THE INFLUENCE OF HALIDE IONS AND ORGANIC SURFACE-ACTIVE AGENTS ON THE DISCHARGE OF HYDROGEN IONS AT A COPPER ELECTRODE IN ACID SOLUTIONS

(UDC 541.138:541.135.8-183)

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Translated from Élektrokhimiya, Vol. 1, No. 2,
pp. 230-233, February, 1965
Original article submitted March 17, 1964

In spite of the large number of papers devoted to the study of the copper electrode, the action of adsorbed substances, including halide anions, has not been studied in detail. The overvoltage of hydrogen on copper in sulfuric and hydrochloric acid solutions was studied in [1-3]. The anodic reaction has been studied in detail by many authors [4-6].

In the present paper we give the results of experiments on the study of the influence of the adsorption of certain substances on the kinetics of the discharge of hydrogen ions in H_2SO_4 solution.

Plates of pure electrolytic copper* were used as electrodes. The electrodes were treated mechanically and chemically to obtain a clean smooth surface and were subjected to electrolytic polishing in H_3PO_4 solution. After washing, the electrodes were subjected to cathodic polarization for a period of 30-40 min at $i = 10^{-2}$ A/cm² in 1 N H_2SO_4 to reduce the oxide film. The reagents were purified by recrystallization or distillation. The halides were then ignited. Before the experiment the H_2SO_4 solution was subjected to prolonged purification on platinized platinum gauze at low current density in an atmosphere of hydrogen. The cathode potential was measured by the usual compensation method at 20°C relative to an auxiliary electrode consisting of Hg_2SO_4 in 1 N H_2SO_4. At each value of the current density the potential was maintained for 2-3 min. In the determination of the cathodic overvoltage, the measured values of the potential were recalculated to the potential of a hydrogen electrode in 1 N H_2SO_4.

The overvoltage curve for the reaction of H_3O^+ ion discharge in 1 N H_2SO_4 (Fig. 1) is a Tafel straight line with coefficients $b = 0.100$ V and $a = 0.770$ V. The exchange current i_0 is equal to $2.3 \cdot 10^{-8}$ A/cm² (obtained by extrapolating the straight line to $\eta = 0$). It can be seen from Fig. 1 that the Cl^- and Br^- anions adsorbed on the copper surface decrease the hydrogen overvoltage, whereas I^- anions increase η. The decrease in η produced by Cl^- ions is greater than that produced by Br^- ions. The slope of the cathodic curves b in the presence of Cl^- ions is greater, and that in the presence of I^- ions smaller, than that in pure 1 N H_2SO_4 solution. Table 1 gives the values in mV for the stationary potentials φ_s, the overvoltage of the cathodic reaction η, and the change in this overvoltage $\Delta\eta$ for the addition of halide ions ($i = 10^{-5}$ A/cm²).

On mercury, the adsorption of halide ions decreases the hydrogen overvoltage in the order $Cl^- < Br^- < I^-$. The above complex influence of these anions in the case of a copper cathode can be attributed to their two-fold action. The specific adsorption of the anions leads to the production of a negative adsorption ψ_1-potential and, in accordance with Frumkin's theory, increases the rate of the cathodic reaction of cation discharge. This effect is observed on a mercury cathode. On certain metals, however, the bond between the halide ion and the surface atoms of the metal may become stronger, with a decrease in the energy of the bond between the hydrogen atoms and the metal. In this case, the chemisorbed halide anions decrease the rate of discharge of H_3O^+ cations and increase the overvoltage of this reaction. An increase in η and retardation of the cathodic reaction (at constant overvoltage) in the order $Cl^- < Br^- < I^-$ is observed on electrodes of iron [7, 8] and cobalt [9].

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*Quantities of impurities: Mn, Mg, Pb $< 10^{-4}$%; Zn, Sb, S $< 2 \cdot 10^{-4}$%; Bi, Se, Ag, Ni $< 4 \cdot 10^{-4}$%.

TABLE 1

Solution	φ_s	η	$\Delta\eta$	b
1N H_2SO_4	190	270	0	100
+0,1 N KCl	30	215	—55	108
+0,1 N KBr	20	240	—30	103
+0,1 N KI	—100	390	120	85

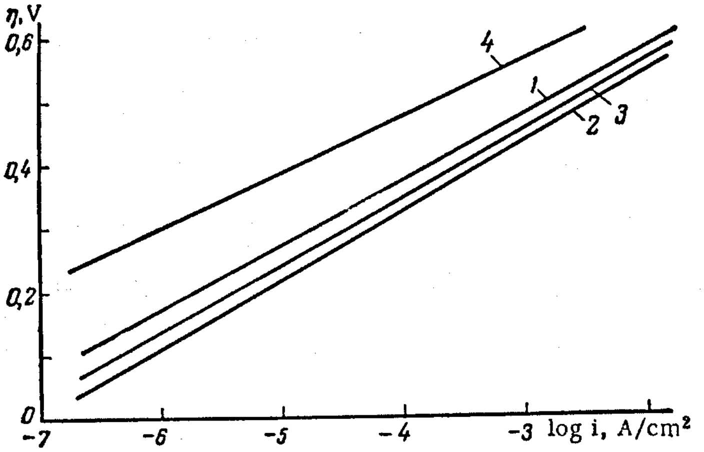

Fig. 1. Curves for the cathodic polarization of a copper electrode in 1 N H_2SO_4 with the following additives (0.1 N): 1) Without additive; 2) KCl; 3) KBr; 4) KL

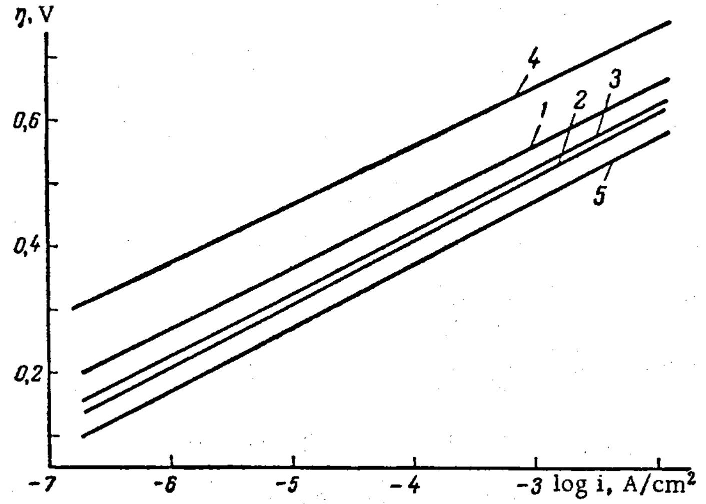

Fig. 2. Curves for the cathodic polarization of a copper electrode in 1 N H_2SO_4 + 0.005 N $N(C_4H_9)_4^+$ with the following additives (0.1 N): 1) Without additives; 2) KCl; 3) KBr; 4) K; 5) 1 N H_2SO_4 without additives.

The behavior of the copper electrode examined here is intermediate between the behavior of mercury and that of iron, as in the case of cathodes of platinum [10] and silver [11]: the specific adsorption of Cl^- and Br^- ions, as in the case of mercury, decreases η, but in the case of Br^- there is a slight increase in the strength of the bond with the copper atom, the increase becoming greater with time, as has been observed in the case of lead [12] and cad-

TABLE 2

Solution	φ_s	η	$\Delta\eta$	Solution	φ_s	η	$\Delta\eta$
1*N* H_2SO_4	190	270	0	+ TBA + KBr	30	320	50
+ TBA 0,005 *N*	210	365	95	− TBA + KI	—100	460	190
+ TBA + KCl 0,1*N*	30	305	35				

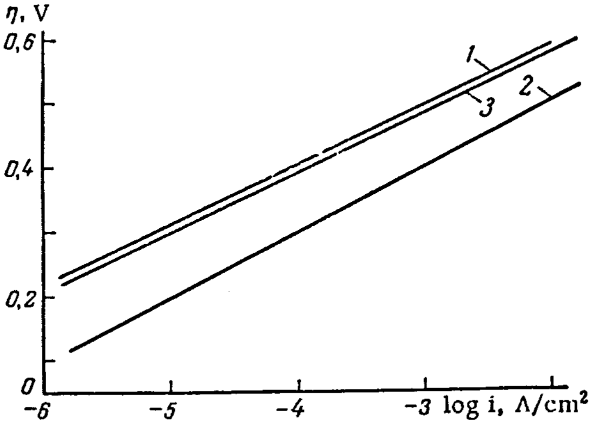

Fig. 3. Curves for the cathodic polarization of a copper electrode in 1 N H_2SO_4 with the following additives: 1) Hexyl alcohol (saturated); 2) 0.05 M sulfosalicylic acid; 3) without additives.

mium [13], so that the decrease in η is less than that observed in the presence of Cl^- ions. In the case of I^- ions a strong chemical bond with the copper atoms is rapidly formed and a considerable increase in η is observed, as in the case of iron and cobalt. The stationary potential in the presence of halide ions is displaced considerably towards more negative values in the order $Cl^- < Br^- < I^-$ as a result of the formation of complex ions of copper. In accordance with [4] this reaction can be represented in the following form: $Cu - e^- \rightarrow Cu^+$; $Cu^+ + X^- \rightarrow CuX$. The Cu^+ ions diffuse through the CuX layer and react with the X^- ions of the solution: $Cu^+ + nX^- \rightarrow CuX_n^{(n-1)}$, where X^- is the halide anion. The instability constant pK, according to the data given in [14], has the values 5.3, 5.89, and 8.76 for $CuCl_3^{2-}$, $CuBr_2^-$, and CuI_2^- respectively. The lower value of pK for the complex CuI_2^- leads to a more marked displacement of φ_s towards more negative values (Table 1).

From the curves in Fig. 2 it may be concluded that tetrabutylammonium cations are readily adsorbed on a copper electrode. This is facilitated by the negative charge of the copper surface.* As a result of the production of the ψ_1-potential of positive sign during the adsorption of these cations, the overvoltage of the cathodic reaction increases. The addition of TBA together with Cl^- and Br^- anions leads to a decrease in the overvoltage, compared with η in the presence of TBA alone. The combined presence of TBA and I^-, however, gives an additional significant increase in η. TBA cations are weakly adsorbed on Fe and Co, evidently as a result of the positive charge of the surface of these metals in H_2SO_4 solutions, and thus have a very weak action, so that in the presence of the halide anions Cl^-, Br^-, or I^-, they give an appreciable increase in the overvoltage of the cathodic reaction [8, 9].

Table 2 gives the values of φ_s and η for a copper electrode, together with the change in these quantities produced by the addition of TBA to a pure solution of 1 N H_2SO_4 and to a solution of H_2SO_4 containing halide anions ($i = 10^{-5}$ A/cm²). An interesting feature is that TBA is also adsorbed in the case of anodic polarization, for its addition to the sulfuric acid solution leads to an appreciable increase in the overvoltage of the anodic reaction of copper ionization (of the order of 100 mV at a TBA concentration of 0.005 N), but the addition of TBA to a solution containing the halide anions Cl^-, Br^-, or I^- has no influence on the anodic potential of the copper anode.

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*The electrocapillary zero for copper, according to the data given in [15], is equal to 0.1 V; the value according to data given in [16] is 0.073 V.

It can be seen from Fig. 3 that hexyl alcohol produces a very slight increase in η. The adsorption of the anions of a sulfonic acid, in accordance with the production of a negative ψ_1-potential, leads to a decrease in η (by approximately 50 mV).

LITERATURE CITED

1. G. M. Maitak, Zap. In-ta Khimii USSR, 6, 31 (1939).
2. A. G. Pecherskaya and V. V. Stender, Zh. fiz. khimii, 24, 856 (1950).
3. N. Pentland, J. O'M. Bockris, and E. Sheldon, J. Electrochem. Soc., 104, 182 (1957).
4. T. Hurlen, Acta chem. scand., 15, 1231, 1239, 1246, 630 (1961).
5. Z. Stephenson and S. Barbest, J. Electrochem. Soc., 101, 571 (1954).
6. E. Matison and J. O'M. Bockris, Trans. Farad. Soc., 55, 1586 (1959).
7. Z. A. Iofa and L. A. Medvedeva, Dokl. AN SSSR, 69, 213 (1949).
8. Z. A. Iofa, Vestn. Mosk. un-ta, No. 2, 139 (1956).
9. Z. A. Iofa and Wei Pao-Ming, Zh. fiz. khimii, 37, 2300 (1963).
10. T. P. Birintseva and B. N. Kabanov, Zh. fiz. khimii, 33, 844 (1959).
11. Ya. M. Kolotyrkin, Trans. Faraday Soc., 55, 455 (1959).
12. Ya. M. Kolotyrkin and N. Ya. Buné, Zh. fiz. khimii, 29, 435 (1955); 21, 581 (1947).
13. Ya. M. Kolotyrkin and L. A. Medvedeva, Zh. fiz. khimii, 31, 2668 (1957); 29, 1477 (1955); 25, 1355 (1951).
14. K. B. Yatsimirskii and V. P. Vasil'ev, The Instability Constants of Complex Compounds [in Russian] (Moscow, 1959).
15. L. I. Antropov, Kinetics of Electrode Processes and Null Points of Metals, New Delhi (1959).
16. B. Iakuszewski and Z. Kozlovski, Roczn. Chem., 36, 1873 (1962).