A Study of the Interaction between the Stearic Acid Monolayer and the Calcium Ions by the Radiotracer Method

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(Received June 5, 1964)

The composition of the calcium stearate formed on the surface of water through the interaction between the stearic acid monolayer and calcium ions has been studied by several authors.[1-3] Langmuir and Schaefer[1] and Havinga[2] collected the monolayer spread on a solution containing calcium ions and ascertained the composition by means of chemical analysis. Later, Sobotka et al.[3] measured the composition of the built-up film by using radioactive calcium. The composition of the calcium stearate in the film thus measured was discussed by these authors as a function of the pH of the underlying solution.

However, these methods involve the disturbing of the monolayer, i. e., "skimming off" or "building up" the monolayer. It has not yet been confirmed whether or not the composition of the film determined by these methods is the same as that on the surface of water itself. Thus it is necessary to measure the calcium content of the monolayers directly, without disturbing the system. The radiotracer method has, therefore, been used in this study; the state of the monolayer has also been discussed.

Experimental

Materials. — Non-radioactive stearic acid was purified from a commercial sample by fractional distillation through a rectifying column of 65 plates at a reflux ratio of 15, followed by repeated recrystallizations from ethanol. The fraction distilled at 225—225.5°C/10 mmHg was collected. Its melting point was 67.2°C. Radioactive stearic acid, labeled with ^{14}C, was obtained from Daiichi Pure Chemicals, Tokyo, Japan. Because of the very minute amount of radioactive stearic acid, we followed the method of purification developed by Gaines,[4] which consists of dissolving the sample in reagent grade *n*-hexane and extracting the impurities first with 1 N hydrochloric acid and then

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[1] I. Langmuir and V. J. Schaefer, *J. Am. Chem. Soc.*, **58**, 284 (1936); **59**, 2400 (1937).

[2] E. Havinga, *Rec. trav. chim.*, **71**, 72 (1952).

[3] H. Sobotka, M. Demeny and J. D. Chanley, *J. Colloid Sci.*, **13**, 565 (1958).

[4] G. L. Gaines, Jr., ibid., **15**, 321 (1960).

with several portions of water. Monolayers of radioactive and non-radioactive stearic acids gave almost the same pressure-area (Π-A) curve, indicating the purity of radioactive stearic acid. The specific activity of this radioactive stearic acid was 2 mc./mmol.

Calcium chloride of a guaranteed grade was purified by recrystallization from its aqueous solution. ^{45}Ca-labeled calcium chloride, with a specific activity of 275 mc./g., was obtained from the Oak Ridge National Laboratory, Oak Ridge, Tennessee, U. S. A. The Π-A curve of the stearic acid monolayer on a solution containing radioactive calcium ions was exactly the same as that on a solution containing purified non-radioactive calcium ions.

The pH of the substrate solution was adjusted by sodium carbonate, sodium bicarbonate and hydrochloric acid, all of which were guaranteed reagents. The water used for these studies was redistilled with a quartz still.

Method.—The procedure of measuring the surface excess by the radiotracer technique was essentially the same as one described previously.[5] The apparatus used in the present experiment is shown in Fig. 1. A brass trough A, 15×30 cm^2 in inner area, was made, and its surface was plated by chromium. An end-window Geiger-Müller tube B, with a mica window 1.5 mg./cm^2 thick was supported by a brass cylinder, C, over the surface of the trough. A brass mount D, with a hole 2 cm. in diameter, was placed on the edges of the trough, A, as is shown in Fig. 1, so that the reproducibility of the geometrical condition could be realized with ease. The inside of the trough and the glass barriers, F, were covered by a thin paraffin film and rinsed with water overnight before use. A radioactive calcium chloride solution of a known concentration and pH was then poured into the trough. The surface of the solution was swept by the barriers, a Geiger-Müller tube was put down to the measuring arrangement and the radioactive counting was started. The same procedure was also carried out after the monolayer of stearic acid had been spread on the surface of the solution.

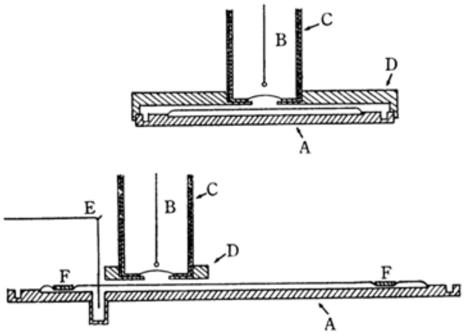

Fig. 1. The measuriug apparatus.

The amount of calcium adsorbed by the stearic acid monolayer, Γ_{Ca}, in mole per cm^2, was calculated according to this equation:

$$\Gamma_{\mathrm{Ca}}=\frac{I_m-I}{SA} \tag{1}$$

where I is the intensity, in count./min., of the radiation due to the substrate without film; I_m, the intensity of the radiation due to that with the stearic acid monolayer; S, the specific activity, in count./min./mol., of the radioactive calcium in the film and A, the surface area, in cm^2 within which the radiation is detectable with the Geiger-Müller tube in the present apparatus. Of these quantities, S and A were determined by using a point source, as has been reported already.[5] Γ_{Ca} was hence obtained from the measurement of I and I_m.

The measurement of the surface pressure of the monolayer was simultaneously carried out by a modified Wilhelmy-type surface balance,[6] E, as is shown in Fig. 1.

All the experiments were carried out at a fixed concentration of calcium ions, 5×10^{-5} mol./l. The temperature of the experiment was ca. 10°C. By preliminary experiments it was confirmed that the variation in temperature from 5 to 15°C modified the Π-A curves slightly, although the change in the surface excess of calcium with the temperature was within the range of experimental error.

Results and Discussion

The Π-A curves of the stearic acid monolayers on the aqueous solutions of calcium

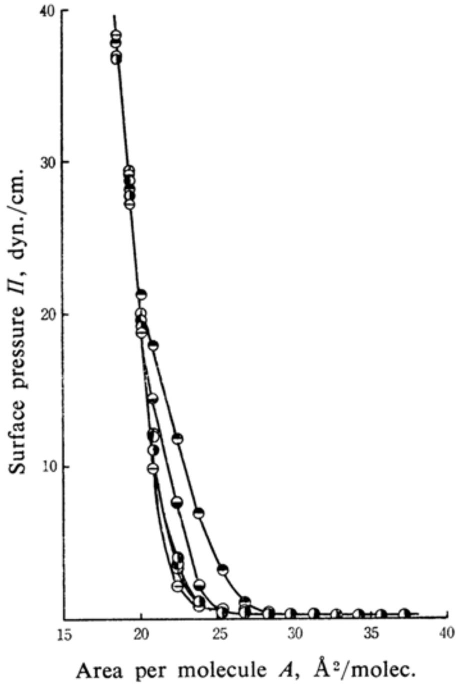

Fig. 2. The Π-A curves for the stearic acid monolayers on the 5×10^{-5} mol./l. CaCl$_2$ solution at pH=5.90 ◓; 6.51 ◒; 7.05 ◑; 7.95 ◐; 8.77 ⊖ and 9.69 ⦶.

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

[6] R. Matuura and I. Hayashi, *Memoirs Fac. Sci., Kyushu Univ., C*, 1, 31 (1948).

chloride of varying pH values are shown in Fig. 2. The general features are the same as those measured by Sasaki and Matuura.⁷⁾ It is obvious from this figure that the condensation of the stearic acid monolayer by calcium ions increases with the increase in the pH of the substrate. This effect has been explained as being due to the formation of calcium stearate, Ca(St.)$_2$.⁸⁾

In the measurement of the surface excess of calcium, the values of I were almost time-independent. On the other hand, the values of I_m increased at once and fluctuated for about thirty minutes or, occasionally, more after the monolayer had been spread. Then, thirty minutes after spreading, the monolayer was compressed at the rate of 1 cm. of a trough scale/min. and at 3 min. intervals and the surface excess of calcium was measured as a function of the surface concentration of stearic acid. In Fig. 3 the amounts of calcium adsorbed on the stearic acid monolayer, Γ_{Ca}, are plotted against a half of the surface concentration of the stearyl chain, $n/2$ in mol./cm^2, for the typical pH values. If it is assumed that the mole ratio of calcium stearate to stearic acid is constant at a given pH, and, in addition, that the film is homogeneous and compressed uniformly, Γ_{Ca} should increase with an increase in the surface concentration of the monolayer along a straight line passing through the point of origin, the slope of the line depending on the pH of the substrate solution. The experimental points in Fig. 3, however, scatter randomly at smaller surface concentrations, especially when the pH of the substrate is high.

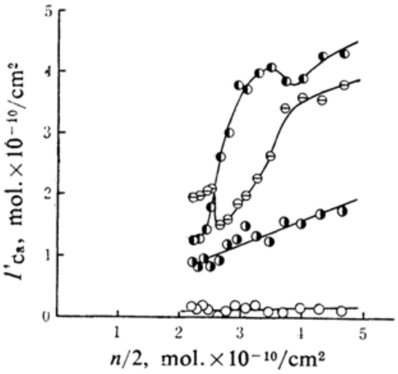

Fig. 3. Γ_{Ca} vs. $n/2$ curves at pH=5.30 ○; 6.45 ◑; 8.00 ⊖ and 10.6 ◐.

The irregularity of the experimental points observed at a smaller surface concentration should be attributed to the inhomogeneity of the monolayer. Harkins et al.⁹⁾ has pointed out the existence of a two-phase region by means of surface potential measurements. Some other authors have also confirmed the inhomogeneity of the stearic acid monolayer at low surface pressures by the electron microscopic¹⁰⁾ and radiotracer¹¹⁾ methods. Unfortunately, these authors have not referred to the large islands of the monolayer. We observed large islands in the present experiment as follows. The ^{14}C-labeled stearic acid was spread over an area of 37.2 Å^2/molec. on the surface of a solution containing non-radioactive calcium ions at pH=8.60, and the counting rate as a function of the position was measured by moving the Geiger-Müller tube horizontally and uni-directionally over the surface film. The results are shown in Fig. 4. It may be seen in this figure that the monolayer is localized as large islands, especially around the position where the spreading solution has been dropped. The inhomogeneity of the monolayer found at lower pH values was less pronounced than that at higher pH's. Thus, it is evident that the monolayer consists of concentrated and dilute regions. As the monolayer is compressed, the area of the dilute region decreases until, finally, the monolayer becomes a homogeneous one composed of closely-packed molecules. The surface pressure increases suddenly from this point.

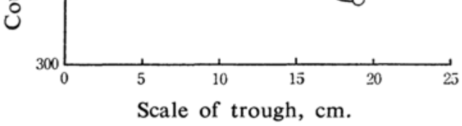

Fig. 4. The radiation from the various position of the C^{14}-labeled stearic acid monolayer at A=37.2 Å^2/molec. on the 5×10^{-5} mol./l. CaCl$_2$ solution at pH=8.60. The measurement was carried out 30 min. after spreading.

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7) T. Sasaki and R. Matuura, This Bulletin, **24**, 274 (1951).

8) W. D. Harkins and R. J. Myers, *Nature*, **139**, 367 (1937); W. D. Harkins and E. Boyd, *J. Phys. Chem.*, **45**, 20 (1941).

9) W. D. Harkins and E. K. Fischer, *J. Chem. Phys.*, **1**, 852 (1933).

10) H. E. Ries, Jr., and W. A. Kimball, *Nature*, **181**, 901 (1958); H. E. Ries, Jr., and D. C. Walker, *J. Colloid Sci.*, **16**, 361 (1961).

11) J. R. Ryan and J. W. Sheppard, *J. Phys. Chem.*, **59**, 1181 (1955); G. L. Gaines, Jr., *J. Colloid Sci.*, **15**, 321 (1960).

From these facts it is clear that the surface excess at each limiting area should be taken into account in determining the true composition of the film. At this area the fraction of the stearyl chain neutralized by, the calcium in the monolayer, Φ_{Ca} is given by:

$$\Phi_{\mathrm{Ca}}=\frac{\Gamma_{\mathrm{Ca}}}{n/2} \tag{2}$$

The calculated values of Φ_{Ca} are plotted against the pH of the substrate solution in Fig. 5. The results obtained by Langmuir and Schaefer(1) and Sobotka et al.(2) are also shown in this figure. The present result is similar to that obtained by Sobotka et al. with regard to the pH range where Φ_{Ca} sharply changes. It may also be seen in this figure that the curve is shifted to the alkaline side as compared to the dissociation curve of fatty acids. Such a kind of shift has frequently been observed in surface chemical phenomena(12) and has been explained there by regarding the pH at the interface as being lower than that in the bulk of the solution.

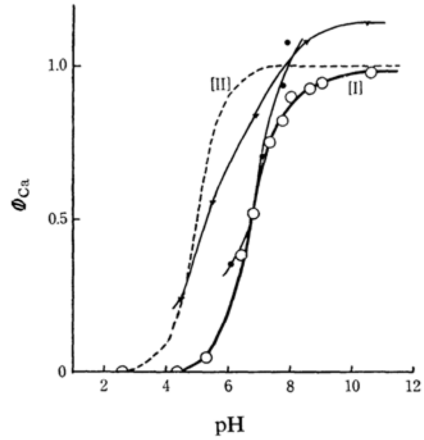

Fig. 5. Φ_{Ca} vs. pH curves. ○ by the present experiment; ▼ by Langmuir and Schaefer; ● by Sobotka et al. The broken line [II] represents the dissociation curve in bulk for fatty acids.

The monolayer of calcium stearate condenses more than that of stearic acid. Furthermore, it has been pointed out already that the more the formation of calcium stearate increases, the more easily the film forms islands, and even over a large area the molecules in these islands are in a closely-packed state. These facts clearly suggest that the cohesive force between calcium stearate molecules is stronger than that between stearic acid molecules. Hence, the energy of the mixing of stearic acid molecules with calcium stearate molecules in the monolayer should not be zero.

For the following relation:

$$2\mathrm{HSt.}+\mathrm{Ca}^{2+}=\mathrm{Ca(St.)}_2+2\mathrm{H}^+$$

$$a_{\mathrm{Ca}^{2+}}/a_{\mathrm{H}^+}^2=Ka_{\mathrm{Ca(St.)}_2}/a_{\mathrm{HSt.}}^2 \tag{3}$$

where K is the equilibrium constant and a's are the activities. If this monolayer is assumed to be a mixture not athermal, $a_{\mathrm{Ca(St.)}_2}$ and $a_{\mathrm{HSt.}}$ are represented by:

$$a_{\mathrm{Ca(St.)}_2}=\Phi_{\mathrm{Ca}}\exp\{2w(1-\Phi_{\mathrm{Ca}})^2\} \tag{4}$$

$$a_{\mathrm{HSt.}}=(1-\Phi_{\mathrm{Ca}})\exp(w\Phi_{\mathrm{Ca}}^2) \tag{5}$$

where w is the interchange energy. Then, by substituting Eqs. 4 and 5 into Eq. 3 the following equation is obtained:

$$a_{\mathrm{Ca}^{2+}}/a_{\mathrm{H}^+}^2=K'\{\Phi_{\mathrm{Ca}}/(1-\Phi_{\mathrm{Ca}})^2\}\exp(-4w\Phi_{\mathrm{Ca}}) \tag{6}$$

where K' is a constant. For an athermal mixture in which w is equal to zero, the following equation is obtained:

$$a_{\mathrm{Ca}^{2+}}/a_{\mathrm{H}^+}^2=K'\Phi_{\mathrm{Ca}}/(1-\Phi_{\mathrm{Ca}})^2 \tag{7}$$

According to Eq. 6, if $a_{\mathrm{Ca}^{2+}}$ is constant, $\log\{(1-\Phi_{\mathrm{Ca}})^2/a_{\mathrm{H}^+}^2\cdot\Phi_{\mathrm{Ca}}\}$ must be linear against Φ_{Ca} and, according to Eq. 7, $\log\{\Phi_{\mathrm{Ca}}/(1-\Phi_{\mathrm{Ca}})^2\}$ must be linear against pH. The former relation was confirmed by the present experimental data as Fig. 6 shows, although the latter one was not confirmed.

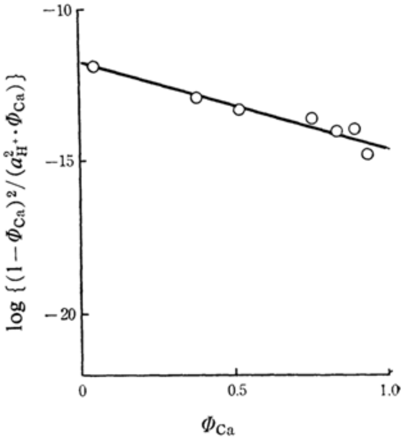

Fig. 6. The test of Eq. 6.

Summary

Direct measurement by the radiotracer method has been carried out in order to determine the surface excess of calcium on the stearic acid monolayer. It did not provoke any disturbance in the monolayer, such as "skimming off" or "building up". At higher pH values the stearic acid monolayer spread

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[12] R. A. Peters, *Proc. Roy. Soc.*, **A133**, 140 (1931); J. F. Danielli, ibid., **B122**, 155 (1937), etc.

on a calcium chloride solution shows a very remarkable inhomogeneity. It has been pointed out that this inhomogeneity must be taken into consideration in determining the composition of the monolayer.

The mixed monolayer of stearic acid and calcium stearate satisfies the equation derived by assuming this monolayer to be a mixture not athermal.

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