Investigation of Thin Layers of Organic Substances at the Mercury-Solution Interface by the Method of Capacity Measurements[1].

II. Compression and expansion of the surface layer

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A detailed investigation of thin layers of organic substances at the mercury-solution interface, such as has been made at the water-air boundary, cannot be carried out without compressing and expanding these layers. The construction of an apparatus corresponding to the "Langmuir trough" involves great experimental difficulties due to glass not being wetted by mercury, which entails the penetration of the organic substance into the interstice between glass and mercury.

The apparatus we used is shown in Fig. 1. It consists of a glass cylinder *a* with a ground piston. The wetting of glass by

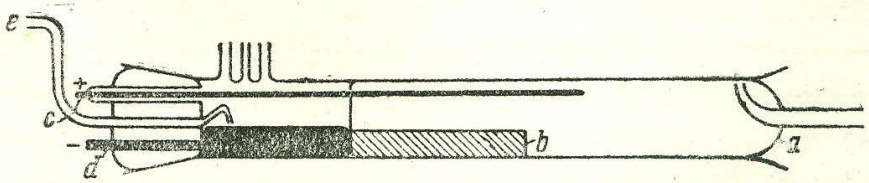

Fig. 1.

mercury was achieved through covering the lower half of the cylinder and the bottom of the piston with a thin layer of pla-

[1] A. Gorodezkaja and A. Frumkin, C. R. de l'Acad. Sci. USSR, 18, 639 (1938).

tinum which adheres well to the opaque surface of the glass[2] (the shaded part *b* in Fig. 1).

A thick platinum wire *c* the end of which passed through an opening in the piston without blocking its movement was used as the anode for polarization by a direct current. The level of mercury in the vessel was maintained through a tube *d* which was connected with a reservoir of mercury kept at a constant level. The same tube served as cathode for polarization. The potential was measured through a syphon *e* leading to the reference electrode. The three tubes in the upper part of the vessel were used to introduce the solution, the organic substance and a small platinum electrode connected with a cathodic voltmeter. The vessel was entirely filled with the solution. The capacity was measured as described by Proskurnin and Borissowa[3].

The organic substance was dissolved in purified ethyl alcohol and applied to the mercury with a micropipette consisting of a cylindrical glass capillary with a bulb-shaped end. The upper part of the pipette and the bulb were filled with mercury. The solution was sucked up by cooling the mercury and expelled by heating it, the end being applied to the mercury surface polarized to the potential corresponding to the optimum spreading of the organic substance. The layer was compressed or expanded by the piston whose movement allowed of a more than threefold increase of the mercury surface (from 7.2 cm.^{2} to 25.5 cm.^{2}). All the measurements were made in a normal Na_2SO_4 solution acidified by H_2SO_4 to 0.002 *N*. The mercury reference electrode was covered by the same electrolyte saturated with Hg_2SO_4.

The experiment shows that on an uncharged surface of mercury (at a potential 0.8 V more cathodic than the reference electrode) none of the organic substances used — myristic and oleic acids, cetyl alcohol, ethyl palmitate and α-bromstearic acid — yield reproducible capacity values upon compression and expansion of the layer. Further measurements were made at a mercury potential of 1 V against the reference electrode. Immediately after the deposition

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[2] To platinize the glass we used the following solution: 1 part of a 2% $PtCl_4$ solution + 4 parts of a 20% solution of hydrazine chloride in 10% NH_3.

[3] T. Borissowa u. M. Proskurnin, Acta Physicochimica URSS, **4**, 819 (1936).

of the layer the capacity equals 2 μF at this potential, as well as at 0.8 V, but on the second compression and expansion its value increases. However, after two or three expansions and compressions of the layer the values of the resulting capacity begin to conform fairly well.

The data obtained with myristic acid in five separate experiments are shown in Fig. 2 where the capacity is plotted against the surface concentration of myristic acid on mercury in mols/cm.^{2}. The minimum capacity observed when using the above method of depositing the substance is 5 μF at 12×10^{-10} mols/cm.^{2} as illustrated by the curve.

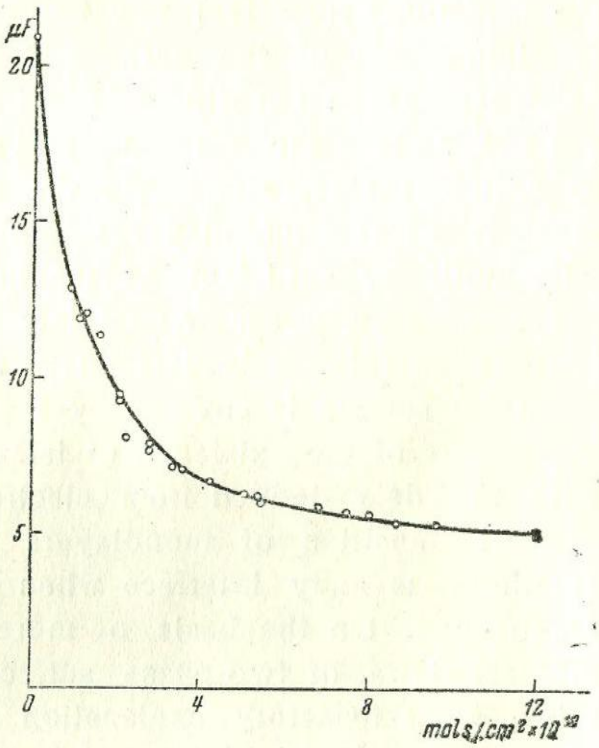

Fig. 2.

In the first part of this investigation[1] we obtained a considerably lower capacity (1 μF) by rubbing the mercury surface with a solid crystal of myristic acid, and decreased the value down to 0.46 μF by compressing the layer. We have shown, however, that these values are not stable and increase on standing. As has already been pointed out in the first paper, the value 1 μF corresponds well to the tickness of a condensed monolayer.

We have not yet succeeded in fully establishing the correlation between the structure of the layers obtained by compression and the layers obtained by rubbing the surface of mercury with solid acids. The ability of fatty acids to produce, at a mercury-solution interface, continuous polymolecular layers several tens of molecules thick was observed on the example of oleic acid[1]. This leads to the supposition that condensed monolayers are stable only in equilibrium with islands of polylayers that have a considerable tickness and can therefore be obtained only in the presence

of a considerable excess of the substance. In fact, applying a quantity of myristic acid up to 2.7×10^{-8} mols/cm.^{2} we succeeded in obtaining a capacity equal to 1.8 μF, and in the case of cetyl alcohol 1.3×10^{-8} mols/cm.^{2} yields 1 μF. At the same time we could observe several small crystals of the substance floating on the mercury; evidently the value of the capacity indicates that the remaining part of the surface is covered by a layer near to the condensed state. On diminishing the total amount of the substance per unit surface the spots of polylayers deaggregate into particles of colloidal size, simultaneously thinning. At the same time the pressure of the monolayer which was in equilibrium with them falls until, by sufficient expansion of the layer, the spots of the polylayers disappear completely and the capacity begins to increase sharply. This last interval is to be observed, apparently, when the surface is covered by less than 4×10^{-10} mols/cm.^{2}. The hypothesis of the existence of islands of colloidal size is in accord with the data derived from electrocapillary measurements [4] on the gradual transition of monolayers into polylayers at a fatty acid solution — mercury interface when the saturation of the solution is approached. On the basis of more simple schemes, applying the ordinary laws of two-phase surface equilibrium to layers of fatty acids, no satisfactory explanation could be given of the observed phenomena. We might attempt to explain our results by supposing that "rubbing" the surface with a crystal produces continuous polylayers which correspond to low values of capacity, while the capacity value for monolayers is always about 5 μF. This, however, — not to mention even the coincidence of the value 1 μF with the capacity calculated for a monolayer — is in contradiction with the fact that immediately after the application of a monolayer, as has already been pointed out, the capacity is about 2 μF.

It would be of interest to make a detailed study of the structure of layers produced by quantities of acid which correspond to several monolayers.

In conclusion I wish to express my gratitude to Prof. A. Frumkin at whose suggestion this research was undertaken.

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[4] A. Frumkin, A. Gorodezkaja and P. Tschugunoff, Acta Physicochimica URSS, 1, 12 (1934).

Summary

An apparatus for compressing and extending thin layers of organic substance at the mercury-solution interface has been constructed. Experiments with myristic acid prove that the formation of a condensed layer of acid on the mercury-solution boundary is only possible in the presence of a large excess of substance.

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