EFFECT OF CATIONS ON OXYGEN OVERVOLTAGE

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INTRODUCTION

The mechanism of electrolytic liberation of oxygen and also anode oxidation processes and, in connection with this, the problem of oxygen overvoltage have not been definitely clarified yet though many authors have studied this problem, which is important from theoretical and practical points of view [1]. As is known, the elucidation of the kinetics of these anode processes in addition to possible conversions of momentarily formed substances (for example, hydroxyl radicals) is hampered mainly by the fact that under the action of oxygen liberated, various oxides are formed on the surface of indifferent electrodes and, depending on the conditions, these oxides also participate in the process. Due to this the effect of experimental conditions on the reaction mechanism of an anode process is extremely varied. Therefore, a detailed study of this problem is of particular importance. The effect of a change in oxygen overvoltage on the current yield of some industrial electrolytic processes is also, in all probability, more considerable than is assumed. Thus, for example, it can be imagined that the effect of the cation of some metals on the current yield in the electrolytic formation of persulfates, which has recently been studied thoroughly by N. A. Izgaryshev and A. A. Petrova [2], may be partially explained by a change in oxygen overvoltage. However, to explain this it is necessary to study the effect of cations on oxygen overvoltage, i.e., on the polarization connected with oxygen liberation. N. A. Izgaryshev and S. Berkmann [3] established long ago that the decomposition voltage of solutions of various sulfates depends on the cation. The authors explained this by the dehydrating action of cations on anions and the acceleration of the anode process associated with it. We considered that a systematic study of the effect of metal cations would also be profitable from the point of view of this aspect of the anode process.

INVESTIGATION PROCEDURE

Polarization curves were measured by the usual method. An anode with a small surface (0.1 cm^2) was connected by means of a tube fitted with a glass tap to a cathode with a large surface immersed in the same solution. The anode potential was measured (without shutting off the current) by means of a Luggin capillary relative to a 0.1 N calomel electrode. The anode potential measured directly was recalculated relative to a normal hydrogen electrode.

Since the potential on a fresh electrode surface at constant current density changed considerably with time (probably due to the formation of surface oxides), before series of measurements the anode was polarized for an hour at a density of 0.1 amperes/cm^2. As experiment showed, the potential of anodes treated in this way did not change appreciably during a measurement at constant current density and was reproducible with an accuracy of approximately 0.01 v.

We used carefully purified, chemically pure substances. The platinum electrode was cleaned with concentrated nitric acid and the nickel electrode was obtained by smooth nickel plating of a platinum electrode.

EXPERIMENTAL RESULTS AND DISCUSSION

To study the effect of metal cations on the overvoltage of the electrolytic liberation of oxygen, we measured the polarization curves with the aid of a smooth platinum anode in 2 and 9 N H_2SO_4 without additives and with the addition of Li^+, Na^+, K^+, NH_4^+, Mg^{2+}, Zn^{2+}, and Al^{3+} and also in solutions of the corresponding sulfates. In choosing the H_2SO_4 concentrations, we were guided by the fact that no persulfuric acid or other peroxide

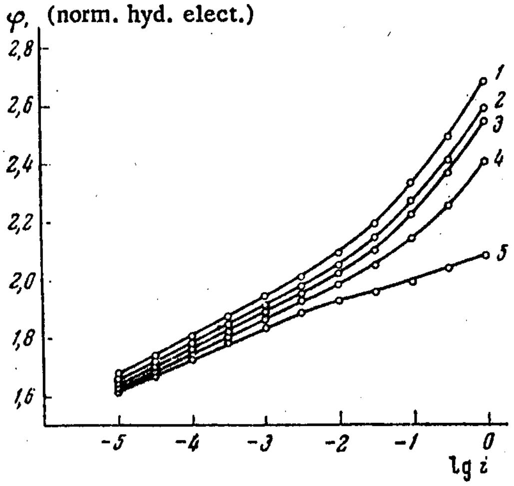

Fig. 1. Polarization curves of a platinum anode in 2 N H_2SO_4 and in the presence of sulfates of monovalent metals (over-all concentration 2 N): 1—1 N H_2SO_4 + 1 N K_2SO_4; 2—1 N H_2SO_4 + 1 N $(NH_4)_2SO_4$; 3—1 N H_2SO_4 + 1 N Na_2SO_4 + 1 N Li_2SO_4; 5—2 N H_2SO_4.

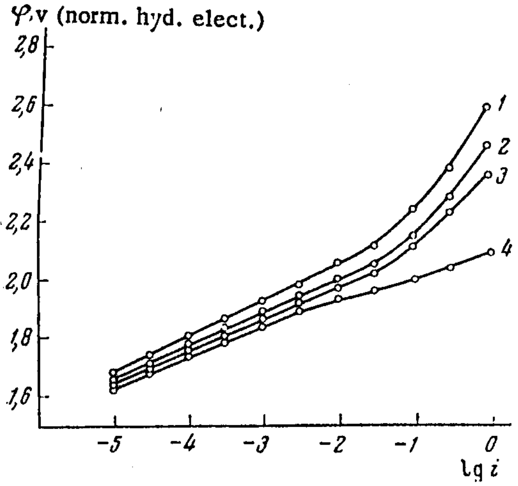

Fig. 2. Polarization curves of a platinum anode in 2 N H_2SO_4 and in the presence of sulfates of polyvalent metals 1— 1 N H_2SO_4 + 1 N $Al_2(SO_4)_3$; 2—1 N H_2SO_4 + + 1 N $ZnSO_4$; 3—1 N H_2SO_4 + 1 N $MgSO_4$; 4— 2 N H_2SO_4.

compound is formed in 2 N solution, even at a high current density, while 9 N H_2SO_4 solution is a medium favoring the formation of persulfuric acid. In addition, we studied the effect of K^+ on the potential of platinized platinum and nickel anodes and on the change in potential of a smooth platinum anode in 2 N H_3PO_4.

In all experiments, we observed (Figs. 1-7) that at low current densities 10^{-5} to $\sim 10^{-2}$ amp/cm²) the anode potential φ changed approximately linearly with the logarithm of the current density i:

$$\varphi = a + b \lg i, \tag{1}$$

where a and b do not depend on the current density. At higher current densities the polarization increased more rapidly than for a linear relationship (with the exception of pure 2 N H_2SO_4). From the change in the appearance of the polarization curve [$\varphi = f$ (lg i)] it follows that beginning at the potential φ = 1.9—2 v, the mechanism of the anode process gradually changed and in addition to the liberation of oxygen, a different electrode process also gradually developed.

Under conditions corresponding to the linear section of the polarization curve, the electrode process in acid solution undoubtedly consisted of the liberation of oxygen from water according to the following over-all equation:

$$2H_2O - 4e \rightarrow O_2 + 4H^+. \tag{2}$$

We consider that the stage determining the rate of the process is the transfer of one electron from a molecule of water adsorbed on the surface of the anode to the electrode:

$$H_2O - e \rightarrow OH + H^+. \tag{3}$$

The very active hydroxyl radical rapidly undergoes further reaction, possibly with the assistance of surface oxides of the anode, and finally forms molecular oxygen. Consequently, this part of the polarization curve shows the change in oxygen overvoltage, assuming that the reversible oxygen potential hardly changes in comparable experiments.

Effect of cations on anode potential (i = 10^{-} amp/cm^2)

Cation	Radius, Å	In 1*N* H_2SO_4 + 1*N* sulfate		In 9*N* H_2SO_4 + 1*N* sulfate		In 1*N* sulfate	
		Δφ, v relative to 2*N* H_2SO_4	*b*	Δφ, v relative to 2*N* H_2SO_4	*b*	Δφ, v relative to 1*N* H_2SO_4	*b*
K^+	1,33	0,073	0,135	0,060	0,147	0,030	0,139
Al^{3+}	0,5	0,068	0,123	0,055	0,151	0,020	0,147
NH_4^+	1,43	0,048	0,128	0,047	0,147	0,000	0,127
Zn^{2+}	0,74	0,046	0,112	0,030	0,140	—0,020	0,138
Na^+	0,95	0,028	0,125	0,030	0,148	—0,020	0,123
Mg^{2+}	0,65	0,022	0,108	0,015	0,139	—0,045	0,133
Li^+	0,60	0,018	0,118	0,015	0,143	—0,040	0,119
Pure acid	—	—	0,106	—	0,141	—	—

The deviation from linearity observed at more positive potentials indicates that, beginning at a current density of approximately 10^{-2} amp/cm^2 the rate of evolution of oxygen becomes insufficient to maintain the given current density and as a result of this, a new electrode process begins with an increase in anode potential. As the investigations of A. N. Frumkin, R. I. Kaganovich, M. A. Gerovich and V. N. Vasil'ev [4] and also E. A. Efimov and N. A. Izgaryshev [5] and other authors show, under such conditions this is apparently caused by the formation of persulfate by indirect oxidation of sulfate ions. The formation of persulfate becomes understandable if we consider that at the anode, the charge on the surface of which is positive under our experimental conditions, sulfate ions or hydrosulfate ions are adsorbed together with water molecules. As the anode polarization increases, i.e., as the electrode becomes more positive, the adsorption of anions with a negative charge increases more sharply than the adsorption of water molecules, which have a dipole character. Consequently, as the

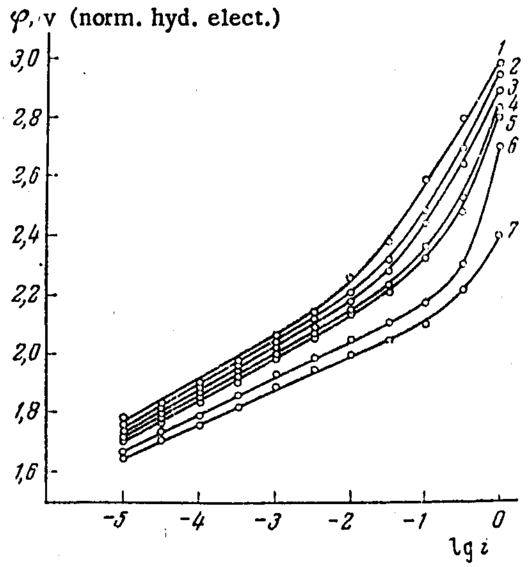

Fig. 3. Polarization curves of a platinum anode in 9 N H_2SO_4 and in the presence of 1 N sulfates of monovalent metals over-all concentration 10 N) and also in 2 N H_3PO_4 and in the presence of potassium dihydrogen phosphate over-all concentration 2 N): 1—9 N H_2SO_4 + 1 N K_2SO_4; 2—9 N H_2SO_4 + 1 N $(NH_4)_2SO_4$; 3—9 N H_2SO_4 + 1 N Na_2SO_4; 4—9 N H_2SO_4 + 1 N Li_2SO_4;5—9 N H_2SO_4; 6—1 N H_3PO_4 + 1 N KH_2SO_4; b = 0.125; 7—2 N H_3PO_4; b = 0.115.

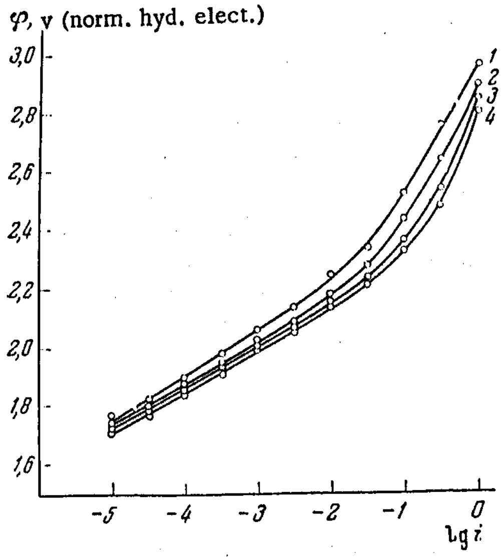

Fig. 4. Polarizarion curves of a platinum anode in 9 N H_2SO_4 and in the presence of 1 N sulfates of polyvalent metals: 1—2 N H_2SO_4 + 1 N $Al_2(SO_4)_3$; 2—9 N H_2SO_4 + 1 N $ZnSO_4$; 3—9 N H_2SO_4 + 1 N $MgSO_4$; 4—9 N H_2SO_4.

anode polarization increases, sulfate ions increasingly displace water molecules from the layers directly in contact with the anode surface. As a result of this, beginning at a certain current density, depending on the experimental conditions, the surface concentration of water molecules, i.e., the replenishment of decomposing water molecules, is insufficient to maintain the given current density and consequently, with a steeper rise in anode potential the direct oxidation of sulfate ions occurs.

In 2 N (and more dilute) H_2SO_4 solutions, at high current densities, the anode polarization increases more slowly than corresponds to a linear relationship. Consequently, under such conditions the oxidation of anions does not occur and the reaction mechanism undergoes other, as yet unexplained changes. What has been stated is confirmed by direct experiment: in the electrolysis of 2 N H_2SO_4 with a current density of 1 amp/cm^2, the anode solution does not liberate iodine from KI, even over a long period. This indicates that the solution does not contain peroxide compounds. However, if the electrolysis occurs in more concentrated solutions, at a more positive potential than that corresponding to a linear relationship, the presence of peroxide compounds is detected by the given method.

When sulfates of various metals are added to H_2SO_4 solution the anode potential increases, both when the over-all electrolyte concentration is unchanged (Figs. 1 and 2) and when the H_2SO_4 concentration is constant (Figs. 3 and 4). Since under our experimental conditions the reversible potential of the oxygen electrode in the presence of various salts changes only insignificantly, the change in anode potential is approximately equal to the change in overvoltage.

Of the cations we investigated, the greatest effect was shown by the ions K^+ and Al^{3+} (at the same current density). The order of effect of the ions from the point of view of increasing the polarization of a solution whose over-all concentration equals 2 N was found to be

$$K^+ > Al^{3+} > NH_4^+ > Zn^{2+} > Na^+ > Mg^{2+} > Zi^+.$$

With an increase in potential, in the case of ions of the same valence, the value b also increases from 0.106, corresponding to pure H_2SO_4, to 0.135*, observed in a solution containing 1 N K^+.

An analogous picture is also observed in 9 N H_2SO_4 (Figs. 3 and 4 and the table), though it is evident that in the presence of metal cations under the given conditions the polarization curve deviates somewhat from a straight line, even at a low current density. In 9 N H_2SO_4 b equals 0.141 but this value increases to approximately 0.148–0.150 under the effect of metal cations. In these concentrated solutions there is hardly any difference between the effects of cations of most metals.

From the polarization increasing action of metal cations it follows that their presence reduces the rate of the stage determining the over-all process rate. If we assume that in processes corresponding to the linear section of the polarization curve, the stage determining the process rate is the transfer of electrons, then according to A. N. Frumkin [6] the following relation is true for the anode potential:

$$\varphi = a - \frac{RT}{\beta F}\ln c + \psi_1 + \frac{RT}{\beta F}\ln i, \tag{4}$$

where a is a constant;

c is the surface concentration of the substance directly transferring electrons (water in the case of the liberation of oxygen from an acid solution);

ψ_1 is a factor ($0<\beta<1$) determining the interrelation between the electrode potential and the activation energy associated with the transfer of electrons.

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*The error in the determination was several units in the third place.

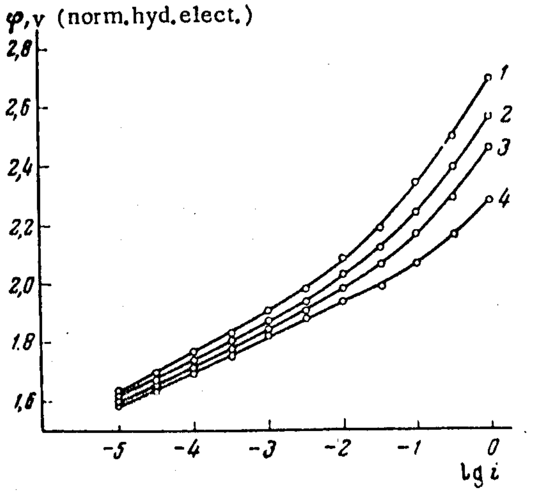

Fig. 5. Polarization curves of a platinum anode in 1 N sulfates of monavalent metals: 1–K^+; 2–NH_4^+; 3–Na^+; 4–Li^+.

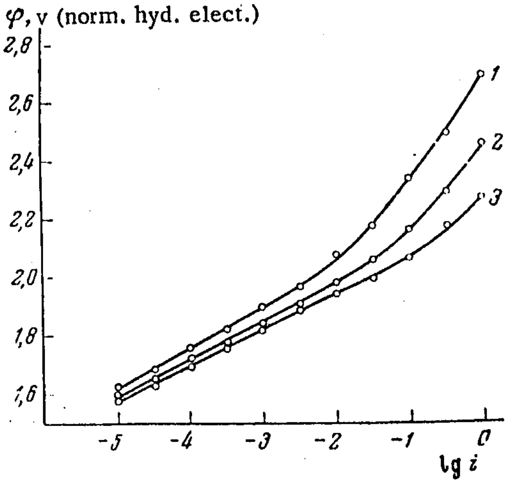

Fig. 6. Polarization curves of a platinum anode in 1 N sulfates of polyvalent metals: 1–Al^{3+}; 2–Zn^{2+}; 3–Mg^{2+}

Converting to logarithms to the base ten for room temperature we obtain

$$\varphi = a - \frac{0{,}058}{\beta} \lg c + \psi_1 + \frac{0{,}058}{\beta} \lg i.$$

Thus, if the surface concentration of the substance determining the rate of conversion and the fall in potential in the diffusive part of the double layer is constant, then according to A. N. Frumkin's theory the potential changes linearly with the logarithm of the current density and the slope of the line will be

$$b = \frac{RT}{\beta F} = \frac{0{,}058}{\beta}.$$

According to the double layer theory [7], ψ_1 depends only on the over-all concentration of the electrolyte if the effect of specific adsorption forces is not observed. Since the metal cations we investigated do not show specific adsorption on platinum and in our experiments in 2 N solutions the over-all electrolyte concentration was constant, the increase in polarization could not occur due to such a change in ψ_1, which is a function of only the over-all electrolyte concentration. In more concentrated solutions the value of ψ_1 is small (due to contraction of the diffusive part of the double layer); consequently, possible changes in it under the action of added salts could not be considerable. However, the fact that the value of the factor b increases approximately parallel with the polarization increasing action indicates that metal cations still change the structure of the double layer with respect to the activation energy of electron transfer. From the values of b obtained in our experiments in pure 2 N H_2SO_4 $\beta = 0.56$ and in 1 N H_2SO_4 β falls to 0.43. In 9 N H_2SO_4 $\beta = 0.41$; under the action of the ions K^+ or Al^{3+} this value falls to 0.39; consequently, the change in a concentrated solution is less appreciable than in a dilute one.

To explain the effect of metal cations it is necessary to assume that they are incorporated in the double layer formed on the surface of the anode. Due to the positive charge on the electrode surface under our experimental conditions, there cannot be a considerable concentration of cations directly on the metal surface; their incorporation must occur through SO_4^{2-} ions adsorbed on the surface in the second or following layers, i.e., mainly in the diffusive part of the double layer. Naturally, as a result of this, the ψ_1 potential may also change.

Metal cations do not only simply replace part of the hydroxonium ions of the double layer formed in pure acid solution, but are incorporated in the double layer to a greater extent and this is more probable as metal sulfates are less soluble in H_2O than in H_2SO_4. The presence of metal cations deforms water molecules adsorbed on the electrode surface and disrupts, i.e., changes their bonds with the other water molecules. The attractive

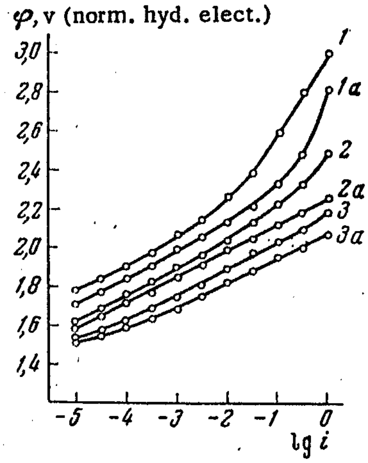

Fig. 7. Polarization curves: Smooth platinum anode—1—in 9 N H_2SO_4 and 1a—in 9 N H_2SO_4 + 1 N K_2SO_4, smooth nickel anode —2—in 9 N H_2SO_4 and 2a—in 9 N H_2SO_4 + 1 N K_2SO_4; platinized platinum anode 3—in 9 N H_2SO_4 and 3a—in 9 N H_2SO_4 + 1 N K_2SO_4.

action of metal cations, affecting the electrons of adsorbed water molecules, hinders the transfer of electrons to the electrode, increases the activation energy of this process and, by thus slowing the rate-determining process, raises the polarization. Metal cations naturally affect adsorbed SO_4^{2-} ions and their hydration envelope.

The charge of the ions is not the only decisive factor in the increase in anode polarization as the effect of the monovalent ion K^+ is greater than that of trivalent Al^{3+} at the same concentration. From this and also from the order of magnitude of the effect of monovalent ions of similar structure we may draw the conclusion that under comparable conditions ions increase polarization more strongly the greater their radius (see table). This is probably explained by the fact that cations hinder the replenishment by new molecules of water molecules decomposed at the anode or the removal of decomposition products the more strongly, the greater the cation volume.

The potential depends on the nature of the cation in pure salt solutions as in the presence of H_2SO_4 (Figs. 5 and 6). The values of b are practically the same in solutions of neutral salts of monovalent cations and in an acid solution (see table), but in a solution of polyvalent cation salts they are higher than in the corresponding acid solution. By making the comparison at identical current densities, it can be seen that the potential is 0.03–0.04 v less positive than in the presence of H_2SO_4.

The effect of metal cations is even shown at low concentrations. For example, even at a concentration of 0.01 N, K^+ ions noticeably increase the polarization in 1 N H_2SO_4. At constant, low current densities the potential increases approximately linearly with the logarithm of the concentration of K^+. This action of the K^+ ion is not connected either with the presence of SO_4^{2-} ions or with the presence of the smooth platinum surface. The potential of a smooth platinum anode immersed in H_3PO_4 solution is also raised under the action of K^+ ions (Fig. 3). An analogous picture is also observed both on platinized platinum and nickel electrodes (Fig. 7). All this confirms the opinion that metal cations increase polarization through their action on water molecules adsorbed in the double layer.

Our investigation on the increase of oxygen overvoltage by metal cations still has not solved many problems which must be solved by further investigations. However, from what has been said it is obvious that this phenomenon is one, but not the only, factor in the effect of cations on the efficiency of individual electrolytic oxidation processes.

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