∂pH and $\partial\varphi_c/\partial pH$, which can be found from Eqs. (4) and (5). Table 1 compares the experimental and theoretical values of these derivatives and also the coefficients θ and γ.

We see that the experimental data favor slow discharge.

For a metal capable of adsorbing hydrogen, with slow electrochemical desorption the kinetic equation of the cathodic process coincides with Eq. (5) and differs from it only in the numerical value of the constant k_c [7], i.e., in this case the mechanisms of slow discharge and slow electrochemical desorption are kinetically indistinguishable. Since the data in [3, 4] indicate slow recombination with hydrogen emission during the corrosion of iron in acidic sulfate and phosphate solutions, we can suppose that the slow stage of the cathode process depends on the anion composition of the medium.

LITERATURE CITED

1. L. I. Antropov, Zh. Fiz. Khim., 27, 1631 (1953).
2. Ya. M. Kolotyrkin, Zh. Fiz. Khim., 25, 1248 (1951).
3. L. I. Antropov and Yu. A. Savgira, Zashch. Met., 3, 685 (1967).
4. M. V. Uzlyuk, Yu. V. Fedorov, L. I. Shatukhina, and L. G. Aleinikova, Zashch. Met., 11, 478 (1975).
5. V. P. Grigor'ev and V. V. Ékilik, Zashch. Met., 4, 582 (1968).
6. R. Chin and K. Nobe, J. Electrochem. Soc., 119, 1457 (1972).
7. V. V. Skorchelletti, Theoretical Electrochemistry [in Russian], Khimiya (1974), p. 402.

USE OF DISK ELECTRODE WITH RING TO INVESTIGATE THE INFLUENCE OF SURFACE-ACTIVE ADDITIVES ON THE CORROSION OF IRON IN ACID MEDIA

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UDC 620.193.01

In interpretations of the inhibiting action of additives on the corrosion of iron, it is usually assumed that iron dissolves by an electrochemical mechanism. However, a number of authors [1-3] suggest that in acid media a chemical solution mechanism is also possible.

In this connection we have attempted to elucidate the action of inhibitors not only on the overall corrosion of iron but also on the chemical and electrochemical components of the process.

We used a disk electrode with a ring in an apparatus built at the Institute of Electrochemistry of the Academy of Sciences of the USSR [4]. The experimental method and the method of calculation were described in [5]. During recording of the charging curves of an iron electrode in 0.1 N H_2SO_4 at potentials from -0.2 to -0.8 V with the potential rise rate v increasing from 0.01 to 100 V/sec, the ratio between the quantities of electricity expended on oxidation of hydrogen, Q_a, and on depositing hydrogen in the cathodic pulse, Q_c, varied as follows: when $v < 1$ V/sec, $Q_a > Q_c$; when $v < 5$ V/sec, $Q_a = Q_c$; when $v > 5$ V/sec, $Q_a < Q_c$. These changes appear to be due to the nature of the deposition of hydrogen on iron, complicated by diffusion of hydrogen into the metal. We can suppose that when $Q_c = Q_a$ the processes of hydrogen adsorption and desorption are predominant. Then the adsorption of an additive can be estimated by comparing the quantities of electricity expended in the cathodic pulse in a solution with an inhibiting additive and in the base electrolyte solution. The rate of solution by a chemical mechanism was determined with the ring electrode potential at E_R = 1.4 V and the disk electrode potential at $E_D = -0.4$ V, and the rate for an electrochemical mechanism with $E_D = -0.15$ V relative to a hydrogen electrode in the same solution. The surface-active additives were benzylamine (BA), tribenzylamine (TBA), cetylpyridinium chloride (CPC), and decyltrihydroxypyridinium chloride (DTHPC); these retard the acid corrosion of iron to different extents [6, 7].

Surface-active additives reduce the current both to the disk and to the ring electrode (Fig. 1). Thus CPC in concentrations of 10^{-6}. . . 10^{-4} mole/liter strongly inhibits the

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Translated from Zashchita Metallov, Vol. 14, No. 6, pp. 714-716, November-December, 1978. Original article submitted June 28, 1977.

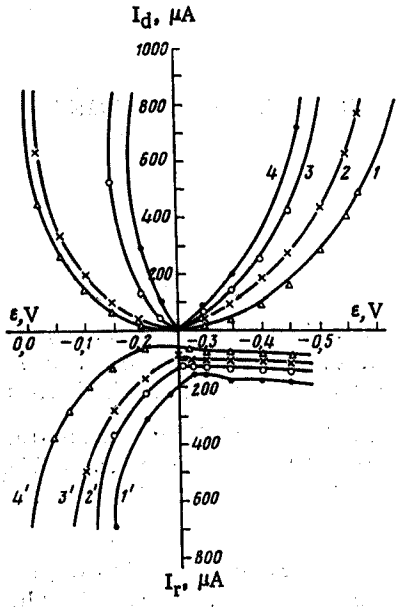

Fig. 1

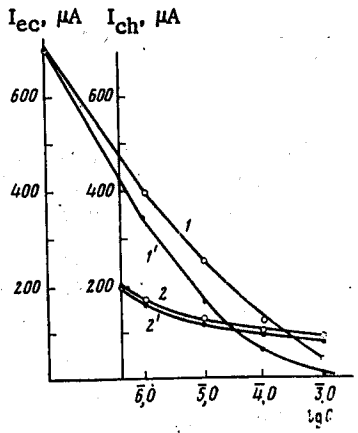

Fig. 2

Fig. 1. Polarization curves of iron disk electrode (1-4) and dependence of current of oxidation of divalent iron ions at platinum ring electrode (1'-4') vs potential of disk electrode in pure solution of 0.1 N H_2SO_4 (1, 1') and with added cetylpyridinium chloride in the following concentrations (moles per liter): 2, 2') 10^{-6}; 3, 3') 10^{-5}; 4, 4') 10^{-4}.

Fig. 2. Rates of solution of iron electrode by electrochemical (1, 1') and chemical (2, 2') mechanisms vs concentration of cetylpyridinium chloride (1, 2) and decyltrihydroxypyridinium chloride (1', 2').

cathodic and anodic processes at the disk electrode (curves 1-4) and markedly reduces the currents to the ring electrode (curves 1'-4'). The rate of solution by an electrochemical mechanism is reduced on addition of CPC or DTHPC. The rate of solution by a chemical mechanism is almost independent of the additive concentration (Fig. 2). Similar results were obtained for BA and TBA.

The predominant inhibition of the electrochemical component in comparison with the chemical component is apparently due to the fact that solution by a chemical mechanism involves direct interaction of iron atoms in a single event with the solution components (H_3O^+ etc.) and ends in direct transfer of electrons to them [2]. At low surface coverages of the metal the presence of additives on a small number of iron atoms cannot exert an appreciable influence on the chemical process. The electrochemical component is affected mainly by changes in the zeta potential, due to adsorption of the surface-active additive [6, 7]. In fact, adsorption investigations have revealed that the maximum electrode surface coverage by CPC, observed near the stationary potential for corrosion of iron, does not exceed 50% in relation to adsorbed hydrogen atoms. In the same potential range we observe maximum inhibition of the overall process.

LITERATURE CITED

1. G. M. Florianovich and Ya. M. Kolotyrkin, Dokl. Akad. Nauk SSSR, 157, 422 (1964).
2. Ya. M. Kolotyrkin, Progress in Science [in Russian], VINITI, (1971), p. 7.
3. M. A. Makhbuba and Z. A. Iofa, Zashch. Met., 3, 4 (1967); 4, 4 (1968).
4. R. Kh. Burshtein, V. S. Vilinskaya, L. L. Knots, V. I. Kushnev, B. I. Lentsner, and M. R. Tarsevich, Electrokhimiya, 8, 1183 (1972).
5. M. A. Marinich, Abstracts of Reports to Fifth All-Union Conference on Electrochemistry [in Russian], Vol. 2, Moscow (1974), p. 222.
6. L. I. Antropov, Zashch. Met., 2, 279 (1966).
7. L. I. Antropov, I. S. Pogrebova, and G. I. Dremova, Elektrokhimiya, 7, 1 (1971).