dividual measurements of the order of 0.04%. These are, of course, arranged in a random manner as to sign so that it can be stated safely that the observed changes in conductance are not due to experimental error. The measured values of the changes in conductance appear to indicate that the observed $\Delta C_{\text{sp.}}$ is about half that calculated by Onsager and Fuoss at higher concentrations and tends to agree with them at lower concentrations. The same statement, it will be remembered, is made by Onsager and Fuoss in connection with the measurements of Bray and Hunt on mixtures of hydrogen chloride and sodium chloride.

The authors would like to make due acknowledgment of a research grant made to one of us (M. K.) by the Faculty Research Committee of the University.

Summary

The conductance of lithium chloride at 25° has been measured and compared with the values in the literature.

The conductances of nineteen mixtures of potassium chloride and lithium chloride have been measured and compared with the theoretical conductances.

PHILADELPHIA, PENNA. RECEIVED JULY 1, 1937

[CONTRIBUTION FROM THE BIOLOGICAL LABORATORIES, HARVARD UNIVERSITY]

Monomolecular Films of α-Aminostearic Acid, Stearic Acid, and Heptadecylamine

BY ELIOT F. PORTER

Monomolecular films of proteins have been studied by many investigators, including ourselves in unpublished work. Unfortunately, the results so far obtained have not added as much as was originally hoped to an understanding of the properties of these large dipolar ions (or zwitterions). In particular, as in the case of other compounds, estimates of the dipole moments based on the contact potentials associated with the films are of a smaller order of magnitude than those calculated from dielectric constant measurements.

In order to throw some light on this difficult problem it seemed desirable to study a simpler type of dipolar ion in a monomolecular film and to compare its behavior, both mechanical and electrical, with that of other related molecules lacking the dipolar ionic structure. Unfortunately the smaller and more familiar amino acids, which at first suggest themselves for the purpose, are too soluble to form monomolecular films on aqueous substrates. For this reason in the following study we have made use of α-aminostearic acid and for comparison of two closely related compounds without the dipolar ionic structure, namely, heptadecylamine and stearic acid. Although it has never been measured directly, there is every reason to believe the dipole moment of this amino acid to be the same as that of other α-amino acids, whose moments, estimated from dielectric constant studies, are found to be very nearly independent of the length of the hydrocarbon chain.[1]

So far as we know the measurements here reported for α-aminostearic acid are the only ones of their kind ever made on dipolar ions, except of course, for the complicated case of the proteins.[2] In the case of heptadecylamine some mechanical, but no electrical, measurements are on record.[3,4] A large number of studies, both mechanical and electrical, have of course been made on long chain fatty acids.

Materials and Solutions.—The aminostearic acid and heptadecylamine used in these experiments were synthesized for us by Dr. T. L. McMeekin of the Department of Physical Chemistry at the Harvard Medical School. The stearic acid was purchased from the Eastman Kodak Company.

The amino acid is insoluble in all common organic solvents with the exception of glacial acetic and formic acids, but uniform films could not be obtained by spreading from solutions in these solvents, partly, at least, because of their high specific gravity. A sufficiently concentrated solution was finally obtained in a mixture of methyl alcohol and diethyl ether by first converting the amino acid into the hydrochloride. The procedure used was to add to weighed samples in a 100-cc. volumetric

---

[1] Wyman and McMeekin, THIS JOURNAL, **55**, 908 (1933).

[2] A preliminary note by van Ormondt [*J. Biol. Chem.*, **114**, lxxvii (1936)], which has just come to our attention, states that he is investigating the mechanical properties of films of certain lipopeptides.

[3] Lyons and Rideal, *Proc. Roy. Soc.* (London), **A124**, 333 (1929).

[4] Adam, *ibid.*, **126**, 526 (1930).

flask 1 cc. of concentrated hydrochloric acid and to warm for a few minutes in a water-bath. Twenty cc. of methyl alcohol was added after cooling and the volume made up to 100 cc. with ether. For some unexplained reason it was impossible to obtain consistent results from this solution on immediate use, but after a day or two of standing the results became reproducible.

The heptadecylamine was dissolved in a 25% methyl alcohol–75% ether mixture. The stearic acid was dissolved in ether.

Methods

The measurement of the force area relations was carried out with an instrument of the type described by Adam, with slight modifications, made in the laboratory shop and capable of detecting pressure changes of 0.1 dyne per cm. The tray was of bronze approximately 13 × 36 × 1 cm.

The study of the potentials was based on a method developed by Zisman,[5-7] which appears to be superior in speed and accuracy to any of the earlier methods. The two conducting media whose contact potential in air is to be measured form the two plates of a condenser. If no compensating electromotive force is introduced into the circuit a field is established in the air gap between the condenser plates proportional to the contact potential. If one of the plates is vibrated so that the capacity of the condenser varies periodically, an alternating current of the same period will flow and give rise to an electromotive force across any resistance in the circuit. This effect, which furnishes the signal, may be abolished by the introduction of a compensating electromotive force drawn from a potentiometer equal and opposite to the contact potential to be measured. The potentiometer setting then gives the contact potential.

Zisman has not given an expression for the effect, and indeed an exact solution of the problem in finite terms is not possible, but the following treatment, due to Dr. Jeffries Wyman, Jr., may be offered, in which E_0 is the contact potential to be measured; E_p is the voltage drawn from the potentiometer, C is the capacity of the condenser, r is the resistance, $\omega/2\pi$ is the frequency of vibration of the moving condenser plate; Q is the charge on one of the plates; I is the current flowing in the circuit.

We may suppose

$$C = C_0 + C_1 \sin \omega t$$

Then by Kirchhoff's law

$$E = E_0 - E_p = Ir + Q/C$$

Now assume that Q may be expressed in terms of a Fourier series as follows

$$Q = Q_0 + \sum_{K=1}^{\infty} (a_K \cos K\omega t + b_K \sin K\omega t)$$

then

$$I = \omega \sum_{1}^{\infty} (Kb_K \cos K\omega t - Ka_K \sin K\omega t)$$

also

$$Q_0 + EC_0$$

The coefficients may be shown to be determined by a set of relations as follows

$$b_1 - r\omega\,(C_0a_1 + C_1b_2) = EC_1$$
$$a_1 + r\omega\,(C_0b_1 - C_1a_2) = 0$$
$$b_2 + r\omega\left(\frac{C_1b_1 - 3C_1b_3}{2} - 2C_0a_2\right) = 0$$
$$a_2 + r\omega\left(\frac{C_1a_1 - 3C_1a_3}{2} + 2C_0b_2\right) = 0$$

. . . .

Each additional relation introduces an additional constant. However, if the higher harmonics are supposed to be weak, we may obtain the following approximate solution for the strength of the signal, provided the amplitude is small

$$rI = E\,\frac{C_1}{C_0}\,\frac{\omega C_0 r}{(1 + \omega^2 C_0^2 r^2)^{3/2}} \cos\ (\omega t - \tan^{-1} \omega C_0 r)$$

In the present investigation the moving electrode was a gold-plated disk vibrated by a well-shielded loud speaker at a frequency of 800 cycles.[8] The liquid, with or without the film, formed the stationary condenser plate and was contained in a glass tray. The gold plate could be brought down to any desired distance above the liquid surface by an accurate screw and could also be swung over the surface of the liquid to test for uniformity of the potential. Both these operations, as well as the movement of the glass barriers for compressing the film, were controlled from outside the metal shield surrounding the system. Electrical contact with the liquid (always containing some chloride ions) was made with a silver–silver chloride electrode.

A pair of telephones in connection with a three-stage amplifier was used for detection of the signal. The author is greatly indebted to Mr. J. P. Hervey, formerly of the Cruft laboratory, for advice in the design of this amplifier.

With this system it was possible to make measurements to an accuracy of a few tenths of a millivolt almost immediately. With freshly cleaned liquid surfaces the potential was in general uniform over the surface to a fraction of a millivolt. The variation of the potential with time depended on the liquid, and in the case of the more acid substrates might amount to 5 mv. in several hours; in the more alkaline substrates to 10–15 mv. It was often found useful to heat the liquid with charcoal and filter before use in order to remove traces of surface active materials which tend to accumulate on the surface and give rise to a drift of potential with time.

Both force–area and potential measurements were made over a range of pH from approximately 3 to 10. For

---

(5) Zisman, *Rev. Sci. Instruments*, **3**, 7 (1932).

(6) Zisman and Yamins, *Physics*, **4**, 7 (1933).

(7) Yamins and Zisman, *J. Chem. Phys.*, **1**, 656 (1933).

(8) Careful experiments showed that neither the frequency nor amplitude of vibration nor the spacing of the plates had any effect on the results within the accuracy of the measurements.

substrates between *p*H 2.7–9 Michaelis acetate–barbital buffers were used, the ionic strength being in all cases 0.011. Above *p*H 9 borate buffers were necessary, the ionic strength being 0.02. The *p*H of the substrate was determined with a glass electrode both before and after a series of measurements. In no case was there a change of more than 0.05 unit.

Films were spread by dropping on to the liquid surface from a specially designed micro-pipet small measured quantities of the standard solution.

The solvents used for making up the standard solutions were tested for capillary active material by control measurements. A film detectable by mechanical means was not produced by either diethyl ether or methyl alcohol when quantities greater than the amounts used in the experimental work were added to the substrate. By the potential method a 3 millivolt increase for ether and a 6 millivolt decrease for methyl alcohol were observed at maximum compression. Both these solvents disappeared very rapidly from the surface.

All the following experiments were conducted at room temperature, which varied between 22–25°.

Mechanical Measurements

A. α-Aminostearic Acid.—It was found in making the mechanical measurements on the amino acid that quite different curves were obtained if the films were compressed immediately than if some time were allowed to elapse before beginning the compression. Therefore, in every case compression was started about one-half hour after adding the film and five to ten minutes was allowed for the film to come to equilibrium between successive compressions.

Between *p*H 7 and 9, where agreement between duplicate runs was best, a steep curve was found, the linear part of which could be extrapolated to zero force, giving an area 30.3 sq. Å./mole (see Fig. 1). At the top of the steep part the curve breaks rather sharply but continues to rise until an area of about 9 sq. Å./mole is reached. This upper part of the curve might find explanation by assuming a rearrangement of the molecules into a double layer, or the formation of aggregates as the film collapses, as shown by Zocher and Stiebel[9] by an ultramicroscopic method, confirmed by Adam and Miller,[10] to be the case for films of fatty acids. Below *p*H 7 a break in the slope appeared in the neighborhood of 18 dynes per cm. which becomes, below *p*H 6, a constant pressure plateau. The final rise in pressure at small areas was very unstable and was not a constant finding. At *p*H 3.06 the film was so unstable that a rise of pressure could be obtained only by very rapid compression. The plateau reappeared at *p*H 11.[11]

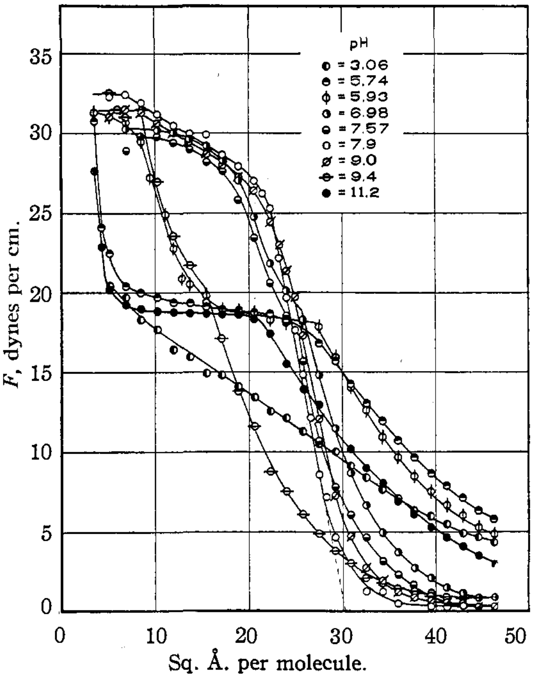

Fig. 1.

B. Stearic Acid and Heptadecylamine.—Films of stearic acid and heptadecylamine came to equilibrium rapidly after formation, making it possible to carry out the compression within a few minutes. The force–area curves for stearic acid (Fig. 2) are in entire agreement with those of previous investigators showing very little change with hydrogen-ion concentration and giving an extrapolated area of 20.6–22.0 sq. Å. per molecule at zero force. However, certain minor *p*H effects were noted. At *p*H 3.2 and also at *p*H 4.9 the curves rose less steeply at first, the films being initially less compressible than at more alkaline reactions. This effect has been described by Lyons and Rideal[3] in studies on the solubility of unimolecular films of palmitic and pentadecylic acids. Another effect of acidity is to diminish the maximum force that the film will support before collapsing. At *p*H 3.2 this maximum is 13 dynes per cm.; at *p*H 5–9 it is between 25 and 30 dynes per cm. Lyons and Rideal[12] and R. J. Myers[13] have reported similar observations on palmitic acid.

---

(9) Zocher and Stiebel, *Z. physik. Chem.*, **147**, 401 (1930).

(10) Adam and Miller, *Proc. Roy. Soc.* (London), **A142**, 401 (1933).

(11) Immediate compression after adding the film gave at every *p*H a curve with a constant pressure plateau in the middle at about 18 dynes per cm. At *p*H 7, however, the length of the plateau was shorter.

(12) Lyons and Rideal, *Proc. Roy. Soc.* (London), **A124**, 322 (1929).

(13) Myers, THIS JOURNAL, **57**, 2734 (1935).

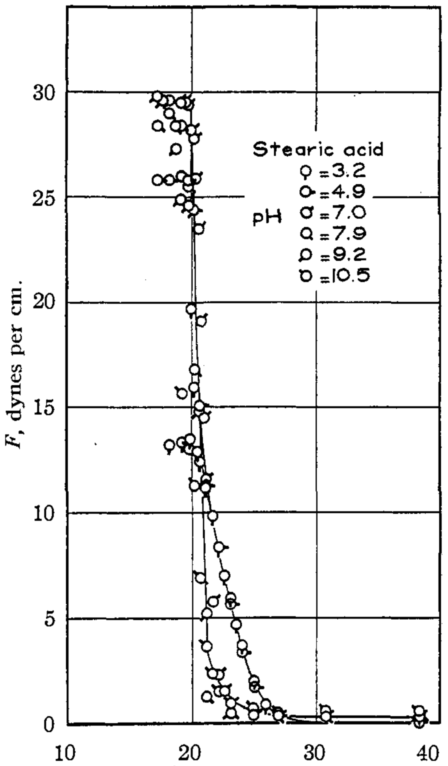

Fig. 2.

Quite different from the behavior of stearic acid is that of heptadecylamine (Fig. 3). On acid substrates, *i. e.*, *p*H 3.0 and 4.9, the force–area curves rise gradually to small areas without collapsing. At *p*H 6.8 a plateau develops at 8.2 dynes, with the curve rising again steeply to the limiting value of about 14 sq. Å. per molecule. When still more alkaline substrates are used the curve rises steeply from the base line, as in the case of stearic acid, extrapolation giving 21.6 sq. Å. per molecule at zero force. On acid substrates heptadecylamine exists in the form of positively charged ions and its films are less stable and more expanded than when the molecules are uncharged.

Amines were first studied by Lyons and Rideal[3] in 1929. They obtained force–area curves for heptadecylamine which varied considerably with *p*H from 6.5 to 11.4. Below 6.5 they were unable to obtain curves because of too great solubility of the amine. On the most acid substrates used the films were greatly expanded, but gave no transition point or plateau as in our results. On the most alkaline substrates steep curves were obtained typical of condensed films with a limiting area at zero force of 26.2 sq. Å. per molecule. In 1930 N. K. Adam[4] studied several of the homologous hydrocarbon amines with from 14 to 20 carbon atoms in the chain. He was unable to confirm Lyons and Rideal's large limiting area. For all amines at room temperature and *p*H 13 he obtained an area of 20.5 sq. Å. per molecule at zero compression. This is certainly about the value to be expected for the simpler straight chain hydrocarbon derivatives. Lowering the *p*H of the substrate produced more expanded types of films but without kinks or transition points. Adam attaches more importance to the kind of salt than to the acidity as determining the kind of film, but since he used a variety of buffers the effect of these factors does not seem to have been clearly separated. In our experiments a single buffer was used over most of the *p*H range studied so that the only variable was the hydrogen-ion concentration.

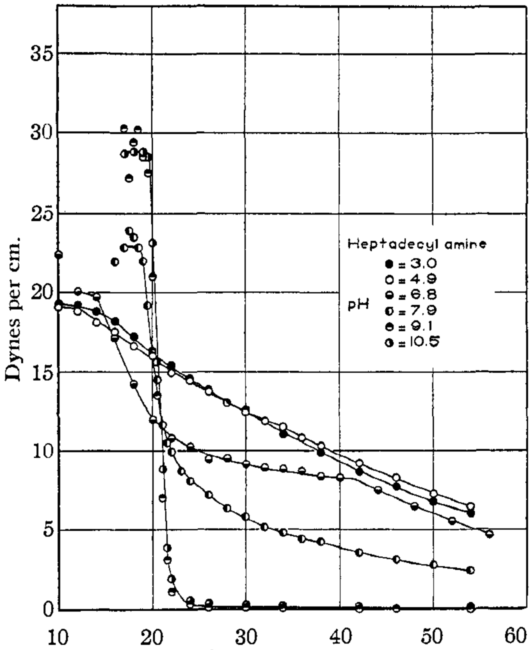

Fig. 3.

The films of the amino acid, which consist of positive ions on acid and negative ions on alkaline substrates should by analogy with the above substance give expanded films at the extremes of the *p*H range. This was the case at *p*H 5.74, 5.93 and 11.2. At *p*H 3.06 the film was both expanded and unstable. The lower part of the curve at *p*H 9.4 seems anomalous. The curve at 5.93 is intermediate between those at 5.74 and 6.98, the latter still showing a slight break in the slope at 18 dynes per cm. It seems useless at present to speculate on the significance of the change in slope at a pressure of 18 dynes per cm. on acid and alkaline substrates.

Potential Measurements

A. α-Aminostearic Acid.—Before making potential measurements on the amino acid, it was necessary as in the case of the mechanical measurements, to allow the films to come to equilibrium. Great variation in potential over the surface was noted immediately after adding the film, but these irregularities gradually diminished in the course of one-half hour to less than 10 millivolts. In Fig. 4, which shows the effect of compression and *p*H on ΔE, the change of contact potential due to the film, the ordinates are the average of values obtained at the same *p*H and equal areas in successive runs. N, the abscissa, gives the number of molecules per sq. cm. of surface. It is to be noted that in this and in all the other cases, positive values of ΔE correspond to a double layer with the negative surface toward the liquid substrate. Potentials of successive runs agreed to within 15 millivolts over most of the range of compression. However, disagreements as great as 30–40 millivolts at the smallest areas were observed on the most acid substrates. This is a divergence from the mean ΔE values over most of the compression range of not more than 1.5% and a maximum divergence of 3% at greatest compression. It is seen that potential differences as great as 800 millivolts existed at high compression and low *p*H values. As the *p*H was increased to 10.8 the maximum ΔE decreased to 400 millivolts.

From *p*H 6.7 to 10.8 inclusive the curves become nearly horizontal in the neighborhood of $N = 6 \times 10^{14}$ (or an area of 16.7 sq. Å. per molecule). In other words the electric moment of the surface double layer per unit area becomes insensitive to compression. In this range the effect on the moment of the film of closer packing of the polar groups is balanced by the effect of change of orientation of the film molecules or squeezing out of adsorbed water or substrate ions.[14] Further compression to larger values of N led to a linear second rise in the surface potential. This is more clearly seen when ΔE is plotted against $1/N$ or A. Here the increase of ΔE with decrease in area must be due to a continued rearrangement of the film molecules. At *p*H 2.7 and 4.9 the curves rise to large values of ΔE without becoming horizontal. The upper parts of these curves are linear. At these hydrogen-ion concentrations there is a smooth change from the initial to the final orientation of the molecules.

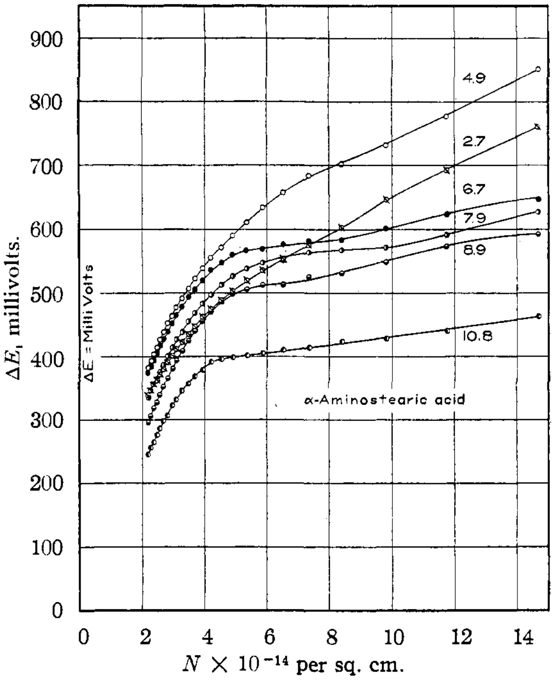

Fig. 4.

B. Heptadecylamine and Stearic Acid.—In the potential measurements of stearic acid and heptadecylamine inability to obtain films of uniform surface potential below compressions of $N = 3 \times 10^{14}$, except at hydrogen-ion concentrations where the molecules are largely ionized, finds partial explanation at least in the fact that the free amine as well as the free acid does not give expanded types of films. The points on the curves in Fig. 5 for values of N smaller than 3×10^{14} were obtained by averaging potentials (which often differed widely from one another) taken at various positions on the surface. At all other values of N the irregularity over the surface was not greater than 10 millivolts in the case of stearic acid and 20–30 millivolts at the steepest parts of the amine curves at *p*H 6.8 and 7.7. Each of the curves given in the figure, except for the amine at *p*H 3.2, is an average of two curves which did not differ at any point by more than 30 millivolts and agreed much better than this at most points.

Perhaps the most interesting consequence of this investigation is the comparison it makes possible of the surface potentials of the amine and

---

[14] This dehydration theory was proposed by Langmuir, *J. Chem. Phys.*, **1**, 756 (1933).

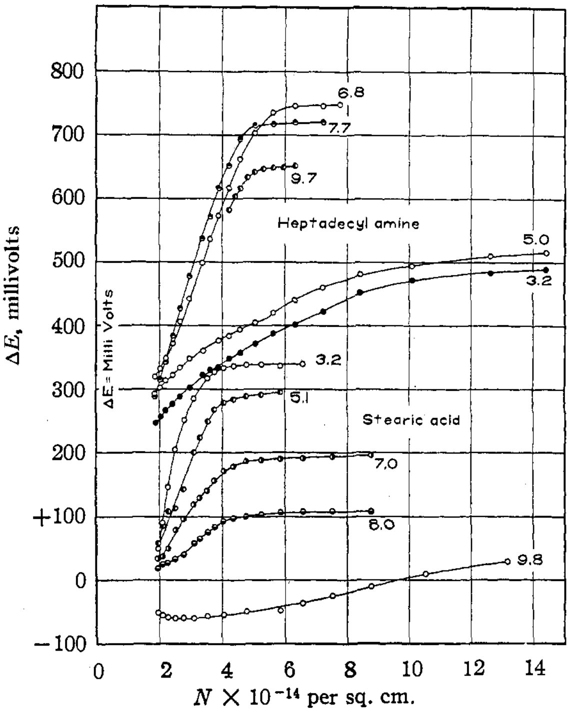

Fig. 5.

stearic acid with those of the amino acid. It is noteworthy that larger ΔE values are obtained with the amine than the acid and that in general the highest potentials given by the amino acid occur when it most closely resembles the amine, namely, on acid substrates; and further that as the amino acid approaches the acid in chemical behavior on alkaline substrates its contribution to the potential difference diminishes. We have not at our disposal sufficient information concerning the structure of films of the amino acid to attempt a complete interpretation of their behavior in terms of the homologous amine and acid.

In Fig. 6 are plotted against *p*H for all three compounds studied the values of ΔE corresponding to the extrapolated areas of the condensed films of stearic acid and heptadecylamine (20.5 sq. Å. per molecule or $N = 4.87 \times 10^{14}$). This shows clearly the opposite effects of ionization on ΔE for the amine, which forms a cation, and for the acid, which gives rise to an anion. In the latter case ΔE actually becomes negative alkaline to *p*H 8, as has been shown previously.[15,16] It is in accordance with this that for the amino acid, which may be regarded as a composite of the two others, ΔE passes through a maximum value at *p*H 5, in the range of the isoelectric point.

From the dielectric constant measurements very much larger dipole moments have been estimated[17] for dipolar ions than for other molecules. If, therefore, the surface potential effects represent in any direct way the dipole moments of the molecules forming the surface layer, we should expect much greater effects for the amino acid than for either stearic acid or the amine. The fact that such is not the case leads to the conclusion that the surface potentials cannot reflect at all exactly the magnitude of the electric moments of the molecules.

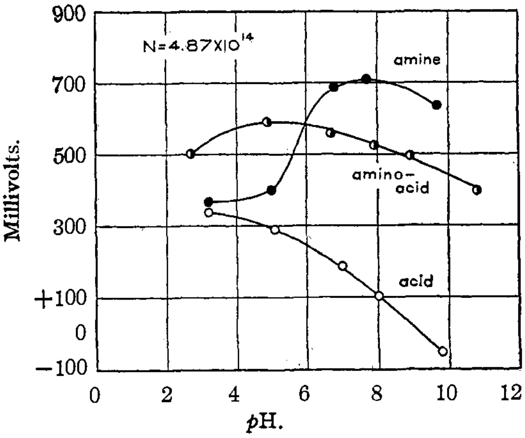

Fig. 6.

Summary

The results are presented of a comparative study of the mechanical and electrical properties of monomolecular films of α-aminostearic acid, a typical dipolar ion, stearic acid, and heptadecylamine, all spread on aqueous substrates of varying *p*H. The area, extrapolated to zero compression, occupied by the amino acid molecules in the isoelectric range is about 50% greater than that of the un-ionized molecules of the acid or amine. On either side of the isoelectric range the amino acid films are more expanded, and exhibit certain characteristic effects. The effect of the amino acid on the contact potential tends to resemble that of stearic acid at alkaline reactions and that of the amine at acid reactions. Notwithstanding its much greater moment in the isoelectric condition, the magnitude of the effect of the amino acid on the potential is never much greater than that of the amine, which shows that the dipole moment is not of primary importance in determining the electrical properties of the films.

CAMBRIDGE, MASS. RECEIVED JUNE 23, 1937

---

[15] Schulman and Rideal, *Proc. Roy. Soc.* (London), **A130**, 284 (1931).

[16] Schulman and Hughes, *ibid.*, **A138**, 430 (1932).

[17] Wyman, *Chem. Rev.*, **19**, 213 (1936).