Wettability of Solid Surface. VI. The Effects of Metallic Cations on Stearic Acid Built-up Film

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Introduction

Formerly, Sasaki and Mitsui⁽¹⁾ reported the nature of wettability of stearic acid built-up film in relation to the number of layers and the condition of building up. The present author has also studied the wettability of stearic acid surface and has been confronted with the necessity of the more precise information on this problem.

It was shown in the fifth report⁽²⁾ of this series that metallic cations were divided into three types, according to their effects on the wettability of stearic acid surface solidified in air, namely (I) wetting ion I (Na, K, Rb, etc.), producing surface dissociation of stearic acid, (II) wetting ion II (Al, Th, Fe, Cu, etc.), forming hydrated metal stearate of a complex structure, and (III) non-wetting ion (Ba, Sr, Ca, etc.), forming simple stoichiometric compound of principal valency. Here the difference between (II) and (III) is the most interesting problem. Matuura and Sasaki⁽³⁾ of our laboratory reported the similar difference in the interaction of metallic ions～stearic acid monolayer, from the study of the pressure～area curve and film elasticity. Muramatsu and

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(1) S. Mitsui and T. Sasaki, *Survey of the Recent Colloid Chemistry*, **1**, 196 (1948).

(2) A. Inaba, This Bulletin, **25**, 174 (1952).

(3) T. Sasaki and R. Matuura, This Bulletin, **24**, 274, 278 (1951).

Sasaki(4) also arrived at the same conclusion in their investigation of built-up film. The purpose of this work is to show the effect of metallic cations for the wettability of stearic acid built-up film.

Experimental

Material.—Materials used were stearic acid, barium chloride, aluminum sulfate, mercuric chloride, calcium nitrate, sodium hydroxide, and hydrochloric acid. These were purified by the usual methods which were described in a former report.(2)

Measurement.—The monolayer of stearic acid was built up on a glass rod under the pressure of oleic acid, excepting the case of B-layer technique, from the surface of aqueous substrate containing various metallic ions of 10^{-3} or 10^{-4} mol. The pH of the substrate was controlled in the range of 4.2~12.0 by adding 0.5 N sodium hydroxide or 0.6 N hydrochloric acid. The glass rod had been successively cleansed with chromic acid mixture, potassium hydroxide~alcohol mixture and distilled water, and dried in the current of dry air. The built-up film thus obtained was used for the wettability experiment. Du Noüy's apparatus was used to measure the degree of wettability.(5)

Results

a. Wettability and the Time of Drying.

—Wettability of stearic acid film built up from the surface of tap water decreased with the time of drying after it was deposited from water surface and came to a certain limiting value after 1.5 hour as shown in Table 1. Therefore in the following experiment, observation was made at least 1.5 hour after the film was built up, unless mentioned otherwise.

Table 1

Time Effect of Drying on the Wettability of Films Built Up from Tap Water (pH 6.8)

Time of drying after built up (hr.)	9-Y layers		19-Y layers	
	θ_a	θ_r	θ_a	θ_r
0	90°	23°	117°	64°
0.5	109	37	108	64
1.5	112	60	114	70
24.0	112	57	113	70

b. Wettability and the Number of Layers.—Wettability of stearic acid film built up from the surface of tap water and substrate containing calcium ion (called Ca-substrate hereafter) was shown in Table 2. The contact angle, especially the receding contact angle of the film increased with increasing number of layers, approaching a certain value. It was noticed that the difference between advancing and receding contact angles was larger in the case of built-up film than in the case of the stearic acid solidified in air. (In the latter case, $\theta_a=110°$, $\theta_r=103°$.) This large hysteresis of wetting of the built-up film may come from an extremely systematic molecular arrangement in the film and the marked difference in the nature on both sides of the outermost monolayer resulting from it. The hysteresis was larger for the film which had a smaller number of layers. In the case of tap water as a substrate, θ_a was large and almost constant, independent of the number of layers, while the Ca- or Ba-substrate film did not give such a large θ_a value for the film which had a small number of layers. The phenomena may be attributed to the trace impurities like ferric or cupric ion in tap water.

Table 2

Wettability and the Number of Layers of Mixed Ca-stearate Y-film Built Up on Glass

Number of layers	Substrate, tap water, pH 6.8		Substrate, $Ca(NO_3)_2$ 10^{-4} mol. pH 6.8*	
	θ_a	θ_r	θ_a	θ_r
1	107°	20°	46°	15°
3	116	23	47	21
5	113	53	55	14
7	117	53	32	15
9	112	60	38	10
11	113	60	108	66
13			38	12
15			116	82
17			103	7
19	115	65	115	65
29	114	70	112	88
39			113	50

* Similar results were obtained in the case of $Ca(NO_3)_2$ 10^{-4} mol. (pH 8.6) and $BaCl_2$ 2×10^{-4} mol. solutions as substrate.

c. Wettability and the Type of Built-Up Film.—X-film could not be deposited directly on the glass surface and could only be deposited on 9 or 11 Y-layers. Therefore, comparison was made between X-film and Y-film both built up on the basis of 15 Y-layers. The results are shown in Table 3.

It is said that X-film has a larger receding contact angle than that of Y-film.(1), (6) This statement is true for the comparison of Y-film

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(4) M. Muramatsu and T. Sasaki, This Bulletin, **25**, 21, 25 (1952).

(5) A. Inaba, *Memoirs of the Faculty of Science, Kyushu Univ., Ser. C*, **1**, 1 (1948).

from solution of pH 6~7 and X-film, which can only be obtained from solution of $p\text{H}>9$ as shown in Table 3. But we should rather insist upon the importance of pH. Namely, Y-film from low pH substrate showed smaller θ_r than that of X-film from high pH substrate. Further, as is shown in Table 3, Y-film deposited from alkaline solution showed the same value of contact angle with that of the X-film occasionally deposited under the same conditions. It is interesting to note that there was no difference in contact angle between the odd and even number of X-layers, contrary to the expectation that odd layers and even layers might show different contact angles because of their different molecular arrangement in the outermost two layers.(7) Importance of pH can readily be recognized when we consider the fact that calcium or barium content in the stearic acid monolayer which appreciably affects the wettability of stearic acid surface(2) is chiefly determined by pH.(8)

Table 3

Wettability of Y-film and X-film of Ba- or Ca-stearate

Substrate, $BaCl_2$ 2×10^{-4} mol., pH 6.8 (Y-film), pH 9.8 (X-film), 10°C

	θ_a	θ_r
$15Y$	46°	8°
$15Y+1X$	117	81
$17Y$	107	25
$15Y+2X$	114	86
$15Y+3X$	112	89
$19Y$	115	82
$15Y+4X$	117	91

Substrate, $Ca(NO_3)_2$ 10^{-4} mol., pH 6.8 (Y-film), pH 9.6 (Y'- and X-films), 10°C

	θ_a	θ_r
$15Y$	114°	71°
$15Y+1X$	118	72
$15Y+2X$	118	80
$15Y+3X$	116	79
$15Y+4X$	113	90
$15Y+2Y'$	117	75
$15Y+4Y'$	112	77
$15Y+10Y'$	114	78
$15Y+20Y'$	114	84
$15Y+28Y'$	115	80
$15Y+30Y'$	116	82

d. Wettability and the Nature of Substrate Cations.—Stearic acid films were built up from redistilled water (pH 4.2~4.5), 10^{-4} mol. Al-substrate (pH 5.0), 10^{-3} mol. Ba-substrate (pH 10.5), and 10^{-3} mol. Hg-substrate (pH 8.8), on 29 Y-layers of barium stearate which was built up from Ba-substrate of pH 7.0. These pH values bracketed are those of optimum conditions for the interaction between stearic acid monolayer and metallic cations specified.(2),(3),(4) The author selected barium and aluminum, because they were typical of the group (II) and (III) mentioned above. Mercuric ion was selected for the sake of its exceptional behavior, that it formed a non-wettable product with solidified stearic acid in spite of its co-ordination tendency,(2) and elasticity of mercuric stearate monolayer.(3) Ions classified in group (I) are known to form no condensed monolayer with stearic acid and we were able to obtain no built-up film of first group metal stearate. A monolayer of stearic acid itself could not be built up directly on glass, but could be built up on the basis of barium stearate built-up film as Y-layer. Monolayer of barium stearate was built up as Y-layer and aluminum stearate as B-layer. The monolayer of aluminum stearate on water showed remarkable elasticity(3) and could not be built up under the piston pressure of oleic acid. Therefore it was built up with the aid of a drop of benzene solution of stearic acid placed near the glass rod as practised by Muramatsu.(4) The monolayer of mercuric stearate was not so elastic at first that it could be built up as Y-layer or sometimes as X-layer by oleic acid as a piston oil; however, the monolayer soon became elastic and it could not be built up as Y-layer or X-layer. It could be built up as A- or B-layer with the pressure of benzene solution of stearic acid placed near the rod. The built-up films thus obtained were hydrophobic, but their wettability was affected by dipping in water of pH about 6. The relation between wettability and dipping time are shown in Figs. 1a~4a. After withdrawing, the films were kept over $CaCl_2$ for about twenty hours and then dipped again in the water. The results of the second dipping are shown in Figs. 2b~ 4b.

e. Wettability and After Treatment of Stearic Acid Built-up Film with Various Metallic Cations.—Stearic acid films built up from distilled water (pH 4.2~4.5) were treated with 10^{-3} mol. barium salt solution (pH 11), 10^{-4} mol. aluminum salt solution (pH 5.0), and 10^{-3} mol. mercuric salt solution (pH 8.8), and the wettability of the treated surface against the same solutions were observed. The results are shown in Figs. 5a~7a. After treating, the films were kept in a desiccator containing $CaCl_2$ for about twenty hours and

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(6) J. J. Bikerman, *Proc. Roy. Soc. (London)*, **A 170**, 130 (1939).

(7) E. F. Porter and J. Wyman Jr., *J. Am. Chem. Soc.*, **58**, 1083 (1938).

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

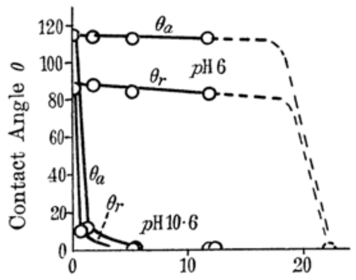

Fig. 1a.—Wettability of 29 *Y* mixed Ba-St+ 10 *Y* H-St, being treated with water of *p*H 6 and 10.6.

again they were dipped into the water. The results of the second dipping are shown in Figs. 5b∼7b.

Discussion

The built-up film of stearic acid was hydrophobic even after immersion for ten hours (Fig. 1a). The fact is the same with the case of stearic acid solidified in air.(2) However, the former was detached or dissolved from the glass surface after prolonged dipping. The dissolution phenomenon was remarkable in the alkaline region as shown in Fig. 1a, which

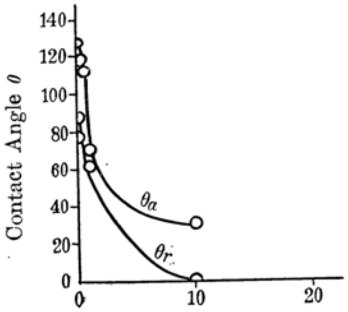

Fig. 2a.—Wettability of 29 *Y* mixed Ba-St+ 10X Ba-St being treated with water of *p*H 6.

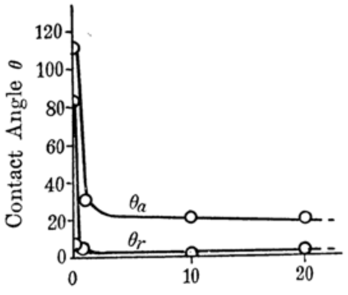

Fig. 2b.—Retreatment after drying of sample of 2a with water of *p*H 6.

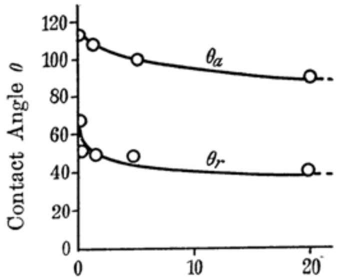

Fig. 3a.—Wettability of 29 *Y* mixed Ba-St+ 1 *B* Al-St, being treated with water of *p*H 6.

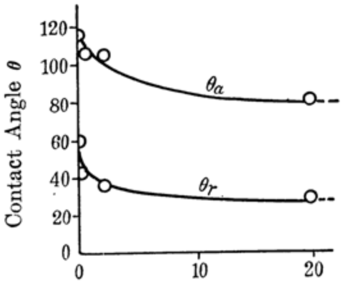

Fig. 3b.—Retreatment after drying of sample of 3a with water of *p*H 6.

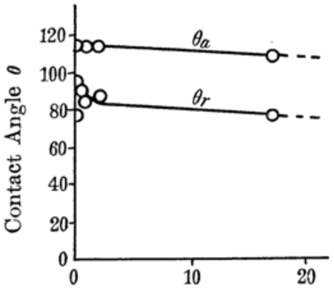

Fig. 4a.—Wettability of 29 *Y* mixed Ba-St+ 1 *B* Hg-St, being treated with water of *p*H 6.

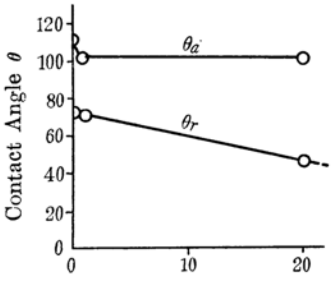

Fig. 4b.—Retreatment after drying of sample of 4a with water of *p*H 6.

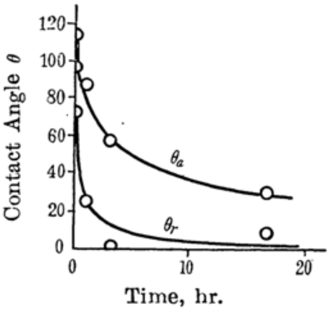

Fig. 5a.—Wettability of 29 *Y* mixed Ba-St+ 10 *Y* H-St towards 10^{-3} mol. Ba^{++} (*p*H 10.5).

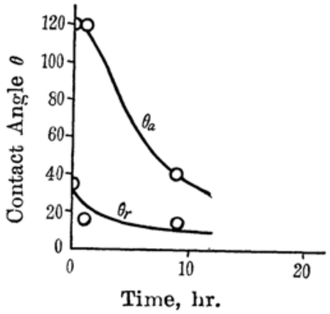

Fig. 5b.—Retreatment after drying of sample of 5a with water (*p*H 6).

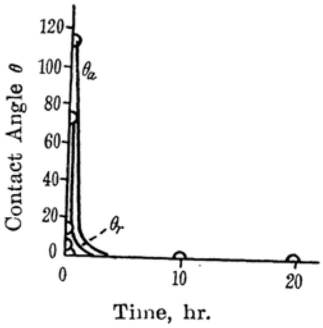

Fig. 6a.—Wettability of 29 *Y* mixed Ba-St+ 10 *Y* H-St towards 10^{-4} mol. Al^{+++} (*p*H 5).

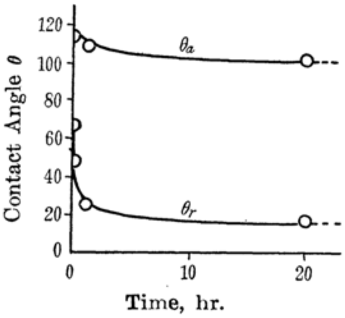

Fig. 6b.—Retreatment after drying of sample of 6a with water (*p*H 6).

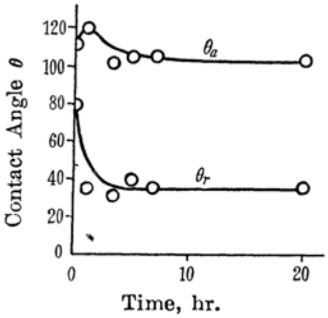

Fig. 7a.—Wettability of 29 *Y* mixed Ba-St+ 10 *Y* H-St towards 10^{-3} mol. Hg^{++} (*p*H 8.8).

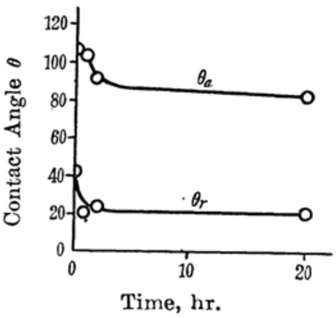

Fig. 7b.—Retreatment after drying of sample of 7a with water (*p*H 6).

was similar to the case of bulk surface previously reported.⁽²⁾ A remarkably large wetting hysteresis hereby encountered may possibly be attributed to the considerable difference in the wetting properties on both sides of the outermost oriented monolayer.

In the case of barium stearate built-up film (ion of the type III), there was not such a detachment and the film became hydrophilic. This may be attributed to the orientation of barium stearate molecules in the surface, which may be not so hydrophilic and soluble as free acid, perhaps due to a weaker dissociation of barium bond. The surface of stearic acid built-up film treated with barium salt solution is also considered to be in a similar state as that of barium stearate built-up film. Here, however, the easiness of orientation should be assumed. The results shown in Figs. 2a, 2b, 5a, and 5b can be explained similarly.

B-layer of aluminum stearate (ion of the type II) was hydrophobic (Fig. 3a). Its θ_a value was large, showing a little decrease after prolonged treatment with water, while θ_r was rather small and practically constant after an initial rapid decrease by treatment with water. Moreover, only one *B*-layer of aluminum stearate on bare glass showed similar properties. B-layer of aluminum stearate is considered to have a complex structure as described in the fifth report.(2)

Wolstenholme and Schulman(9) obtained the results that a monolayer of myristic acid was in an expanded state on the distilled water containing no metallic ion except for sodium, while it condensed and exhibited high rigidity on the solution containing aluminum, cobaltous, ferric ions etc. They explained their results under the assumption that basic metal ion forms a large network structure in the range of pH proper to that ion. Their explanation is similar to ours in that metallic ion and stearic acid combine in a complex manner and that the extended network is produced. But we are rather inclined to the non-stoichiometric composition between metal and stearic acid while they assumed the stoichiometric one. Moreover we pointed out the distinct difference in nature between the ions of (II) and (III) as far as the wettability was concerned,(2) while they arranged them in the order of ease of hydroxide formation.

Anyway, in aluminum stearate B-layer, the network structure of aluminum stearate may prevent the overturning of molecules. Therefore hydrocarbon groups remain to be exposed in the outermost surface of the film, giving a large and unaffected value of θ_a.

In the case of the treatment of stearic acid built-up film with aluminum solution, a loose hydrophilic network may be formed in the outermost surface of the built-up film, making the surface extremely hydrophilic. Therefore both θ_a and θ_r may be small (Fig. 6a). When it is, however, withdrawn from the solution, it may happen that stearate radicals loosely interlocked in the surface, overturn themselves, directing carboxyl groups inside, and then the network forms again firmly as the time elapses. Now the surface may be considered to have similar structure with that of aluminum stearate B-layer. In fact, the results of the present experiment can be accounted for by these considerations (Fig. 6b). Relating to the results of aluminum salt∼stearic acid system, an interesting phenomena was also observed for the interaction of octadecyl amine and sodium alginate. In this case, amine monolayer on alginate solution was so rigid that it was difficult to build up amine film even as B-layer. On the other hand, the film of free amine built up at pH 7.5 was remarkably hydrophobic even after prolonged contact with water, but it became hydrophilic by treating it with sodium alginate solution, which finally dissolved amine into the solution. Similar experiments were conducted by Muramatsu and Sasaki.(10)

B-layer of mercuric stearate behaved similarly as that of aluminum stearate. However, treatment of stearic acid built-up film with mercuric salt solution was different from the corresponding case for aluminum. They rather had resemblance in behavior to B-layer of mercuric stearate treated with water. This may be explained as follows. The network formation in this case is delayed and the overturning of the mercuric stearate molecules precedes already in the solution. Mercuric stearate molecules thus overturned gradually interlock and give a surface just like B-layer of aluminum stearate. Thus it can be reasonably understood that the film behaves similarly to barium initially but is essentially different from it as shown in Fig. 7a and 7b. The film also showed larger resistance against the treatment with an aluminum salt solution like aluminum stearate than the barium stearate film.

It is noticed that the treatment of solidified stearic acid surface with metallic salt solutions reported in the preceding paper,(2) gave a little different results from those of the stearic acid built-up film. The difference may be attributed to the difference in molecular arrangement between the two cases.

Summary

1. Wettability of mixed built-up film of stearic acid and barium or calcium stearate decreased with the number of layers, the advancing contact angle tending to the value of about 115°. The difference between θ_a and θ_r of built-up film was larger than that of solidified surface.

2. X-film and Y-film of barium or calcium stearate prepared occasionally at almost the same condition showed the same wettability. Increase of barium or calcium content in the film was considered to result in the wettability decrease.

3. Of the three types of metallic ion classified according to the influence on wettability of stearic acid, the following two were studied precisely.

(a) Ions of the type III, forming relatively simple stoichiometric compound with stearic acid, the stearates being able to overturn themselves easily in the surface, and the

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(9) G. A. Wolstenholme and J. H. Schulman, *Trans. Faraday Soc.*, **46**, 475 (1950).

(10) M. Muramatsu and T. Sasaki, to be published in a near future.

wettability changing with the condition. (Ba, Ca)

(b) Ions of the type II, forming a network of a complex structure with stearic acid, which overturn themselves with difficulty in the surface and their wettability does not change with the condition.

II—1. Ions, rapidly forming network and render the surface hydrophilic tempolarily. (Al, Cu)

II—2. Ions, slowly forming network and rendering the surface hydrophobic (Hg).

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