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INVESTIGATION OF THIN LAYERS OF ORGANIC SUBSTANCES AT THE MERCURYSOLUTION BOUNDARY BY THE METHOD OF CAPACITY MEASUREMENTS

I. HIGH-MOLECULAR ALCOHOLS AND ACIDS

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The examination of thin layers on the surface of mercury in solutions of electrolytes presents considerable interest since it affords the possibility of studying the influence of the electric field upon the properties of the layer. Moreover, at this boundary it is possible to obtain thin polylayers since, as it was shown in one of the foregoing papers (¹), a drop of organic acid spreads completely over the surface of the mercury electrode polarized to the potential corresponding to the maximum of the electro-capillary curve. Yet, the application of the basic methods used in studies of monolayers on the surface of water to investigations of the boundary mercury/solution encounters greaf difficulties.

In the present paper we propose a new method for the study of thin layers at this boundary, based on the fact that the capacity of the double electrical layer of a metallic electrode, in the case of the penetration of organic molecules into that double layer, ought to be considerably reduced. In the case of soluble capillary-active organic substances this effect is well-known from measurements of electro-capillary curves and has of late found additional support in direct measurements of capacity (²). The method of capacity measurements made use of in the present work does not differ essentially from the method formerly developed by M. A. Proskurnin at this Institute (³).

All measurements were effected with a current of 50 Herz in norm. Na_2SO_4 acidulated by H_2SO_4 up to 0.001 norm. acidity*. The potential of mercury was measured against the reference electrode Hg/norm Na_2SO_4 saturated with Hg_2SO_4. For control of surface purity the capacity of the mercury electrode was always measured before the organic substance was applied.

The curves characterizing the dependence of the capacity of the clean mercury surface on cathodic polarization in norm. Na_2SO_4 are represented in all graphs by dotted lines.

The application of the organic substance was effected by means of the contact with the solid substance or else by pressing a drop out of a micropipette on the mercury surface polarized to the potential, corresponding

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* In a neutral solution the fatty acid layers on mercury are unstable.

to the optimum spreading of the given substance over mercury. Palmitic acid dissolved in benzene was applied upon a surface which had not yet been covered with the solution of the electrolyte.

1. Measurements of Electrode Capacity with Constant Surface

Cetyl alcohol (Fig. 1). The film was produced by prolonged contact of the solid substance with the surface. The shape of the curve which gives the relation between capacity and polarization shows that the film is retained on the surface only within the interval 0.1—1.7 V; in the middle portion of the curve, between 0.6 and 1.1 V, the capacity is constant and equals 1.03 μF/cm².

Palmitic and oleic acids (Fig. 2 and 3) give curves differing from the curve for alcohol by the existence of a second horizontal part corresponding to ~5 μF/cm². The minimum capacity for a single monolayer of palmitic acid equals 2.4 μF/cm² and for 10 layers—0.80 μF/cm²*; while even after 2 or 3 hours of «rubbing» the surface with a crystal, the capacity failed to drop below 3.5 μF/cm².

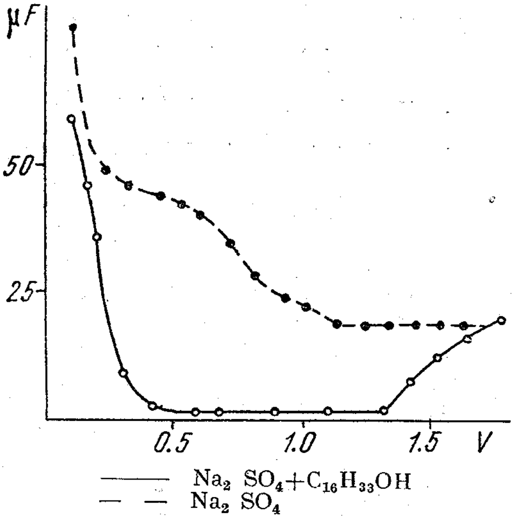

Fig. 1. Cetyl alcohol.

The minimum capacity for a thickness equal to 0.8 of a monolayer of oleic acid equals 5 μF/cm² while it reaches 0.32 μF/cm² for 8 monolayers.

Sharp maxima for potential values corresponding to the limits of stability of the film are clearly to be seen on the capacity curves of fatty acids. The reason for the appearance of these maxima was explained formerly; the theory thereof will be examined more elaborately in another paper.

A number of experiments were also carried out with a large amount of oleic acid (50—1000 monolayers). [The oleic acid, of «Kahlbaum» grade, was not subjected to further purification. It is certain that the preparation was not sufficiently pure.] With such quantities, and when observations are made at a small angle to the surface, interference colours can be observed

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* Under the term «monolayer» we understand an amount of organic matter which corresponds to an area of 20.5Å² per molecule.

on the mercury at polarization corresponding to the maximum spreading, the colour of the surface varying with the potential.

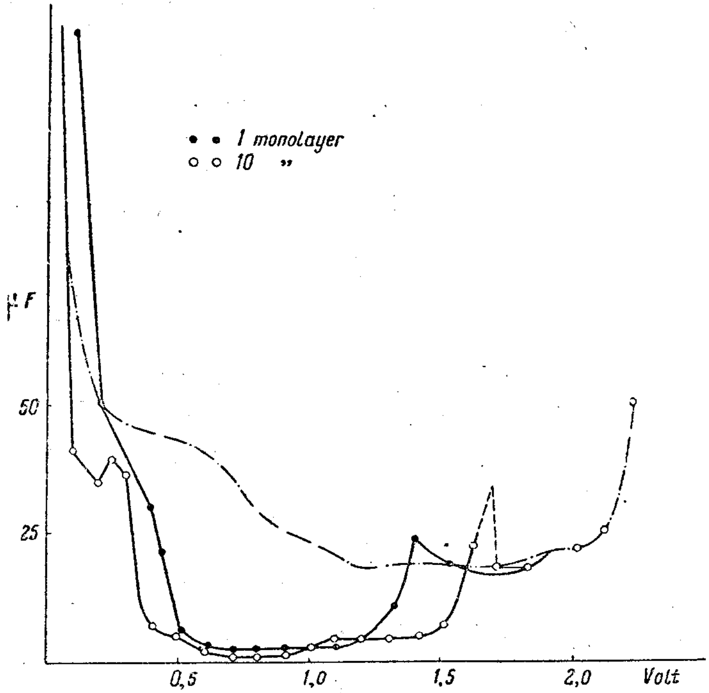

Fig. 2. Palmitic acid.

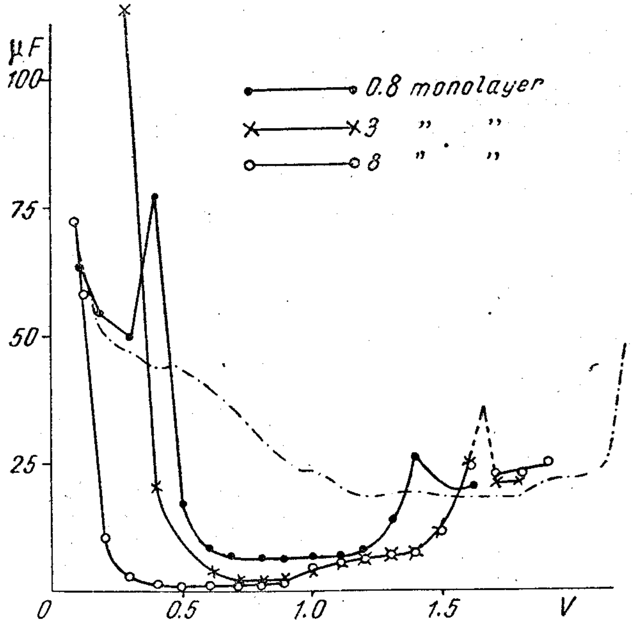

Fig. 3. Oleic acid.

As polarization recedes from values corresponding to the region of maximum spreading, the film breaks up into separate coloured spots whose edges have sometimes a colour differing from that observed in the middle.

With further change of polarization the spots coalesce into colourless lenses and finally into spherical drops, as was already described previously(¹).

In order to clear the question of the equilibrium of such polylayers, experiments were carried out with gradual application of the acids.

Measurements of Capacity with Gradual Application of Oleic Acid. Polarization 0.75 V

Number of monolayers of acid	Capacity in μF/cm^2	Colouring of mercury surface
1.25	1.16	Not coloured
4	1.16	» »
7	1.21	» »
13	1.15	Small faintly coloured spots
18.5	1.15	Fairly well visible red spots
25	1.19	Spots brighter and larger
43.5	1.08—1.18	Spots coalesce to form network
43.5 vessel heated to 60°	1.84	Red and green spots
43.5 vessel cooled to 20°	1.55	» » » »
68.5	0.71	Whole surface red
117	0.30	» » »

The curve taken with a film of 117 layers fully coincided with the curve for 8 layers when these have been applied at once (Fig. 3).

It will be seen that with the gradual application of the acid, the capacity reaches a certain limiting value, provided the amount slightly exceeds a monolayer. The excess of the acid remains in the form of spots in equilibrium with the monolayer and affects but little the magnitude of the capacity. This continues till, with about 60 layers, the spot covers almost the whole surface, when a new reduction of capacity takes place. As can be readily seen from the values of capacity given in Fig. 3, practically continuous polylayers are obtainable from a much smaller amount of the substance, provided the substance be applied at once. However, even though these layers may exist for several hours, they are not in equilibrium and when kept for a long time spots appear on them, the capacity increasing simultaneously. At the same time polylayers of a thickness of 50—100 molecules are apparently quite stable. It is interesting to note that in the case of oleic acid at the boundary mercury/solution—notwithstanding the absence of a measurable angle of contact—within a certain interval of the layer thickness the layers are unstable.

2. Experiments with Compression of the Mercury Surface

In these experiments the mercury was placed in a conical funnel and the change of the surface was effected by lifting or lowering the mercury level.

In the case of cetyl alcohol, the capacity of the layer at first decreased somewhat under the action of compression and then assumed a constant value in the neighbourhood of 0.91 μF/cm^2.

Palmitic and particularly myristic acids yield under compression polylayers with lower values for the capacity; thus, with a threefold diminution of the surface, the capacity of the layer of myristic acid falls down from 1.26 to 0.46 μF/cm^2. Yet these polylayers are unstable and their capacity increases with time.

Calculation of Layer Thickness

Our measurements afford the possibility of calculating the effective thickness of a layer d from its capacity C, according to the formula for surface condensers: $C=\frac{\varepsilon}{4\pi d}$, where ε is the dielectric constant. In this case it will obviously be necessary to take for ε a value which would be free from the dipole effect (in the adsorbed layer the dipoles are certainly oriented and have lost their freedom of rotation); e. g. in the case of cetyl alcohol ε calculated from the index of refraction or from the sum of polarizabilities of all bonds in the molecule equals 2.07. Moreover, in order to obtain a value of C which would equal $\frac{\varepsilon}{4\pi d}$, it will be necessary to introduce a correction for the capacity of the ionic layer C_2 into the observed value of capacity C_1, using the formula $\frac{1}{C}=\frac{1}{C_1}+\frac{1}{C_2}$, since the whole system may be considered as two condensers in series. However, as the value C_2, known from measurements taken with a clean mercury surface, equals 20—30 μF/cm², i. e. by far surpasses C_1, the respective correction is very small. The following values of d were obtained:

A layer of cetyl alcohol under maximum compression, $d=1.9\cdot 10^{-7}$.

A layer of oleic acid in equilibrium with polylayers, $d=1.5\cdot 10^{-7}$.

The value for cetyl alcohol is fairly close to the length of the molecule determined by other methods, e. g. from the amount of matter in a condensed layer on the free surface of water; the value for oleic acid lies lower. It should, however, be borne in mind that in the case of even a partial penetration of the solution of the electrolyte between the molecules of a monolayer, the effective thickness of the monolayer as calculated from capacity measurements will be much lower than its true value. In this way capacity measurements provide a sensitive criterion for investigating the structure of these layers.

At present an apparatus is being designed by us which will permit to carry out measurements of capacity at different values of the area per molecule.

In the case of polylayers calculations of the thickness from capacity afford quite reasonable results until the thickness of the layer does not exceed 2 to 3 monolayers. For thicker layers too low values are obtained. This is, however, just the thing to be expected, since, in case of sufficiently thick layers, our method of measurement should give no longer the thickness of the layer of the organic substance, but the thickness of a diffuse double layer, produced by the ions of the electrolyte penetrating into the layer of the organic substance from the water phase, at least at such frequencies of alternating current, at which the equilibrium distribution of ions has time to become established.

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