STUDY OF THE MECHANISM OF THE ELECTROCHEMICAL FORMATION OF OXYGEN COMPOUNDS OF CHLORINE BY ANODE POLAROGRAPHY

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The formation of a whole series of oxygen compounds of chlorine in addition to Cl_2 and O_2 is possible in the electrolysis of solutions of Cl^- and HCl. The anode formation of the ClO_4^- ion by oxidation of the Cl^- ion may be represented as a stepwise oxidation [1, 2]:

$$Cl^- \xrightarrow[+O]{-2e} ClO^- \xrightarrow[+O]{-2e} ClO_2^- \xrightarrow[+O]{-2e} ClO_3^- \xrightarrow[+O]{-2e} ClO_4^-. \tag{1}$$

Schemes of oxidation-reduction of chlorine in acid and alkaline solutions [3] show that Cl_2, HClO, ClO^-, ClO_3^-, and ClO_2 are thermodynamically stable in acid solutions. ClO^- may also be thermodynamically stable in alkaline media. In certain potential regions, these intermediate products may exist in measurable concentrations together with the starting materials and final reaction products [4]. Therefore, the kinetics of the subsequent oxidation of these products has a substantial effect on the direction of the electrochemical process.

In the present work we studied the kinetics and mechanisms of separate stages of the anode oxidation of chlorine: $ClO^- \rightarrow ClO_2^-$ and $ClO_2^- \rightarrow ClO^-$ (or ClO_2^-). The results of the investigation of the stages $Cl \rightarrow ClO_3^-$ and $ClO_3^- \rightarrow ClO_4^-$ have already been published [5]. It was shown that the rate and mechanism of the oxidation of Cl^- ions on a platinum electrode depends to a considerable extent on the HCl concentration.

Little light has been shed on the theory of the electrochemical oxidation of these compounds in the literature [6-8]. On the basis of a comparison of polarization curves plotted in solutions of alkali, chloride, and hypochlorite, Foerster and Müller [9] found that ClO^- is oxidized at a potential of approximately 1.1 v, i.e., less positive than the potential of Cl_2 liberation. The mechanism of the oxidation of ClO^- to ClO_3^-, according to three schemes presented by Foerster [9], excludes the possibility of the stepwise oxidation $ClO^- \rightarrow ClO_2^- \rightarrow ClO_3^-$ and does not allow for the effect of the state of the surface of the anodically polarized electrode on the kinetics of the electrochemical process.

In the present work we used anode polarography with a rotating platinum microelectrode, described by K. I. Rozental' and V. I. Veselovskii [10]. The current strength-potential curves were plotted on a Heyrovsky polarograph. The electrode was a platinum wire, 8 mm long and 0.5 mm in diameter, rotating at a constant rate of ~ 1000 rev/min. The cathode and at the same time the reference electrode was a normal hydrogen electrode. All experiments were carried out in a nitrogen atmosphere. In addition to the polarographic investigations, we electrolyzed solutions containing ClO^- and ClO_2^- with the platinum anode at potentials corresponding to the half-wave potentials of the oxidation of ClO^- and ClO_2^- ions and determined the current yields of the main electrolysis products.

ANODE OXIDATION OF HYPOCHLORITE

Figure 1 shows curves of anode current $\underline{i}$ against φ for KClO with NaCl and KOH as base electrolytes. These curves clearly show waves for ClO^- oxidation, beginning at a potential which is considerably more negative (~ 0.3 v) than the potential of O_2 and Cl_2 liberation on platinum.

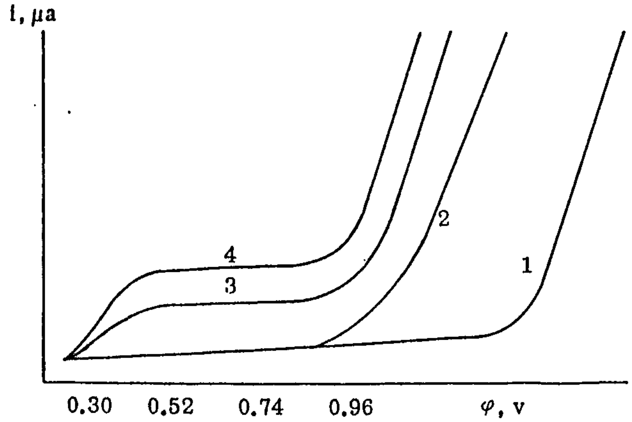

Fig. 1. Anode polarograms obtained for the following solutions: 1) 1 N NaCl; 2) 1 N KOH; 3) 1 N KOH + $4.7 \cdot 10^{-3}$ M KClO; 4) 1 N KOH + $9.4 \cdot 10^{-3}$ M KClO.

The limiting current i_d was directly proportional to the concentration of ClO^- ions (within the limits 10^{-2} - 10^{-4} M). The half-wave potential ($\varphi_{1/2}$) equaled ~0.4 v. The slope of the line of φ against $\lg \frac{i_d - i}{i}$, (0.042 v), corresponded approximately to the slope characterisitc of the two-electron oxidation of ClO^- to ClO_2^-. Similar waves for ClO^- were obtained for alkaline, neutral, and acid solutions of NaCl and Ca_2SO_4.

Figure 2 gives polarograms of ClO^- in a base electrolyte of NaCl, plotted with rotating and stationary platinum electrodes. The polarograms have a somewhat unusual form. Two different slopes were observed on the rise of the ClO^- wave. With a decrease in the KClO concentration to $2.2 \cdot 10^{-4}$ M, two waves appeared on the curve, characterizing the stepwise oxidation of ClO^- to ClO_2 with $\varphi_{1/2}$ = 0.40 v and then the oxidation of ClO_2^- to ClO_3^- (or ClO_2) with $\varphi_{1/2}$ = 1.15 v. Curves plotted under the same conditions with a stationary electrode showed only one wave for the oxidation of $ClO^- \rightarrow ClO_2^-$ since, as will be shown below, i_d of the wave for $ClO_2^- \rightarrow ClO_3^-$ (or ClO_2) depends strongly on the rotation rate of the electrode, and on a stationary electrode it is a factor of 4–5 less than on a rotating electrode.

The possibility of stepwise oxidation of ClO^- in neutral solutions has been confirmed by the work of L. M. Elina and T. S. Filippova, devoted to a study of the relation between the differential capacity of an electrode and the potential in a solution containing NaCl.

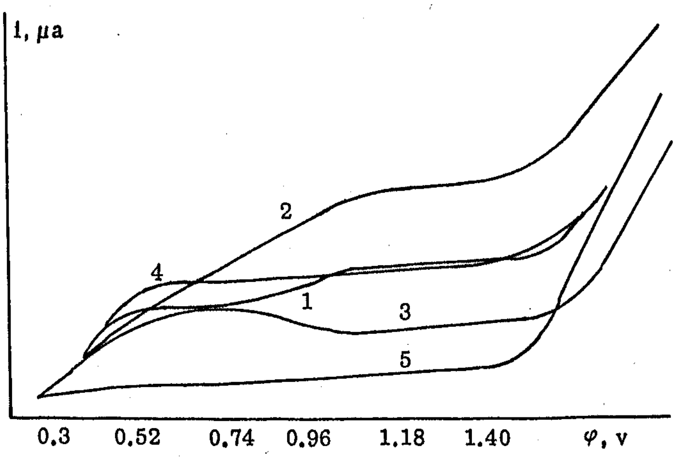

Fig. 2. Anode polarograms obtained in the following solutions:
1 N NaCl + $4.4 \cdot 10^{-4}$ M KClO
1 N NaCl + $8.8 \cdot 10^{-4}$ M KClO } on a rotating electrode
1 N NaCl + $4.4 \cdot 10^{-4}$ M KClO
1 N NaCl + $8.8 \cdot 10^{-4}$ M KClO
1 N NaCl. } on a stationary electrode

As our experiments showed, the electrochemical characteristics of ClO^- waves plotted with a base electrolyte of NaCl depended strongly on the pH. Figure 3 gives curves of i_d and the slope of the line of φ against $\lg \frac{i_d - i}{i}$ in relation to the alkalinity of a chloride solution with a constant ClO^- concentration. The curves show two sharply expressed regions:

1) A region of strongly alkaline solutions (> 0.3 N KOH) where $\varphi_{1/2}$ ClO^- = 0.38–0.40 v, i_d does not change with a change in alkali concentration, and the slope of the ClO^- wave (0.042 –0.048 v) corresponds approximately to the slope of a two-electron reaction.

2) A region of weakly alkaline and neutral solutions, where $\varphi_{1/2}$ increases to 0.65 v, i_d increases sharply, with a decrease in the concentration of OH^- ions, and the slope of the ClO^- wave increases to 0.100–0.190 v.

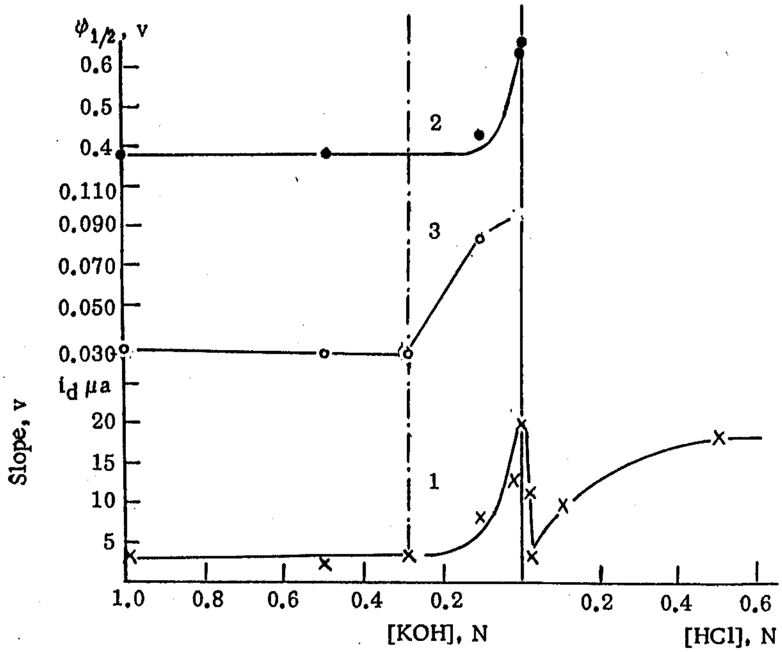

Fig. 3. Curves of the relation of $\varphi_{1/2}$, the slope of the line of φ against $\lg\frac{i_d - i}{i}$, and i_d of the oxidation wave of ClO^- ions to the concentration of OH^- ions in 1 N NaCl + 2.2 · 10^{-4}M KClO.

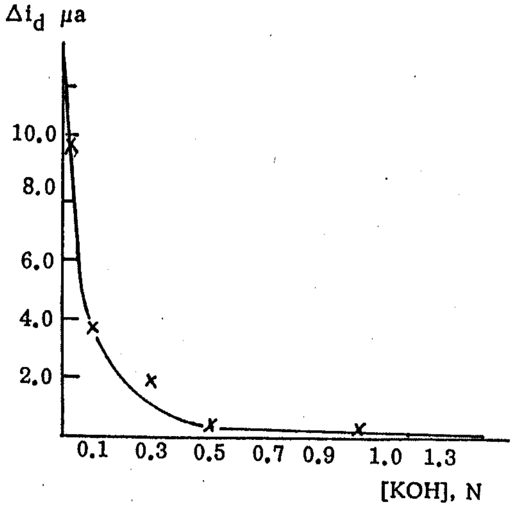

Fig. 4. Relation of the difference in the limiting currents of the oxidation waves for ClO^- ions measured on rotating and stationary electrodes to the KOH concentration. Solution composition: 1 N NaCl + 4.4 · 10^{-4} M KClO.

The complex relation of the characteristics of the ClO^- oxidation wave to the alkalinity of the electrolyte indicates a change in the mechanism of the electrochemical process with the transition from strongly alkaline to weakly alkaline and neutral solutions and also the participation of OH^- ions in the anode oxidation of ClO^-.

The electrolysis of 0.015 M alkaline solutions of KClO at low temperatures (-10-0°) and a platinum anode potential of 0.9-1.0 v showed that KClO is actually oxidized to ClO_2^- with the simultaneous discharge of OH^- ions and the liberation of free oxygen. The current yields of these processes depended on the pH of the electrolyte. The maximum ClO_2^- yield (~35%) was obtained in weakly alkaline electrolytes (0.01 N NaOH). Under these conditions, in addition to ClO_2^-, the electrolyte was found to contain ClO_3^- and ClO_2, which were probably formed as a result of further anode oxidation of ClO_2^-. In strongly alkaline solutions, the bulk of the current was consumed in the discharge of OH^- ions and the ClO_2^- yield was only 9-10%. On the basis of the experimental material presented, it may be considered that in strongly alkaline solutions, ClO^- is oxidized to ClO_2^- according to the reaction:

$$ClO^- + 2OH^- \rightarrow ClO_2^- + H_2O + 2e.$$

In neutral and weakly alkaline solutions, the anode oxidation is more extensive, proceeding through two successive stages: $ClO^- \rightarrow ClO_2^- \rightarrow ClO_3^-$ (partly to ClO_2).

As our experiments showed, i_d is independent of the rate of change of the potential and the state of the surface of the polarized electrode. The latter circumstance indicates that the kinetics of the process, which occurs at low anode potentials, are not determined by the rate of oxidation of ClO^- ions by oxygen adsorbed on the surface of the platinum electrode.

Figure 4 gives a curve of the relation of the difference in i_d of ClO^- waves plotted on rotating and stationary electrodes to the alkalinity of the electrolyte. As this figure shows, in neutral and weakly alkaline solutions i_d changes to a considerable extent with a change from a stationary to a rotating electrode. It is probable that in this case the rate of anode oxidation of ClO^- may be limited by the rate of diffusion of the oxidizable ions to the anode. In strongly alkaline solutions, where i_d depends little on the rotation rate of the polarizable electrode, the slow stage determining the kinetics of the anode process is the electrochemical act of the donation of electrodes by the reagent.

ANODE OXIDATION OF CHLORITE

Polarograms plotted on rotating and stationary electrodes in 1 N NaCl containing $1.2 \cdot 10^{-4}$ and $2.4 \cdot 10^{-4}$ M $KClO_2$ are characterized by the presence of sharp waves for the oxidation of ClO_2 with $\varphi_{1/2}$ equal to 1.07 v. A linear relation between i_d and the concentration of ClO_2^- ions is found over the concentration range 10^{-2} - 10^{-4} M $KClO_2$. The value of i_d of the wave depends on the conditions of diffusion of ClO_2^- ions to the electrode; on a rotating electrode, i_d is 4.5 times greater than on a stationary electrode. The electrolyte pH substantially affects the characteristics of the process studied. Reproducible ClO_2^- waves are obtained only in neutral and acid electrolytes.

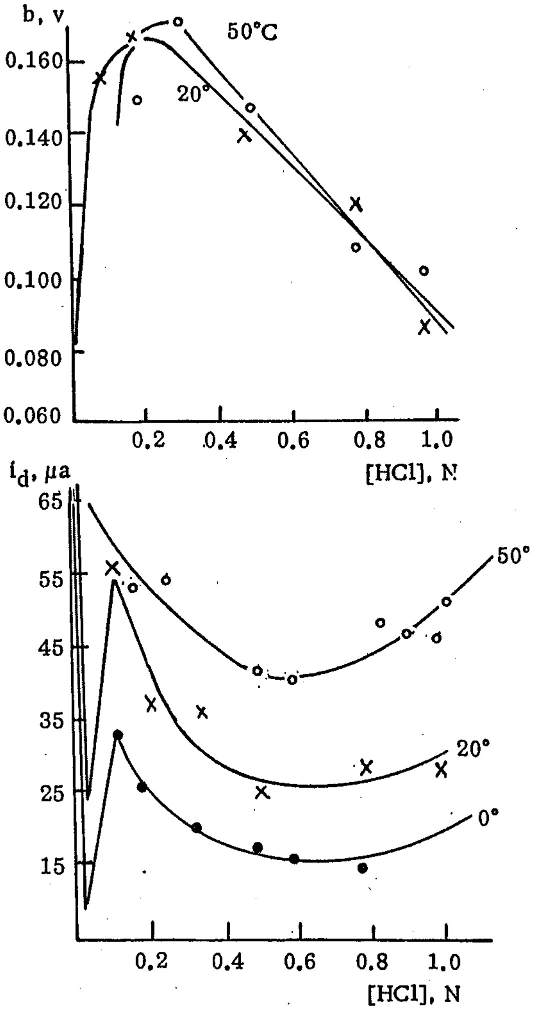

Fig. 5. Relation between the electrochemical characteristics of the chlorite oxidation wave and the acidity of the base electrolyte (1 N NaCl) at 0, 20, and 50°.
1) Slope of the line of φ against $\lg\frac{i_d - i}{i}$;
2) i_d.

Figure 5 shows curves of the relation of i_d and the slope of the line of φ against $\lg\frac{i_d - i}{i}$ of the ClO_2^- wave to the concentration of H^+ ions in the NaCl solution at 0, 20, and 50°. The curves show three clearly expressed regions of dependence of polarographic characteristics on pH, which indicates, apparently, a change in the mechanism of anode oxidation of ClO_2^- with a change from neutral to acid solutions. Analysis of the products from electrolysis of ClO_2^- solutions with a potential of 1.07-1.15 v on the platinum anode showed that ClO_2^- is oxidized to ClO_3^- and ClO_2, whose current yields depend on the pH of the electrolyte. From the data obtained it follows that at pH 7-6, ClO_2^- is oxidized mainly to ClO_3^-, whose yield reaches 75%. The remainder of the current is consumed in the formation of ClO_2. In this pH region, the limiting current of the ClO_2^- wave depends not only on the diffusion conditions, concentration of ClO_2^- ions in the solution, and the electrolyte pH and temperature, but also the rate of change of the potential and the stage of the surface of the platinum anode. This shows that under stationary diffusion conditions, the kinetics of the given anode process are determined by the rate of oxidation of ClO_2^- to ClO_3^- by oxygen electrochemically adsorbed on the surface of the platinum electrode:

$$PtO^+(O)_n + ClO_2^- \rightarrow ClO_3^- + PtO^+(O)_{(n-1)}.$$

With an increase in the acidity of the electrolyte, the ClO_3^- yield falls and the ClO_2 yield correspondingly increases, reaching a maximum value of 80% at pH 3. At pH 6-3, i_d is independent of the state of the surface of the polarizable electrode. The high slope of the ClO_3^- wave (~ 0.170 v) apparently indicates the irreversibility of the anode oxidation of ClO_2^- to ClO_2 according to the following scheme:

$$ClO_2^- \rightarrow ClO_2 + e^- .$$

The kinetics of the given process are determined by the rate of discharge of ClO_2^- ions.

Finally, at pH < 3.0, the main anode process is the oxidation of $HClO_2$ to $HClO_3$. The yield of the latter equals 70-75%. In parallel, 10-15% of the current is consumed in the formation of ClO_2.

In the region of strongly acid electrolytes, i_d of the $HClO_2$ wave depends on the state of the surface of the polarizable electrode. In this case, apparently, the rate of the anode process may be limited by the rate of oxidation of $HClO_2$ to $HClO_3$ by surface oxygen of the platinum.

LITERATURE CITED

[1] N. A. Izgaryshev, Proceedings of Conference on Electrochemistry [in Russian] (Acad. Sci. USSR Press, Moscow, 1953), p. 335.

[2] T. S. Filippov and R. D. Chausovskaya, Tr. Voenno-khozyaistvenno i Akad. RKKA 4, 117 (1951); K. G. Il'in and D. P. Semchenko, Tr. Novocherkassk. Politekh. Inst. 19, 95 (1948).

[3] W. M. Latimer, Oxidation States of the Elements and Their Potentials in Aqueous Solutions. [Russian translation; (Foreign Lit. Press, Moscow, 1954), p. 59.

[4] A. N. Frumkin, V. S. Bagotskii, Z. A. Iofa, and B. N. Kabanov, Kinetics of Electrode Processes [in Russian] (Moscow State University Press, 1952), p. 194.

[5] E. I. Yakovleva, K. I. Rozental', and T. S. Filippov, Zhur. Fiz. Khim. 30, 937 (1956).

[6] G. Holst, Chem. Rev. 54, 169 (1954); Ind. Chem. 42, 2359 (1950).

[7] F. Foerster and P. Dolch, Z. Elektrochem. 23, 137 (1919).

[8] F. Foerster and E. Müller, Z. Elektrochem. 8, 633 (1902).

[9] F. Foerster, Trans. Electrochem. Soc. 46, 23 (1924).

[10] K. I. Rozental' and V. I. Veselovskii, Zhur. Fiz. Khim. 27, 1165 (1953).