Studies on Monomolecular Films. VII. The Effect of Metallic Ions on the Monomolecular Film of Stearic Acid

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Introduction

It is of great importance in the study of monomolecular films of fatty acids on the surface of water to know precisely the effect of ions in the underlying water on the properties of the monolayers. Harkins and Myers(1) noticed that the decrease in the area per molecule of a fatty acid on the surface of alkaline water is chiefly caused by the contamination of divalent ions (especially calcium ion) which make the chains close-packed (20.5 Å.^{2}); in the absence of such ions the molecules may be arranged with their heads close-packed giving approximately the area of 25 Å.^{2}, the area found on dilute acid solutions. Extensive work on the effect of dissolved salts on insoluble monolayers of stearic acid was carried out by Langmuir and Schaefer,(2) who studied

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(1) W. D. Harkins and R. J. Myers, *Nature*, **139**, 367 (1937).

(2) I. Langmuir, and V. J. Schaefer, *J. Am. Chem. Soc.*, **59**, 2400 (1937).

in detail the remarkable effect of such metallic ions as calcium, barium and aluminum and proposed a theory of the interaction between ions in the substrate and stearic acid in the film, assuming that the modification of a stearic acid monolayer by the presence of salts is due to the adsorption of salt to the undersurface of the monolayer. It has not been studied systematically, however, how each metallic ion affects the property of a fatty acid monolayer under varying hydrogen ion concentration and, particularly, how the effect can be explained from the standpoint of molecular structure of the resulting metallic soap. Recently studies on metallic soaps have been carried out colloid chemically by many workers and the interesting results have been obtained concerning the structure as well as the colloid chemical properties of metallic soaps.(3), (4), (5) It is the purpose of the present work to investigate the effect of the various metallic ions on the monolayer of stearic acid spread on the surface of the solution of varying hydrogen ion concentration and to discuss the result by taking into consideration the recent studies on metallic soaps as well as the characteristic properties of each metallic ion.

Experimental

The monolayer of stearic acid was prepared from benzene solution on the surface of water containing a salt of concentration of 10^{-4} mol/l.. The salts were used as chloride, nitrate and sulfate. They were purified by the repeated recrystallization. From the preliminary experiment the effect of inorganic anion on the monolayer of stearic acid was found negligible. The tray was made of brass and was coated thickly with paraffin. It was found that, when the surface of the tray was covered thickly with paraffin, the effect of the metallic ions which might come from the tray material on the acid monolayer was not measurable at least in the case where *p*H of the substrate ranged from 2 to 10. The value of *p*H of the substrate was controlled by hydrochloric acid and ammonium hydroxide. The use of ordinary buffer salts were particularly avoided since the possibility was considered that the buffer salts might frequently cover the remarkable effect usually encountered in the presence of metallic ions for investigation. The pressuie∼area diagram was measured for each monolayer of stearic acid by the method described already.(6)

Results

Various metallic ions were examined how they affect the pressure∼area curve of the monolayer of stearic acid on the surface of the solution and it was found that they can be classified into two groups according to the difference in the effect. One involves those which cause the monolayer to condense on the alkaline solution and the other those which make it expand in a proper *p*H range of the solution, characteristic of each metallic ion.

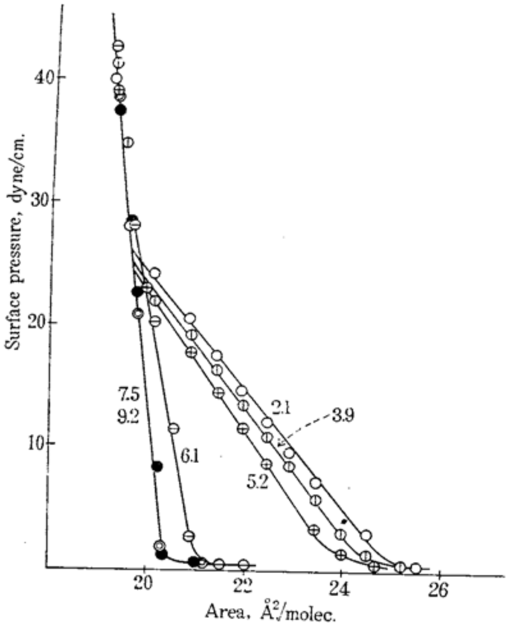

Fig. 1.—Pressure∼area curves of the monolayer of stearic acid on water containing calcium ion: The numeral for each curve represents *p*H of the substrate.

The typical example of the first group is calcium ion. The pressure∼area diagram of the monolayer of stearic acid on the surface of water containing calcium ion is shown in Fig. 1. It is obvious from this figure that the effect of calcium ion on the monolayer of stearic acid varies with *p*H of the substrate. In order to make this relation more distinct, the zero-compression area per molecule of stearic acid is plotted against *p*H of the substrate as shown by crosses in Fig. 2. The curve shown by small circles in the same figure represents the result of the blank experiment carried out on the surface of water containing no metallic ion. In the absence of metallic ions the monolayer of stearic acid is unstable,

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(3) C. G. McGee, *J. Am. Chem. Soc.*, **71**, 278 (1949).

(4) V. R. Gray and A. E. Alexander, *J. Phys. Coll. Chem.*, **53**, 9, 23 (1949).

(5) R. D. Vold and G. S. Hattiangdi, *Ind. Eng. Chem.*, **41**, 2311 (1949); G. S. Hattiangdi, and M. J. Vold, *ibid.*, **41**, 2320 (1949); etc.

(6) T. Sasaki, *J. Chem. Soc. Japan*, **62**, 796 (1941); R. Matuura and I. Hayasi, *Memoirs of the Faculty of Science, Kyūshū University, Ser. C*, Vol. 1, 31 (1948).

presumably a little soluble, on the alkaline substrate and the area per molecule of stearic acide diminishes sometimes to as small as 15 or 16 Å². On the contrary when calcium ion is present, the monolayer becomes stable enough even on the alkaline substrate to give a definite area of so-called close-packed chain, 20.5 Å². per molecule. On the acid substrate the monolayer of stearic acid is stable irrespective of the presence of calcium ion and gives the area of about 25 Å²., the area of so-called close-packed head. The metallic ions which show the similar effect as calcium ion are barium, magnesium, lead and manganese, but the effect of the last two is rather ambiguous. The pressure~area curve of the monolayer of stearic acid affected by these ions is similar, depending little upon the difference in the nature of these metallic ions.

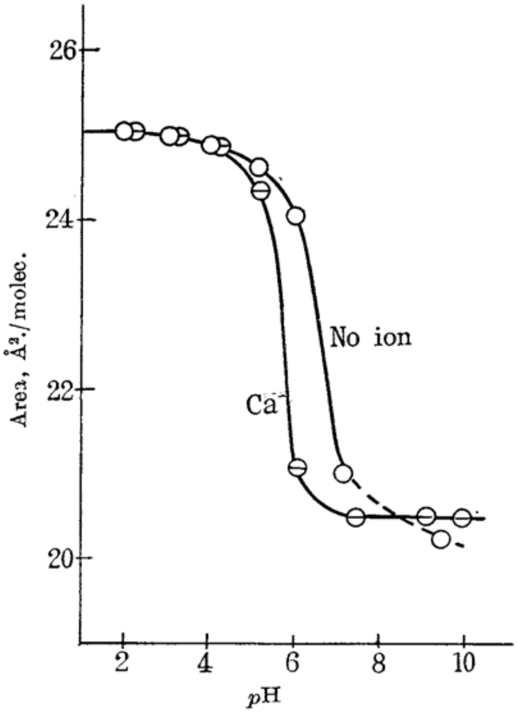

Fig. 2.—Area-*p*H curve of the monolayer of stearic acid on water containing calcium ion.

An example of the second group of metallic ions is aluminum. The pressure~area curve of the monolayer of stearic acid spread on the substrate containing $AlCl_3$ is shown in Fig. 3. It is noticed that aluminum ion remarkably expands the monolayer in a certain range of *p*H, the maximum expansion occurring at *p*H near 7. This is more clearly illustrated in Fig. 4, where the zero-compression area per molecule of stearic acid is plotted against *p*H of the substrate. When *p*H increases beyond the value of maximum expansion, the film becomes gradually unstable. It is noteworthy that the monolayer which is made to expand by aluminum ion has a large compressibility and its collapse pressure is rather small compared with that of the film unaffected by metallic ions, as seen in Fig. 3. In this group of the metallic ions copper, zinc, mercury, cobalt, nickel, iron, cerium and thorium ions are included in addition to aluminum ion. The optimum *p*H of the film expansion is proper for each ion as shown in Fig. 4 in the case of a few metallic ions of this group.

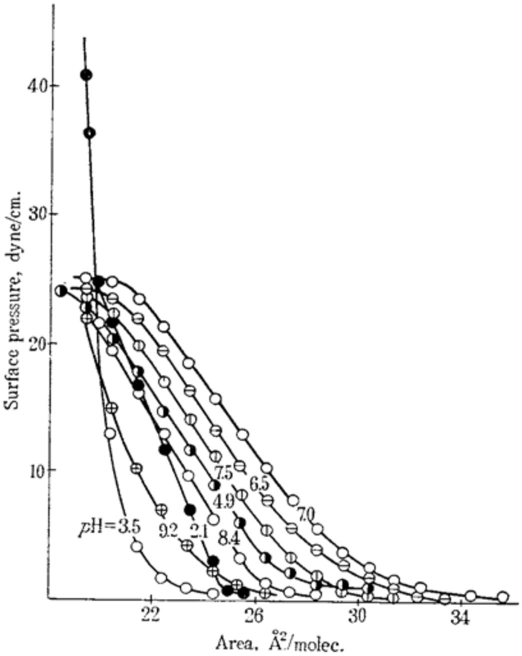

Fig. 3.—Pressure~area curves of the monolayer of stearic acid on water containing aluminum ion.

Discussion

It is evident from the experiment of Langmuir and Schaefer⁽⁷⁾ that the metallic soap is formed in the film when stearic acid is spread on the surface of water which contains both metallic ions and a suitable amount of hydrogen ion. Hence the remarkable effect of those metallic ions on the monolayer of stearic acid should be discussed from the standpoint of the resulting metallic soaps.

It was shown that ions of the first group, namely calcium, barium and magnesium,

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(7) I. Langmuir and V. J. Schaefer, *J. Am. Chem. Soc.*, **58**, 284 (1936).

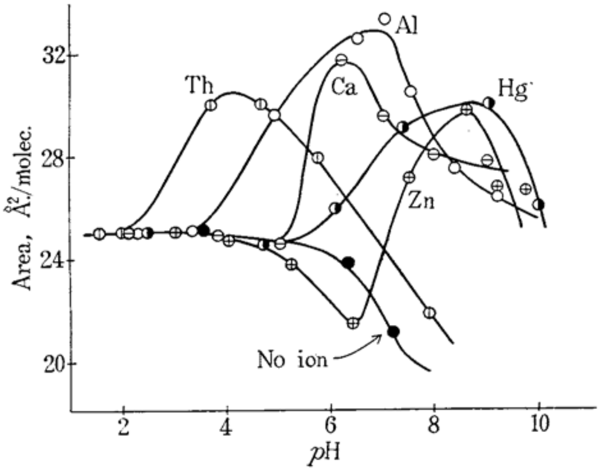
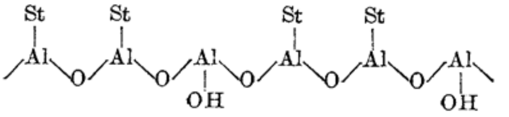


Fig. 4.—Area∼pH curves of the monolayer of stearic acid on water containing some metallic ions.

clearly condensed the monolayer of stearic acid on the alkaline solution. This is due to their bivalent bond joining two molecules of stearic acid, thus forming a stoichiometric compound of the type $Me(St)_2$, as has been pointed out by Harkins.(1),(8) This causes the chain close-packed and gives the area of $20.5\ \text{Å}^2$. per stearate radical, while without these metallic ions the heads are close-packed, giving the corresponding value of $25\ \text{Å}^2$. Notwithstanding this difference, the structure of the monolayer of these metallic soaps is not essentially different from that of stearic acid, since in both films the long chain molecules are oriented vertically with their nonpolar chains being arranged side by side.

The situation is wholly different in the case of metallic ions of the second group, namely ions of aluminum, thorium, iron, copper, zinc, mercury, cobalt, nickel, etc. The effect of these ions on a stearic acid monolayer causing it to expand and rendering it remarkably compressible suggests that the resulting metallic soap may not be so simple as the soap of calcium, barium and magnesium but may have a rather complicated structure. Since McBain(9) reported for the first time a non-existence of aluminum trisoap, many workers have investigated the properties and structure of aluminum soap but concordant results have not been obtained yet.(3),(4),(5),(10) In fact the properties of aluminum soap depend greatly upon the method of preparation, especially upon whether or not water takes part in the process.(4),(11) Such a fluctuation of the properties can also be considered as an indication of a complicated structure of aluminum soap. Eigenberger(12) proposed aluminum stearate of a polymeric structure. Recently McGee(3) presented a model for the structure of aluminum mono- and di-laurate in which two adjacent alumina octahedra are joined by sharing their edges or corners. Gray and Alexander(4) also reported a linear polymer structure for aluminum soaps, especially for those prepared using aqueous media. Although the opinion somewhat differs in detail from each other, these authors agree at least in adopting the polymeric structure for aluminum soaps, which can also be assumed in the present experiment. It is difficult to determine precisely the molecular structure of aluminum stearate formed in the film, but taking into consideration the model presented for aluminum soap by McGee, and Gray and Alexander, it might schematically be depicted as follows.



If this high-molecular structure is allowed for aluminum stearate, the backbone of –Ai—O– linkage will lie flat on the surface of water, from which stearyl groups attached to aluminum atom in the backbone will be directed to air. This explains well the experimental results obtained in this work. First, it is expected from this molecular structure of aluminum stearate that the area per stearyl group in this film is larger than the area per stearic acid in the film formed on water containing no metallic ion. Next, since –Al—O– chain is considered flexible, the compressibility of the film should be large compared with that of the film of stearic acid without metallic ion. Further, it may be expected that this film can not resist so large a pressure, as is usually the case with the film of long chain high-molecular substances in which the molecules lie flat on the surface of water.(13) All these presumptions

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(8) W. D. Harkins and E. Boyd, *J. Phys. Chem.*, **45**, 20 (1941).

(9) J. W. McBain and W. L. McClatchie, *J. Am. Chem. Soc.*, **54**, 3266 (1932).

(10) Wo. Ostwald and R. Riedel, *Kolloid-Z.*, **69**, 185 (1934); G. H. Smith, H. H. Pomeroy, C. G. McGee and K. J. Mysels, *J. Am. Chem. Soc.*, **70**, 1053 (1948); etc.

(11) T. C. McRoberts and J. H. Schulman, *Nature*, **162**, 101 (1948).

(12) E. Eigenberger and A. Eigenberger-Bittner, *Kolloid-Z.*, **91**, 287 (1940).

(13) W. D. Harkins, E. F. Carman and H. E. Ries, *J. Chem. Phys.*, **3**, 692 (1935).

were proved to be the case by the present experiment.

It is reasonable to assume that the rest of metallic ions of the second group will also form soaps of similar molecular structure as aluminum soap in a certain *p*H range characteristic of each ion. The *p*H value for the maximum of the film expansion seems to depend on the basicity of each ion. It should be emphasized that these metallic ions exhibit a high co-ordination valency and readily form co-ordination compounds with various substances. In presenting a polymer structure of aluminum soap McGee(3) also took the linkage by co-ordination valency into consideration. Presumably all the metallic ions classified into the second group in this experiment will form with stearic acid a soap, complex in structure supported by co-ordination valency. In this point they are different from those classified into the first group, *i. e.*, calcium, barium and magnesium. Now, it is to be noted that all the metallic ions of the second group prove to be either transition elements or elements being trivalent or higher. The ionic radius of these elements is known to be generally small and its ionic potential large, which are considered to be favorable conditions for the formation of complex salts. The fact that metallic ions are also classified largely into two groups similar to those in the present experiment according to the difference in some other surface chemical properties was confirmed by the studies on the effect of metallic ions both on the built-up film of stearic acid carried out by Muramatsu(14) and on the wettability of stearic acid surface carried out by Inaba,(15) both of our laboratory.

Summary

The effect of various metallic ions on the pressure～area curve of the monomolecular film of stearic acid spread on the surface of the solution was studied. It was found that they were classified into two groups; one involves those which make the film condense such as calcium, barium and magnesium and the other those which make it expand such as thorium, aluminum, iron, copper, zinc, mercury, cobalt and nickel. This classification was explained from the standpoint of molecular structure of the resulting metallic soaps. It was suggested that while the soap of the former metals has a simple structure the soap of the latter metals has a complicated polymeric structure. These structures were explained by the characteristic nature of metallic ions of two groups.

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(14) M. Muramatsu and T. Sasaki, in press.

(15) A. Inaba, to be published recently.