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# The Polarization Capacity and Adsorption Properties of the Silver Electrode

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The establishment of a valid molecular-kinetic picture of the state of an electrode surface and of the processes which determine the localization of the total potential difference at the phase boundary is at present one of the main problems of theoretical electrochemistry. The principal points have already been established in the works of a number of investigators [1,2,3] and experimental methods have been developed for the study of that part of the metal-solution potential difference which is determined by the ionic double layer and the dipole layer of atoms and molecules.

The study of the electrode process on silver is of considerable interest. Silver is a typical metallic electrode, the potential of which is determined, over a considerable range, by the concentration of its own ions.

Owing to the electrochemical properties of silver it may be studied by the methods which have been developed for the study of platinum and mercury — the two metals on which the electrode process has been particularly well studied [4,5]. Finally, silver has been the object of a number of investigations which give us some ideas of the state of its surface.

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[1] Bowden a. Rideal, Proc. Roy. Soc., **A 120**, 59 (1928).

[2] Frumkin, Erg. Exact. Naturwiss., **7**, 235 (1928).

[3] Stern, Z. Elektrochem., **30**, 508 (1924).

[4] Šlygin a. Frumkin, Acta Physicochimica URSS, **3**, 791 (1935); **4**, 911 (1936); **5**, 820 (1936).

[5] Proskurnin a. Frumkin, Trans. Farad. Soc., **31**, 110 (1935).

In order to make an advantageous study of the behaviour of an electrode in solutions of electrolytes it is of particular interest to know the properties of the surface of the metal in simpler systems, such as when the metal is in contact with a gas, or vacuum. It is particularly, desirable to know the adsorption properties of the electrode studied and to know the influence of the adsorbed layers on the energy characteristics (the work function of an electron, the catalytic properties and so on) of the metallic surface which is being studied.

Unfortunately there exist very few direct investigations of the adsorption properties of a silver surface; nevertheless the indirect data of a number of authors make it possible to draw perfectly definite conclusions relative to the adsorption of hydrogen and oxygen on silver in which we are interested.

From the investigations of Chapman and Hall[6] and of Chapman and Ramsbottom[7] and also from the work of Benton and Elgin[8] who studied the catalytic behaviour of a silver surface in the synthesis of water, it may be considered that the adsorption of oxygen by silver at room temperature is established. Chapman and Hall found that if a silver surface with adsorbed oxygen is heated, it becomes more difficult for the oxygen film to be reduced by hydrogen, and the catalytic activity of the silver surface is decreased. The adsorption of oxygen by a silver surface was also observed earlier by Sieverts[9].

The conclusion that hydrogen is adsorbed on the surface of silver cannot be drawn quite so definitely from the available data. Chapman and Hall, as well as Benton and Elgin, did not establish any noticeable adsorption of hydrogen on silver at room temperature. However, at higher temperatures, Chapman observed a certain adsorption of hydrogen which was not released when the silver was cooled.

Sieverts, in the work quoted above, found that "solid and molten silver do not adsorb hydrogen". Indirect data on the adsorp-

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[6] Chapman a. Hall, Proc. Roy. Soc., **A 124**, 478 (1929).

[7] Chapman, Ramsbottom a. others, Proc. Roy. Soc., **A 107**, 92 (1925).

[8] Benton a. Elgin, J. Am. Chem. Soc., **48**, 302 (1926).

[9] Sieverts, Z. physik. Chem., **60**, 179 (1907).

tion of gases are provided by investigations of the photoelectric effect on silver surfaces treated in various manners. Here there are definite indications of the adsorption of oxygen by a silver surface, the oxygen having the effect of shifting the long-wave limit towards shorter wave-lenghts. **Suhrman's**[10] work also provides evidence for a marked influence of hydrogen on the photoelectric properties of a silver surface. Silver treated with hydrogen shows a marked shift of the long-wave limit of the photoelectric effect towards longer wave-lenghts as compared with the surface of pure silver treated by electronic bombardment. It is to be regretted that the works on the influence of gases on the photoelectric emission offer no information as to the quantity of gases adsorbed.

Amongst the investigations which might provide some idea of the state of a silver surface there must be included a number of papers devoted to the study of the electro-kinetic properties of silver[11, 12, 13]. Without entering into an examination of the physical concepts used as a basis for the execution and elucidation of the experiments, it must be mentioned that the authors did not take into account the influence of gases (oxygen from the air) on the measured electrokinetic effects on silver, and this fact must undoubtedly be borne in mind in explaining the results obtained by them. The main conclusion drawn by these investigators (**Billitzer**, **Garrison** and others) consists in that the electrokinetic potential of a silver surface changes in sign at a concentration of silver ions corresponding to $\varepsilon_h = +0.475$ V.

**Bennewitz**[12], using the method of scraping, observed a change in the direction of the electric current flowing from the tested silver electrode at a potential $\varepsilon_h = +0.475$ V.

Measurements of the adsorption of silver ions by a silver surface from a solution were carried out by **Euler** and **Rudberg**[14] and also by **Proskurnin** and **Frumkin**[15]; these latter obser-

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[10] Suhrman, Z. Elektrochem., 35, 681 (1929).
[11] Billitzer, Monatsh. Chem., 53/54. 813 (1929).
[12] Bennewitz, Z. physik. Chem., 124, 115 (1926).
[13] Garrison, J. Am. Chem. Soc., 45, 37 (1923).
[14] Euler a. Rudberg, Z. Elektrochem., 28, 446 (1912).
[15] Proskurnin a. Frumkin, Z. physik. Chem., 155, 9 (1931).

ved a change in the sign of adsorption of silver ions (zero charge of silver) at a potential $\varepsilon_h = +0.510$ V.

Bowden and Rideal[1] measured the quantity of electricity necessary to alter the potential of a silver plate by 100 mV in a sulphuric acid solution. According to their measurements the polarization capacity of 1 cm.$^2$ of silver electrode with a polished surface is 100 μF; when the surface is etched the value becomes 310 μF. These values for the polarization capacity of a silver electrode are approximately twenty times less than the values obtained from adsorption measurements in the work of Proskurnin and Frumkin quoted above.

In the present work we give the results of our investigations of the electrochemical properties of a silver surface in solutions of electrolytes, obtained by the method of measuring the adsorption of silver ions and by that of measuring the polarization capacity of a silver electrode.

## Measurements of the polarization capacity

Measurements of the polarization capacity of a silver electrode were carried out with direct current of low current density with preliminary vacuum treatment of the metal and solution.

In order to reduce the expenditure of electricity on processes which are not of interest in making capacity measurements it may be advisable to apply vacuum treatment of the solution and electrode, and the solution should contain a low concentration of the potential-determining ions. The best conditions for taking charging curves of a silver electrode over quite a wide potential range are obtained with solutions of NaOH and $KNO_3$.

Vacuum treatment should first of all remove oxygen from the solution, since the electric equivalent of the latter in solutions in equilibrium with air under ordinary conditions might be considerably greater than the polarization capacity effects to be measured. In control experiments, made to guarantee the removal of oxygen, the solution was degassed, saturated with hydrogen and again degassed with a high vacuum.

Heating the electrode in hydrogen at 400° C with subsequent degassing at 500° C in a high vacuum ensured the removal of oxides and adsorbed oxygen which might occur on the electrode (cf. Chapman a. Hall[6]).

The apparatus used for the treatment of both solution and electrode and for the polarization measurements is shown in Fig. 1.

A piece of Kahlbaum silver with a surface of 60—100 cm.² was formed into a loose roll, freed from grease in a solution of NaOH and carefully washed. It was then etched in a 35% solution of $HNO_3$ at a temperature of 30° C. After etching the foil was again washed by boiling in twice distilled water.

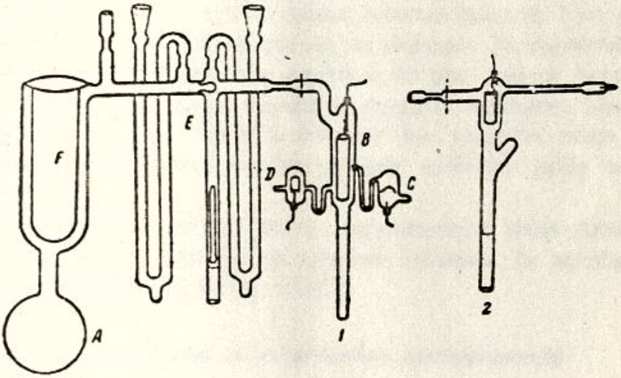

Fig. 1. Apparatus for measuring the polarization capacity (*1*) and the adsorptive properties (*2*) of a silver electrode.

The foil was dried and placed in the part of the apparatus denoted by *B*, which was then sealed off. Contact with the foil was made by means of a silver wire which had previously been fused in. The auxiliary platinum electrode for polarization was situated in *D*. The reference electrode (silver oxide on a silver wire) was situated in *C*. The two latter parts of the apparatus, *C* and *D*, were connected to *B*, in which the electrode to be tested was situated, by sufficiently long tubes with glass filters to reduce diffusion and convection. The electrolyte was poured into the vessel *A* which was connected to *B* by the tube *E*. Both parts of the apparatus could be connected independently to vacuum and to a hydrogen source through two U-tubes with liquid air traps. The electrode was heated in hydrogen at 400° C and degassed in a high vacuum for three hours at 500° C. The vessel $F$ was cooled with liquid air during the degassing. The degassing was continued until all of the solution had condensed on the cooled walls of the vessel. After this treatment the bulb sealing off the electrolyte in $E$ was broken and the electrolyte was poured into the reaction vessel $B$, $C$, $D$. The potential of the electrode was measured with a cathodic voltmeter. The density of the polarizing current varied between 0.2 and 1 μA per square centimeter of apparent surface of the electrode. No appreciable changes in the capacity with the variation of the current density were observed over the range of current densities employed. Under these conditions the time taken to measure the potential when it changed from anodic values to the extreme cathodic value was 10—20 min.

With the method discribed above, measurements were carried out of the polarization capacity of a silver electrode in solutions of $KNO_3$, NaOH, KCl and $KNO_3 + HCl$.

### Experimental results of polarization measurements

The results of measurements of the polarization capacity of a smooth and etched silver electrode in 0.1 $N$ $KNO_3$ are given in Fig. 2 (curves *1* and *2*). The abscissae denote the quantity of electricity in microcoulombs per 1 cm.$^2$ of electrode surface and the ordinates the corresponding potentials referred to a normal hydrogen

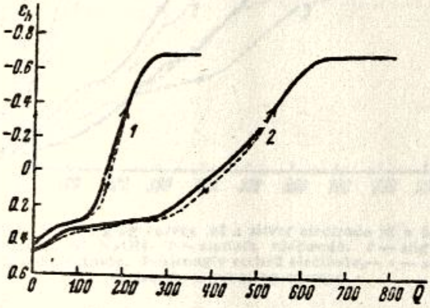

Fig. 2. Charging curves of a silver electrode in a 0.1 $N$ solution of $KNO_3$. *1* — smooth electrode, *2* — etched electrode.

electrode. The solid lines indicate the charging curves obtained with cathodic polarization, and the dotted ones with anodic polarization.

The potential change on a smooth silver electrode, from a potential close to that of silver/silver oxide in the solution used to the potential of steady evolution of hydrogen, requires the expenditure of a quantity of electricity equal to 270 microcoulombs per cm.$^2$ of silver surface. In the case of cathodic polarization the first 130 microcoulombs per cm.$^2$ change the potential of the plate by 250 mV, whilst the last 140 microcoulombs per cm.$^2$ change it by 1000 mV.

There is a clearly expressed delay in the charging curve at a potential of $\varepsilon_h = +0.330$ V, which corresponds to a concentration of silver ions of about $1.10^{-8}$ $N$. The charging curve obtained in 0.1 $N$ $KNO_3$ with etched silver differs only in that there is an increase in the quantity of electricity necessary to change the potential from the limiting anodic value to a cathodic one. This quantity is equal in this case to 645 microcoulombs per cm.$^2$. A large number of measurements were carried out in a 0.1 $N$ solution of NaOH in order to elucidate the influence of various factors on the value of the capacity of the electrode, such as the degree of etching of the electrode, the preliminary treatment of the surface and so on.

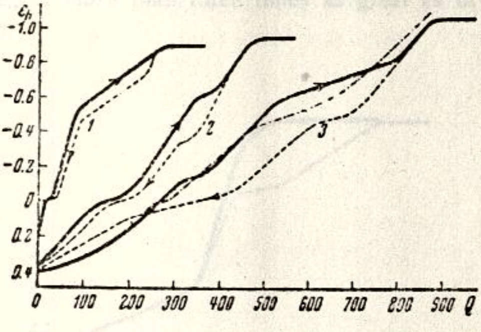

Fig. 3. Charging curves of a silver electrode in a 0.1 $N$ solution of NaOH. 1 — smooth electrode, 2 — slightly etched electrode, 3—strongly etched electrode,— · — same electrode, alternating current.

In Fig. 3 there are given charging curves of silver electrodes with a smooth surface and with different degrees of etching as measured in 0.1 *N* NaOH. The notation is the same as in Fig. 2. The dash-and-dot line gives values of the capacity of a deeply etched silver electrode which we obtained using alternating current. All curves show delays or large values of capacity in the potential range from —0.4 to —0.8, which was not observed with $KNO_3$.

The charging curve of the smooth electrode consists of two parts with very different slopes characterizing the values of the polarization capacity. The presence on the curve of a small delay in the potential variation at $\varepsilon_h = 0$ is characteristic.

A more clearly expressed delay on the cathodic curves at a potential $\varepsilon_h = 0$ and also the shift of the main delay on the anodic curve to a potential $\varepsilon_h = 0$ are features which distinguish the charging curves for etched silver apart from the general increase of the capacity.

The total quantity of electricity necessary to change the potential of etched silver from the potential of silver oxide ($\varepsilon_h = +0.416$ V.) to the potential of steady evolution of hydrogen ($\varepsilon_h = 1.0$ V. with the current density applied) is equal to about 900 microcoulombs per cm.², *i. e.*, is more than three times as great as in the case of smooth silver.

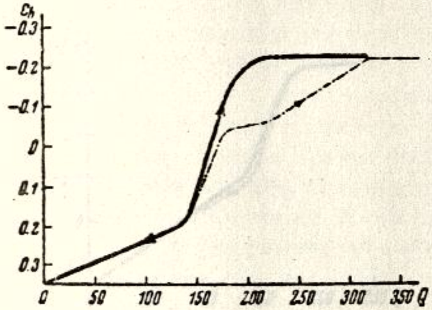

Fig. 4. Charging curves of a silver electrode in 0.01 *N* HCl and 0.1 *N* $KNO_3$ solutions.

Using a 0.1 *N* solution of NaOH we carried out also experiments with an atmosphere of hydrogen and nitrogen. We shall not describe them here, since the results obtained are in general agreement with those of the vacuum series of experiments.

It is of interest to note here an observation made during the taking of the charging curves, which in our view is of essential importance. If the electrode and solution treated *in vacuo* are brought into contact with air, the weakly expressed delay on the charging curve at about $\varepsilon_h = 0$ with cathode polarization increases very markedly and cannot be overcome with the current densities employed, which are of the order of 1 $\mu$A per cm.$^2$, *i. e.*, owing to the depolarizing effect of the oxygen of the air the potential of silver remains constant in the neighbourhood of this value at small current densities.

Measurements of the polarization capacity in a solution 0.1 $N$ $KNO_3 + 0.01$ $N$ HCl were carried out with smooth silver degassed *in vacuo* (without hydrogen) at $T = 20°$ C. When introduced into the solution the silver foil attained the potential of silver chloride. The charging curve obtained with the first cathodic polarization is represented by a dotted line (Fig. 4). It will be seen from Fig. 4 that the charging curve obtained consists of two parts with different slopes. The total quantity of electricity necessary to change the potential of silver from that of silver chloride in the solution used ($\varepsilon_h = +0.35$ V) to that of the steady evolution of hydrogen from this solution ($\varepsilon_h = -0.23$ V.) is equal to 220 microcoulombs per cm.$^2$ of surface. The charging curve obtained with anodic polarization coincides with the cathodic curve. A characteristic effect was also observed in this series of measurements, which is observed in all

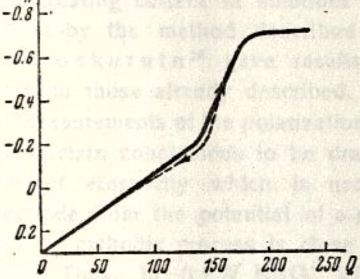

Fig. 5. Charging curves of a silver electrode in a 0.1 $N$ solution of KCl.

cases when hydrogen is not used in the preliminary treatment; the first charging curve obtained with cathodic polarization displayed a large delay (in addition to that observed between $\varepsilon_h = 0.33$ and $\varepsilon_h = 0.2$) of about 130 microcoulombs per cm.$^2$ at a potential close to that of the evolution of hydrogen.

With the usual treatment of the electrode (heating in hydrogen at $t = 400°$ C and degassing at 500° C) the first cathodic charging curve displayed no essential difference from the subsequent ones.

With a solution of 0.1 $N$ KCl, measurements of the polarization capacity were carried out with smooth silver treated in the usual manner. In this case the initial potential of the silver on immersion in the solution was about $\varepsilon_h = 0$. The charging curve obtained is shown in Fig. 5. The principal difference between it and the charging curve taken in $HCl + KNO_3$ consists in that the anodic delay is very much drawn out. The total quantity of electricity necessary to, change the potential of the electrode from that of silver chloride in this solution to that of the steady evolution of hydrogen is, in this case, equal to 210 microcoulombs per cm.$^2$. Of these about 130 microcoulombs are expended in overcoming the delay.

Preliminary measurements of the polarization capacity of a silver electrode with alternating current in solutions of NaOH, $KNO_3$ and others, carried out by the method described in the work of Borissowa and Proskurnin[16] gave results which were not essentially different from those already described.

The results of measurements of the polarization capacity of a silver electrode permit certain conclusions to be drawn.

1. The quantity of electricity which is necessary to charge a smooth silver electrode from the potential of a stable anodic process to that of a stable cathodic process is close to a single value in various solutions. Thus, in 0.1 $N$ $KNO_3$, 270 microcoulombs per cm.$^2$ were necessary to change the potential of a silver electrode from that of silver/silver oxide to that at which the steady evolution of hydrogen takes place (with the current density applied). In 0.1 $N$ NaOH the corresponding value is 275 microcoulombs

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[16] Borissowa u. Proskurnin, Acta Physicochimica URSS, **4**, 819 (1937).

per cm.$^2$; in 0.1 $N$ KCl it is 200 microcoulombs per cm.$^2$ and in 0.1 $N$ HCl + KNO$_3$, it is 220 microcoulombs per cm.$^2$ (in the latter two experiments the anodic limit of the electrode potential change was the potential of formation of silver chloride).

When the electrodes were not subjected to special treatment with hydrogen, the quantity of electricity necessary for the electrode to attain the potential of the steady evolution of hydrogen for the first time was some 100—200 microcoulombs per cm.$^2$ greater than the above value.

An electrode etched with acid requires a total quantity of electricity some 3—4 times greater than is necessary in the case of a smooth electrode in order to change the potential to the same extent. The average polarization capacity for the range of polarization used is 640 $\mu$F per cm.$^2$ in the case of an etched silver electrode in a solution of 0.1 $N$ KNO$_3$. The values of the minimum capacity (region of formation of a double layer) of a silver electrode calculated from the given charging curves were 100—120 $\mu$F per cm.$^2$ for smooth silver and 350—400 $\mu$F per cm.$^2$ in the case of deeply etched silver. These values are in good agreement with the ones obtained by Bowden and Rideal[1] who obtained values of 100—310 $\mu$F per cm.$^2$ for silver surfaces treated in various ways.

2. The charging curves of a silver electrode in various electrolytes all consist of two characteristic parts. In the first the potential rises rapidly with a constant current density (the polarization capacity of the electrode is small), in the second the potential increases slowly (the polarization capacity of the electrode is great). It is natural to suppose that the region of the charging curves in which the capacity is small is determined mainly by the formation of an ionic double layer, whilst the potential region in which the electrode capacity is large is one in which surface compounds are formed and destroyed on the electrode. These processes frequently overlap one another, which considerably complicates the form of the charging curves. This latter circumstance may explain the fact that, in the region of minimum capacity, the capacity of a silver electrode is still considerably greater than can be attributed to the formation of an ionic double-layer alone.

From an analysis of all the polarization measurements obtained and taking into account the known data concerning the adsorption properties of a silver surface, it follows that the principal process which takes place during the charging of a silver electrode in the solutions described (in addition to the formation of an ionic double layer) is the process of formation or removal of an oxide film on the surface of the silver or of a surface film of silver chloride in the case of solutions which contain chlorine ions. We found no definite indications of the formation of hydrogen films on silver, such as are observed with platinum.

3. Owing to the presence of an oxide film on a silver surface, a silver electrode may acquire in the presence of oxygen a fairly well defined potential corresponding to the deposition and remova of an oxide film.

4. Preliminary measurements of the polarization capacity with alternating current make it possible to draw the conclusion that the processes which determine the polarization capacity of a silver electrode take place with high velocity.

## The adsorption method of measuring the capacity of a silver electrode

The method of measuring the adsorption capacity of a silver electrode which we applied was on the whole similar to that described in the article of Proskurnin and Frumkin[15].

The adsorbing silver surface and the solution were first treated in a vacuum by the method described on page 819. The functions of the various parts of the apparatus are obvious from its diagram (Fig. 1, right-hand side) and from the subsequent description of the results. The effect of changing the concentration was determined from the potential difference of silver electrodes of very small area, one of which was situated in the initial solution and the other in the solution which was in equilibrium with the adsorbent, the silver foil.

In considering our method it is necessary to mention one of the effects which may lead to incorrect conclusions under the described conditions of measurements.

It is well known that adsorbed layers of dipole molecules, atoms, and, particularly, of ions on metals change the potential of the metal relative to vacuum very considerably, as may be observed from the change in the work function of electrons.

Such layers also change the potential liquid/gas. But in solutions with a given concentration of ions which determine the potential, the equilibrium potential of the electrode will be determined only by the activity of these ions, and the deposition of a dipole film on the surface of the electrode only changes the form of the potential curve on the surface. The distribution of the ions between the metal, the solution and the double layer changes in such a way that the total value of the potential difference between the metal and the solution remains the same as it was before deposition of the dipole film.

The influence of a dipole film on the potential of the electrode is rather different when there is a noticeable change in the quantity of ions which determine the potential, owing to the expenditure of ions on the formation of the double layer. In this case the potential of a metallic plate is not determined in a single-valued manner by the given concentration of ions, since this latter may itself change to various extents, depending on the state of the electrode.

Thus the state of the electrode surface will, to a certain extent, determine the final value of the potential of the electrode in solution in which the concentration of ions which determine the potential changes considerably on formation of the double layer.

The rate of establishment of phase equilibrium, and consequently of the equilibrium potential of the electrode, on appreciable change in the concentration of ions which determine the potential, will not be practically instantaneous as in the case when there is an excess of these ions, but will be determined mainly by the rate of diffusion of ions from the bulk of the solution and by the rate of the processes of formation and destruction of surface films. A marked reduction in the concentration of ions which determine the potential may radically alter the mechanism of establishment of the electrode potential, and the rôle of "potential determinants" may be transferred to ions of a different sort from those of the metal of the electrode, in the first place to the ions $H^\cdot$ and $OH'$ (in aqueous solutions). The above remarks must be taken into account in analysing the results of adsorption measurements on a silver electrode.

Using the method described we carried out measurements of the adsorption of ions of silver from solutions of silver nitrate in pure water and in the presence of a foreign electrolyte, 0.1 $N$ $KNO_3$. A piece of silver foil etched with 35% nitric acid served as the adsorbent. An experiment carried out with an initial concentration of $1 \times 10^{-4}$ $N$ $AgNO_3$ in the presence of 0.1 $N$ $KNO_3$ gave a potential difference of 40 mV between small electrodes in the initial solution and in a solution in communication with the adsorbent, which, with the quantity of solution used, corresponds to an effect of adsorption of $Ag^{\cdot}$-ions equivalent to 301 microcoulombs per cm². of silver surface with a final concentration of $Ag^{\cdot}$-ions equal to $2.04 \times 10^{-5}$ $N$ (Table 1).

Table 1

| Initial concentr of $Ag^{\cdot}$-ions | Change of potential in mV | Final concentr. of $Ag^{\cdot}$-ions | Volume of the solution cm.³ | Surface of the electrode cm.² | Adsorption effect in microcoul./cm.² | Electrolyte added |
|---|---|---|---|---|---|---|
| $1 \times 10^{-4}$ $N$ | 42.2 | $1.9 \times 10^{-5}$ $N$ | 3.1 | 67 | 364 | No foreign electrolyte |
| $1 \times 10^{-4}$ $N$ | 40.0 | $2.0 \times 10^{-5}$ $N$ | 2.4 | 61.4 | 301 | 0.1 $N$ $KNO_3$ |
| $1 \times 10^{-4}$ $N$ | 40.0 | $2.0 \times 10^{-5}$ $N$ | 3.3 | 74.6 | 340 | 0.1 $N$ $KNO_3$ |
| $1 \times 10^{-5}$ $N$ | 280 (140) | $1.5 \times 10^{-10}$ $N$ | 5.0 | 60 | 80.5 | 0.1 $N$ $KNO_3$ |
| $1 \times 10^{-5}$ $N$ | 317 (185) | $3.4 \times 10^{-11}$ $N$ | 4.0 | 60 | 64.4 | 0.1 $N$ $KNO_3$ |
| $1 \times 10^{-5}$ $N$ | 190 (182) | $5.3 \times 10^{-9}$ $N$ | 4.0 | 70 | 55.1 | 0.1 $N$ $KNO_3$ + + 0.01 $N$ $HNO_3$ |
| $1 \times 10^{-5}$ $N$ | 406 (216) | $1 \times 10^{-12}$ $N$ | 2.5 | 70 | 34.5 | 0.1 $N$ $KNO_3$ + + $1 \times 10^{-4}$ $N$ NaOH |
| $1 \times 10^{-5}$ $N$ | 330 (230) | $2 \times 10^{-11}$ $N$ | 5.0 | 60 | 80.5 | 0.1 $N$ $KNO_3$ + + $1 \times 10^{-4}$ $N$ NaOH |

Experiments with a $AgNO_3$ solution of $1 \times 10^{-4}$ $N$ initial concentration either in the presence or in the absence of a foreign electrolyte did not show a considerable change in the adsorption effect. The small variations obtained in the values of the adsorption effect may be explained as due to insufficient uniformity of corrosion of the silver.

The results of adsorption measurements with an initial concentration of $1 \times 10^{-4}$ $N$ $AgNO_3$ are of good reproducibility; the absolute values of the effects are sufficiently close to the results of measurements carried out by other authors (Euler and Rudberg[14], Proskurnin and Frumkin[15]). Owing to the rapid establishment of adsorption equilibrium and potential stability at these comparatively high concentrations this process of measurement affords the possibility of obtaining reliable values for the adsorption effect. Using an initial concentration of $AgNO_3$ equal to $1 \times 10^{-5}$ $N$, determination of the adsorption effect was found to be considerably more complicated.

With an initial concentration of $1 \times 10^{-5}$ $N$ $AgNO_3$ the adsorption effects (positive) obtained by the original method gave, in the majority of the experiments, a potential difference of 110—130 mV between an electrode in the initial solution and one in a solution communicating with the adsorbent, but this value fell to 10—15 mV in certain experiments. The results obtained with an initial concentration of $AgNO_3$ equal to $1 \times 10^{-6}$ $N$ were still less satisfactory. The potential changes varied from 40 to 20 mV at these concentrations, and a change in the apparent sign of the charge of the adsorbing electrode (negative adsorption of silver ions) was observed in one experiment.

As a result of a number of experiments carried out to elucidate the observed anomalies in the determination of the adsorption effect with a concentration of $AgNO_3$ of less than $1 \times 10^{-5}$ $N$, it was established that the small silver electrode used to measure the concentration of silver ions only gives satisfactory results with concentrations of $Ag^{\cdot}$-ions exceeding $1 \times 10^{-6}$ $N$. When the concentration of $Ag^{\cdot}$-ions is smaller than this value, as well as in a solution of $KNO_3$ or in pure water which do not contain silver ions, a silver wire which has not been subjected to a special treatment assumes a potential corresponding to a concentration of $Ag^{\cdot}$-ions of $10^{-6}$—$10^{-7}$ $N$.

This fact, as will be shown below, depends on the presence of an oxygen film on the silver, which begins to be removed at this potential.

Some changes were introduced into the method of measurement in order to remove the described defect — namely, in measuring the potential between the electrode in the initial solution and that in the solution in communication with the adsorbing surface, the adsorbing surface was brought into contact with the latter electrode.

The results of adsorption measurements with an initial concentration of $AgNO_3$ $1 \times 10^{-5}$ $N$ are given in Table 1. The values of the potential obtained without contact between the small electrode in the final solution and the adsorbing surface are given in brackets. The potential of the silver foil introduced into the initial solution was markedly negative at the first moment of measurement (up to 450 mV against a small silver electrode in $1 \times 10^{-5}$ $N$ $AgNO_3$) and then slowly reached a value of 300—320 mV as measured against this electrode. A small electrode which is not in contact with the adsorbing surface always shows a more positive potential of 140—200 mV against an electrode in the initial solution. When the small electrode was not brought into contact with the adsorbing surface at all, its potential, as in the case of the old method, was unstable and usually had a value of 110—120 mV as measured against an electrode in the initial solution.

The adsorption effect calculated from the potential of the adsorbing electrode with an initial concentration of $1 \times 10^{-5}$ $N AgNO_3$ is equal to 64.4 microcoulombs per cm.$^2$ of silver surface, and in another experiment it was found to be equal to 80.5 microcoulombs per cm.$^2$ with final concentrations of $Ag^{\cdot}$-ions of $3.4 \times 10^{-11}$ and $1.5 \times 10^{-10}$ $N$ respectively.

In experiments with acidified and alkalized solutions all of the observed effects are preserved, but in alkaline solutions the potential of the adsorbing electrode is more negative in both the initial and steady conditions. In a control experiment in which the possible influence of hydrogen was excluded, the adsorption effect was measured with an electrode which had been carefully heated and degassed in vacuum without application of hydrogen. No essential difference was observed between the results thus obtained and the previous ones.

There is one interesting effect which should be mentioned: the admission of air into the reaction vessel rapidly brings the potential of the adsorbing electrode to a value corresponding to a concentration of silver ions of $1 \times 10^{-5}$ $N$ and sometimes to even more positive values.

Fig. 6 gives the results of measurements of the adsorption effects expressed in microcoulombs per cm.$^2$ of silver electrode surface plotted against the final concentrations to which the effect corresponds. The circles with marks directed upwards and downwards refer to acidified and alkalized solutions respectively.

The straight line which is drawn through the points gives, to a first approximation, the dependence of the charge of the electrode on the logarithm of the concentration of silver ions in the solution. The average capacity of the silver electrode as determined by the slope of this line is found to be equal to 620 μF per cm.$^2$ of surface, which is in good agreement with the values of the average capacity obtained by the polarization method (640 μF per cm.$^2$).

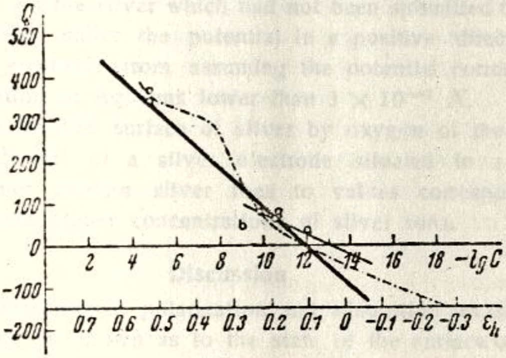

Fig. 6. Dependence of the charge of a silver electrode on the potential in a 0.1 $N$ solution of $KNO_3$ from adsorption and polarization measurements.

The point of intersection between the abscissae axis and the straight line giving the dependence of the charge on the logarithm of the concentration gives also, to a first approximation, the position of the point of zero charge of the silver electrode. It will be seen from the figure that it is situated at $C_{Ag^{\cdot}} = 1 \times 10^{-12}$ $N$. As will be shown below, the values of the differential capacity of a silver electrode in this region, obtained by polarization measurements, necessitate the location of the point of zero charge at $C_{Ag^{\cdot}} = 1 \times \times 10^{-13}$ $N$.

Silver foil introduced in a $10^{-5}$ $N$ solution of its ions assumes at the first instant a potential close to that corresponding to the zero charge of a silver electrode (in our experiments up to 450 mV more negative than the potential of the electrode in the initial solution). Later, during the process of attainment of equilibrium, the silver ions are deposited on the plate and give it a positive charge, but as a result of the drop in the concentration of silver ions the adsorbing electrode does not attain the potential of the electrode in the initial solution.

The difference between the values corresponding to the small electrodes and the adsorbing electrode at low concentrations is due to the oxide film on the silver which had not been submitted to special outgassing which shifts the potential in a positive direction and prevents the electrode from assuming the potential corresponding to a concentration of $Ag^{\cdot}$-ions lower than $1 \times 10^{-7}$ $N$.

Oxidation of the surface of silver by oxygen of the air may bring the potential of a silver electrode situated in a solution which does not contain silver ions to values corresponding to $1 \times 10^{-5}$ $N$ and higher concentrations of silver ions.

## Discussion

From the results of polarization and adsorption measurements conclusions may be drawn as to the state of the surface of a silver electrode and as to the processes which proceed on it during the establishment of various values of the potential.

Fig. 6 shows a charging curve for a silver electrode in a 0.1 $N$ solution of $KNO_3$ obtained from polarization measurements (dotted line). The curve is plotted from values of the concentration of $Ag^{\cdot}$-ions corresponding to zero charge of the silver electrode equal to $1 \times 10^{-12}$ $N$ which was obtained as a first approximation from the dependence of the adsorption effect on the potential (solid line). As is obvious from Fig. 6, the dependence of the charge of the electrode on the potential as obtained by two independent methods shows fully satisfactory coincidence.

It will be seen from the charging curve given in Fig. 6 that using the value of the capacity of the electrode, observed in the neighbourhood of the point of zero charge, the position of this point can be determined more accurately; it corresponds for a silver electrode in a neutral solution of $KNO_3$ to a $C_{Ag^{\cdot}} = 1 \times 10^{-13}$ $N$ ($\varepsilon_h = +0.046$ V.).

It further follows from the charging curve of a silver electrode in 0.1 $KNO_3$ that in this solution, at potentials exceeding $\varepsilon_h = 0.200$ V. corresponding to $C_{Ag^{\cdot}} = 5 \times 10^{-11}$ $N$, the silver surface becomes covered with an oxide layer, the process of deposition of which finishes at a potential $\varepsilon_h = 0.365$ V. corresponding to $C_{Ag^{\cdot}} = 3 \times 10^{-8}$ $N$.

It is obvious that the point of zero charge of a clean silver electrode in a neutral solution of $KNO_3$ cannot lie at concentrations of $Ag^{\cdot}$-ions greater than $5 \times 10^{-11}$ $N$. It is difficult to establish unambiguously from our experiments whether in addition to a point of zero charge of a clean silver surface there exists also a definite point of zero charge of an oxidized surface.

The potential difference of 0.3 V. between a silver surface covered with an oxide layer and silver at the point of zero charge might depend on the dipole moment of the oxide layer, but it is of course possible that processes of the formation of an ionic double layer also take place in the same interval, which makes it impossible to draw any quantitative conclusions from our measurements regarding the position of the point of zero charge of an oxidized surface.

The supposition of the existence of a point of zero charge of an oxidized silver surface is supported by the results of measurements of electrokinetic effects on silver which establish the change in sign of ζ-potential at $\varepsilon_h = 0.4$—$0.5$ V. ($C_{Ag^{\cdot}} \sim 10^{-6}$). Almost all these investigations (Billitzer[11], Bennewitz[12], Garrison[13]) were carried out under conditions in which the surface of the silver was covered with an oxide film.

In addition to the possibility of displacement of the zero point considered above, the previous formation of an oxide film also changes the value of the effect of silver ion adsorption by a silver surface.

If silver with an oxide film is immersed in a solution with a concentration of silver ions of $1 \times 10^{-4}$ $N$, the quantity of silver ions which is deposited on the electrode during the process of attainment of adsorption equilibrium will be less than that which is deposited on a pure silver surface, since the oxide film plays the rôle of a positive charge. With an initial concentration of about

$10^{-6}$ $N$ of Ag˙-ions the adsorption effect will be zero on such a surface and it will be negative with lower concentrations. It is possible that the point of zero charge found by adsorption measurements in the paper of Proskurnin and Frumkin[15] also referred to an oxidized surface.

If a perfectly clean silver surface is introduced into a solution which does not contain oxygen and which has a concentration of Ag˙-ions of the order of $10^{-4}$ $N$ the adsorption of Ag˙-ions will be accompanied by the formation of an oxide film at the expense of adsorption of hydroxyl ions from the water and of an additional equivalent quantity of Ag˙-ions.

With very small initial concentrations of Ag˙-ions the potential of a silver electrode may not be sufficiently positive for the formation of an oxide film.

It seems to us that these considerations can explain the divergence between the values of the potential of zero charge and of the adsorption effect obtained in our work and those in the investigations quoted above which dealt with the measurement of the electrokinetic and adsorption (from solution) effects on silver.

According to our measurements the energy of adsorption of oxygen on silver from a neutral solution is equal to 0.5 V. However, data on the first cathodic polarization (see above) and, in particular, an analysis of the charging curves of a silver electrode in a solution of NaOH suggest the supposition that the oxide film on silver may be more firmly bound to the silver and that the reduction of this film necessitates considerably greater cathode potentials. The bond energy between this film of the second kind and the metal will be about IV. in alkali. This is all the more interesting because Chapman and Hall[6] observed two types of adsorption of oxygen on silver, the oxygen film which was firmly attached to the silver possessing a lower catalytic activity.

The charging curves of a silver electrode in solutions containing Cl′-ions have a very pronounced region corresponding to adsorption and desorption of chlorine. The linear dependence of the quantity of adsorbed chlorine on the potential (*i. e.*, on the logarithm of the pressure of chlorine) is of particular interest. An analogous behaviour of hydrogen on platinum is reported in the papers of Frumkin and Šlygin[4] and may be explained either by a non-uniformity of the surface of the adsorbent or by repulsion forces between adsorbed atoms. The absolute value of the quantity of adsorbed chlorine on 1 cm.$^2$ of surface of a smooth silver electrode was equal to $0.9 \times 10^{15}$ atoms of chlorine (1 cm.$^2$ of ideally smooth surface of silver has about $1.5 \times 10^{15}$ atoms of silver).

Let us examine the last conclusion which can be drawn from our experimental results. The zero charge potential of a silver electrode which we established is at $\varepsilon_h = 0.046$ V. The electromotive force of a cell consisting of silver and mercury electrodes at their zero charge potentials will be $\Delta\varepsilon = 0.046 - (-0.22) = 0.266$ V. The difference between the work functions of silver and mercury surfaces is equal to $4.78 - 4.53 = 0.25$ V. and, consequently, the electromotive force of a cell composed of silver and mercury electrodes at the zero charge potentials is determined mainly by the difference between the work functions of these metals. This shows that the molecules of water are oriented in a similar way at the mercury-water and silver-water interfaces (cf. **Frumkin**[16]).

In conclusion the author considers it his pleasant duty to express his gratitude to Prof. A. N. **Frumkin**, at whose suggestion and under whose guidance the present investigation was carried out. The author also wishes to express his gratitude to M. A. **Proskurnin** for his valuable advice and help, in particular in working out the experimental technique.

## Conclusions

1. Direct current with a current density up to $0.1 \times 10^{-6}$ A/cm.$^2$ may be used to measure the polarization capacity of electrodes under conditions close enough to those of equilibrium. For this purpose it is necessary that the electrode and solution be specially outgassed in vacuum.

2. Measurements of the quantity of electricity necessary to change the potential of a silver electrode from that of the steady discharge of anions to that of the steady evolution of hydrogen in solutions of 0.1 $N$ $KNO_3$, 0.1 $N$ NaON, 0.1 $N$ $KNO_3$ + 0.01 $N$ HCl and 0.1 $N$ KCl gave values of 200—1000 microcoulombs per cm.$^2$

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[16] **Frumkin**, J. Chem. Phys., 7, 552 (1939).

depending on the treatment of the electrode and on the solution applied.

The polarization capacity of silver electrode in the double-layer region was equal to:

100—120 μF per cm.$^2$ for a smooth electrode,
350—400 μF per cm.$^2$ for an etched electrode.

3. The surface of metallic silver is covered with an oxide film which is removed in a solution of $KNO_3$ at $\varepsilon_h = 0.330$ V., whilst in alkali partial removal takes place at $\varepsilon_h = 0$ and the remainder is removed at considerably greater cathodic potentials.

4. In solutions containing Cl′-ions the silver is covered with a layer of adsorbed chlorine. About $0.9 \times 10^{15}$ atoms of chlorine are deposited on 1 cm.$^2$ of a smooth silver electrode; there is a linear dependence of the quantity of adsorbed chlorine on the potential of the electrode.

5. The dependence of the charge of a silver electrode on the potential, obtained by measurement of the adsorption of silver ions by silver foil, coincides well with the data of polarization measurements. The point of zero charge of a silver electrode established from adsorption measurements and from values of the polarization capacity is found at $\varepsilon_h = 0.046$ V. which corresponds to a concentration of silver ions of $1 \times 10^{-13}$ *N*.

6. The electromotive force of a galvanic cell consisting of a silver electrode at the zero charge potential and a mercury electrode at the zero charge potential is, as established in this paper, 0.266 V. This is in good correspondence with the value of the difference between the work functions of silver and mercury (0.25 V.).

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