Electro-Capillary Phenomena and the Wetting of Metals[1,2].

III. Influence of surface-active substances on wetting. Properties of multi-molecular layers

By *B. Kabanov* and *N. Ivanishenko*

The nature of the elementary act in the process of flotation — sticking of a gas bubble to the surface of an ore particle — is a question which occupies an important place in flotation theory. Valuable information concerning this problem can be acquired from the study of the equilibrium conditions of a bubble located at a smooth boundary of two phases, in spite of the fact that, during actual flotation, equilibrium is probably never reached. The study of equilibrium states is considerably simpler, and doubtless aids the understanding of non-equilibrium states.

Probably the simplest and most definite conditions can be obtained with a hydrogen bubble on a mercury surface in an electrolytic solution.

Frumkin, Gorodetzkaya, Kabanov and Nekrassov have shown [1] that, under such a bubble, there is not a clean, „dry" mercury surface, as supposed by Möller [3], but a surface covered with an adsorbed layer of the electrolyte. Actual calculation of the interfacial tension at this boundary, carried out with the aid of Neumann's equation, gives values not exceeding 418 dynes per cm, while the tension at the interface mercury — dry gas or vacuum is 488 dynes per cm [4]. Furthermore, the interfacial tension of

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[1] Frumkin, Gorodetzkaya, Kabanov and Nekrassov. Sow. Phys., **1**, 255 (1932).
[2] Gorodetzkaya a. Kabanov, Sow. Phys., **5**, 418 (1934).
[3] Möller, Z. phys. Chem., **65**, 226 (1908).
[4] Burdon, Trans. Farad. Soc., **28**, 866 (1932).

the mercury-bubble boundary strongly depends on the composition of the solution and on the potential of the electrode. The latter fact indicates that the adsorbed layer has a finite electrical conductivity.

The present work is devoted to a more detailed study of the layer of electrolytic solution adsorbed at the mercury-bubble boundary.

Experimental

The methods used by us for measuring contact angles and for calculating the mercury-bubble interfacial tension, are described in the above-mentioned papers [1]. In order to obtain constant values of the contact angles of the hydrogen bubbles in the presence of surface-active substances, it was necessary to carefully remove mercury ions and oxygen from the solution by prolonged cathodic polarization of the mercury electrode. When traces of mercury ions are present, at certain potentials the contact angle sharply changes from time to time.

Considering the great significance for our method of the question, whether or not the contact angles measured by us represent equilibrium values, the change of the contact angles with time was investigated by us once more.

The results obtained confirm the conclusion reached in the above-cited article [1] that bubbles of different sizes come to the equilibrium value of the contact angle at different rates, but that the final value to which the contact angle tends does not depend on the size of the bubble.

Bubbles of a diameter of 0,15 mm reach the equilibrium value within 5 minutes, but if the diameter is 1,1 mm, the process takes several hours. Inasmuch as we worked with bubbles of 0,15 to 0,25 mm in diameter, and after deposition waited for 15 — 20 minutes, we unquestionably obtained equilibrium values.

The error in measuring contact angles amounted to $\pm 1{,}5$ degrees.

The accuracy of the value of the calculated interfacial tension of the mercury-bubble boundary amounted to 2 dynes per cm for contact angles of about 90°, and 1,4 dynes per cm for angles in the neighbourhood of 25°.

Our electrocapillary measurements were made by G o u y's method [5]. The diameter of the capillary at the narrow end was 0,036 mm. The interfacial tension at the mercury-solution boundary is denoted by σ_{12}.

All measurements were made with a normal solution of sodium sulphate which was twice recrystallized from redistilled water. The surface-active substances added to this solution: phenol, normal amyl alcohol and normal heptyl alcohol were highest grade

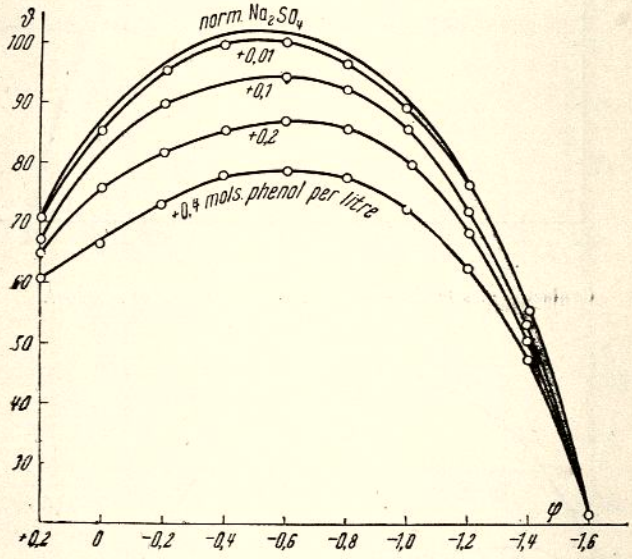

Fig. 1.
Contact angles in sodium sulphate + phenol solutions.

products of Kahlbaum, further purified by distillation *in vacuo*. To prevent the phenol solutions from oxidation the phenol was directly distilled in a solution of sodium sulphate saturated with hydrogen.

The results of measurements with phenol (0,01, 0,1, 0,2 and 0,4 mols per litre), normal heptyl alcohol (0,00175, 0,0035 and 0,007 mols per litre) and normal amyl alcohol (saturated) are reproduced in Figs 1, 2 and 3. The abscissae, φ, are the electrode

[5] G o u y, Ann. chim. phys., (7) **29**, 145 (1903).

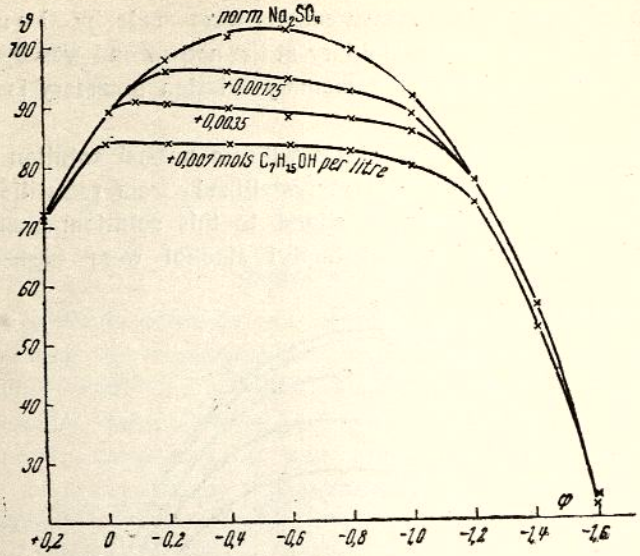

Fig. 2.
Contact angles in sodium sulphate + heptyl alcohol solutions.

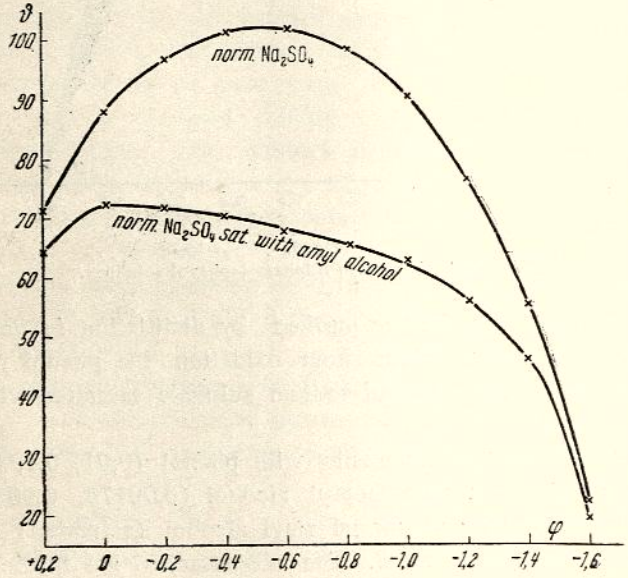

Fig. 3.
Contact angles in sodium sulphate + amyl alcohol solutions.

potentials, referred to a normal calomel electrode (negative values of φ corresponding to cathodic polarisations), while the ordinates, ϑ, are the contact angles of the bubbles. The upper curves were obtained in a pure normal solution of sodium sulphate. In addition, preliminary and less accurate measurements were also carried out (Fig. 4) with *p*-toluidine (0,05 mols per litre), thiourea (0,5 mols per litre) and *p*-cresol (0,1 mols per litre).

The measurements were carried out at temperatures from 18 to 21° C. Considering the small value of temperature coefficient of surface tension, no temperature correction was made.

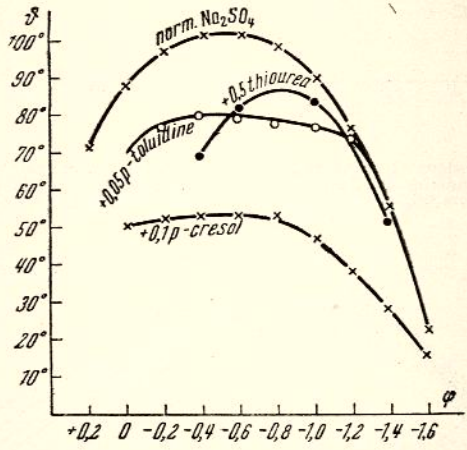

Fig. 4.
Contact angles in solutions of sodium sulphate + thiourea, *p*-toluidine, *p*-cresol.

All the surface-ative substances investigated by us reduce the contact angles of the bubbles, that is, increase the wetting power of the solution, especially in the neighbourhood of the maximum of the electrocapillary curve [6].

The contact angle curves have the same shape as the corresponding electrocapillary curves in the same solutions, which

[6] Results obtained in this part of the curves (where the mercury is hydrophobic) are similar to those obtained by P. A. Rehbinder on paraffin whose wettability also increases on adding surface-active substances to the solution (cf. P. Rehbinder, M. Lipetz, M. Rimskaya and A. Taubman: „Physical Chemistry of Flotation Processes", Moscow, 1933).

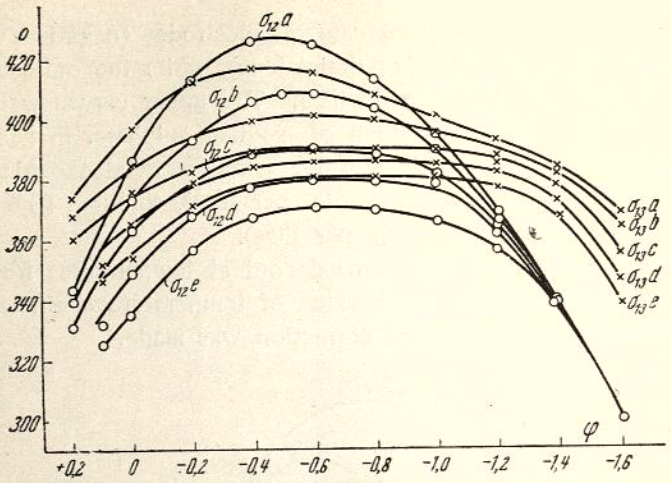

Fig. 5.

Interfacial tensions of the mercury-solution (circles) and the mercury-bubble (crosses) boundaries in Na_2SO_4 + phenol: *a* — Na_2SO_4, *b* — Na_2SO_4 + 0,01 C_6H_5OH, *c* — Na_2SO_4 + 0,1 C_6H_5OH; *d* — Na_2SO_4 + 0,2 C_6H_5OH; *e* — Na_2SO_4 + + 0,4 C_6H_5OH (mol per litre)

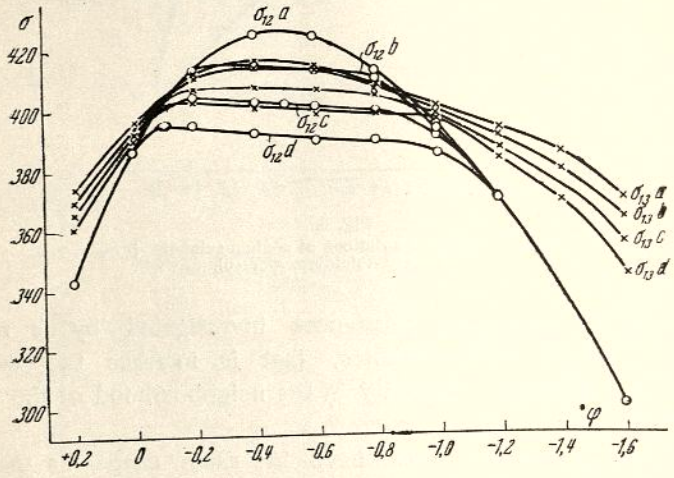

Fig. 6.

Interfacial tensions of the mercury-solution (circles) and of the mercury-bubble (crosses) boundaries in Na_2SO_4 + heptyl alcohol.

a — Na_2SO_4; *b* — Na_2SO_4 + 0,00175 $C_7H_{15}OH$; *e* — Na_2SO_4 + 0,0035 $C_7H_{15}OH$; *d* — Na_2SO_4 + 0,007 $C_7H_{15}OH$ (mol per litre).

give the interfacial tension solution-mercury, σ_{12}, as a function of the potential difference (cf. Figs. 5, 6, 7, and 8, circles). The positions

of the maxima of the two sets of curves agree to within 0,1 volt. The lowering of the contact angles produced by surface-active

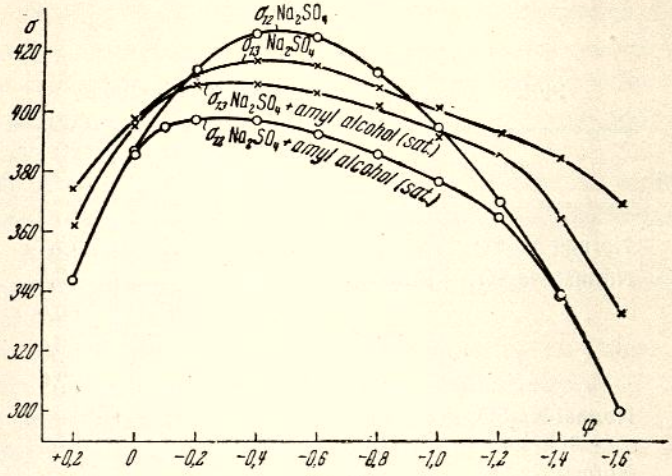

Fig. 7.
Interfacial tensions of the mercury-solution (circles) and of the mercury-bubble (crosses) boundaries in Na_2SO_4 + amyl alcohol solutions.

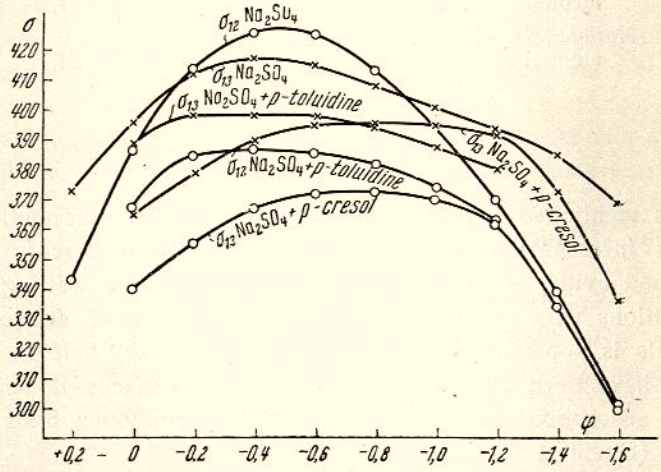

Fig. 8.
Interfacial tensions of the mercury-solution (circles) and of the mercury-bubble (crosses) boundaries in Na_2SO_4 + *p*-cresol and Na_2SO_4 + *p*-toluidine solution.

substances becomes smaller as the distance from the maximum is increased on either side.

The measurements of surface tension at the gas-solution boundary, σ_{23}, were carried out by the method of maximum bubble pressure. The reasults of measurements are reproduced in Table 1.

Table 1

Surface tension of the solution-gas boundary

Solution	Conc. of surface-active substance, mols per litre	σ_{23}
Normal Na_2SO_4	—	73,2
Normal Na_2SO_4 +phenol	0,01	69,8
" " "	0,1	60,0
" " "	0,2	50,6
" " "	0,4	42,0
Normal Na_2SO_4 +heptyl alcohol	0,00175	65,1
Normal Na_2SO_4 +heptyl alcohol	0,0035	56,6
Normal Na_2SO_4 +heptyl alcohol	0,007	47,2
Normal Na_2SO_4 + amyl alcohol	Saturated	34,7

Discussion of results

As mentioned above, we have found that surface-active substances increase the degree of wetting of a clean mercury surface. Published evidence concerning the reduction of the wetting power of solutions with respect to metals on addition of surface-active materials is apparently to be explained by the fact that the experiments have been carried out with oxidized surfaces of metals, on which adsorption may be irreversible, hydrophobic films being formed (chemical fixation).

From the results of our measurements of contact angles (ϑ) and measurements of surface tension at the mercury-solution (σ_{12}) and gas-solution (σ_{23}) boundaries (Table 1), we have calculated the interfacial tension, σ_{13}, of the mercury-bubble boundary with the aid of Neumann's triangle (cf. the first paper of this series).

On examining the σ_{13} curves obtained at different concentrations of the surface-active substance (Figs. 5, 6, 7 and 8, crosses) the following characteristic property is at once evident. On increasing the distance from the maximum of the electrocapillary curve, the σ_{13} curves converge just as the electro-capillary curves do in the same solutions. But upon further increase of the cathodic or, correspondingly, the anodic polarization, the σ_{13} curves once more diverge fan-like.

It is natural to explain the decrease of adsorption of the organic substance at the mercury-bubble boundary on increasing the distance from the electrocapillary maximum, as in the case of the mercury-solution boundary, by the salting-out action of the increased charge of the surface [7].

The second process, leading once more to the increase of adsorption on increasing the polarization, can be explained, in our opinion, only by an increase in the thickness of the adsorbed layer of solution at the mercury-bubble boundary. In general it is natural to expect a thickening of the layer of solution on increasing the charge of the double layer, because the ions must draw molecules of water into the layer.

When the solution layer becomes thicker, the adsorption of surface-active substances can proceed not only at the surface of the mercury (as in the case of the mercury-solution boundary), but at the upper boundary of the solution layer as well. At this surface, which behaves more like a solution-gas boundary, adsorption does not depend directly on polarization, whereas at the mercury surface, adsorption decreases with increasing charge. It should be mentioned, that the divergence of the end points of the $\sigma_{13} - \varphi$ curves is far beyond the limits of experimental error. In order that the $\sigma_{13} - \varphi$ curves should not diverge at strong polarizations, that is, that the adsorption in the layer under the bubble should not increase with polarization, it would be necessary, that the contact angles in the presence of surface-active substances should be reduced to 0° at an electrode potential of $-1{,}4$ volts which is actually never observed. That is to say, from this potential on, the equilibrium of a bubble at the metal-solution boundary should become

[7] A. Frumkin, Z. Physik, **35**, 792 (1926).

impossible. Experiment shows that, in all solutions of surface active non-electrolytes, the contact angle curves converge when polarization becomes considerable. Thus, at a potential of —1,6 volts, the contact angles in all cases are close to 20°. For these values of the contact angle, the tension of the mercury-bubble boundary (σ_{13}) differs by only a few dynes from the sum of the tensions at the two other boundaries ($\sigma_{12} + \sigma_{23}$) (cf. Table 2).

Table 2

Solution	Potential	Dynes per cm		
		σ_{13}	$\sigma_{12}+\sigma_{23}$	Difference
Normal Na_2SO_4	—1,2	393	433	50
" "	—1,6	368	373	5
Normal Na_2SO_4 + phenol (0,4 mols per litre)	—1,6	340	342	2
Normal Na_2SO_4 + heptyl alcohol (0,007 mols per litre)	—1,2	383	419	36
Normal Na_2SO_4 + heptyl alcohol (0,007 mols per litre)	—1,6	344	348	4

We arrive at the conclusion that, near the electrocapillary maxima, where the thickness of the layer between mercury and bubble is small, adsorption of the surface-active substances takes place directly on the mercury surface, along with the adsorption of water and electrolyte [8]. On increasing the charge of this surface, the adsorption of organic matter is reduced, similarly to what occurs at a mercury-solution boundary. At the same time, adsorption of the electrolyte increases, which involves thickening of the layer. Beginning with a certain layer thickness, it becomes possible to speak

[8] It should be mentioned that, near the maxima of the curves, adsorption of the surface-active substances at the mercury-bubble boundary is less than at the mercury-solution boundary. For example, in a nearly saturated phenol solution, the lowering of the interfacial tension at the first boundary is about 1,5 times less than at the second.

of two surfaces of the composite layer. Adsorption appears at the upper surface, which behaves like a solution-gas boundary. Transformation into a new phase, however, takes place gradually, and the mutual interaction between the surfaces does not disappear at once. In some solutions (heptyl and amyl alcohols, cf. especially anodic parts of curves in Figs. 6 and 7), the adsorption on mercury ceases sooner than the adsorption on the upper surface of the layer begins; in a certain transition region, adsorption in the layer underlying the bubble ceases altogether and the different $\sigma_{13} - \varphi$ curves practically merge together. In other solutions (phenol, Fig. 5), in which the electrocapillary curves converge only at greater distances from the maximum, adsorption at the upper surface begins sooner than adsorption on the mercury itself disappears, and the $\sigma_{13} - \varphi$ curves do not come so close together.

We attempt, in the second part of this paper, to give a quantitative determination of the thickness of the layer at the mercury-gas boundary.

Determination of the thickness of the layer adsorbed on the mercury-bubble boundary

Method

After a rapid change in electrode polarization, the contact angle does not reach its new equilibrium value instantaneously, but at first assumes values larger or smaller than the equilibrium one, depending on the size of the bubble. The kinetics of this phenomenon are shown in Fig. 9. In this case the mercury potential was changed from $-1{,}6$ to $-0{,}6$ in norm. Na_2SO_4. It can be concluded from the form of these curves that the process proceeds through two stages. We suppose that the first stage is characterized by a rapid expansion of the layer of electrolyte under the bubble, its total volume remaining constant [9], the second, by a gradual change in the total volume of the electrolyte layer, followed by a gradual change in the contact angle, the latter approaching the equilibrium value, corresponding to the new potential of the mercury. The study of the first stage of the process makes it pos-

[9] This is to be considered as a stretching of the mercury surface under the bubble caused by an increase of the tension at the mercury-solution boundary.

sible to determine the ratio of the thicknesses of the electrolyte layer corresponding to two definite values of interfacial tension. In order to do this, we measure (microscopically) the area of contact between the bubble and mercury (i. e., the area of the electrolyte layer) before and immediately after changing the polarization: the thickness of the layer is reduced in the same ratio as the area increases. From the value of the contact angle at which the break in the contact angle-time curve occurs, Fig. 9, we can find the value of the surface tension corresponding to the calculated thickness of the electrolyte layer.

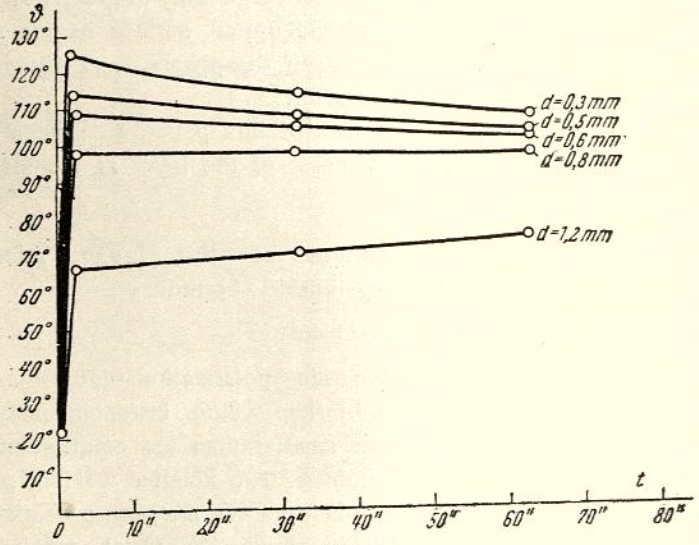

Fig. 9.

Contact angle-time curves observed after changing the mercury potential from — 1,6 volts to—0,6 volts with bubbles of different size in norm. Na_2SO_4. d — diameter of the bubble.

Having effected the transitions from an equilibrium state of the electrolyte layer at certain polarization (e. g., at — 1,6 volts) to different thicknesses of the electrolytic layer at some other polarization (e. g., — 0,6 volt) corresponding to different contact angles, it is possible to find the relative thickness of the layer, δ, for different values of the interfacial tension σ_{13}. It must be emphasized that our determination of the thickness of the electrolyte layer was not based upon direct measurements, but calculated by us on the

assumption that the first stage of change upon changing the polarization consists entirely in an expansion of the electrolyte layer under the bubble, without any change in the total volume of the layer. Inasmuch as this assumption has a hypothetical character, our quantitative results cannot be considered as quite conclusive.

In order to find the relation between the interfacial tension and the thickness of the electrolyte layer, it was necessary to obtain layers of different thicknesses for an identical change in polarization, for example, from —1,6 to — 0,6 volts. This was possible because the change in the contact area depends upon the size of the bubble. The explanation is as follows: small bubbles, 0,1—0,2 mm in diameter, are practically not deformed by the force of gravity, and maintain a spherical shape. Large bubbles are strongly deformed. This deformation leads to a reduction of the mercury-bubble contact area which is especially pronounced at small contact angles. Therefore, large bubbles change the contact area on changing the angle of contact in a larger ratio, as do small ones. For example, during the transition from —1,6 to —0,6 volts, the contact area of a bubble of 1,4 mm diameter, is changed 160 times, but in the case of a diameter equal to 0,5 mm, only 9 times.

It should be mentioned that, during the course of our work, in some cases we observed bubbles whose contact angles came to equilibrium very quickly, as the bubble passed from one polarization to another, so that it was difficult to make the corresponding measurements. In these cases, the characteristic break on the kinetic curve was not observed. On careful examination of the contact area between such a bubble and the mercury with a microscope, a lens of electrolyte could be discerned. The latter is probably formed when a particle of hydrophilic dust falls on the mercury-bubble boundary. As study of this phenomenon did not come within the scope of our problem, we did not investigate the behaviour of these bubbles any further.

The error in determining the ratio of areas, and consequently the relative thickness of the layer, amounted to $4 - 12\%$, and was larger for large bubbles (the bubbles had diameters from 0,3 to 1,4 mm at — 1,6 volts).

Inasmuch as, on expanding the layer, the density of the surface charge is decreased, a surface with a low charge is the first

result of a transition from a large polarization to a smaller one. It can be shown, using the relation between interfacial tension and surface charge given by the electrocapillary curve, that the influence of the remaining charge on the tension can be neglected as well as the influence of the charge present in an equilibrium layer at — 0,6 V. Thus we practically obtain an uncharged layer after reducing the polarization. A transition from a smaller to a larger cathodic polarization, which means reducing the contact area, would, on the other hand, lead to a large charge, which must strongly influence the interfacial tension. As a result of this, data obtained in this way do not fall on the $\sigma_{13} - \delta$ curve (cf. below).

The dependence of the interfacial tension, σ_{13}, on the relative thickness of the layer of electrolyte between the mercury and the bubble, δ, (the thickness of an equilibrium layer at an electrode potential of —1,6 volts being taken as unity) is shown in Fig. 10. As seen from the form of this curve, the tension at the mercury-bubble boundary in the case of a practically uncharged surface is the smaller the thicker the layer of electrolyte between bubble and mercury. It is to be held in mind that the points on this curve do not represent equilibrium states.

In addition to the transition from — 1,6 to — 0,6 volts, we also carried out transitions between other values of potentials.

Using these transitions, we determined the relative thickness of the electrolytic layer for bubbles in equilibrium at different mercury potentials. For example, on bringing a bubble (of a certain size) from a polarization of — 1,5 to — 0,6 volts, the contact area changed by a factor of 19,5, whilst with a transition of a different bubble from — 1,4 to — 0,6 volts, it changed but 9,7 times. In both cases nearly identical values of the interfacial tension after the expansion of the mercury-bubble boundary were obtained. This indicates that the initial electrolytic layer thicknesses were different and enables to determine their ratio. As a check we carried out measurements with bubbles of different sizes, and obtained identical values for the layer thickness in the initial states. We tried to determine not only the relative thickness of the equilibrium layers, but also its absolute value. To do this, some data concerning the adsorption of water vapours on mercury must be taken into consideration.

According to Iredale [10], water vapor is adsorbed by mercury and near the saturation point lowers the surface tension by 25 units. Cassel and Salditt [11] found no adsorption of water vapor on mercury, but their experiments were carried out at a higher temperature (50°C), and they did not reach the saturation point. The authors consider it quite likely that a multi-molecular layer of adsorbed water is formed near the saturation point.

The surface tension of clean mercury we assume in what follows to be equal to 488 dynes/cm — the mean of three more reliable values, taken from the literature: 500 dynes/cm [12]; 488 dy-

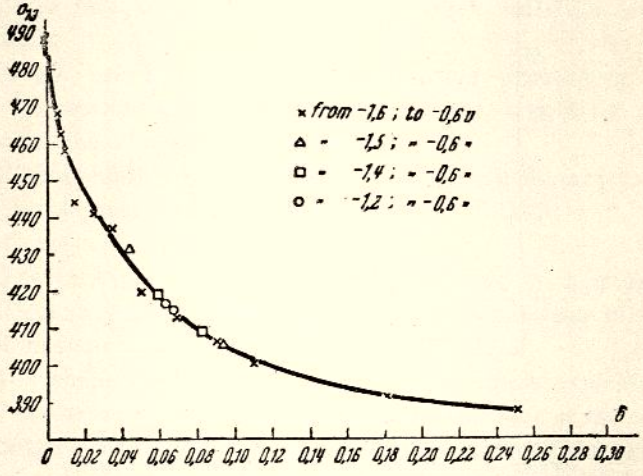

Fig. 10.
Relation between the tension and the relative thickness of the freshly expanded layers.

nes/cm [4] and 476 dynes/cm [13]. This value is taken as the initial point of the curve in Fig. 9.

It was explained above how the relative thicknesses of the equilibrium layer as compared with the thickness at —1,6 V can be determined. To find the absolute values it was tentatively assumed that a lowering of interfacial tension by 25 dynes/cm corres-

[10] Iredale, Phil. Mag., **48**, 182 (1924).
[11] Cassel a. Salditt, Z. physik. Chem., (A) **155**, 321 (1931).
[12] Bradley, J. Physic. Chem., **38**, 231 (1934).
[13] Harkins a. Ewing, J. Am. Chem. Soc., **42**, 539 (1920).

ponds to the formation of a monomolecular layer of solution. Then, using the curve of Fig. 10, we found the absolute value of the layer thickness for any desired value of the potential of mercury. This assumption may involve an error amounting to 100 per cent. The thickness of the equilibrium layer, δ_1, expressed in $\mu\mu$, obtained in this way, is plotted against the electrode potential on Fig. 11. Up to a potential of — 1,2 volts, the thickness of the layer changes little; from — 1,2 volts on, it increases rapidly.

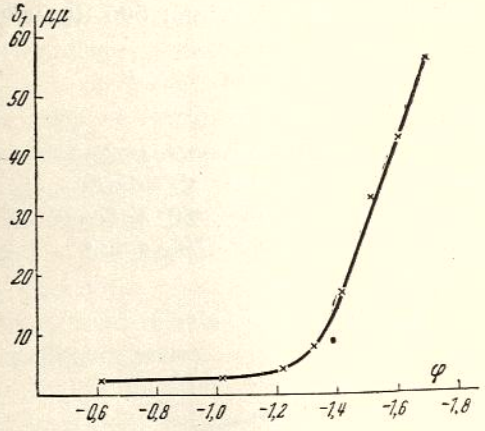

Fig. 11.

Thickness of the equilibrium layer at the mercury-bubble interface in norm. Na_2SO_4 at different potentials.

This agrees well with the picture of the adsorption at the mercury-bubble boundary, developed in the first part of this paper. The beginning of adsorption on the upper side of the layer (cf. above) corresponds to the beginning of the rapid thickening of the layer. In the region of the maximum of the electrocapillary curve, the layer is so thin ($\sim$ 2,5 $\mu\mu$) that it cannot act as a separate phase, and adsorption can take place only on the surface of the mercury. At a potential of — 1,6 volts, a layer of about 40 $\mu\mu$ is formed. Such a layer should exhibit, to a considerable degree, the properties of a new phase. Actually, we did see that at this potential the tension of the layer is almost completely additive in all solutions (Table 2).

However, even at a layer thickness of about 200 water molecules, i. e. about 60 μμ (— 1,7 volts), the tension is not exactly additive, the difference $\sigma_{13} - (\sigma_{12} + \sigma_{23})$ in normal Na_2SO_4 being equal to about 3 dynes. Thus we have a case of gradual transition from an adsorbed layer to a new phase on increasing the charge of the surface.

Summary

1. The influence of surface-active substances (phenol, heptyl and amyl alcohols, *p*-cresol, thiourea and *p*-toluidine) on the contact angle of bubble at the mercury-electrolyte interface has been investigated.

2. It has been found that surface-active substances always increase the wetting of a clean mercury surface, especially near the maximum of the electro-capillary curve.

3. Electro-capillary curves, and the surface tension of the solution — gas boundary of solutions containing Na_2SO_4 and surface-active substances have been measured.

4. The interfacial tension of the mercury-bubble boundary (σ_{13}) has been calculated from these data for different values of the potential of mercury φ.

5. The shape of the $\sigma_{13} - \varphi$ curves has been explained with the help of the assumption that the electrolyte layer at the mercury-bubble boundary thickens on increasing the surface charge. In the neighbourhood of the maximum of the electro-capillary curve, adsorption of surface-active substances at the mercury-bubble boundary takes place directly on the mercury. On increasing the electric charge of the mercury surface, the magnitude of this adsorption decreases. On further increase of this charge, adsorption begins at the upper boundary of the electrolyte layer, which behaves like a solution-gas boundary.

6. A relation has been established between the change of the contact area bubble-mercury on changing the polarization of the mercury, and the magnitude of the contact angle observed at the first moment after changing the polarization. This relation can be explained with the help of certain assumptions concerning the expansion of the layer of electrolyte under the bubble, and was used for an approximate calculation of the thickness of this layer.

7. It has been found in this way that on increasing the cathodic polarization the layer begins to thicken rapidly at a potential of — 1,2 volts; and at — 1,7 volts, it reaches a thickness of hundreds of water molecules.

We are deeply indebted to Prof. A. Frumkin for his advice, which has made possible the carrying out of this work.

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Received
January 13, 1937.