

POLAROGRAPHIC REDUCTION OF HALOGENATES AND THEIR OXIDATION POTENTIALS

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The value of the equilibrium potential of an oxidizing agent containing oxygen is known to be dependent on the acidity of the solution. Theoretically, this relation can be expressed by the formula:

$$E = E_0 + \frac{RT}{nF} \ln \frac{a_{\text{oxid.}} \cdot a_{\text{H}}}{a_{\text{red.}}}$$

However, calculations based on this formula cannot be carried out in practice, since the activity values are not always known, while substitution of concentration for activity leads to values which do not agree with the values determined experimentally. As an example one may instance the work of Kolthoff and Luther [1], in which it was shown that the change in the potential of the system $\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}$ arising from a unit pH change, not only did not agree with the calculated value, but differed in sulfuric and hydrochloric acid solutions.* In a number of papers, Syrokonskii, Avilov, et al. [3-7] also demonstrated disagreement between the oxidation-reduction potentials measured in various media and the theoretical and published values. In addition, published values of the potentials cannot characterize the reducibility of halogenates under the currents applied during polarography with a dropping-mercury electrode or with a platinum rotating electrode. Thus, according to published results [8], chlorate has the highest normal oxidation potential (in the halogen series), while iodate has the lowest; on the other hand, it is well known that chlorate is not reduced during electrolysis with a dropping-mercury cathode, and iodate and bromate are polarographed quantitatively, the half-wave potentials and the wave height being functions of the pH [9-14].

However, the work carried out already referred to a comparatively narrow acid concentration range, and, in general, no work has been carried out in sulfuric acid. Accordingly, the work described here was devoted to establishing the effect of sulfuric acid concentration (from 2 to 32 N) on the polarographic reduction of halogenates.

Since hydrogen invariably participates during the electrical reduction of most oxygen-containing anions, the material from which the electrode is made should play an important part; accordingly, we polarographed the halogenates not only on a dropping-mercury electrode but also on a platinum electrode.

In order to compare the polarographic reduction potentials of the halogenates (i.e., potentials when current is applied) with the oxidation potentials, we measured the potentials in solutions of the halogenates with varying sulfuric acid concentrations in the absence of a current.

1. Polarography of the Halogenates with a Dropping-Mercury Cathode. Polarographic experiments were carried out on a PPT-1 visual polarograph made by the experimental shop of the Institute of Energetics, Academy of Sciences, Kazakh SSR. The M-21 type galvanometer had a sensitivity of 10^{-9} amp/mm/m. The half-wave potentials were determined graphically as the point of intersection of the straight line constructed within the

*It was shown in Ptitsyn and Petrov's paper [2] that the potential of this system is completely independent of trivalent chromium ions.

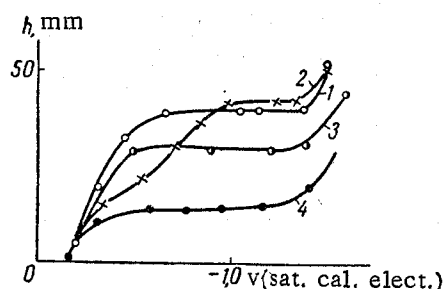


Fig. 1. Polarograms for 4×10^{-3} M chlorate solutions. Sulfuric acid concentration: 1) 18 N; 2) 22 N; 3) 24 N; 4) 32 N.

coordinates $\log i/(i_d - i) - E$ with the potential axis. The potential values given below are corrected for IR and refer to the saturated calomel electrode. Dissolved oxygen was removed by passing hydrogen or carbon dioxide through the solution prior to addition of the halogenate (0.1 ml).

a) Chlorate. Results obtained during the polarographic study of chlorate* are given in Fig. 1 and in Table 1. A reduction current was only observed on the polarograms when the sulfuric acid concentration was not less than 10 N. During oscillographic polarography, which is more sensitive, it was possible to observe reduction of chlorate at lower sulfuric acid concentrations [15]. A clearly defined wave was observed in 16 N and in higher concentrations of sulfuric acid when ordinary polarography was used.

The wave height is proportional to the chlorate concentration and depends on the sulfuric acid concentration, passing through a maximum at approximately 16 N sulfuric acid, and again increasing somewhat in 32 N acid. Such a relation is connected, probably, with the viscosity of the medium; starting at concentrations higher than 16 N, the viscosity of the sulfuric acid solutions increases, in the range 29-31 it changes to a small extent, while in the range 32-35 N there is again a certain drop in viscosity.

However, the effect of sulfuric acid concentration on the reduction process is also connected with chemical interactions between chlorate and sulfuric acid, in the course of which it is known [16] that chlorine dioxide, chlorous, and perchloric acids are formed, as well as free chlorine, all of which can be reduced on the cathode (with the exception of perchloric acid and its anions, which, according to published results [10, 11] and according to our results, do not give polarographic waves in the absence of special catalysts).

The most probable participants in the electrode process are chlorine dioxide and chlorine, the presence of which can be observed from the yellow-green color of the solution and from its odor. It should be pointed out that during polarographic investigation of a solution from which chlorine dioxide and chlorine had been removed by extraction with organic solvents or by heating, no reduction waves were observed.

Qualitative changes in the composition of the solution are reflected in changes in the values of the half-wave potentials (Table 1).

b) Bromate. Bromate is known to be reduced on the dropping-mercury cathode in weakly alkali and acid media of varying composition [9, 11, 12, 14]. We established that in a supporting electrolyte of 2 N sulfuric acid, bromate forms one very clearly defined reduction wave ($E_{1/2} = -0.4$ volt). However, even in 4 N sulfuric acid, another wave appears which precedes the main bromate wave, and starting at 0 volt, it persists at higher acid concentrations (Fig. 2). We think that this wave is determined by the reduction of mercury ions formed as the result of the direct interaction of bromate with mercury metal. Exactly the same wave is also obtained in solutions of other oxidizing agents—dichromate, permanganate [17]—which oxidize metallic mercury.

TABLE 1

Characteristics of the Polarograms of Sulfuric Acid Solutions of Chlorate. Chlorate Concentration $4 \cdot 10^{-3}$ M $2/3 t^{1/6} = 2.4$

Sulfuric acid concentration, N	$I_d, \mu a$	$I_d/m^{2/3}t^{1/6}$	$E_{1/2}, V$	n
16	20,0	8,3	-0,67	0,1
18	16,8	7,0	-0,59	0,1
20	14,0	5,8	-0,54	0,2
22	16,0	6,6	-0,39	0,3
24	12,0	5,0	-0,33	0,3
26	8,0	3,3	-0,39	0,3
28	6,8	2,8	-0,35	0,3
30	4,8	2,0	-0,25	0,3
32	6,4	2,7	-0,25	0,3
34	8,0	3,3	-0,25	0,3
36	8,0	3,3	-0,30	0,3

*The experiments were carried out by R. Sh. Nigmatova.

TABLE 2

Characteristics of the Polarograms of Sulfuric Acid Solutions of Iodate. Iodate Concentration $2.4 \cdot 10^{-3} \text{ M}$; $m^{2/3} t^{1/6} = 1.7$

Sulfuric acid concentration	$I_d, \mu a$	$I_d/m^{2/3} t^{1/6}$	$E_{1/2}, v$	n
First wave (reduction of mercury ions)				
2	No wave			
6	No wave			
8	3,6	2,1	+0,34	—
10	4,6	2,7	+0,36	—
14	4,1	2,4	+0,37	—
16	4,1	2,4	+0,30	—
18	4,6	2,7	+0,30	—
20	4,1	2,4	+0,25	—
Second wave (reduction of iodic acid molecules)				
2	13,3	7,8	—0,13	0,6
6	18,9	11,1	—0,03	—
8	15,3	9,0	—0,09	—
10	10,7	6,3	—0,08	—
14	6,1	3,6	—0,10	0,6
16	4,1	2,4	—0,10	—
18	2,6	1,5	—0,16	—
20	Wave poorly expressed			
Third wave (reduction of iodate anions)				
2	17,9	10,5	—0,69	0,6
6	25,1	14,8	—0,89	0,3
8	30,2	17,8	—0,95	0,3
10	28,2	16,6	—0,93	0,3
14	29,7	17,5	—0,99	0,3
16	2,6	1,5	—0,56	—
18	1,5	0,9	—0,56	—
20	No wave			

At acid concentrations of 6 N and higher, between the first (mercury) and second, main (bromate) wave, there is observed yet another wave which is not very clearly defined; this is the result, apparently, of the reduction of the bromic acid molecule [13, 14]. Since bromic acid is a fairly strong acid, the concentration of its undissociated molecules in equilibrium with its anions is relatively low, and the wave does not have a clearly defined shape; at higher sulfuric acid concentrations this "molecular" wave, in general, disappears.

The absence of clear lines of demarcation between the waves prevents one from calculating the polarographic characteristics. The height of the total wave depends on the acid concentration, and attains a maximum in approximately 10 N acid. The chemical interaction of bromate with acid is more clearly marked the higher the acid concentration; this chemical interaction gradually leads to a complete change in the composition of the solution, an idea of which can be gained from the external appearance of the solution, which acquires a rosy-orange or yellow color (extracted by chloroform or carbon tetrachloride), the latter is caused by the formation of free bromine, and possibly bromine dioxide. Under these conditions, the total wave height decreases sharply and disappears in approximately 22 N acid. When the acid concentration is increased further, this wave is replaced by another (curve 5, Fig. 2) located at a considerably more negative potential ($E_{1/2} = -0.6$ volt) than in less acid solutions (Curve 3, Fig. 2).

c) Iodate. Results of these experiments are given in Table 2 and Figs. 3 and 4. It is clear from these results that reduction of iodate in general proceeds in a way

similar to that of bromate: depending on the acid concentration, waves for the reduction of mercury ions (Fig. 3, curve 3 step I), iodic acid (curves 1, 2, 3 step II), and of iodate (step III on the same curves) are observed. In these experiments the second step on the polarogram is expressed very clearly, since iodic acid dissociates to a very small extent. The limiting current in this case is observed at potentials close to the null discharge potential (-0.2 volt), i.e., under conditions which are most favorable for the reduction of uncharged particles.

The relation between the heights of the individual waves and the acid concentration, is, in general, similar to that described above for bromate. However, already in 18 N acid, there is observed an "infinite" current at a potential which is more positive than the reduction potential of hydrogen in the given supporting electrolyte (curves 1 and 2, Fig. 4); in this case the height of the other steps (as compared with curve 3, Fig. 4) decreases sharply, and in 30 N acid these steps disappear completely (curve 3, Fig. 4)—there remains only a sharp increase in the current at -0.6 volt. Since this potential is approximately 0.4 volt more positive than the hydrogen liberation potential (curve 1, Fig. 4), it remains to suggest that this wave appears as the result of some new electrode process, or, most probably, has a catalytic character. We should point out incidentally, that similar catalytic waves have been observed by Lingane [18] during reduction of perrhenate in various buffer solutions, and, later by us during the reduction of perrhenate in a sulfuric acid medium [19].

As is evident from Tables 1 and 2, in which the number n calculated from the slope of the straight lines constructed within the coordinates $\log i/(i_d - i) - E$, is given, reduction of the halogenates is irreversible. This might have been expected since the anion being reduced suffers profound changes in composition.

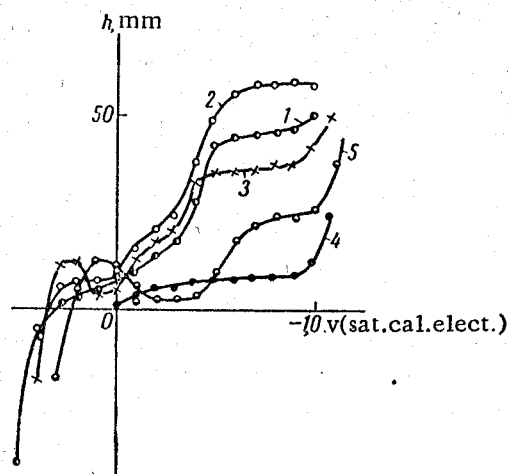


Fig. 2. Polarograms of 8×10^{-3} M iodate solution. Sulfuric acid concentration: 1) 6 N; 2) 10 N; 3) 14 N; 4) 22 N; 5) 26 N.

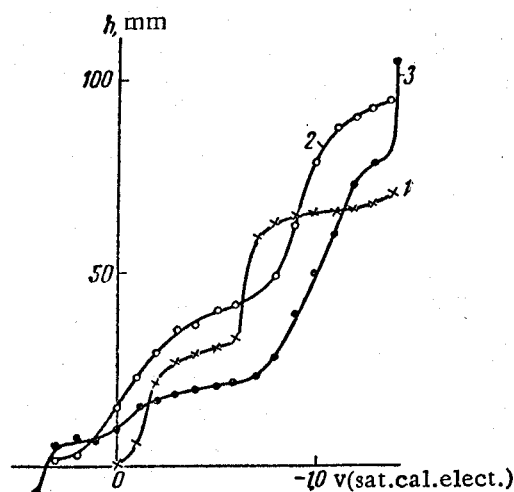


Fig. 3. Polarograms of 2×10^{-3} M iodate solution. Sulfuric acid concentration: 1) 2 N; 2) 6 N; 3) 14 N.

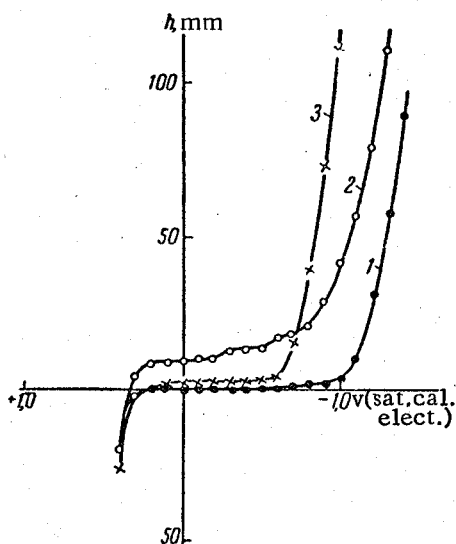


Fig. 4. Polarograms of 10^{-3} M iodate solution in a supporting electrolyte of concentrated sulfuric acid solutions: 1) 18 N sulfuric acid without iodate; 2) 18 N sulfuric acid; 3) 30 N sulfuric acid.

Comparison of the results obtained during polarographic studies of chlorate, bromate, and iodate, shows that the reducibility of these ions increases from chlorate to bromate and iodate.

The presence of several waves on the polarograms of iodate and bromate confirms the qualitative changes which occur in solution under the influence of sulfuric acid, while the inconstancy of the half-wave potential within the limits of these separate waves testifies to the instability of the systems formed, and to their simultaneous coexistence in the test solution.

Results of potential measurements in the absence of a current also point to these qualitative changes which are connected with the appearance of new forms which are distinguished by higher oxidation potentials.

2. Measurement of Potential in the Absence of Current. The potentials were measured on a PPTV-1 potentiometer. * The indicator electrode was a smooth platinum wire. The reference electrode was a saturated calomel electrode. The temperature of the solution was $25 \pm 1^\circ$. Measurements are carried out 5 minutes after addition of the halogenate to the acid solution.

It should be pointed out that the experimental determination of the potentials of the systems halogenate-halide are impossible in actual fact, since halide ions in an acid medium are oxidized by halogenate with formation of a free halogen (the values given in textbooks are obviously calculated on the basis of Luther's law from the potential values of the systems halogenate-halide and halogen-halide). Accordingly, in our experiments, the solutions only contained halogenate (4×10^{-3} M) and from 2 to 36 N sulfuric acid.

Results of these measurements are given in Fig. 5. When the values which we obtained in 2 N sulfuric acid are compared with the values of the normal potentials (as is well-known, the values of the normal potentials of

*V. P. Gladyshev took part in this work.

the oxidizing agent correspond usually to 2 N sulfuric acid), what is immediately striking is the directly contradictory way in which the potentials change, namely

	Chlorate	Bromate	Iodate
The potential which we measured in a 10^{-3} solution of halogenate in 2 N sulfuric acid	± 0.39	+ 0.41	+ 1.12
The normal potential of the halogenate system (free halogen according to Latimer [20])	+ 1.47	+ 1.52	+ 1.20
The normal potential of the system halogenate-halide ions [8]	+ 1.44	+ 1.42	+ 1.08

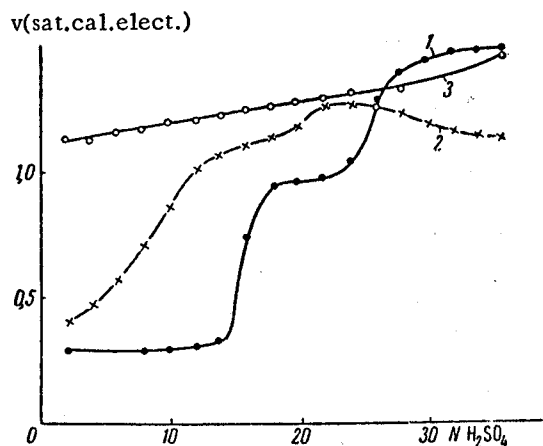


Fig. 5. Relation between the potential of 10^{-3} M solutions of the halogenates (in the absence of a current) and the sulfuric acid concentration: 1) chlorate; 2) bromate; 3) iodate.

Thus, in 2 N sulfuric acid, iodate is the stronger oxidizing agent. This fact is in good agreement both with the results given above of our experiments, and with the observations and calculations of Sammet [21], who found that the equilibrium constant, on switching from halogen decreases from chlorate to iodate, and that consequently, the oxidizing capacity of iodate is higher than that of the other halogenates.

With increasing sulfuric acid concentration, the potential of the iodate increases uniformly, while the potential of the chlorate increases stepwise, indicating sudden changes in the composition of the solution. Bromate occupies an intermediate position between iodate and chlorate (Curve 2, Fig. 5). The slight drop which occurs at high sulfuric acid concentrations should presumably be related to the limited solubility of bromine in concentrated sulfuric acid. Where this is not the case, then, in all probability, at high acid concentrations, the curve for bromate would be located at approximately the same potentials as for the chlorate curve, and would intersect the iodate curve just like the chlorate curve does. Or, putting it in another way, the published order of the sequence of the potentials according to their potentials (chlorate, bromate, and iodate) could be achieved in real conditions when the sulfuric acid concentration exceeds 27 N (Fig. 5).

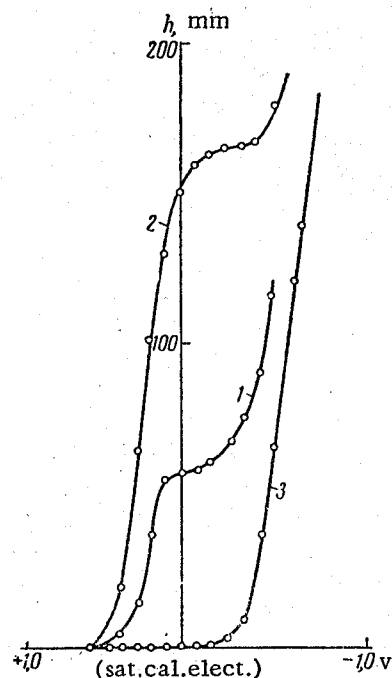


Fig. 6. Polarograms of a 10^{-4} M solution of iodate in a supporting electrolyte of sulfuric acid (platinum electrode). Sulfuric acid concentration: 1) 2 N; 2) 4 N; 3) supporting electrolyte, the curves coincide for all acid concentrations.

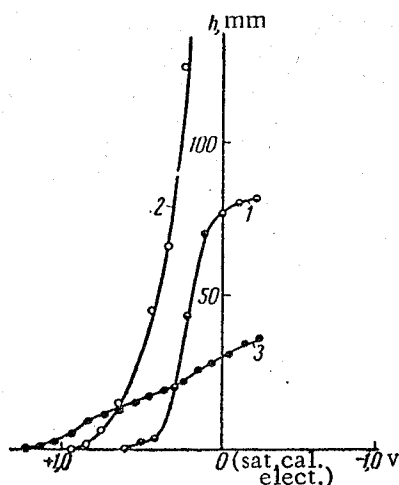


Fig. 7. Polarograms of 10^{-3} M solutions of the halogenates (platinum electrode). 1) Iodate; supporting electrolyte 16 N sulfuric acid; 2) bromate, supporting electrolyte 16 N sulfuric acid; 3) chlorate; supporting electrolyte 22 N sulfuric acid.

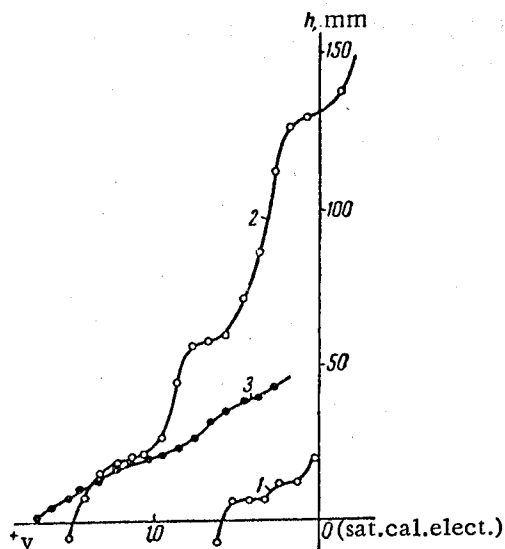


Fig. 8. Polarograms of 10^{-3} M solutions of the halogenates (platinum electrode) in a supporting electrolyte of 30 N sulfuric acid; 1) Iodate; 2) bromate; 3) chlorate.

3. Polarography with a Rotating Platinum Electrode. The setup used was the same as that described above, with the exception that the dropping-mercury electrode was replaced by a rotating platinum electrode (a wire ~ 3 mm long and 0.5 mm in a diameter; the rotational rate was ~ 400 rpm).

Results of the experiments are given in Figs. 6-9.

In Fig. 6, which relates to 2-10 N acid, are given typical reduction curves for iodate alone. The wave height is proportional to the acid concentration. The potential at which the wave starts is + 0.6 volt., i.e., it appears at a considerably more positive potential (by almost 0.6 volt) than on a dropping-mercury electrode. At the acid concentrations indicated, no reduction curves were observed on the polarograms for chlorate and iodate. It should be emphasized that reduction of chlorate on a platinum electrode generally does not occur in practice, even at the hydrogen reduction potentials: a specially conducted "macro test" (current density 0.2 amp/cm^2 , electrode surface 1 cm^2) showed that after prolonged electrolysis (more than 2 hours) of a solution of chlorate in 2 N sulfuric acid (chlorate concentration 10^{-2} M) which was accompanied by intense liberation of hydrogen, only a slight opalescence appeared on addition of silver nitrate. When the same experiment was repeated with a mercury electrode, the chlorate was reduced almost completely in a matter of minutes.

At acid concentrations ranging from 12 to 22 N (Fig. 7), reduction currents are observed for all three halogenates. Iodate gives a wave similar to that described above, but its height is lower, presumably, as a result of an increase in the viscosity of the sulfuric acid solution. The reduction potential does not change with increasing acid concentration—this indicates that either the same products that were reduced at lower acid concentrations are reduced at the cathode, or that the new materials formed in the solution are reduced at the same potential as the iodate itself. Actually, on taking polarograms of a solution containing known amounts of iodate and free iodine simultaneously, we again observed only one wave which coincided in potential with the wave obtained when no free iodine had been added.

It should also be pointed out that the final product of the electrode reduction of iodate—iodide ions cannot exist in acid solutions at the same time as iodate, since it reacts with the latter according to the equation $10 \text{ IO}_3^- + \text{I}^- + 6\text{H}^+ \rightarrow \text{I}_2 + 3\text{H}_2\text{O}$.

Free iodine, as is well-known, is readily reduced on a platinum electrode, and the reduction product (iodide) is again oxidized by iodate according to the equation just given. Thus, apparently, only free iodine is subjected to electrode reduction, while reduction of the iodate proceeds mainly as the result of a chemical reaction in solution.

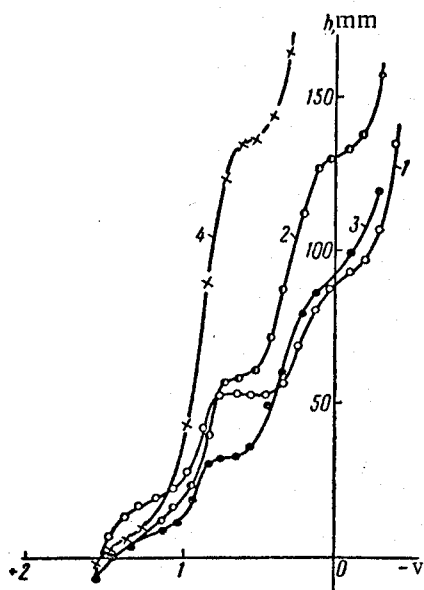


Fig. 9. Polarograms of a $8 \cdot 10^{-4}$ M solution of bromate in a supporting electrolyte of concentrated sulfuric acid. Acid concentrations: 1) 28 N; 2) 30 N; 3) 32 N; 4) 34 N.

reduction wave starts at approximately + 1.5 volt. The presence of three steps on the wave indicates reduction of the three different interaction products mentioned above, which are formed from the bromate and the concentrated acid, namely—bromine dioxide, free bromine, and, possibly, free oxygen [20]. It should be pointed out that in such solutions liberation of gas bubbles can be observed. The complexity of the relation between the wave height and acid concentration is brought out very well in the curves in Fig. 9, particularly by Curve 4. On this curve the first step (starting from positive potential values) dropped considerably in comparison with Curve 1, the second step increased by four times, while the last step went off the galvanometer scale. The start of this step occurs at a potential approximating to that for reduction of oxygen on a platinum electrode, which enables one to suggest that the wave is connected with the reduction of oxygen, and, apparently, is catalytic in character.

The results described which were obtained on taking polarograms on a platinum electrode agree very well with the way in which the potentials of the halogenates change with the sulfuric acid concentration in the absence of a current (Fig. 5). The iodate potential which is relatively high already in 2 N sulfuric acid: + 0.87 volt. (+ 1.12 volt relative to the saturated calomel electrode) does not undergo any sharp changes as the sulfuric acid concentration increases; in agreement with this, when solutions of iodate are polarographed with a platinum electrode in a supporting electrolyte of acid, only one wave is observed whatever the acid concentration.

The potentials of chlorate and bromate change very rapidly with increasing acid concentration, and the polarographic behavior of these anions on a platinum electrode changes accordingly. Thus, the potential of the chlorate remains almost constant and very low—about + 0.05 volt (+ 0.3 volt with respect to the saturated calomel electrode) right up to sulfuric acid concentrations of the order of 14 N, after which it sharply increases up to + 0.7 volt (+ 0.95 volt with respect to the saturated calomel electrode). It is precisely at the acid concentration indicated that the reduction current appears on the platinum electrode, starting at a potential of about + 1.05 (+ 1.3 volt with respect to the saturated calomel electrode). The appearance of the second step on the polarogram, when the latter is taken in a supporting electrolyte of concentrated acid (higher than 22 N), is in good agreement with the second increase in the potential in the absence of a current, which is observed at this acid concentration.

The Mechanism of the Polarographic Reduction of the Halogenates. Comparison of the experimental results obtained with the platinum and mercury electrodes draws attention to the fact that reduction on platinum occurs at considerably higher positive potentials than on mercury. Under such conditions the reduction wave is located at

In bromate solutions, in a supporting electrolyte of 12–22 N acid, the reduction currents appear at a potential of about + 1.2 volt, and the current increases so strongly that the galvanometer needle goes off the scale (even when the galvanometer is shunted to its limit). Apparently, reduction of the products formed by the interaction of bromate and sulfuric acid occurs, while the sharp increase in the current is catalytic in character.

In chlorate solutions the reduction currents only appear at acid concentrations of ~ 16 N. The potential at which reduction starts is strongly dependent on the acid concentration, and shifts to more positive values with increasing acid concentration. This is readily explained by the fact that with increasing acid concentration, the amount of the products formed by the interaction of the acid and chlorate increases. The fact that the reduction processes occur at the same time leads to a wave which is not clearly defined (Curve 3, Fig. 7).

In Fig. 8 are shown polarograms which are typical of those obtained in 24–36 N acid. The wave height of the iodate in 30 N acid is insignificant, but its potential is almost the same as of the waves in less concentrated acids. Bromate, as is evident from Fig. 8 (Curve 2) gives very clearly defined waves in 30 N sulfuric acid; the

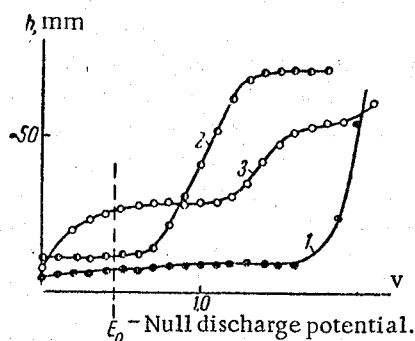


Fig. 10. Polarograms of a 10^{-4} M solution of iodate in a supporting electrolyte of dilute (10^{-3} M) solutions of sodium sulfate and sulfuric acid: 1) Sodium sulfate solution; 2) iodate in a supporting electrolyte of sodium sulfate; 3) iodate in a supporting electrolyte of sulfuric acid.

of hydrogen. Similar experiments with bromate and iodate solutions * showed that during electrolysis with a platinum electrode, in iodate solutions, immediately after switching on the current, there is observed liberation of free iodine; while in solutions of bromate, free bromine only appears several minutes after the beginning of electrolysis.

Reduction of all three halogenates occurs on a dropping mercury electrode, iodate and bromate give well defined polarographic waves; chlorate ions, which are the most electronegative as compared with bromate and iodate, do not give waves because of the overwhelming liberation of hydrogen (the wave which appears in ~ 16 N acid is caused by the reduction, not of chlorate as such, but of chlorine dioxide).

One cannot but notice that in their behavior during electrolysis the halogenates are similar to polar organic compounds, which, as is known [22], can only be electrolytically reduced on cathodes made of metals with a high overvoltage for liberation of hydrogen, in particular, on mercury.

The mechanism of the reduction of oxygen-containing anions of the halogenate type on a mercury cathode, apparently, differs essentially from the reduction mechanism of the readily reducible anions studied by A. N. Frumkin et al. In the work of Kryukova [23], Frumkin and Florianovich [24, 25], and in other articles of the Frumkin school [26, 27] it has been shown that during the polarographic reduction of persulfate, chloroplatinate, chloroiridate, and some other anions, a minimum current is observed on the polarization curve in a potential region which is more negative than the potential of the mercury zero discharge. The current drop can be eliminated by adding excess of an indifferent electrolyte. The authors of the articles cited above explain these phenomena by the fact that the electrostatic repulsion of the anion from the negatively charged surface of the cathode leads to a drop in the concentration of the anion near the cathode. Cations which enter into the composition of a double salt on addition of an excess of an indifferent electrolyte facilitate the approach of the anions to the cathode.

However, during reduction of such anions as MnO_4^- and HgI_4^{2-} , Florianovich and Frumkin [25] did not observe current minima. This phenomena has not been explained in the articles cited above. In our opinion the most likely reason for such "anomalous" behavior on the part of anions of the type MnO_4^- , is that these anions oxidize the mercury of the electrode, and the wave which is observed when polarograms are taken of solutions of these oxidizing agents is determined by the reduction of mercury ions formed as the results of the chemical reaction of the latter with the solution. It should be noted that Kolthoff and Orlemann [14] when working with iodates and bromates pointed out the necessity of removing the mercury pool from the electrolyzer in order to avoid accumulations of mercury ions in solution. We have pointed out the fact that permanganate oxidizes mercury during polarographing earlier [17]. Kivalo and Laitinen hold the same view with respect to chloroplatinate [28]. As for the complex anion HgI_4^{2-} , which was mentioned above, it too is an oxidizing agent as far as mercury metal is concerned.

*K. Sagadieva took part on this work.

potentials where reduction of hydrogen does not yet occur. This fact compels one to assume that the mechanism of reduction on platinum and on mercury is different, thus: on a platinum electrode, in the main, it is not halogenate anions that are reduced, but the products of the interaction of the halogenates with sulfuric acid—molecules of the halogen dioxides and free halogens. Direct reduction of a halogenate anion on platinum can occur, apparently, only in the case of the iodate, the one that is most readily deformed of the three anions considered, and the one which possesses a sufficiently high oxidation potential in solutions of acids of any concentration (Fig. 5). However, as soon as electrode reduction of iodate occurs, then, near the electrodes there appear iodide ions which react directly with iodate; as a result free iodine is liberated, which is subsequently reduced on the electrode.

It was shown above that reduction of chlorate on platinum does not occur even during intensive liberation

In order to compare our results with those obtained by the Frumkin School, we carried out a series of experiments in which iodate solutions were polarographed in the absence of excess of an indifferent electrolyte. As is evident from the curves in Fig. 10, no current minima were observed at potentials more negative than the mercury zero discharge potential either in neutral (Curve 2) or in weakly acid solutions (Curve 3).

If it is assumed that the reduction of persulfate according to the scheme $\text{S}_2\text{O}_8^{2-} + 2e \rightarrow 2 \text{SO}_4^{2-}$, i.e., without participation of hydrogen ions, does not differ in principle from the reduction of the oxygen-containing anions which we examined, and which only proceeds with the participation of hydrogen ions, then the absence of current minima on the polarograms becomes understandable; it is explained by the fact that during the electrical reduction of the halogenates on a mercury electrode, the first act of the electrode process is the discharge of hydrogen ions. Reduction of the anions is carried out by hydrogen at the moment of its formation. The hydrogen ions in the layers near the electrode facilitate the approach of the anions to the cathode, playing, in this way, a part similar to that of the cations of the supporting electrolyte in the experiments of Frumkin, et al.

The authors wish to express their thanks to M. T. Kozlovskii for his valuable advice and help in carrying out this work.

SUMMARY

It has been shown that when polarograms are taken with a dropping mercury electrode in a supporting electrolyte of sulfuric acid:

a) chlorates are not polarographed directly; in concentrated sulfuric acid solutions (not less than 16 N) it is the products formed by the interaction of chlorate with sulfuric acid that are polarographed;

b) bromates and iodates are polarographed even in dilute sulfuric acid, and in the case of bromates one clearly defined wave is observed, while in the case of iodates two clearly defined waves are observed.

It has been shown that bromate and iodate oxidize the mercury of the electrode, as a result of which a wave for the reduction of mercury ions appears on the polarograms.

It has been shown that, in the main, it is not the halogenates which are subjected to reduction on a platinum electrode, but the products of their interaction with sulfuric acid.

It has been shown that there is a complex relation between the wave height and the sulfuric acid concentration, as a result of simultaneous changes in the composition of the solution and in its viscosity.

The potentials of the halogenates in sulfuric acid of various concentrations have been measured in the absence of a current, and a relation has been established between the value of these potentials and the reducibility of the halogenates on dropping mercury and platinum cathodes.

On the basis of the experimental results obtained, some observations are made regarding the mechanism of the reduction of the halogenates.

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