INFLUENCE OF ORGANIC SURFACTANTS ON THE COURSE OF THE DISCHARGING OF HYDROGEN IONS ON A CADMIUM ELECTRODE IN AQUEOUS SOLUTIONS

Z. A. Iofa and Saad Abdel' Vakhab

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In early studies of the kinetics of the discharging of hydrogen ions on cadmium, little attention was paid to the purity of the solutions and the state of the electrode surface; therefore, the results of these studies could not give a correct value of the overvoltage of hydrogen (η_{H_2}) and its dependence on the composition of the solution and other factors. In some studies (for example, [1]), η_{H_2} and the coefficients in the Tafel equation b are greatly elevated; in others η_{H_2} is too low, while b is elevated [2, 3]. A detailed and careful investigation of the overvoltage of hydrogen on cadmium was conducted by Kolotyrkin et al. [4-6]. They have shown that curves of η versus log i on Cd, just as on Pb and Tl, consist of two straight-line segments, corresponding to "high" and "low" hydrogen overvoltage with a 140 mV drop in 1 N H_2SO_4 and 100 mV drop in 1 N HCl, decreasing with decreasing acid concentration. This voltage drop occurs in the region of potentials close to the zero charge potential of the cadmium electrode and is associated with the adsorption of anions of the acid. The influence of the concentration of the acid and halide ions on the corrosion of cadmium was also studied.

This article presents the results of a measurement of the polarization curves (φ versus log i) under static conditions in 1 N H_2SO_4 on an electrode of high-purity cadmium (Kd-000) with an area of 3-4 cm^2. The electrode surface was cut with a sharp knife or polished with fine glass powder until a clean, smooth, shining surface was obtained, then the electrode was washed and cathodically polarized for 2-3 h with a current of 20-30 mA in a solution of acid, which was preliminarily purified by cathodic polarization on a platinized Pt mesh for 20 h. The influence of hydrogen bubbles on the measured potential was detected; in the region close to the zero charge concentration, as a result of the large angle of wetting, they adhere to the surface of the electrode, which leads to an increase in the cathode potential of 100 mV or more and of 20-40 mV in the case of a negatively charged surface. The bubbles can be removed by a stream of hydrogen or by tapping along the ground joint on which the electrode is held; in this case the potential is lowered, but in 1-3 min the bubbles again cover the electrode. The results obtained in this way were verified by experiments with a rotating electrode, representing a ring of cadmium ($\phi = 8$ mm), in the center of which there is a Teflon disk ($\phi = 3$ mm). In the case of rotation, there were no bubbles on the electrode; only one bubble appeared after some time on a Teflon disk, and this grew more rapidly the higher the current density.

The results cited below were obtained in a measurement of the potentials after the removal of bubbles from the electrode and during the establishment of bubbles from the electrode and during the establishment of adsorption equilibrium. The potentials are given according to a normal hydrogen electrode at 20°C.

The curve of φ versus log i for 1 N H_2SO_4 (Fig. 1) does not differ from that obtained in [4, 6]. From the curve of 1 N $HClO_4$, it is evident that the drop in the overvoltage occurs at lower current densities, and the overvoltage corresponding to the lower branch is 40-60 mV higher than in 1 N H_2SO_4, which is an indication of the lower adsorption activity of ClO_4^- ions in comparison with SO_4^{2-} ions.

Tribenzylamine (TBzA) cations increase the hydrogen overvoltage on cadmium (Fig. 2), as do tetrabutylammonium cations [6]. In the region of negative charges of the electrode at $i = 10^{-3}$ A/cm^2, the increase in η_{H_2} is 170, 225, and 275 mV, respectively, at concentrations of TBzA of 10^{-5}, 10^{-4}, and 10^{-3} M. At low current densities and positive charges of the electrode surface, there is a desorption of TBzA, the curves of φ versus log i approach the lower branch of the curve for the pure acid and merge with it for the indicated concentrations of TBzA at log i = 5.75, 5.10, and 6.50, respectively.

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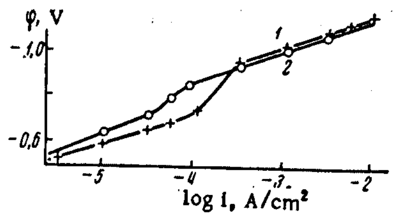


Fig. 1

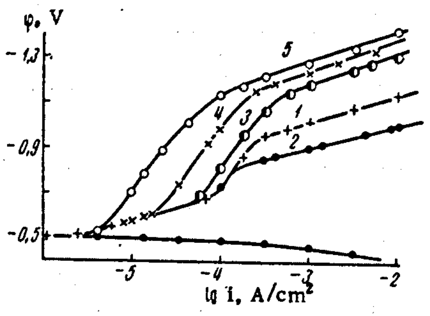


Fig. 2

Fig. 1. Cathodic polarization curves of cadmium (φ versus log i) in 1 N H_2SO_4 (1) and in 1 N $HClO_4$ (2).

Fig. 2. Curves of φ versus log i of the cathodic and anodic polarization of cadmium in 1 N H_2SO_4 (1) and with additives: 2) sat. diphenylamine; 3-5) tribenzylamine in concentrations of 10^{-5}, 10^{-4}, and 10^{-3} M.

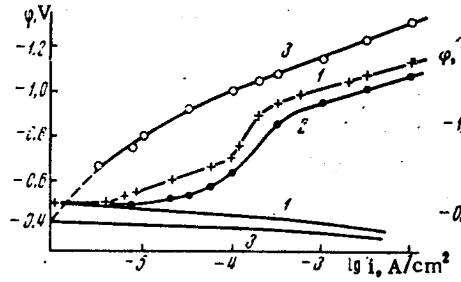


Fig. 3

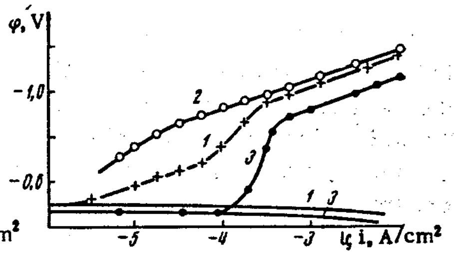


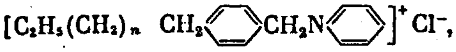
Fig. 4

Fig. 3. Curves of φ versus log i of cadmium in 1 N H_2SO_4 (1) and with additives: 2) 0.1 M potassium sulfosalicylate; 3) 0.65 g/liter catapine.

Fig. 4. Curves of φ versus log i of cadmium in 1 N H_2SO_4 (1) and with additives: 2) sat. $C_5H_{11}COOH$; 3) 10^{-6} Na_2S.

Diphenylamine (DPA), which is a weak base, also exists in acid solution partially in the form of cations; however, it does not increase, but lowers the hydrogen overvoltage (Fig. 2, curve 2). The acceleration of the reaction of discharging of hydrogen ions evidently occurs as a result of a catalytic reaction of evolution of hydrogen, which has been studied in detail for a mercury electrode [6-8]. At positive charges of the electrode surface, DPA is desorbed, and the indicated catalytic reaction stopped.

The anodic curves of the ionization of cadmium in solutions of TBzA and DPA coincide with the curve for the pure acid.

The addition of a cationic type catapine inhibitor  $[C_2H_5(CH_2)_n\ CH_2C_6H_4CH_2NC_5H_5]^+Cl^-$, where n=10, in a concentration of 0.65 g/liter leads to an increase of 150 mV in η_{H_2} and to a shift of the static potential (φ_S) by 70 mV in the positive direction. The curves of anodic polarization are also shifted in the direction of positive potentials, which leads to a slowdown of the ionization of cadmium (Fig. 3).

Sulfosalicylic acid (SSA), which dissociates into hydrogen ions and surface-active anions in solutions, lowers the hydrogen overvoltage (Fig. 3). As a result of the stronger adsorption of SSA anions on the electrode surface, which carries a positive charge, this decrease in η_{H_2} on the lower branch of the curve is larger ($\Delta\eta_{H_2} \cong 100$ mV) than at high current densities, corresponding to negative charges of the electrode surface ($\Delta\eta_{H_2} = 60-70$ mV).

Neutral molecules of caproic acid (CA), which is a weak acid, increase the hydrogen overvoltage on cadmium in a saturated solution within a broad region of potentials (Fig. 4).

TABLE 1

Solution	$\rho_g \cdot 10^6$, g/cm^2·h	$\rho_{H_2} \cdot 10^6$, g/cm^2·h
5 N H_2SO_4	2,1	2,0
Same +0,001 M TBzA	1,5	1,4
» +0,2 M SSA	5,6	5,8
» +0,1 M SSA	7,4	7,5
» +10^{-4} H_2S	36	35
» +½ sat. CA	0,30	0,28

The HS^- anions significantly lower the overvoltage of hydrogen on cadmium even in a very low concentration. In 1 N H_2SO_4, it is lowered by 80-100 mV at a HS^- concentration equal to 10^{-6} N. The potential drop begins at higher current densities than in a pure solution of H_2SO_4 at a more positive potential (Fig. 4).

The cations of tetraalkylammonium salts, as well as amines and other surfactants of the onium type, slow down the reaction of discharging of hydrogen ions in the region of potentials and charges of the surface in which their adsorption on cadmium is possible and increase the hydrogen overvoltage. The anions of strong organic acids, for example, sulfosalicylic acid, act in the opposite direction – they accelerate the indicated reaction and lower the hydrogen overvoltage. In accord with the classical theory, in all these cases the influence of the Ψ_1 potential on the kinetics of the discharging of hydrogen ions is manifested. In the case of weak organic bases, for example, diphenylamine, a catalytic process can occur [9], leading to an acceleration of the discharging of hydrogen ions and to a decrease in the hydrogen overvoltage.

Neutral molecules of organic compounds are adsorbed on the surface of cadmium, carrying both a slightly negative and a slightly positive charge. In this region of charges they increase the hydrogen overvoltage. Their action is evidently associated with an increase in the distance between the clouds of the electrical double layer and blocking of the electrode surface when large molecules are introduced into this layer.

For a comparison of the results obtained with the influence of organic surfactants on the rate of corrosion, we conducted experiments on the measurement of the rates of self-dissolution of cadmium in 5.0 N H_2SO_4 according to the weight loss of the samples (ρ_g) and the volume of hydrogen liberated (ρ_{H_2}). The results obtained (see Table 1) qualitatively confirm the conclusions that can be drawn with respect to the rate of corrosion from the polarization curves.

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