (type FC-16, Japan Radiation and Medical Electronics, Inc.) proved successful for the measurement of the soft beta-radiation of tritium from aqueous surfaces, a measurement which had hitherto been impossible with the ordinary Geiger-Muller tube with a thick window. The optimal thickness of the polycarbonate film used was 15—20 μg/cm^2. The overall counting efficiency attained for tritium was 9% of that obtained by using a windowless gas-flow 2π counter when polyvinyl alcohol-treated polycarbonate windows of 17.5 μg/cm^2 were used at a distance of 1 mm from an infinitely thin tritium sample in air. Further, th film proved to suffer no perceptible change in counting efficiency over several months. The details of the method of preparation and the properties of the film may be found in a former report.[14]

The Trough and Surface Balance. The surface tension of the aqueous sodium stearate solution was measured by a self-recording Wilhelmy-type surface balance[15]; the surface radioactivity was simultaneously measured. The apparatus is shown in Fig. 1. A Teflon trough ($120 \times 61 \times 5.6$ mm) was put in a jacket

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[9] N. L. Jarvis, *J. Colloid Sci.*, **17**, 501, 512 (1962).

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

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

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

[13] G. Nilsson and G. Aniansson, *Nucleonics*, **13**, 38 (1955).

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

[15] K. Ohbu, T. Seimiya and T. Sasaki, 18th Colloid Symposium (Shimane University 1965).

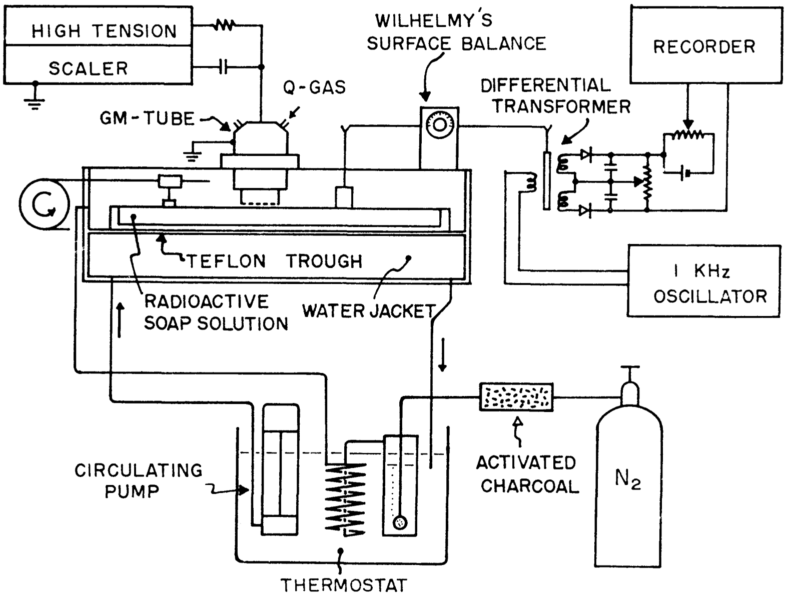

Fig. 1. Apparatus for simultaneous measurements of amount of adsorption and surface tension.

box, and the temperature of the solution in the trough was kept constant by the circulation of thermostatted water through the jacket surrounding the trough. The evaporation of water from the aqueous surface was prevented by slowly introducing nitrogen gas saturated with water vapor into the space above the trough. The radioactivity and surface-tension measurements were started just after the sweeping of the surface by a Teflon barrier which could be operated outside the lagged box. The Wilhelmy surface balance was equipped with a differential transformer (type DS-36-LM, Shinkoh Electric Works, Tokyo) which converted the minute displacement of the hanging plate to a proportional electrical output.[15] The primary input for the differeytial transformer was supplied by a 1-kHz oscillator. The output was then rectified and recorded by means of a Hitachi QPD 33 recorder after an appropriate application of bias voltage in order to put the desired part of the surface-tension change into the range of the recorder scale. Thus, the surface tension change could be recorded within an accuracy of ±0.09 dyne/cm.

Materials. The tritium-labelled sodium stearate used was prepared[16] by dissolving tritium-labelled stearic acid[17] (specific activity, 7 Ci/mol) in absolute alcohol freshly distilled over sodium hydroxide; an amount of sodium hydroxide slightly less than that required for the neutralization of the acid was added as an alcoholic solution. The soap solution thus prepared was evaporated to dryness in vacuo, and the residue was washed with benzene to remove excess stearic acid by using a Soxhlet extractor. The water used in this experiment was obtained by first refluxing distilled water in an alkaline permanganate solution for 24 hours, and by then distilling it three times from a Hysil flask. The carbon-dioxide contamination from the air was removed by boiling the water for about ten minutes and then cooling it in a nitrogen atmosphere. The supernatant solution of saturated aqueous sodium hydroxide, after being centrifuged, was used to control the pH of the stearate solution.

Procedures. The conversion factor used for calculating the amount of adsorption from the observed counting rate was obtained by measuring the counting rate of a known amount of a radioactive stearic acid monolayer spread on the water surface. For this purpose, tritium-labelled sodium stearate was spread on distilled water from a 2.40×10^{-4} mol/l benzene solution by means of a microsyringe. At a low surface concentration, the heterogeneity of the monolayer and its time dependence were usually observed.[16] However, when left standing at 20°C for at least several hours, the film became homogeneous and the time dependence practically disappeared as far as the surface radioactivity was concerned. As the surface concentration increased, the surface film became more homogeneous and the time effects disappeared. The counting rate versus surface concentration curve was obtained from radioactivity measurements made at various surface concentrations by means of the compression and expansion of the monolayer. A linear relationship was confirmed within the limits of counting errors. For the measurement of the adsorption of sodium stearate at the air/water interface, a radioactive sodium stearate solution with a $1.0—5.0\times10^{-5}$ mol/l concentration was put in the Teflon trough used in the monolayer measurement, and the counting of the surface radioactivity was started immediately after the sweeping of the surface by the barrier. The bulk-count rate should be subtracted from the total count rate observed to give the surface radioactivity due to the adsorption of stearate at the air/water interface. In this experiment, the bulk-count rate was comparable to the background, so it was negligibly small compared with the total count rate. This

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[16] K. Sekine, T. Seimiya and T. Sasaki, This Bulletin, **43**, 629 (1970).

[17] M. Muramatsu and T. Sasaki, *Radioisotope*, **10**, 100 (1961).

can reasonably be expected from the extremely low concentration of the solution used and the small range of beta-rays, about 1 micron in water. It is also confirmed by the fact that, for some solutions, the surface count rate at the initial stage of adsorption is comparable to that of the background. Therefore, the bulk-count rate can safely be neglected within the limits of counting error in the present experiment. The pH of these solutions was kept constant (within +0.1) throughout the experiment by keeping the trough in a humidified nitrogen atmosphere and by avoiding the dissolution of carbon dioxide from the air. The measurements were carried out at both 40°C and 30°C for the solutions with pH values from 8 to 11, and at concentrations from 1 to 5×10^{-5} mol/*l*.

Results and Discussion

Effect of Propane Gas. As for the measurement of tritium radioactivity using windowless gas-flow 2π counter mentioned above,[13] the aqueous surface must be exposed to the propane gas, and an appreciable change in the adsorption of the surface-active agent can subsequently be expected to occur. In this connection, the surface tension was measured for the aqueous sodium dodecyl sulfate solution in atmospheres of both nitrogen and propane gas. The results are shown in Fig. 2. In this figure, a remarkable drop in surface tension was observed upon the introduction

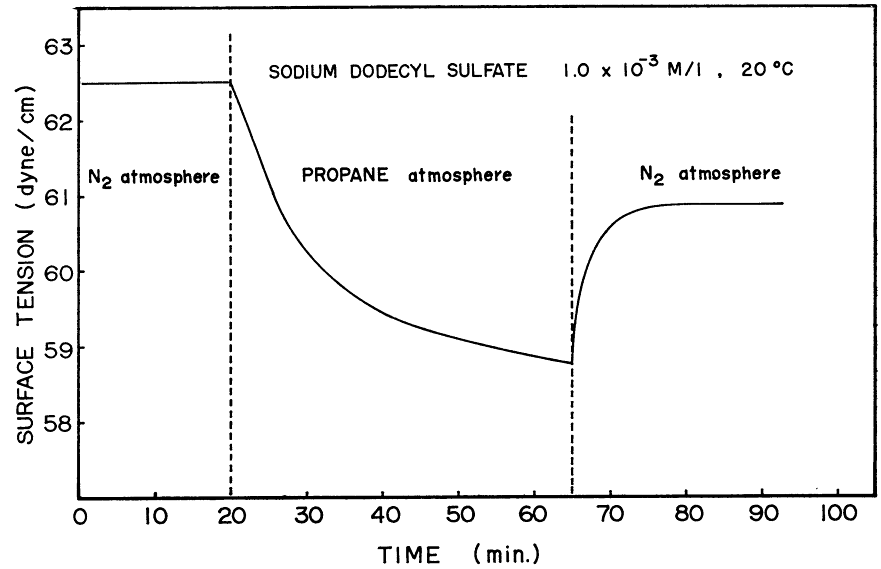

Fig. 2. Effect of propane gas on surface tension of aqueous sodium dodecylsulfate solution.

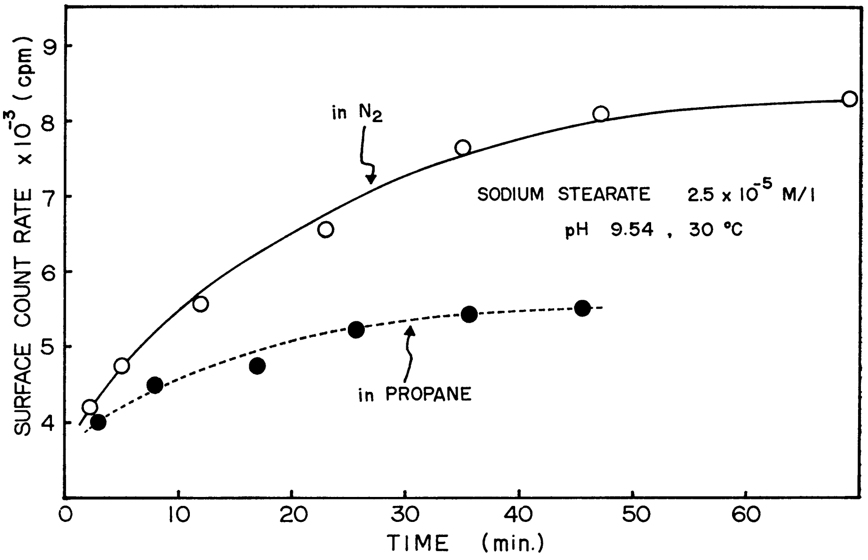

Fig. 3. Effect of propane gas on adsorption of sodium stearate at aqueous surface.

of propane gas to the aqueous surface of the sodium dodecylsulfate solution. The original value was only partially recovered by flushing the propane out with nitrogen. The effect of propane gas on the adsorption was further examined for the aqueous sodium stearate solution, as is shown in Fig. 3. An appreciable difference in the amount of the adsorption of stearate can be seen between the propane/water and nitrogen/water interfaces. The adsorption of stearate is lower for the propane/water interface than the nitrogen/water one, presumably because of the formation of a mixed film of stearate and propane at the aqueous surface, as was to be expected from the surface tension lowering shown in Fig. 2. The dissolution of propane into the aqueous stearate may also be expected to affect the stearate adsorption, although no tacit proof was found in this experiment. These experiments clearly show the considerable influence of atmospheric propane gas upon the adsorption of soap at the air/water interface.

Kinetic Aspects of Adsorpsion. Typical examples of the simultaneous measurement of the surface tension and the amount of adsorption at 30 and 49°C are presented in Fig. 4. The surface tension decreases and the amount of adsorption increases with the lapse of time. An amount of adsorption of about 8.5×10^{-10} mol/cm², nearly equal to that corresponding to the closely-packed monolayer of stearic acid, can be seen for the adsorption curve at 30°C. The surface tension curve in its early stage of aging, within 10 min, exhibits a gradual change which indicates the expanded nature of the adsorbed film at this stage. This tendency is more pronounced for the solution with a lower temperature (Fig. 4), pH (Fig. 5), and soap concentration (the third factor is not shown in the figure); the initial plateau appears in the surface tension, though a considerable increase in the amount of adsorption with time occurred during this stage. From the observed adsorption rate at an early period of aging, the diffusion coefficient of the solute can be calculated according to the equation of Ward and Tordai,[18] assuming the rate-determining process of adsorption to be the diffusion of the solute from the bulk to the sublayer of the surface, and assuming that the electrostatic potential barrier does not affect the diffusion practically in this early period of adsorption. The diffusion coefficient was calculated by the following equation;

$$\left(\frac{d\Gamma}{dt}\right)^2\cdot\frac{\pi t}{C_0^2}=D$$

where Γ denotes the amount of adsorption at time t, C_0 the bulk concentration of solute, and D, the diffusion coefficient. The observed D values for various C_0 and pH values at various temperatures are listed in Table 2, along with the values obtained by various other workers.[19-22] Although no comparison can be made between these data in a strict sense, it can at least be noted that the

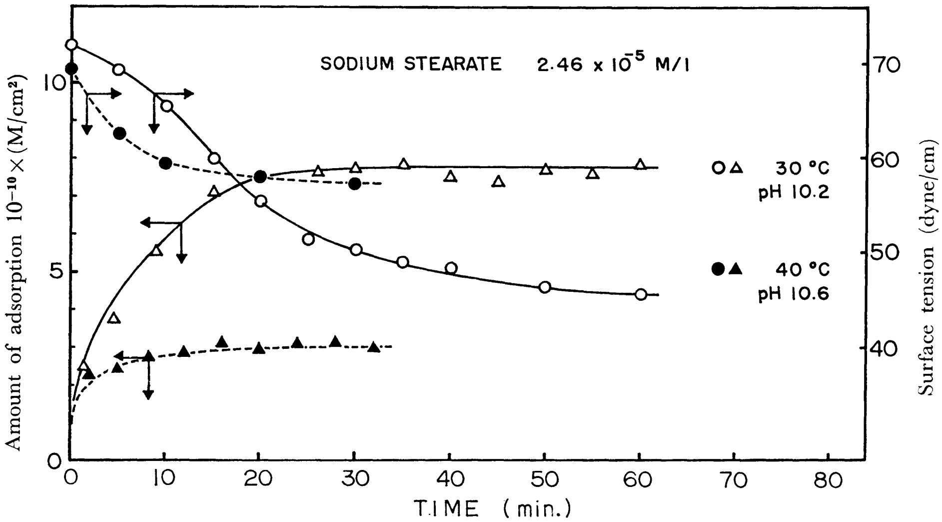

Fig. 4. Simultaneously measured amount of adsorption and surface tension for aqueous sodium stearate.

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18) A. F. H. Ward and L. Tordai, *J. Chem. Phys.*, **14**, 453 (1946).

19) R. Matsuura, H. Kimizuka, S. Miyamoto, R. Shimozawa and K. Yatsunami, This Bulletin, **32**, 404 (1959).

20) D. J. Salley, A. J. Weith, Jr., A. A. Argyle and J. K. Dixon, *Proc. Roy. Soc.*, **A203**, 42 (1950).

21) S. N. Flengas and E. Rideal, *Trans. Faraday Soc.*, **55**, 339 (1959).

22) C. C. Addison and S. K. Hutchinson, *J. Chem. Soc.*, **1949**, 3387.

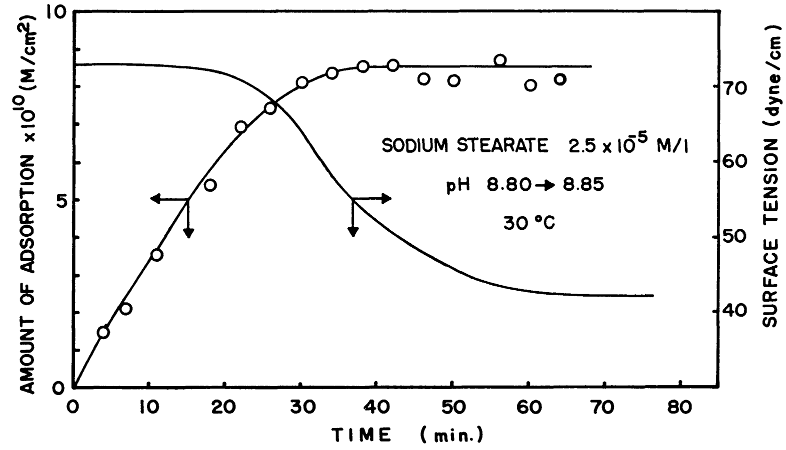

Fig. 5. Simultaneously measured amount of adsorption and surface tension for aqueous sodium stearate.

Table 2. Diffusion coefficient of surface active substances in aqueous solution

Surface active substance	C_0 (mol/l)	Temp., °C	pH	D_{obs} (cm^2/sec)	D_{cal} (cm^2/sec)
Sodium stearate	1.00×10^{-5}	40	11.0	1.88×10^{-6}	
	2.00		10.6	1.64×10^{-6}	
	3.00		10.7	1.40×10^{-6}	
	4.00		10.5	8.49×10^{-7}	
	5.00		10.7	1.51×10^{-7}	
	2.46×10^{-5}	30	10.2	9.35×10^{-7}	
Sodium hexadecylsulfate[19,20]		28		6.32×10^{-7}	4.01×10^{-6}
Sodium stearate[21]	3.26×10^{-5}	25	10.0	1.29×10^{-6}	
n-Octanol[22]	3.26×10^{-5}	20		5.94×10^{-6}	6.0×10^{-6}

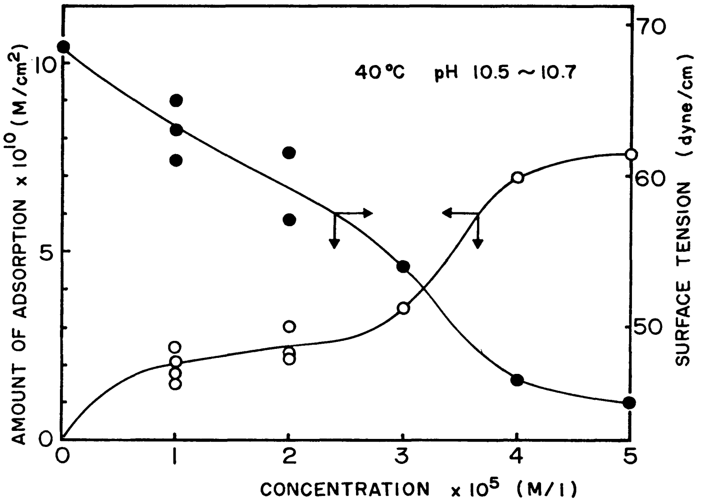

Fig. 6. Equilibrium values of surface tension and amount of adsorption for various concentrations of sodium stearate.

results of the present experiment are comparatively direct and accurate as far as the diffusion to the surface is concerned. There is also a tendency for the D value for a stearate to decrease with an increase in the solute concentration C_0. This presumably due to the effect of the electrostatic barrier assuming some importance.

Concentration Dependence of the Adsorption and Surface Tension. From these time-dependent curves of the surface tension and adsorption for various concentrations of stearate at a constant temperature and pH, equilibrium values were obtained; they are plotted against the concentration in Fig. 6. The adsorption isotherm appears step-by-step, on the whole, and shows two plateaus. The amount of adsorption in the lower concentration region is about one-third of that in the higher concentration region. The former corresponds closely to the state of saturation of the ionized monolayer,[23] while the latter corresponds to that of stearic acid. Such a step-by-step adsorption may presumably be interpreted as the superposition of two isotherms for species differing in the area of surface occupation, such as a stearate ion and a stearic acid molecule, the latter being the hydrolysis product of a stearate in the solution. The stearate ion, requiring a larger area, is predominant in the low concentration region, while the stearic acid molecule, with a smaller molecular area, appears in the higher concentration region at constant pH. Although the amount of stearic acid adsorbed is not in agreement with that expected from the bulk hydrolysis calculated by using the ordinary pK of the stearate, the discrepancy may be explained by the difference in pK between the bulk and the surface, or by the adsorption of some surface active associates between stearate and the stearic acid molecule.[4] These explanations are further supported by the pressure-area characteristics of the film, which will be described below.

Pressure-area Curve. From the time-dependence curves of the amount of adsorption, $\Gamma(t)$, and the surface tension, $\sigma(t)$, shown in Figs. 4 and 5, a Γ-σ or F-A plot can be constructed by eliminating the parameter, t, where $F=\sigma_0-\sigma$ denotes the surface pressure, σ_0 being the surface tension of water, and $A=1/\Gamma$ the area occupied by a stearate ion or a stearic acid molecule in the monolayer. In Fig. 7 such plots are constructed for varying concentrations of stearate solutions. The plots for F and A values in equilibrium appear at the end of the series of plots for each solution concentration. F-A curve thus obtained for the non-equilibrium state runs closely to that in the equilibrium state. Namely, Γ and σ change with the time in such a manner as F-A plot moves along the equilibrium F-A curve, and the successive steps of the kinetic state closely resemble that of equilibrium. In this respect, we cannot distinguish between the compression of an insoluble monolayer by a barrier in the usual monolayer technique and the compression of the soluble film due to the increase in the amount of adsorption. Thus, an automatic scanning of the pressure-area curve is made for the soluble monolabers by the simultaneous measurement of the surface tension and the amount of adsorption. The slower compression is more desirable for the surface-pressure measurements from the viewpoint of the homogeneity of the monolayer.[16] Here, the time re-

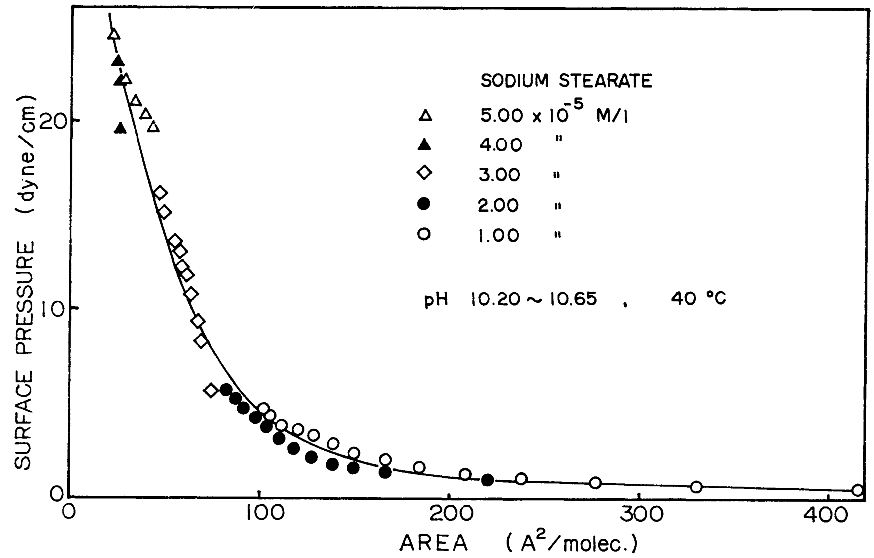

Fig. 7. Pressure-area relationship for adsorbed stearate films.

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[23] E. H. Lucassen-Reynders, *J. Phys. Chem.*, **70**, 1777 (1966).

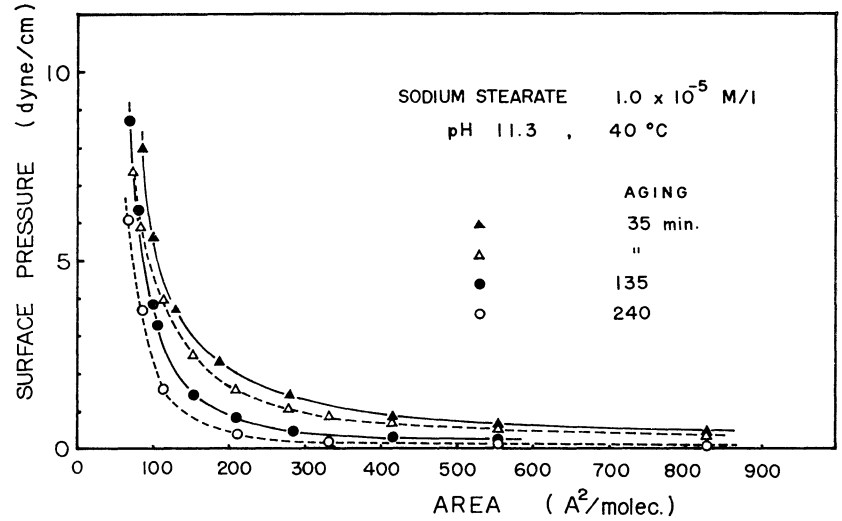

Fig. 8. Effect of bulk aging of stearate solution on pressure-area characteristics.

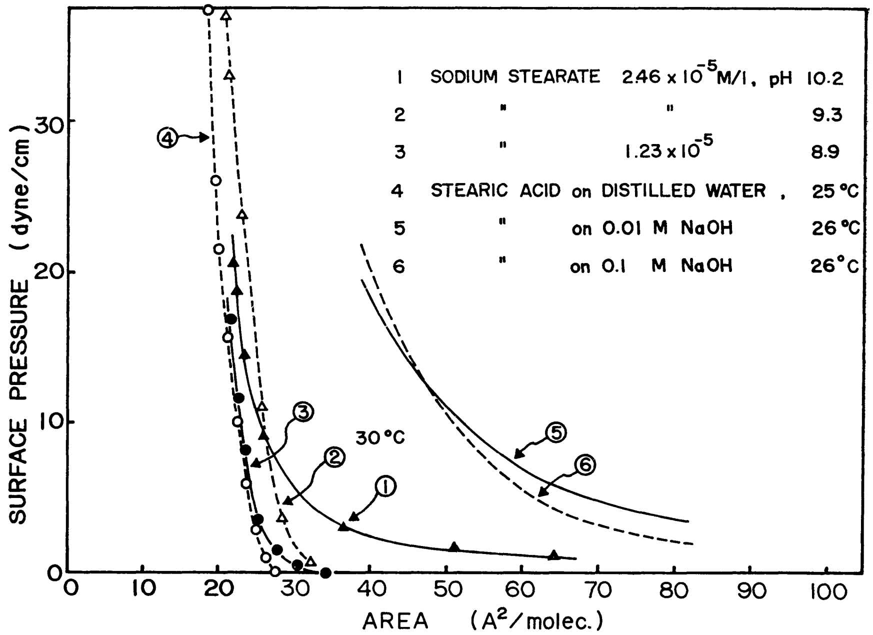

Fig. 9. Effect of pH on pressure-area relationship of adsorbed stearate films at 30°C.

quired for the establishment of the adsorption equilibrium is about 60 min, while in the usual monolayer technique about 10 min or so is required for complete compression.

The method of preparing a stearate solution markedly affects the pressure-area characteristics of the adsorbed monolayer (Fig. 8). The amount of adsorption increases, but the surface pressure decreases, with the increase in the age of the solution from 35 to 240 min before use. The effect of the pH of the stearate solution on the pressure-area relation is shown in Fig. 9, together with, for the sake of comparison, the curves for stearic acid on alkaline and neutral substrates at 30°C.[7] There is a close resemblance between the monolayer of stearic acid on neutral water and the adsorbed films on the stearate solution at pH values from 8.85 to 9.30. The difference in pH from 10 to 12 dose not produce any appreciable difference in the pressure-area relation, as is shown in Fig. 10.

The adsorption of stearic acid as a result of surface hydrolysis[24] is also expected to occur in these films. In the case of a stearate film adsorbed at

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[24] M. A. Cook and E. L. Talbot, *ibid.*, **56**, 412 (1952).

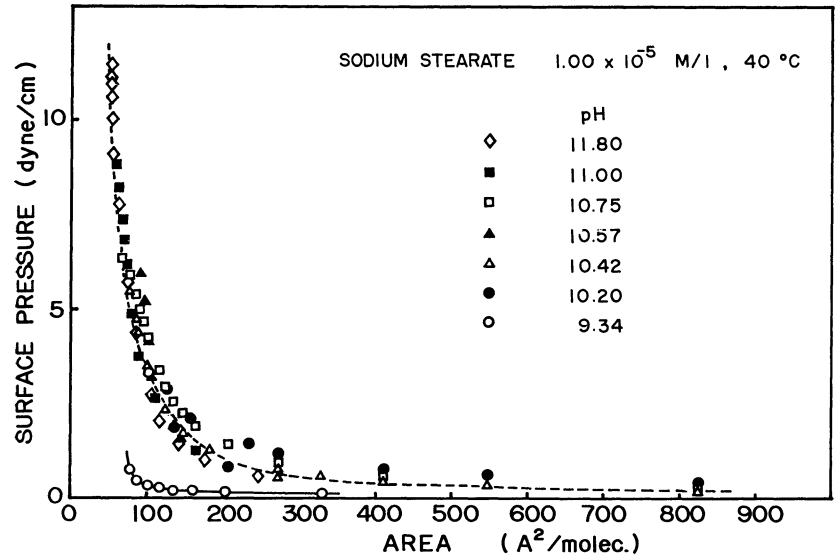

Fig. 10. Effect of pH on pressure-area relationship of adsorbed stearate films at 40°C.

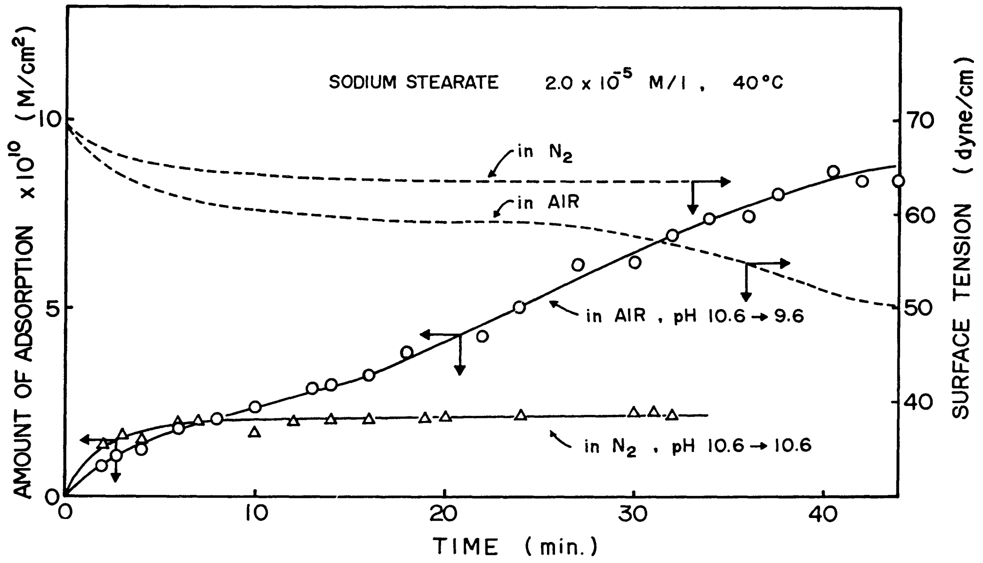

Fig. 11. Effect of atmospheric carbon dioxide on stearate adsorption.

pH 10.2, a transition from a condensed state at a higher surface concentration to an expanded state at a lower concentration can be observed. This behavior is in accord with the explanation of the step-by-step increase in Γ shown in Fig. 6, although the details are somewhat different because of the difference in temperature. The surface properties of soap are greatly affected by the presence of carbon dioxide either in solution or in atmosphere, as has been predicted by various workers.[3,5,25] In this experiment, extreme care was taken to avoid the contamination of either the surface or the bulk of the solutions by using carbonate free sodium hydroxide and sodium stearate, and by performing the experiments in a nitrogen atmosphere. In Fig. 11, the effects of carbon dioxide on the surface tension of stearate solution and on the amount of adsorption are shown by comparing the measurements in atmospheres of air (containing carbon dioxide) with those in carbon dioxide-free nitrogen. The exposure of an aqueous surface to air containing carbon dioxide increases the amount of adsorption and decreases the surface tension compared with the corresponding values obtained in nitrogen. From the observed change in the pH of the bulk solution, it is evident

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25) J. Lucassen, *ibid.*, **70**, 1824 (1966).

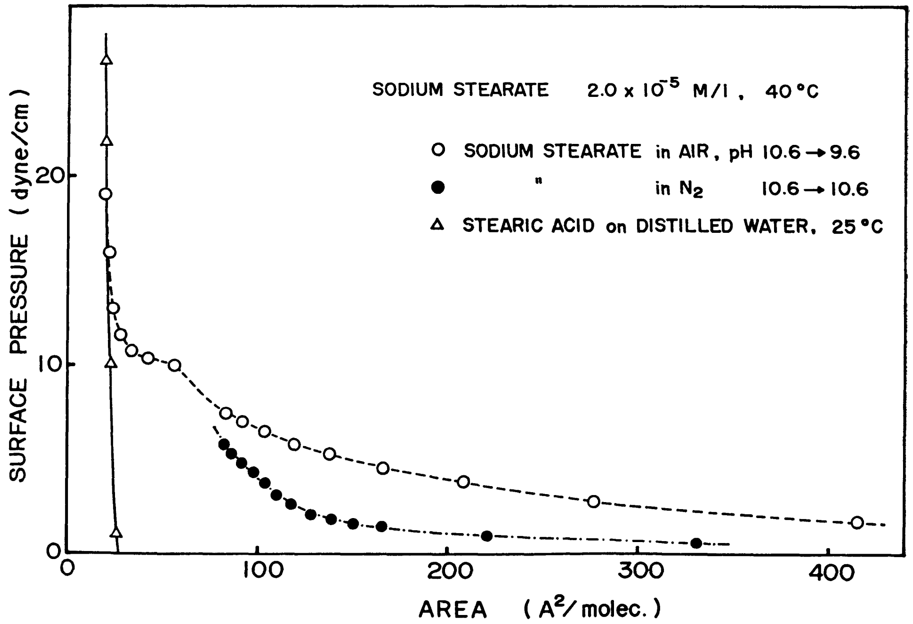

Fig. 12. Effect of atmospheric carbon dioxide on stearate adsorption.

that a considerable amount of carbon dioxide was absorbed by the solution from the air. This carbon dioxide distinctly lowers the pH of the surface layer of the solution and accelerates the hydrolysis to form free stearic acid or other surface-active associates[4,21,26)] of a solute containing stearic acid, associates which preferentially adsorb at the surface and which often produce an abnormally large amount of adsorption. This tendency is also apparent in the pressure-area characteristic as shown in Fig. 12, which takes a form different from that obtained in an nitrogen atmosphere because of the dissolution of carbon dioxide into the solution. However, the curve coincides with that for stearic acid at a high surface pressure.

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26) J. Marsden and J. H. Schulman, *Trans. Faraday Soc.*, **34**, 748 (1938).