Wettability of Solid Surface. IV. Wettability of Palmitic Acid Surface towards Aqueous Salt Solutions

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Introduction

The phenomena of wetting of solid surface have been studied by numerous investigators. The present author has also continued the theoretical studies upon these phenomena and reported some results chiefly concerning the wetting of paraffin, palmitic acid, and cetyl alcohol surfaces. According to the preceding report,(1) the surface of palmitic acid proved to be non-wettable at the moment of contact with water, while it showed increase in wettability with time of contact. However, the results of later experiments, made on apparently the same conditions, showed that the surface of palmitic acid remains evidently unwettable even by a long time contact with water. A careful examination of experimental conditions, which lead us to such an apparent contradiction, revealed the fact that the minute impurities especially ions in distilled water have a great influence upon the wetting phenomena. Such a presumption is also confirmed by the experimental facts reported by Langmuir(2) upon the action of polyvalent metallic ion for monolayers on water as well as for built up films. Therefore the present author has studied the wettability of palmitic acid towards some aqueous solutions of electrolytes.

Experimental

a. Material.—Paraffin, palmitic acid and cetyl alcohol were purified similarly as described in the preceding reports.(1)(3) Potassium, calcium and thorium nitrates, and aluminum sulfate (of extra-pure grading of Takeda Pure Chemical Co.) were used after recrystallization. Water was redistilled,

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(1) Inaba, *Memoirs of the Faculty of Science, Kyūsyū University*, **Ser. C, 1**, 19 (1948).

(2) Langmuir and Schaefer, *J. Am. Chem. Soc.*, **59**, 1406, 1762, 2075, 2400 (1937).

(3) Inaba, *Memoirs of the Faculty of Science, Kyūsyū University*, **Ser. C, 1**, 1 (1948).

using the apparatus made of "Vidrex" glass of Mitsuya Glass Co.

b. Method of Measurement.—Wettability of paraffin, palmitic acid and cetyl alcohol was measured for their solidified surface by means of the modified Du Nōuy tensiometer, the details of which have been described in the preceding paper.(3) The apparatus employed was essentially the same as used by Sasaki for the surface pressure measurement.(4) ζ-potential of palmitic acid in contact with solution was measured for its sol by means of electrophoresis, using the apparatus modified also by Sasaki,(5) which is illustrated in Fig. 1. This apparatus eliminates the troublesome operations of both obtaining ultrafiltrate and making sharp initial boundary between a sol and ultrafiltrate, because the semipermeable membrane of the apparatus acts to produce ultrafiltrate and form a sharp boundary automatically as the electrophoresis proceeds. The moving boundary can be seen in position below the membrane as shown in Fig. 1. The two platinum electrodes B serve to measure the potential gradient applied for sol, which is done by means of the compensation method.

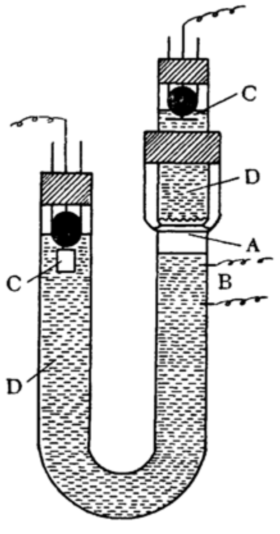

Fig. 1.—Simple apparatus for electrophoresis: A, semipermeable membrane; B, platinum auxiliary electrodes; C, platinum electrodes; D, colloidal solution.

Experimental Results and Discussion

Wettabilities of the solid surface of paraffin (both crude and purified), palmitic acid and cetyl alcohol towards 0.1 N aqueous solutions of potassium, calcium, aluminum and thorium salts were measured, the results of which are shown in Table 1 and are partly illustrated in Figs. 3 and 4, where the wettability is expressed in terms of the work of adhesion, W_a, in the unit of erg/cm^2. The subscript "a" means that the work of adhesion is calculated using the value of the advancing contact angle.

Table 1

Soln	pH of soln	Time of contact in min.	W_a, erg/cm.^{2} of Purified paraffin	Crude paraffin	Palmitic acid	Cetyl alcohol
Water	6.0	0	46.5	46.3	50.3	108.8
〃	〃	60	49.5	77.4	49.4	112.2
0.1 N KNO_3	6.4	0	53.5	46.6	48.6	103.7
〃	〃	60	54.7	81.0	52.1	96.7
0.1 N $Ca(NO_3)_2$	6.0	0	48.8	55.8	59.2	102.2
〃	〃	60	47.9	77.0	64.7	96.0
0.1 N $Al_2(SO_4)_3$	2.4	0	44.9	58.2	56.1	112.6
〃	〃	60	48.7	73.8	55.8	109.7
0.1 N $Th(NO_3)_4$	1.5	0	46.7	55.7	120∼66	115.7
〃	〃	60	52.1	70.1	143.4	111.2

(Wettabilities are measured both at the moment and after one hour of contact with solutions.)

The table shows that crude paraffin generally exhibits an increase in wettability after one hour's contact both with water and aqueous solutions, while such an effect is absent for pure paraffin. In the case of palmitic acid surface the wettability increases only in the case of thorium nitrate solution, where a remarkable effect is observed. The value of 140 erg/cm.^{2} listed in the table corresponds to 0° of contact angle. In the case of cetyl alcohol the wettability changes in a complex manner, showing even a decrease in the case of potassium and calcium salt solutions. Thus we have many problems to make clear, but here we are chiefly interested in the remarkable effect of enhanced wettability due to thorium salt for palmitic acid surface. The aqueous solution of 0.1 N thorium nitrate shows as low pH value as 1.5 due to its hydrolysis. However, this low pH value of the solution proved not to be the cause of the increase in wettability mentioned above, because we cannot observe such an increase in wettability as exhibited by thorium salt in any other solution, though its pH value is controlled to 1.5.

Then, the enhanced wettability of palmitic acid surface by thorium salt solution may be ascribed to the change in ζ-potential(6) of palmitic acid surface in the solution due to the ionic adsorption. To know the effect of ζ-potential upon the wettability, the following experiments were carried out. The palmitic acid hydrosol was prepared by the radiation

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(4) Sasaki, *J. Chem. Soc. Japan*, **62**, 769 (1941); Sasaki and Takeuchi. *J. Chem. Soc. Japan*, **63**, 372 (1942).

(5) Sasaki and Hidemura, *Kindai Koshitsugaku no Tenbo* (*The Review of Recent Advance in Colloid Science*), **1**, 304 (1948).

(6) *Bull*, *Trans. Faraday Soc.*, **28**, 597 (1932); *J. Phys. Chem.*, **38**, 401 (1934).

of ultrasonic wave of medium intensity upon the mixture of water and molten palmitic acid, to which various salt solutions were added. The electrophoretic velocity of sol particles in such solutions was measured, from which ζ-potential was calculated. The results are shown in Fig. 2. We can see in this figure that ζ-potential of palmitic acid hydrosol particle in pure water is -0.12 volt and addition of the salt in increasing amount gradually changes it to more positive value. The effect is particularly remarkable for thorium salt even in extreme dilution. In the thorium salt solution of sufficient concentration the surface charge of particle becomes positive. The effect gradually decreases in the order of aluminum, calcium and potassium salts. To facilitate a comparison, we may illustrate the degree of wettability and ζ-potential together with the *p*H of solution for varying concentration of solutions of aluminum and thorium salts in Figs. 3 and 4 respectively.

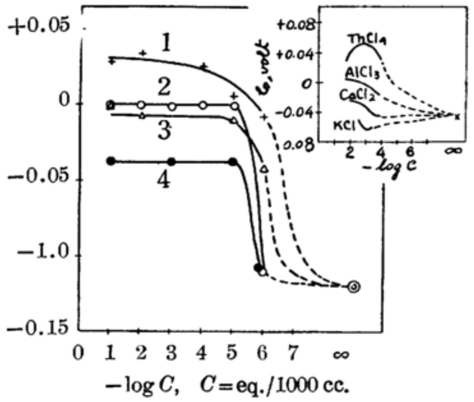

Fig. 2.—ζ-potential of palmitic acid sol particle in various salt solutions: Curve 1, $Th(NO_3)_4$; Curve 2, $Al_2(SO_4)_3$; Curve 3, $Ca(NO_3)_2$; Curve 4, KNO_3.

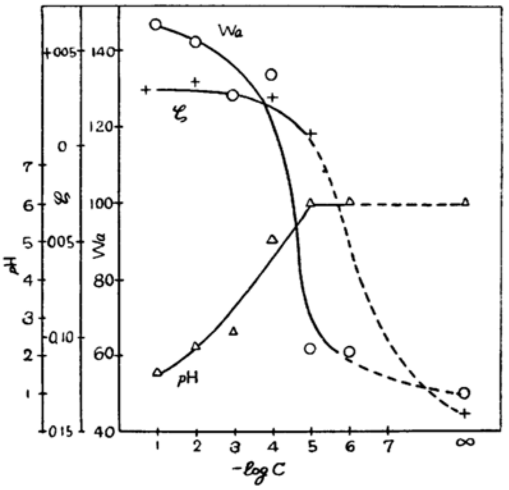

Fig. 3.—Wettability and ζ-potential of palmitic acid surface in $Th(NO_3)_4$ solution of various concentrations: ○, W_a (work of adhesion) in erg/cm.^{2}; +, ζ-potential in volt; △, *p*H of $Th(NO_3)_4$ solution; *C*, concentration of $Th(NO_3)_4$ in equiv./1000 cc.

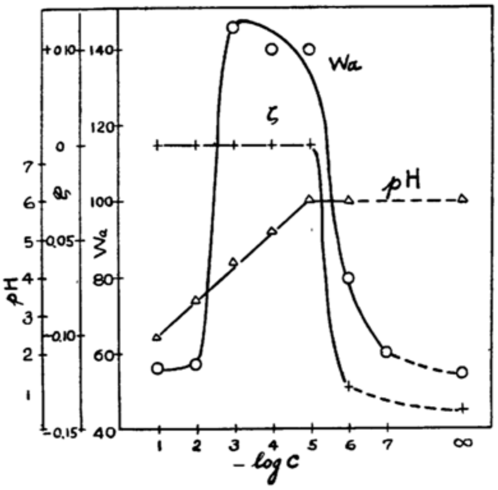

Fig. 4.—Wettability and ζ-potential of palmitic acid surface in $Al_2(SO_4)_3$ solution of various concentrations: ○, W_a (work of adhesion) in erg/cm.^{2}; +, ζ-potential in volt; △, *p*H of $Al_2(SO_4)_3$ solution; *C*, concentration of $Al_2(SO_4)_3$ in equiv./1000 cc.

Under the assumption that ζ-potential of the surface of palmitic acid sol particle is the same as that of the bulk surface, and ignoring a few details, we can see as a whole in these figures that the wettability of palmitic acid surface towards various salt solutions changes parallel with the ζ-potential of the surface. Namely thorium salt solution, showing the most remarkable effect of changing the sign of ζ-potential, exhibits the most pronounced effect on wettability, and aluminum salt solution changing ζ-potential from negative to zero still shows a considerable effect, while the solutions of calcium and potassium salts which merely decrease the value of negative ζ-potential have no influence on wettability. There has been a view concerning the relation between the wettability and the electrical charge of solid surface, that if both the surface of solid and air bubble in solution have the electrical charge of the same sign towards water, solid surface remains in wet condition because the bubble cannot contact with the surface as the results of electrical repulsion between them. On the contrary, when the signs of the charges are opposite to each other, the solid surface is considered to be unwettable for the similar reason. The wetting porperty of palmitic acid in contact with the concentrated thorium salt solution may be explained from such a reasoning. It fails however to explain the non-wettability of palmitic acid towards the salt solution of sufficient dilution, where again both the surfaces of solid and bubble have the charges of the same negative sign. Furthermore, it is pointed out that although the ζ-potential curve of paraffin oil measured by Mooney(7) is similar to that of palmitic acid as shown in the diagram inserted in Fig. 2, thorium salt is not effective for the increase in wettability in the case of paraffin surface. Therefore ζ-potential by itself is not sufficient for the explanation of wettability.

According to Langmuir(2) the barium stearate built-up film becomes wettable in the solution of thorium salt because the stearate molecules overturn themselves in the surface layer and polar groups thus exposed contribute to the hydrophilic property of the surface. However, the view can hardly give any explanation of the fact that the ζ-potential of palmitic acid surface which may suffer a remarkable change in magnitude if the overturning occurs, is practically the same as that of paraffin where the possibility of the overturning of molecules cannot be expected.

The explanation has furthermore been offered that the increase in surface potential causes the decrease in the surface free energy and so the change in wettability.(8) But this theory also does not give sufficient explanation to the experimental results mentioned above.

It is worth while to emphasize here the possibility that the increase in wettability depends on the chemical reaction taking place on the solid surface layer. We can expect that the surface of palmitic acid in contact with salt solution is covered by the corresponding metallic soap.(9) Then the remarkable wettability due to aluminum and thorium salts is ascribed to the formation of corresponding metallic soaps. In this relation, it may be noteworthy that special features of such metallic soaps, particularly the macromolecular nature of them have attracted much attentions of several investigators.(10) In fact we have confirmed that the polyvalent metallic soap such as aluminum or thorium stearate is the only constituent which causes the enhanced wettability of crude paraffin by the contact with water. The details of experiments and discussions upon these phenomena will be reported in the following papers.

Summary

Wettabilities of purified paraffin, crude paraffin, palmitic acid and cetyl alcohol are measured towards aqueous solutions of potassium, calcium, aluminum and thorium salts. It is pointed out that palmitic acid surface becomes remarkably wettable by the contact with aqueous solution of thorium or aluminum salt even in the extreme dilution. Such an increase in wettability can neither be explained simply by ζ-potential change of the palmitic acid surface in those solutions nor overturning of the molecule in surface layer. Alternative explanations are suggested.

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(7) Mooney, *J. Phys. Chem.*, **35**, 331 (1931).

(8) Kabanov, *Kolloid-Z.*, **65**, 101 (1933); Adam, "The Physics and Chemistry of the Surface," Oxford, 350 (1938).

(9) It has also been suggested by Dr. T. Tachibana (Faculty of Science, the University of Tokyo) in his private communication to the present author that the adsorption of metallic hydroxide towards the palmitic acid surface may be considered to play an important rôle in wetting.

(10) McGee, *J. Am. Chem. Soc.*, **71**, 278 (1949); Gray and Alexander, *J. Phys. Colloid Chem.*, **53**, 26 (1949).