On the Nature of Built-Up Film. III. Effect of Dissolved Anion on Mono- and Multilayers of Octadecylamine

By Tunetaka SASAKI and Mitsuo MURAMATSU

(Received August 14, 1952)

Introduction

In the preceding papers(1), (2) the effects of metallic ions on the built-up film of stearic acid were reported. There it was suggested that some metallic ions, e. g., copper, aluminum or thorium, are adsorbed from an aqueous solution in their characteristic pH range as a fairly large and complex unit. This suggestion is in agreement with the experiments of Matuura and one of the present authors,(3), (4) who have arrived at the same conclusion based upon the remarkable expansion and rigidity exhibited by the monolayer of fatty acid spread on an aqueous solution containing the ions mentioned above. A certain wetting phenomena can also be explained from the same point of view which was reported by Inaba(5) of our laboratory. Wolstenholme and Schulman(6), (7) obtained the similar experimental results and explained these phenomena from a different point of view

The fact(2) that the intensity of water-repellency of metal stearate built-up film, after the treatment with or without aqueous salt solution, is parallel to the presumed complexity or macromolecular structure of the film, seems to suggest a profound effect for the wettability of the easiness of overturning of the molecules which is hindered by two-dimensional molecular network in the film. To confirm this, we have further studied the interaction between the film of long chain amine and the organic anion of the known structure.

Experimental

Material. — Octadecylamine was prepared by reduction(8) of nitrile which was synthesized(9) from Merck's pure stearic acid and was purified by distillation in vacuo. The final product was recrystallized repeatedly from benzene. Its melting point was 83~84°C. Bigelow, Glass and Zisman(10) however obtained the free amine of melting point ranging from 51.5 to 52.5°C., and amine bicarbonate of melting point being about 80°C., while the Beilstein value of the former was reported to be 53°C. This leads us to the conclusion that we actually obtained the amine bicarbonate. In fact, the result of micro nitrogen determination of this sample agreed with theoretical value for the bicarbonate within an error (Nobs., 4.37%; Ncalc. for $C_{18}H_{37}NH_2 \cdot H_2CO_3$, 4.23 %, whilst Ncalc. for $C_{18}H_{37}NH_2$, 5.21%). The molecular area of octadecylamine in monolayer spread on water surface was calculated, taking into account of this bicarbonate formation.

Dibasic organic acids were of Takeda's or Riedel de Haën's pure grade and recrystallized

---

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

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

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

(4) R. Matuura, This Bulletin, **24**, 277 (1951).

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

(6) G. A. Wolstenholme and J. H. Schulman, *Trans. Faraday Soc.*, **46**, 475 (1950); **47**, 788 (1951).

(7) G. A. Wolstenholme and J. H. Schulman, *Trans. Faraday Soc.*, **46**, 498 (1950).

(8) F. Kraft, *Ber.*, **15**. 1728 (1883); N. K. Adam and J. W. W. Dyer, *J. Chem. Soc.*, **1925**, 72.

(9) H. Stephen, *J. Chem. Soc.*, **1925**, 1875.

(10) W. C. Bigelow, E. Glass and W. A. Zisman, *J. Colloid Sci.*, **2**, 563 (1947).

several times. A highly purified sample of sodium alginate was given by Mr. S. Miyamoto of our laboratory.

Apparatus and Method.—The surface pressure of monolayer was measured by the Wilhelmy balance modified by one of the authors of this paper.(11) The monolayers were deposited onto the metal slide by either of the two methods, namely by the ordinary Langmuir-Blodgett technique(12) and by the special method of using benzene solution of amine as a piston oil placed near the slide, the details of which were reported in the preceding paper.(2) Optical thickness of built-up films was determined by means of the interference method as used in the preceding reports.(1), (2) The experimental error associated with the apparatus was ±1.5 A. All experiments were carried out at room temperature from 7 to 14°C.

Results

Monolayers Spread on the Surface of Distilled Water.—The pressure $\sim$ area curve of the amine monolayer spread on the surface of distilled water proved to be of a typical condensed film. The cross-sectional area of molecules at zero compression lies in the range of 21.7—25.6 A.^{2}/molecule depending upon various factors. It seems to be characteristic for this film that the reproducibility is poor presumably due to its sensitivity towards pH,(13) or to the presence of carbon dioxide(10) in water, and also due to the aging of the film.(14) Moreover, it was observed thet the shape of curve was profoundly affected by velocity of compression, as reported by Marsden and Schulman,(15) and Hoffman, Boyd and Ralston,(16) though the other conditions were the same. The similar result was reported in the case of the monolayer of antifoaming agent.(17)

Deposition of Multilayers from Water Surface.—By use of the Langmuir-Blodgett technique(12) attempts were made to build multilayers of free base from the surface of water, pH of which was adjusted to larger than 5, to prevent the formation of ammonium salt.(14) Under the pressure of tricresyl phosphate, castor oil and oleic acid as piston oils, through all pH region, the monolayer did not adhere to a bare surface of stainless steel slide both for down- or up-trip. On the other hand, it could be deposited onto the barium stearate base as successive Y-multilayers when the substrate pH was smaller than 10 and each double layer was sufficiently dry after withdrawal. Under the piston pressure of tricresyl phosphate, the films of 4—6 layers showed an optically perfect homogeneity when they were deposited from the substrate water of pH 5—8.6. However, in the case of the film exceeding six layers, optical contrast of the echelon became weak indicating the heterogeneity of the film, which was seen already in the first double layer when pH of substrate water was 8.6—10. Using castor oil or oleic acid as a piston oil, on the other hand, an optically homogeneous film could be obtained only up to 2—4 layers when it was built from substrate water of pH 5—6, while heterogeneous film resulted in the other range of pH. In the case of homogeneous film, the spacings in multilayer were found between 24.0—25.3 A. (24.5 A. for the mean value of twelve experiments) per layer irrespective of the conditions of building-up. It should be noted that remarkable fogging occurred in the built-up films of amine when more than about ten layers were deposited. Similar results were reported in the cases of the films of long chain esters(18) and phthiocerol.(19)

At pH$>$10, the films were deposited as X-layer independent of the piston pressure. The slide was withdrawn from the solution completely wetted with water but it quickly peeled back soon after.

Interaction of Amine Monolayer with Organic Anions in the Underlying Solution.—In Fig. 1 are shown the effects of some dibasic organic acids and sodium alginate dissolved in a substrate water, on the pressure$\sim$area curve of the amine monolayer. The solutes were dissolved to 10^{-4} mol./l. for acids and 0.1% for sodium alginate, and pH of the substrate was kept to 4.5—5.0. The same result was also obtained when the oxalic or succinic acid was injected in water beneath the monolayer. It was seen, in general, that the monolayer expanded with increasing distance between the polar groups in each anion of the substrate. The curve of sodium alginate, in this connection, lies between succinic and

---

(11) T. Sasaki, *J. Chem. Soc. Japan*, **62**, 796 (1941).

(12) K. B. Blodgett and I. Langmuir, *Phys. Rev.*, **51**, 964 (1937).

(13) C. G. Lyons and E. K. Rideal, *Proc. Roy. Soc. London*, A **124**, 333 (1929).

(14) N. K. Adam, *Proc. Roy. Soc. London*, A **126**, 526 (1930).

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

(16) E. J. Hoffman, G. E. Boyd and A. W. Ralston, *J. Am. Chem. Soc.*, **64**, 498 (1942).

(17) A. L. Jacoby and C. E. Johnson, *J. Phys. Colloid Chem.*, **53**, 1417 (1949).

(18) E. Stenhagen, *Trans. Faraday Soc.*, **34**, 1328 (1938); G. Knott, J. H. Schulman and A. F. Wells, *Proc. Roy. Soc. London*, A **176**, 534 (1940).

(19) S. Ställberg and E. Stenhagen, *J. Biol. Chem.*, **143**, 171 (1942).

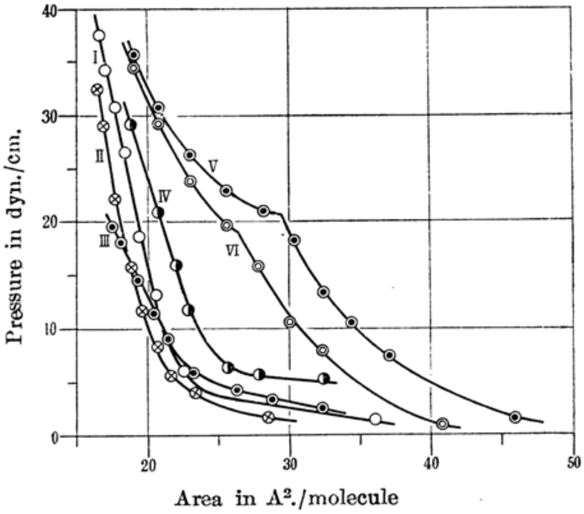

Fig. 1.—Pressure∼area curve of octadecylamine monolayer spread on various substrate: I, distilled water; II, oxalic acid; III, malonic acid; VI, succinic acid; V, adipic acid; VI, Na alginate.

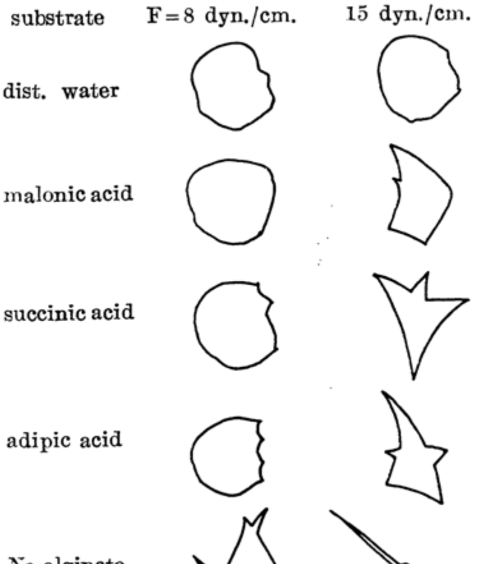

Fig. 2.—Expansion pattern of octadecylamine monolayer.

adipic acids. With respect to the mechanical properties, however, sodium alginate behaved remarkably different from the other anions. It rendered the amine monolayer highly rigid, while such an effect was not so remarkable in the case of dibasic acids. This behavior is shown in Fig. 2, in which the expansion patterns of camelia oil⁽⁴⁾ are schematically illustrated for different solute and surface pressure.

Multilayers of Amine Built Up from the Surface of Organic Anion Solution. — The monolayer of amine formed on the surface of the solution as described above could easily be deposited onto the barium stearate echelon, excepting the case of sodium alginate, as successive Y-layers which showed an optical homogeneity up to six layers. On the other hand, X-film alone was obtained in the case of adipic acid, and this film was so patchy indicating the incomplete deposition that we could not measure its spacing. The opticallv perfect film was obtained by the method of deposition as described in the preceding report.⁽²⁾ It was confirmed with dibasic acids except for adipic acid, that the thickness of a monolayer is unaffected by the method of deposition.

Table 1 shows the apparent spacing of these films under the piston pressure (15 dyn./cm.) of castor oil, together with the cross-sectional area of a molecule at the same pressure. All these films, especially those built up from the solutions of organic ions, proved to have an extremely hydrophobic property, as well as a strong resistance against corrosion and dissolution in contrast with the built-up film of stearic acid.⁽²⁰⁾⁽¹⁾ Thus the film transferred from the aqueous oxalic acid substrate, for instance, showed no change in the film thickness as well as the water-repellent property, even when it was soaked in distilled water for a long time (44 hrs. or more). It is a very interesting fact that it became wettable towards water, when it was immersed in the sodium alginate solution. The minimum time of immersion necessary for wetting is shown in Table 2. In this table, the case of KH_2PO_4 (buffered to pH=7.2 with

Table 1

Cross-sectional Area of Molecules and Apparent Spacing in Built-up Film

Substrate Solution	Apparent Spacing per Layer in A.	Cross-sectional Area in A.²/molecule
distilled water	24.5	20.0
$(COOH)_2$	34.7	19.1
$CH_2(COOH)_2$	32.5	19.1
$(CH_2)_2(COOH)_2$	32.6	22.1
$(CH_2)_4(COOH)_2$	20.9	31.2

---

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

Table 2

Minimum Time of Immersion in Aqueous Sodium Alginate(0.1%) Required to Wet Built-Up Film Transferred from Various Aqueous Substrate

Aqueous Substrate	Time of Immersion in min.
distilled water	1-3
$(COOH)_2$	7
$CH_2(COOH)_2$	10
$(CH_2)_2(COOH)_2$	15
$(CH_2)_4(COOH)_2$	25
KH_2PO_4	∞

NaOH) was listed in addition to the cases of dibasic acids. Amine monolayer spread on this substrate was as rigid as that spread on the alginate, and it could be transferred onto the slide but was extremely heterogeneous.

Discussion

Easiness of Building-Up of Amine Film. —There are several experimental evidences that the affinity between the metal surface, e. g., platinum,$^{(10)}$ silver or copper surface,$^{(7)}$ and long chain amine when the molecules of free amine were adsorbed from non polar solvent, is as strong as that between metal and long chain acid. Then, it seems to be a contradiction that the monolayers of free base spread on water do not adhere, as was mentioned already, to the bare surface of metal. This may be explained by the stronger affinity of amine molecules towards water surface, than towards nonpolar solvent. However when the echelon of barium stearate was dipped into water carrying the monolayer, it took up the amine molecules as an A-layer, its polar group orienting towards bulk water. On withdrawal, moderately strong anchorage of amine molecules to echelon by non polar group and to the next amine layer by polar group enables the formation of AB-double layer. This interaction can reasonably by assumed from the following facts. A strong cohesion of long chain amine was predicted from the formation of islands in the monolayer$^{(15)}$ and from the lower value$^{(21)}$ of c. m. c. of long chain amine than that of the corresponding anionic soap. Also in our experiments the heterogeneity or the fogging in the film may presumably be an indication of the tendency of transformation into the three-dimensional microcrystal which may be a more stable form than the two-dimensional one. That the homogeneous thicker film could only be obtained using the lower piston pressure, and that the successive layer could be better transferred onto the echelon from the surface of aqueous substrate containing organic acid than from that without acid, may be considered to have some relation to this phenomenon.

Surface Interactions between Amine and Organic Anions. — In Fig. 1 a somewhat distinct condensation was observed for amine oxalate film* compared with the case of free base, while, for amine malonate, pressure~area curve at low pressure was nearly the same as the control test, and a remarkable expansion was seen with succinate and adipate. It is probable that the cross-sectional area of molecules in monolayer is chiefly affected by the distance between carboxyl groups in substrate anion, to which amine molecules in monolayer are considered to attach. Thus in the film of, say, amine adipate, octadecyl radicals attach separately to the carboxyl groups of adipate ion under low pressure. This idea is also supported by the decrease in apparent spacing shown in Table 1, which can be interpreted to be the increase in distance of octadecyl radicals in the film as was already pointed out$^{(2)}$ referring to the metal stearate. We may also find Schulman's strong polar and weak van der Waals' type interaction$^{(22)}$ in the behavior at a high pressure region. On the other hand condensation of amine oxalate would be accounted for by the attachment of the amine monolayer to carboxyl groups which are located closely in the acid molecules.

The effects of dissolved alginate ion upon the mono- and multilayers of amine are of very great interest. It can be pointed out from Figs. 1 and 2, and is also expected from X-ray data$^{(23)}$ on alginate solution, that the distance between ionic groups in the alginate ion is slightly smaller than between groups in adipate, and that a large number of polar groups in anion interact with amine molecules. This interaction renders the film highly rigid. Such a type of interaction was called multiple-point polar association by Cockbain and Schulman.$^{(22)}$ The remarkable rigidity due to the interaction of this type has also been shown by several investigators for amine film on

---

(21) A. W. Ralston, C. W. Hoerr and E. J. Hoffman, *J. Am. Chem. Soc.*, **64**, 97 (1942); **68**, 2460 (1946); I. M. Kolthoff and W. Stricks, *J. Phys. Colloid Chem.*, **52**, 915 (1948); M. Nakagaki, *J. Chem. Soc. Japan*, **72**, 113 (1951).

* The term "amine oxalate (malonate, succinate, and so on) film" is used hereafter as the abbreviation for the monolayer of amine spread on the surface of solution of oxalic (malonic, succinic, and so on) acid.

(22) E. G. Cockbain and J. H. Schulman, *Trans. Faraday Soc.*, **35**, 716 (1939).

(23) Wo. Pauli and L. Sternbach, *Kolloid-Z.*, **84**, 291 (1938).

aqueous tannin(22),(24), silicate(6) and metaphosphate(25) and for amide film on aqueous tannin.(17)

Now we should draw attention to the fact that the interaction between monolayers of stearic acid and the polyvalent salt in the aqueous substrate closely resembles the interaction between amine monolayer and alginate in aqueous substrate, in that both can form a macromolecular complex as has been reported in the case of aluminum stearate.(26)

In this connection, the experimental data upon wettability shown in Table 2 appear to be of much value. Langmuir(27) has found the remarkable wettability of the built-up film of stearic acid and stearate when it was conditioned with the solution of various metallic ions, and explained this phenomenon by the overturning effect of molecules in the film. In the previous report(2) authors have correlated the two-dimensional network in the film with the difficulty of overturning or re-overturning which seems to be one of the chief factors for the wettability of this film. Inaba(5) also arrived at the same conclusion. The high wettability of the built-up film of amine towards a solution of sodium alginate is similar to the case of stearic acid or stearate towards metallic ion solution. The molecules of amine overturn themselves, and are fixed to the alginate ions and form a network of polyoctadecylamine alginate so that the re-overturning is not allowed and an extremely wettable surface results. In the case of amine phosphate, as shown in Table 2, a remarkable rigidity as described already also acts to hinder the overturning of amine molecules and the surface remains non-wettable. Further, we can also see in this table, though not so distinctly, that the resistance to wetting increases with increasing distance between the hydrocarbon chains attached to organic di-acids. Again the authors have inclined to the opinion that the easiness of overturning when treated with alginate solution is chiefly determined by the magnitude or complexity of amine$\sim$organic acid compound formed in the film.

Summary

Attempts were made to transfer the monolayers of octadecylamine on distilled water both onto the metal surface and onto the optical gauge of barium stearate. They did not adhere to the former surface, while with the latter it was shown that the homogeneous film was obtained when the substrate pH and the piston pressure were favorable for preventing the film from aggregating.

Effects of organic anions upon the mono- and multilayers of amine were investigated. The increase of the distance between the ionic groups of dicarboxylic acids caused the corresponding expansion and change in thickness of amine monolayer spread on the solution containing these anions. The solution of sodium alginate caused a somewhat large expansion and gave a remarkable rigidity towards the amine monolayer spread on it.

The built-up film of amine transferred from the substrate of various organic acids showed a variety of resistance for wettability when treated with aqueous sodium alginate solution. It was found that the resistance for wetting increased with the increasing complexity of the two-dimensional network formed in the film prior to the treatment. These results were discussed with regard to the easiness of overturning.

The authors wish to thank Mr. T. Tsutsumi for the micro nitrogen analysis of octadecylamine. They also wish to express their thanks to the Ministry of Education for the grant given for this research.

Department of Chemistry, Faculty of Science,
Kyūshū University, Fukuoka.

---

(24) F. Sebba and E. K. Rideal, *Trans. Faraday Soc.*, **37**, 273 (1941).

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

(26) V. R. Gray and A. E. Alexander, *J. Phys. Colloid Chem.*, **53**, 23 (1949); C. G. McGee, *J. Am. Chem. Soc.*, **71**, 278 (1949); etc.

(27) I. Langmuir, *Science*, **87**, 493 (1938).