The Influence of Adsorption on the Surface Motion of Dropping Mercury

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The problem of polarographic maxima and the effect of surface-active substances on them has been repeatedly discussed in the literature. However, the possibility of the polarographic curve being distorted by surface-active substances in cases when the ordinary maxima were thought impossible has not as yet been considered.

Under certain conditions, when ions are reduced in concentrated solutions of indifferent electrolytes, the current-potential curves, instead of smooth steps, have an unusual form with maxima often closely resembling polarographic waves. Such curves have been reported by various authors [1,2,3,4].

These phenomena were either left unexplained or explained incorrectly. For example, Orlemann and Kolthoff[2] observed an unexpected current increase on the polarographic curve and took it for a wave corresponding to a reduction process. Inasmuch as under their conditions no reduction was possible they suggested that the molecules of water were reduced forming hydrogen amalgam. It follows, however, from the work of Frumkin and co-workers[5] that not only is hydrogen not dissolved in mercury, but it is not even appreciably adsorbed. As will be seen below, the effect described by Orlemann and Kolthoff has nothing in common with any reduction process.

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[1] T. Krjukova, Zavodskaya Laboratoria, (Russ.), **9**, 691, 699 (1940).

[2] F. Orlemann and J. M. Kolthoff, J. Am. Chem. Soc., **64**, 833 (1942).

[3] T. Krjukova and B. Kabanov, J. Gen. Chem. (Russ.), **15**, 294 (1945).

[4] Maas, Coll. de trav. chim. Tschechosl., **10**, 42 (1938).

[5] A. Frumkin, Acta Phys. Chim., **18**, 23 (1934).

Maas [4] believes that distortion of the current-voltage curve is due to irregularities of the capillary. He does not, however, explain the mechanism of this phenomenon.

Distortions of form and spurious waves on the polarographic curves have been described by us in detail [3]. We have shown that these distortions are especially great for certain rates of flow of mercury from the capillary and that in these cases the current intensity is considerably greater than the diffusion current obtained in the presence of gelatine, a substance which suppresses the maxima at all the potentials of the polarographic curve. Our tentative experiments have shown that very few surface active substances completely eliminate these distortions of the curve, many, on the contrary, even increasing them. These considerations induced us to undertake a systematic study of the effect of surface-active substances on the form of the current-potential curves.

It can be considered proven that the appearance on the i—E curve of a current greater than the diffusion current in an unstirred solution is connected with tangential motions of the mercury [6,7]. Two causes of these motions have been established, *viz.* an unequal polarization of the drop (maximum of the first kind), and the flow of mercury from the capillary (maximum of the second kind).

A combination of the two effects brings to very involved forms of motion and to a complicated polarization curve. This question will be more thoroughly treated in a following paper. The influence of surface-active substances was so far studied mainly on such complex maxima, and hence no clear-cut simple results were attained.

A maximum of the second kind not complicated by a maximum of the first kind can easily be obtained in sufficiently concentrated solutions of an indifferent electrolyte and the motion causing it can be observed within the range of almost two volts. We therefore studied the effect of surface-active substances on maxima of the second kind, carrying out a number of polarographic investigations both in the practically complete absence of surface-active substances and with surface-active admixtures, and also in the presence of substances which could contaminate the solution with surface-active components under the conditions of practical polarographic work.

[6] A. Frumkin u. B. Bruns, Acta Phys. Chim., 1, 232 (1934).
[7] H. Antweiler, Z. Elektrochem. 44, 663, 831, 888 (1938).

Experimental part

Method

The experiments were carried out in a previously described closed cell with a dropping mercury cathode[3]. The capillaries were 230 mm long and 0.053 and 0.065 mm in radius. Neither the apparatus nor the electrolytic set-up delivering hydrogen contained any rubber connections. Special care was taken to purify the reagents from traces of organic admixtures.

Twice recrystallized potassium chloride was calcined for one hour in air at red heat. The other salts which could not be calcined were repeatedly recrystallized and in no case was filtration performed with paper filters. Birchwood charcoal was washed in hydrochloric acid and distilled water and heated in a stream of hydrogen at $\sim 500°$. Charcoal was added when observations of the motion were made visually and bore a qualitative character. When the i—φ curves were determined quantitatively no charcoal was added.

Electrolytic hydrogen was purified in the usual way over a palladium catalyst and sodium plumbite. The distilled water for the solutions was boiled for a long time with alkaline potassium permanganate to oxidize organic impurities and then redistilled in a glass apparatus without rubber connections. Mercury, purified by means of 5% solution of nitric acid and 5% solution of mercurous nitrate was washed several times in distilled water. Before the experiment hydrogen was bubbled through the solution for four hours.

The potential of the drop was measured with a 1 N calomel electrode the siphon of which contained the same solution as the cell and was set at a distance of 0.1—0.01 mm from the drop. Only such solutions were used in which the concentration of the reducible ion was small (no more than 0.001 M) and that of the indifferent electrolyte large (1.0 M and higher).

Results of the experiments

The polarization curve of 0.0003 N $HgCl_2$+sat. KCl obtained when contaminations are excluded with greatest care is represented in Fig. 1 (curve I). It may be seen from the curve that the current increases up to —0.5V, then gradually takes off. Thus under these

conditions the i—φ curve has a simple form. The curve for 0.001 N lead chloride in concentrated potassium chloride shown in the same figure (curve 2) is similar in form.

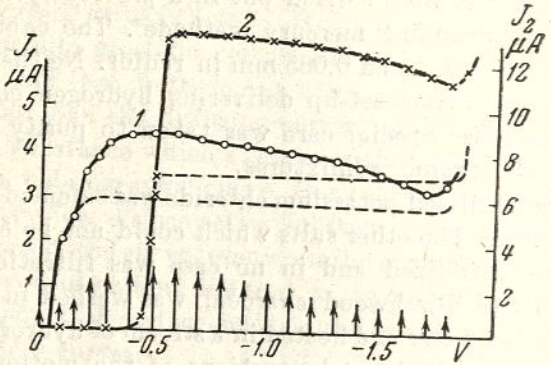

Fig. 1. Polarographic curves: 1—0,003 N $HgCl_2$+sat. KCl: 2—0.001 N $PbCl_2$+sat. KCl. The arrows depict the velocity of motion of the mercury surface (estimated from visual observations of charcoal particles). The dotted lines give the magnitudes of the normal diffusion currents.

When surface-active substances[8] are added the curve becomes distorted; new waves which we shall call spurious appear on it. Such curves are shown in Figs. 2 and 3; they were obtained in solutions which contained in varying concentrations surface-active substances: amyl alcohol, phenol, methylene-blue, potassium oleate, starch, gelatine, agar-agar and saponin from the root of «saponaria officinalis». The latter are used in polarography to suppress the maxima.

Discussion of results

In concentrated solutions of non-reducible electrolytes, stirring of the solution is caused by the motion of the surface of the mercury drop as it flows out of the capillary [3,9]. The charges of the double electric layer are displaced by this motion to the upper part of the drop. Frumkin and Levich[10] have derived an equa-

[8] Kahlbaum reagents were used without any further purification, or recrystallization.

[9] T. Krjukova and B. Kabanov, J. Phys. Chem. (Russ.), **13**, 1454 (1939); **15**, 475 (1941).

[10] A. Frumkin and B. Levich, Acta Phys. Chim., **21**, 193 (1946).

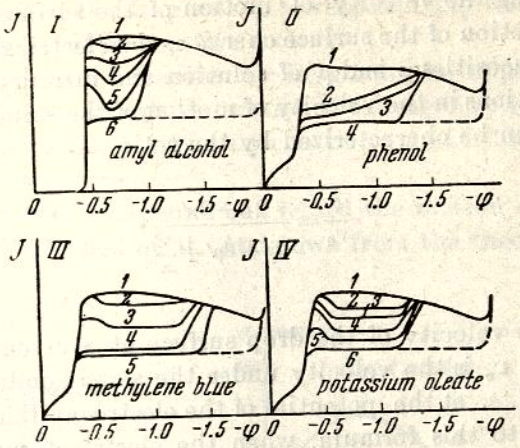

Fig. 2. Influence of surface-active substances. *I*. Amyl alcohol *1*—KCl sat.+0.001*N* $PbCl_2$; *2*—same+1×10^{-5} *M* amyl alcohol; *3*—same+2×10^{-5} *M*; *4*—same+$3\times10^{-3}M$; *5*—same+$5\times10^{-3}M$; *6*—same+$1\times10^{-2}M$. *II*. Phenol *1*—*N* KCl+0.001 *M* $CuSO_4$; *2*—same+3×10^{-6} *M* phenol; *3*—same+$1\times10^{-4}M$; *4*—same+$5\times10^{-4}M$. *III*. Methylene blue *1*—*N* KCl+0.001 *M* $CuSO_4$; *2*—same+3×10^{-7} *M* methylene blue; *3*—same—$2\times10^{-6}M$; *4*—same+$2\times10^{-5}M$; *5*—same+$1\times10^{-4}M$. *IV*. Potassium oleate *1*—*N* KCl=0.001 *M* $CuSO_4$; *2*—same+1×10^{-6} *M* potassium oleate; *3*—same+$5\times10^{-5}M$; *4*—same+1×10^{-4} *M*; *5*—same+$+3\times10^{-4}$ *M*; *6*—slme+3×10^{-3} *M*.

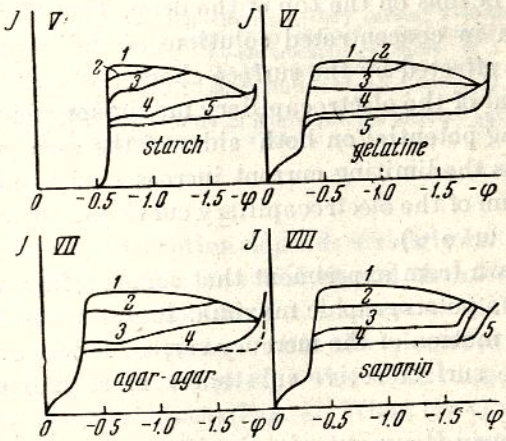

Fig. 3. Influence of surface-active substances *V*. Starch *1*—*N* KCl+0.001 *M* $CdCl_2$; *2*—same+4×10^{-3}% starch; *3*—same+1×10^{-2}%; *4*—same+4×10^{-2}%; *5*—same+0.1%. *VI*. Gelatine *1*—*N* KCl+0.001 *M* $CuSO_4$; *2*—same+4×10^{-4}% gelatine; *3*—same+1×10^{-3}%; *4*—same+5×10^{-3}%; *5*—same+3×10^{-2}%. *VII*. Agar-agar *1*—*N* KCl+0.001 *M* $CuSO_4$; *2*—same+3×10^{-3}% agar-agar; *3*—same+1×10^{-2}%; *4*—same+3×10^{-2}%. *VIII*. Saponin *1*—*N* KCl+0.001 *M* $CuSO_4$; *2*—same+4×10^{-5}% saponin; *3*—1×10^{-4}%; *4*—same+$+6\times10^{-4}$%; 5—same+7×10^{-3}%.

tion expressing the velocity of motion of the surface of a mercury drop as a function of the surface charge ε, the electrical conductivity $\varkappa$, and the viscosities μ and μ' of solution and mercury respectively.

The variations in the velocity of motion of the solutions observed in our case can be characterized by the ratio

$$\frac{v}{v_0} = \frac{2\mu + 3\mu'}{2\mu + 3\mu' + \frac{\varepsilon^2}{\varkappa}},$$

where v is the velocity of the drop surface at a given value of the charge ε, and v_0 is the velocity under the same conditions of flow but for $\varepsilon = 0$, *i. e.* at the potential of the electrocapillary maximum.

According to this formula, when the electrical conductivity is small, the electric field due to the convection current, *i. e.* to displacement of the charges towards the upper part of the drop, retards the motion, the degree of retardation depending on the surface charge.

In concentrated solutions of indifferent electrolytes, *i. e.* with a large conductivity of the solution, the convection current of ions along the surface is compensated to a great extent by currents through the adjacent layers of the solution and there can be no appreciable accumulation of ions on the top of the drop. That is why the motion of the surface in concentrated solutions of indifferent electrolytes is but weakly affected by the surface charge. The motion is greatest at the potential of the electrocapillary maximum and falls off slowly with increasing potential on both sides of the zero point. In agreement with this the limiting current increases with the potential up to the maximum of the electrocapillary curve and then slowly decreases (Fig. 1, curve *1*).

It was known from experiment that some surface-active substances suppress the polarographic maxima. Inasmuch as all the maxima are due to the motion of the mercury surface it was evident that the effect of these surface-active substances must be to retard such motions.

When mercury flows out of a capillary the surface of the drop moves upward. Substances adsorbed on the surface will move in the same direction. If adsorption does not proceed rapidly enough the concentration of surface-active substance on the upper part of the drop will be greater than on the lower. Hence the surface tension

on the upper part of the drop will be correspondingly less and a downward force arises opposing the motion.

This effect, like the transfer of charges to the upper part of the drop by the motion, retards the motion of the mercury surface. Under certain conditions the retardation can be so great that the motion is practically suppressed.

A surface-active compound can retard the motion of the surface only by being adsorbed on it. As known from the theory of electro-

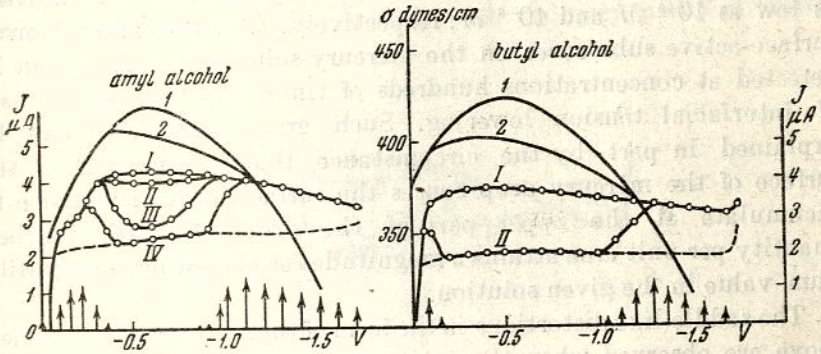

Fig. 4. Comparison of polarization and electrocapillary curves: *1*—0.003 *N* $HgCl_2$+sat. KCl without amyl alcohol; the same+amyl alcohol in concentrations: *II*—$1\times10^{-4}M$. *III*—$1\times10^{-3}M$; *IV*—$1\times10^{-2}M$. *I*—electrocapillary curve of 1 *N* NaCl; *2*—the same+$1\times10^{-2}M$ amyl alcohol. In the right-hand side of the figure the same is shown for norm. butyl alcohol: *I* and *1*—pure solution of 1 *N* Na_2SO_4; *II* and *2*—the same+ +0.1*M* butyl alcohol.
The arrows depict the velocity of motion of the mercury surface for the curves with the highest concentration of alcohol.

capillary phenomena, adsorption depends strongly on the potential. A similar dependence on the potential should therefore be observed for the retardation of the motions of the mercury. Indeed, a comparison of our polarization curves with the electrocapillary curves shows that the motion is retarded in the same range of potentials in which adsorption takes place (Fig. 4). When the charge of the surface is sufficiently great, so that adsorption is completely absent, the motion takes place unhindered. Our experiments show that both potential ranges broaden as the concentration of surface-active compound increases.

The quantitative dependence of the adsorption on the potential

was given by Frumkin[11]. It can be calculated from the data in these papers that the lowering of the mercury-solution interfacial tension $\Delta\sigma$ becomes less than 0.5 dynes if the concentration of amyl alcohol is reduced to 3×10^{-3} mole. Thus, at the given concentration the surface-active substance lowers the surface tension by a quantity only slightly greater than the experimental error. At the same concentration of amyl alcohol the motion of the mercury surface is almost completely suppressed.

The retardation effect can be detected by the decrease of the limiting current even at concentrations of amyl alcohol and β-naphtol as low as 10^{-5} M and 10^{-8} M, respectively, *i. e.* the adsorption of surface-active substances on the mercury-solution interface can be detected at concentrations hundreds of times less than in the case of interfacial tension lowering. Such great sensitivity can be explained in part by the circumstance that the motion of the surface of the mercury drop causes the surface-active substance to accumulate at the upper part of the drop and the adsorbed quantity per unit area attains a magnitude far exceeding the equilibrium value in the given solution.

The saddle-like distortions in the form of the $i-\varphi$ curve mentioned above are observed when the cations are reduced at a sufficiently positive potential, so that the potential range of the limiting current is wider than that of the adsorption potentials, and when the concentration of surface-active substances is small. If the reduction of the cations (*e. g.* Pb, Cd) begins at potentials close to the electrocapillary maximum and the concentration of surface-active substance is large enough, the motions starting after desorption caused by increased cathodic polarization give rise to a second polarographic wave, which is a typical spurious wave (Fig. 2).

In practical polarography there are many possibilities for contamination of the solution by small amounts of highly surface-active substances. The surface of crystals of commercial chemically pure salts and of salts that have been exposed to the laboratory atmosphere is covered with surface-active substances which in many cases cannot be removed even by repeated recrystallization; this was first

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[11] A. Frumkin, Trans. Karpov Chem. Inst., No. 5, 3 (1926); Z. Physik, **35**, 792 (1926).

concluded by Proskurnin and Frumkin[12] from the lowering of the capacity of the double layer at a mercury surface.

If the solution is prepared from potassium chloride twice recrystallized but not heated, one obtains a characteristic distortion of the curve (see Fig. 5), curve *3*, 0.001 *N* $PbCl_2$ in saturated KCl. When water twice redistilled in an apparatus without rubber connections, but not previously boiled with permanganate is used, the polarization curve for the same solution is appreciably distorted too (Fig. 5, curve *2*) revealing the presence of surface-active substances. A considerably stronger effect is obtained with ordinary distilled water.

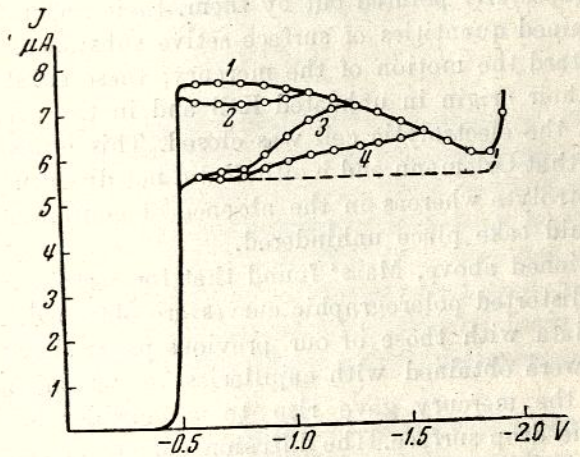

Fig. 5. Appearance of spurious waves on the polarographic curves: *1*—0.001 *N* $PbCl_2$+sat. KCl; *2*—the same solution prepared with twice distilled water not preliminarily boiled with permanganate; *3*—the same solution: the KCl used was twice recrystallized but not heated; *4*—the pure solution was filtered through a paper filter.

If a clean rubber stopper is dipped into a perfectly pure solution for one second the i—φ curve is appreciably distorted. If the rubber stopper is left in contact with the solution for several hours a very great distortion of the polarographic curve results. A similar effect is obtained if powdered charcoal washed but not heated in a current

[12] M. Proskurnin and A. Frumkin, Trans Farad. Soc., **31**, 110 (1935).

of hydrogen is kept in the solution for a long time (5—6 hours). This was shown in one of our earlier papers[3], where we used such charcoal washed in acids and bases but not preheated for the detection of motions.

Especially great distortions of the polarographic curve result if the solution under investigation is preliminarily drawn through a paper filter (Fig. 5, curve *4*).

This dependence of the form of the polarographic curve on the adsorption of surface-active substance shown by us explains the phenomena described by Orlemann and Kolthoff[2]. Despite the fact that these authors used salts carefully purified by recrystallization, as especially pointed out by them, their apparatus undoubtedly contained quantities of surface-active substances quite sufficient to retard the motion of the mercury; these substances could have had their origin in unheated KCl and in the rubber stopper with which the electrolytic cell was closed. This is also borne out by the fact that Orlemann and Kolthoff did not discover any motion of the electrolyte whereas in the absence of contaminations such motion should take place unhindered.

As mentioned above, Maas[4] found that for certain forms of the capillaries distorted polarographic curves are obtained. A comparison of his data with those of our previous paper shows that these distortions were obtained with capillaries in which the velocity of flow of the mercury gave rise to a considerable tangential motion of the drop surface. The diffusion current of cadmium with which Maas worked sets in at potentials near the maximum of the electrocapillary curve. The motion which should have taken place in this case was suppressed by the impurities probably present in the solution.

According to the viewpoint here developed, in order that the motion of the mercury surface be suppressed at small concentrations of surface-active susbtances enough time must elapse for diffusion of the substance from the depth of the solution and its accumulation on the upper part of the drop to take place. It is therefore to be expected that an increase in the frequency of dropping should lower the effect of surface-active substances on the motion of the mercury surface. Upon rapid dropping some of the surface-active substance is carried off together with the drop, and the solution is in a way purified. When the linear velocity of motion of the mercury increases

to very large values retardation due to lowering of the surface tension should become relatively smaller also, since in rapid motion the concentration is more easily evened out by convective diffusion. In fact, experiment shows that if for a given capillary the rates of flow and of dropping of the mercury are increased, the distortions of the polarographic curves due to retardation of the motion diminish, and at small concentrations of the surface-active substances they can disappear entirely. We shall return to this question in a subsequent paper.

In conclusion I wish to express my grateful acknowledgement to Prof. A. Frumkin and Dr. B. Kabanov for their interest in this work and valuable suggestions.

Summary

The influence of the adsorption of surface-active substances on the motion of the surface of a mercury drop emerging from a capillary has been investigated. It is shown that the substance adsorbed on the mercury-solution interface retards the motion of the mercury surface in the range of potentials in which it is adsorbed. At all other values of the potential the motion proceeds unhindered. Such a variation of the velocity of motion with the potential leads to a distortion of the polarographic i—φ curves and to the eventual appearance of spurious waves.

Under the conditions of practical polarography spurious waves are formed as a result of contamination of the solution by surface-active substances coming from not calcined salts, rubber tubing, paper filters, *etc.*

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