ROLE OF INORGANIC IONS IN THE ELECTROLYTIC LIBERATION OF HYDROGEN FROM ACID SOLUTIONS ON A ROTATING CATHODE

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Using platinum and nickel cathodes in some of their work, G. S. Vozdviszhenskii et al. [1] established that during the electrolysis of H_2SO_4 solution the concentration of sulfates increased in the space adjacent to the cathode. This increase was even greater during the electrolysis of solutions containing added neutral salts and was accompanied by a considerable increase in pH in the layer adjacent to the cathode.

In the present communication we present the results of studying the nature of the action of some inorganic cations on the discharge of hydrogen ions on a rotating copper cathode in dilute H_2SO_4 solution.

As the cathode we used the tip of a cylindrical form, 1.3 cm in diameter, pressed onto a rotating rod and covered with a layer of electrolytic copper. The cathode polarization of the copper electrode was measured potentiometrically at +18° over a range of current densities from $5 \cdot 10^{-5}$ to $4 \cdot 10^{-2}$ a/cm^2. To the base electrolyte, which consisted of $5 \cdot 10^{-3}$ M H_2SO_4, were added Na_2SO_4, K_2SO_4, $MnSO_4$, $MgSO_4$, and $Al_2(SO_4)_3$. The concentration of added cations in the solution investigated equaled 0.2 M.

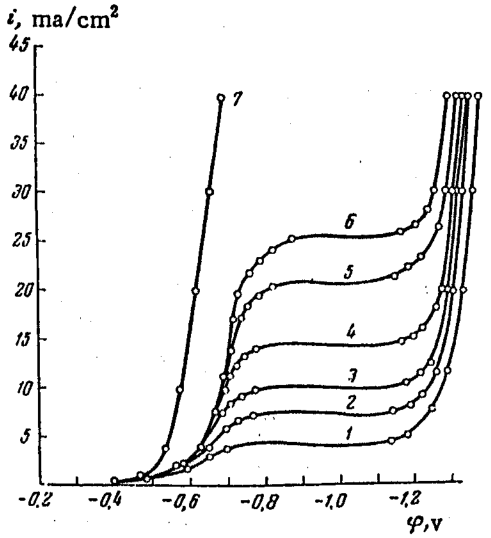

Fig. 1. Relation of copper cathode potential to current density and electrode rotation rate in $5 \cdot 10^{-3}$M H_2SO_4 + 0.2 M Na_2SO_4. 1) 3.3 rev/sec; 2) 8.3 rev/sec; 3) 16.7 rev/sec; 4) 33.3 rev/sec; 5) 66.7 rev/sec; 6) 100 rev/sec; 7) $5 \cdot 10^{-3}$ M H_2SO_4 without Na_2SO_4–3.3 rev/sec.

The results of measuring the cathode polarization of copper in a solution consisting of $5 \cdot 10^{-3}$ M H_2SO_4 and 0.2 M Na_2SO_4 with various cathode rotation rates are given in Fig. 1. The curves presented show that the presence of sodium ions in the basic electrolyte resulted in the appearance of a limiting current and a sharp displacement of the hydrogen ion discharge potential in a negative direction of approximately 0.6 v. The limiting current depended to a considerable extent on the electrode rotation rate. An increase in the cathode rotation rate from 3.3 to 100 rev/sec led to an increase in the limiting current by a factor of approximately six. A comparison of the results of investigating the cathode polarization of copper in a pure solution of $5 \cdot 10^{-3}$M H_2SO_4 (curve 7) and in H_2SO_4 with Na_2SO_4 added (curves 1-6) shows that with the addition of Na^+ ions to the electrolyte, up to the appearance of limiting current, the hydrogen ion discharge potential increased relative to the potential in pure H_2SO_4 by approximately 0.1 v. Curve 7 also shows that in $5 \cdot 10^{-3}$ M H_2SO_4 without added sodium sulfate no limiting current appeared up to a current density of $4 \cdot 10^{-2}$ a/cm^2 even at the lowest cathode rotation rate used in our experiments (3.3 rev/sec). It should be noted that in the electrolytic liberation of hydrogen from the same solution of H_2SO_4 on a stationary copper cathode, a limiting current was observed even at $2 \cdot 10^{-2}$ a/cm^2.

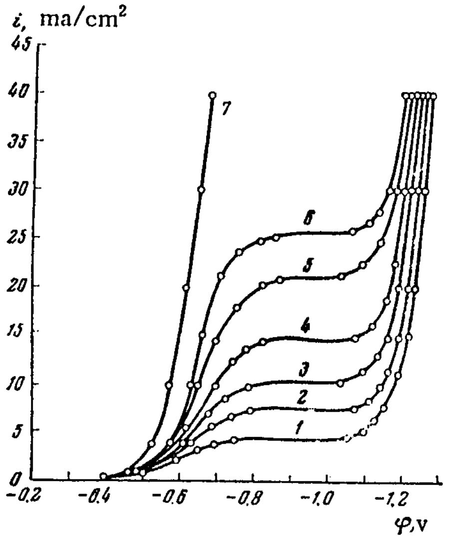

Fig. 2. Relation of copper cathode potential to current density and electrode rotation rate in $5 \cdot 10^{-3} M\ H_2SO_4 + 0.2 M\ MnSO_4$. 1) 3.3 rev/sec; 2) 8.3 rev/sec; 3) 16.7 rev/sec; 4) 33.3 rev/sec; 5) 66.7 rev/sec; 6) 100 rev/sec; 7) $5 \cdot 10^{-3} M\ H_2SO_4$ without $MnSO_4$–3.3 rev/sec.

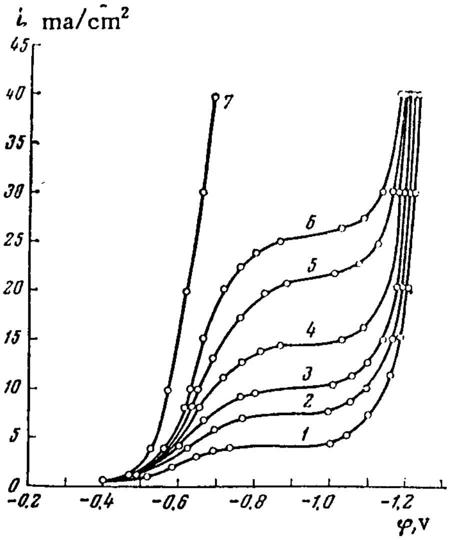

Fig. 3. Relation of copper cathode potential to current density and electrode rotation rate in $5 \cdot 10^{-3} M\ H_2SO_4 + 0.2 M\ MgSO_4$. 1) 3.3 rev/sec; 2) 8.3 rev/sec; 3) 16.7 rev/sec; 4) 33.3 rev/sec; 5) 66.7 rev/sec; 6) 100 rev/sec; 7) $5 \cdot 10^{-3} M\ H_2SO_4$ without $MgSO_4$–3.3 rev/sec.

A study of the cathode polarization of a rotating copper electrode in a solution of $5 \cdot 10^{-3} M\ H_2SO_4$ with added K_2SO_4 showed that sodium and potassium ions act identically.

Figure 2 gives data obtained in a solution of $5 \cdot 10^{-3} M\ H_2SO_4$ and $0.2 M\ MnSO_4$. The curves show that the limiting current in the discharge of hydrogen ions, produced by the addition of Mn^{2+} ions, also depends on the cathode rotation rate and changes with an increase in the rotation rate in the same sequence as under the action of Na^+ ions. The slight difference observed between the effect of sodium and magnesium ions on the electrolytic liberation of hydrogen consisted of a different increase in the hydrogen ion discharge potential at current densities above and below the limiting values. Thus, for example, while there was a difference of 0.6 v in the hydrogen-liberation potentials on a rotating copper cathode in a solution of $5 \cdot 10^{-3} M\ H_2SO_4$ with added Na_2SO_4 before and after the appearance of the limiting current, this difference produced by the addition of $MnSO_4$ was only 0.55 v.

By comparing the curves in Fig. 1 with those obtained on a rotating copper cathode in $5 \cdot 10^{-3} M\ H_2SO_4$ with added $MgSO_4$ (Fig. 3), it is easy to see that the difference in the increase in hydrogen overvoltage above the limiting current produced by Na^+ and Mg^{2+} ions is expressed even more clearly. Figure 3 shows that with the appearance of the limiting current caused by the action of Mg^{2+} ions, the hydrogen ion discharge potential is displaced by approximately 0.5 v, i.e., 0.1 v less than under the action of monovalent ions Na^+ or K^+.

A more detailed analysis of the data on cathode polarization obtained on the same electrode in $5 \cdot 10^{-3} M$ H_2SO_4 with added monovalent ions Na^+ and K^+ and divalent ions Mn^{2+} and Mg^{2+} shows that not only above but also below the limiting current is there some difference in the increase in the hydrogen overvoltage produced by the mono- and divalent cations. This is shown by a comparison of the hydrogen ion discharge potentials established in pure $5 \cdot 10^{-3} M\ H_2SO_4$ and in the same solution containing 0.2 M sulfates of the corresponding cations. While the difference between these potentials observed in the presence of Na^+ and K^+ ions is about 0.1 v, in the presence of the divalent ions Mn^{2+} or Mg^{2+}, it is less and equals approximately 0.05 v. Moreover, as Figs. 1 - 3 show, all the cations studied have the same effect on the limiting current, its dependence on the copper electrode rotation rate, and thus on the hydrogen ion diffusion rate.

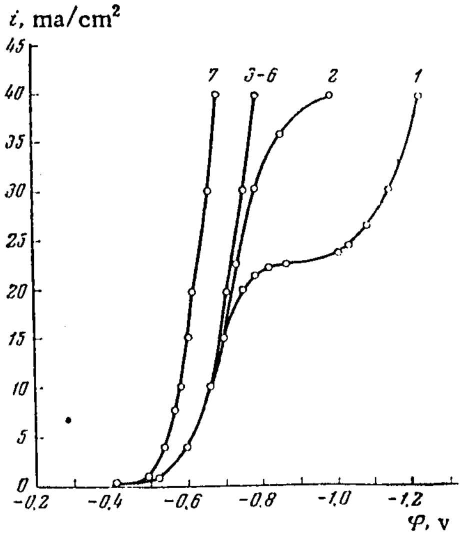

Fig. 4. Relation of copper cathode potential to current density and electrode rotation rate in $5 \cdot 10^{-3}$ M H_2SO_4 + 0.2 M $Al_2(SO_4)_3$. 1) 3.3 rev/sec; 2) 8.3 rev/sec; 3) 16.7 rev/sec; 4) 33.3 rev/sec; 5) 66.7 rev/sec; 6) 100 rev/sec; 7) $5 \cdot 10^{-3}$ M H_2SO_4 without $Al_2(SO_4)_3$ – 3.3 rev/sec.

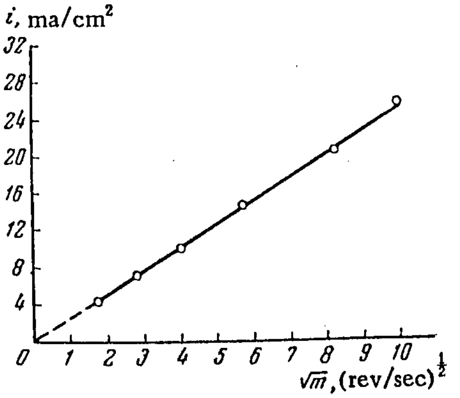

Fig. 5. Relation of the limiting current of hydrogen ion discharge to the square root of the rotation rate of the copper electrode in the solution $5 \cdot 10^{-3}$ M H_2SO_4 + 0.2 M Na_2SO_4.

Although the data presented are as yet insufficient for a conclusive elucidation of the reasons for the different actions of the cations investigated on the hydrogen ion discharge potential before and after the appearance of the limiting current, they provide grounds for considering that the action of Na^+, K^+, Mn^{2+}, and Mg^{2+} ions is closely connected with their actual nature, important characteristics of which are the solvation energy [2] and the degree of dissociation of their hydroxides [3]. These factors may play all the more important a role in that, as the investigations show, the limiting current of hydrogen ions arising under the action of these inorganic cations is closely connected with a sharp change in pH, not in the whole mass of the electrolyte, but mainly in the layer adjacent to the cathode alone.

The hypothesis presented on the role of the very nature of inorganic ions, which are capable of producing a limiting current, is confirmed by data obtained by the addition of 0.2 M $Al_2(SO_4)_3$ (Fig. 4). The polarization curves presented show that the limiting current of hydrogen ion discharge is observed only at the slowest rotation rate of the copper cathode, i.e., at 3.3 rev/sec. With an increase in the rotation rate of the cathode to 8.3 rev/sec, a limiting current arises only at the highest current densities used in the present experiments, i.e., equal approximately to $4 \cdot 10^{-2}$ a/cm². A further increase in the electrode rotation rate increased the limiting current so much that it was beyond the limits of the current densities we investigated.

The considerable increase in the supply of hydrogen ions to the cathode surface in the presence of aluminum ions in comparison with other cations, used as additives, may apparently be explained by the very nature of aluminum ions.

According to literature data [3], the following reactions occur in aluminum sulfate solutions:

$$Al^{3+} + H_2O + SO_4^{2-} = AlOHSO_4 + H^+; \quad (1)$$

$$2AlSO_4^+ + 2H_2O = (AlOHSO_4)_2 + 2H^+. \quad (2)$$

As a result of these reactions and also due to the amphoteric properties of aluminum hydroxide in the layer adjacent to the cathode, there is considerable hindrance to the sharp change in pH which is observed when mono- and divalent cations are present.

By comparing the polarization curves presented in Figs. 1 - 4 and considering the effect of the cathode rotation rate on the magnitude of the limiting current of hyrdogen ion discharge, we made an attempt to check some aspects of the diffusion theory in a stirred solution, developed by V. G. Levich [4]. According to this theory, the limiting current with concentration polarization is proportional to the rotation rate of a disc electrode to the power 0.5. As is known, this relation, which was checked in practice, gave results which agree well with theory for amalgamated copper and silver disc electrodes [5]. As Fig. 5 shows, the relation of the limiting current to the square root of the rotation rate of the copper electrode in $5 \cdot 10^{-3}$ M H_2SO_4 with the addition of 0.2 M Na_2SO_4 is also expressed by a straight line. Analogous data were also obtained with the addition of K^+, Mn^{2+}, and Mg^{2+} ions. We used the results obtained to calculate the diffusion coefficient of hydrogen ions in $5 \cdot 10^{-3}$ M H_2SO_4 + 0.2 M Na_2SO_4; it equaled $2.0 \cdot 10^{-5}$ cm^2/sec. The same value for the diffusion coefficient was also obtained in the other electrolytes investigated both with mono- and divalent cations.

A comparison of the results obtained by studying the effect of inorganic ions on the hydrogen overvoltage on copper and also chromium and aluminum rotating cathodes, which we investigated previously [6], leads to the conclusion that the mechanism of the action of the cations studied is analogous in all cases and appears mainly as a change in the concentration polarization of hydrogen ions in the layer adjacent to the cathode.

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