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Corrosion Effect on Iron Electrode in Presence of Heterocyclic Amines

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ABSTRACT

A relationship between the adsorption capacity of 2,2' -dipyridyl, 4,4' -dipyridyl heterocyclic amines, 1,10-phenanthrolin and Fe (dipy)₃²⁺ complex on mercury with the corrosive activity of these compounds on the iron electrode by cyclic voltammetry was established. The use of this method made it possible to establish a regularity between the process of the iron electrode ionization and the appearance of a current maximum due to the electroreduction of corrosion products on the cathode volt-ampere curves. It was found that 4,4' -dipyridyl, isomer of 2,2' -dipyridyl, has a stronger interaction of π -electrons with the surface of mercury and a flat arrangement on the surface of the electrode, which contributes to its more corrosive activity. It should be noted that 4,4' -dipyridyl is able to form polymer low solubility compounds with metal ions, whereas 2,2'-dipyridyl and 1,10-phenanthroline form chelate soluble complexes with Fe (II). Unlike molecules of 2,2' -dipyridyl, which inhibit corrosion processes, complex compounds Fe (dipy)₃²⁺, being corrosion products, lead to increased corrosion.

Keywords: Anodic dissolution, Cathodic maximum, Cyclic voltammetric curves, Initial potential, potential sweep rate.

INTRODUCTION

For conducting corrosion tests it is necessary to have information about the course of both cathode and anode processes. The most complete information can be obtained by using cyclic voltammetry allowing to establish the relationship between ionization processes and cathodic processes of their recovery. Based on the fact that many organic surfactants lead to inhibition of corrosion processes, it was expedient to use the proposed voltammetric method for evaluating the inhibitory ability of a number of heterocyclic compounds.

Gatos¹, who studied the adsorption of amines on mercury, found that the surface activity of amines on mercury changes in the same way as the inhibitory effect of these compounds in acid corrosion. The greatest inhibitory effect is possessed by nitrogen-containing amine compounds. The inhibitory effect of these compounds depends on the size and structure of organic molecules, the nature of their adsorption on the metal surface, and the protective properties of the formed or adsorbed films. The potential scale used by Andropov² makes it possible to establish a clear quantitative dependence between the surface activity of a number of compounds on mercury and their inhibitory properties in acid corrosion. The established regular dependence makes it possible to determine the inhibitory effect of the compounds on the basis of their electro capillary curves. According to Hakerman^{3,4}, the inhibitory properties of organic compounds are determined by the electron density at the atom, which is a special reaction center. With the increase of the electron density near the center adsorption (chemisorption) between the inhibitor and the metal are enhanced. It has been established^{3,4} that the protective properties of pyridine derivatives increase with increasing electron density at the nitrogen atom in the sequence of pyridine < 3-picoline < 2-picoline < 4-picoline. Along with the enhancement of the electron density at the nitrogen atom, aromatic substances have the ability to be adsorbed due to π -electrons, being oriented flat to the surface of the mercury electrode5.

It was of interest to establish a relationship between the adsorption capacity of heterocyclic amines: 2,2' -dipyridyl, 4,4' -dipyridyl, 1.10phenanthroline and Fe (dipy)₃²⁺ on mercury with the corrosive activity of these compounds on an iron electrode using the voltammetric method.

MATERIALS AND METHODS

Cyclic current-voltage curves were obtained at the potentiostat-galvanostat AUTOLAB (Netherlands) in a sealed cell, thermo stated at 25°C with a LOIPLT-105 (Russia) thermostat. The working electrode was a disc, compact iron electrode ($C_{T.3}$) with a visible surface of 0.03 cm². Rotation of this electrode was carried out on the AUTOLAB RDE-2 (Netherlands). To update the working electrode surface using abrasive paper grade MIRKA 2000 (Finland) with the electrode rotating at 2500 rpm followed by washing with distilled water. Before reproduction the current-voltage curves, the electrode was kept in a solution of sodium sulfate at E = -1.1 V for 5 minutes. As an auxiliary electrode, a platinum wire with a visible surface exceeding the working electrode surface more than 100 times was used. The potentials presented in the article were measured with respect to silver chloride electrode firm Metrohm (Switzerland) with a potential of 198 mV relative hydrogen electrode. The potential sweep rate was 15 mV / s, with the exception of cyclic volt-ampere curves obtained at different potential sweep rates. Deaeration of the solution in the cell was carried out with an inert gas of argon "x.µ". Distilled water was used to prepare the solutions. The reagents Na₂SO₄, 2,2[/]-dipyridyl and 4,4/-dipyridyl used in the work had the mark "x.µ" and "oc.µ", 2,2'-dipyridyl and 4,4'-dipyridyl of the company 'Reanal' Hungary, 1,10-phenanthroline of the company "Chemapol" Czech Republic.

RESULTS AND DISCUSSION

Figure. 1 shows cyclic voltammetric curves on an iron electrode in solutions of 0.3 M Na₂SO₄ and 0.3 M Na₂SO₄ + 5.7·10⁻⁴ M 2,2[/] -dipyridyl at different potential sweep rates, which varied from 5 to 300 mV / s. Cyclic volt-ampere curves were taken as follows: first, a cathode part of the current-voltage curves was obtained from -0.35 to -1.1 V, after reaching the potential E = -1.1 V, the direction of the potential sweep was reversed and the anode part of the current-voltage curves was obtained, reaching a value of the initial potential E = -0.35 V. Comparing the current-voltage curves in Fig. 1 it should be noted that in the presence of 5.7.10⁻⁴ M 2,2'-dipyridyl, the current value of the maximum (A) is significantly less than in the solution not containing 2,2'-dipiridyl. In this case, it should be noted that the potential of the maximum (A) at the same potential sweep rate does not depend on the content of 2,2'-dipyridyl in the solution.

A relationship is established between the current value of the maximum (A) on the cathode curve and the ionization current on the anode curve at a constant value of the initial potential E = -0.35 V. Increase of the ionization current leads to increase of the cathode current of the maximum (A). In other words, increase in the degree of the iron electrode filling with ionization products leads to increase of the cathode current of the maximum (A), caused by the electroreduction of this products.

The presence in the solution of 0.3 M $Na_2SO_4 + 5.7 \cdot 10^{-4}$ M 2,2'-dipyridyl leads to a decrease of the current maximum (A). This is due to the adsorption of 2,2'-dipyridyl on the iron electrode surface, which prevents its ionization. The decrease in the degree of filling of the iron electrode surface by the products of its ionization due to the adsorption of 2,2'-dipyridyl leads to decrease of the current value of the maximum (A) on the cathode volt-ampere curves.

The change of the current value of the maximum (A) from the potential sweep rates (V) in the coordinates IgI - IgV (Figure 2) is shown for solutions of 0.3 M Na₂SO₄ (curve 1), 0.3 M Na₂SO₄ + $1.9 \cdot 10^{-4}$ M Fe (dipy)₃²⁺ (curve 2), 0.3 M Na₂SO₄ + $5.7 \cdot 10^{-4}$ M 2,2' -dipyridyl (curve 3), 0.3 M Na₂SO₄ + $5.7 \cdot 10^{-4}$ M 1.10'-phenanthroline (curve 4).

From Fig. 2 it follows that the IgI - IgV dependence for all the solutions has a similar character. So, at a potential sweep rate (V) from 15 to 50 mV / s, the value IgI / Igv ~ 1.3, while at V > 50 mV / s this value is equal to ~ 0.3. It is established that at a potential sweep rate of V > 300 mV / s, the current value of the maximum (A) remains practically constant.

-120-80 --30--40--40--40--12--40--12--40--12--1

Fig. 1. Cyclic voltammetric curves of iron electrode in solution of $0.3 \text{ M Na}_2\text{SO}_4$ with presence of of 2,2'-dipyridyl

1) Electrolyte 0.3 M Na₂SO₄; pH = 5.9

2) 0.3 M Na₂SO₄ + 5.7·10⁻⁴ μ 2,2′-dipyridyl

The observed events are apparently related to the lifetime of the particles formed. At low potential sweep rates, the particles formed during the ionization of the iron electrode succeed in breaking down. As the sweep speed of the potential increases, these particles do not have time to undergo destruction. Under these conditions, a sharp increase of the current value of the cathode maximum (A) is observed. A further increase of the potential sweep rate leads to the fact that the proportion of particles that have not undergone destruction increases more and more, and finally, when practically all the particles that are formed do not undergo destruction, the current value of the maximum reaches a constant value.

The destruction of the formed compounds on the surface of the iron electrode at active dissolution potentials is facilitated not only by a decrease in the potential sweep rates, but also by an increase in the rotation speed of the disk electrode. Thus, at a rotational speed of the disk electrode w = 80 rpm, the current maximum at the cathode part of the cyclic volt-ampere curves is not observed. This effect is associated with an increase in the mass exchange between the particles on the surface of the electrode and the ions of the electrolyte $(0.3 \text{ M Na}_2\text{SO}_4)$.



Fig. 2. The dependence of the current value (IgI) of the cathode maximum on potential sweep rates (IgV) in solutions of:

- 1) Electrolyte 0.3 M Na SO
- 2) Electrolyte + 1.9.10⁻⁴ μ Fe(dipy),²⁺
- 3) Electrolyte + 5.7.10⁻⁴ μ 2,2[/]- dipyridyl
- 4) Electrolyte + 5.7·10⁻⁴ μ 1,10- phenanthrolin

Increasing the concentration of 2,2'dipiridyl from $1.4 \cdot 10^{-3}$ to $2 \cdot 10^{-5}$ M in 0.3 M Na₂SO₄ solution at a constant potential sweep rate of 15 mV / s results in a reduction of the maximum current (A) (Fig. 3). A similar effect occurs in the presence of 1,10-phenanthroline in 0.3 M Na₂SO₄ solution in a concentration ranging from $1.4 \cdot 10^{-3}$ to $2 \cdot 10^{-5}$ M. The presence of $2,2^{\prime}$ -dipyridyl and 1,10-phenanthroline in 0.3 M Na₂SO₄ solution leads only to a decrease in the current value of the maximum (A) without a significant change in its potential. The observed decrease of the current maximum (A) without



Fig. 3. Cyclic voltammetric curves of iron electrode in solution with presence of different concentrations of 2,2[/]-dipyridyl, V=15ìÂ/Ñ. Electrolyte - 0.3 M Na₂SO₄; pH = 5.9; Concentrations of 2,2-dipyridyl (M): 1-0; 2 -2.10⁻⁵; 3 - 6.95.10⁻⁵; 4 - 1.67.10⁻⁴; 5 - 5.39.10⁻⁴; 6 - 1.4.10⁻³



Fig. 4. Cyclic voltammetric curves of iron electrode in solution with presence of different concentrations of 4,4'-dipyridyl, V=15mV/S. Electrolyte- 0.3 M Na₂SO₄; pH = 5.9; Concentrations of 4,4'-dipyridyl (M): 1-0; 2 - $2 \cdot 10^{-5}$; 3 – 6.95 $\cdot 10^{-5}$; 4 – 1.67 $\cdot 10^{-4}$; 5 - 5.39 $\cdot 10^{-4}$; 6 – $1.4 \cdot 10^{-3}$

changing its potential and decrease the ionization current led to the conclusion that the observed effect is caused by shielding the surface of the iron electrode by heterocyclic amines.

In the works of Kolotyrkin et al.,5,6 it is noted that in the wide range of concentrations of sulfate ions and hydroxyl ions, the participation of these ions in two parallel reactions is excluded, while SO,²⁻ ions are not able to displace OH- ions. If the sulfate ions replaced the OH⁻ ions, then a decrease in the total speed would be observed, and not an increase in it. Using cyclic voltammetric curves obtained at the iron electrode in sodium sulfate solutions of various concentrations from 0.3 to 1 M, it is established that the ionization current increases with increasing of Na₂SO₄ concentration, and an increase of the current maximum (A) is observed on the cathode curves without changing its potential E = -0.97 V. If OH ions were displaced by sulfate ions, an opposite effect would be observed on the anode and cathode curves.

Dissolution of iron occurs according to the following reactions^{5,6}:

$$Fe + H_2O \leftrightarrow (FeOH)_{ads} + H^+$$
 ...(1)

$$(FeOH >)_{ads} \leftrightarrow (FeOH)_{ads} + e \qquad ...(2)$$

$$(FeOH)_{ads} + SO_4^{2-} \rightarrow FeSO_4 + OH + e$$
 ...(3)

In many respects similar data were obtained in⁷. In solutions close to neutral the anodic dissolution proceeds according to the reactions:

 $Fe + H_2O \leftrightarrow (FeOH)_{ads.} + H^+ + e$...(4)

 $Fe(OH)_{ads} \leftrightarrow FeOH^+ + e$...(5)

$$FeOH^{+} + H^{+} \leftrightarrow Fe^{2+}_{ads} + H_{2}O$$
(6)

With an increase of pH>5.5, the degree of electrode coating with the complex $(FeOH)_{ads}$ increases, and the formation of an intermediate complex Fe $(OH)_{2 ads}$ is possible.

$$(\text{FeOH})_{\text{ads.}} + \text{H}_2\text{O} \leftrightarrow \text{Fe}(\text{OH})_{2 \text{ ads.}} + \text{H}^+ + \text{e} \qquad ...(7)$$

$$[Fe(OH)_2]_{ads.} + H^+ \leftrightarrow FeOH^+ + H_2O \qquad \dots (8)$$

In the presence of anions the intermediate complexes Fe $(OH)_{2 ads}$ come into reaction:



Fig. 5. Cyclic voltammetric curves of iron electrode in solutions of (V=15mV/S):

- 1) Electrolyte 0.3 M Na₂SO₄
- 2) Electrolyte + 5.7·10⁻⁴ µ 2,2[/]- dipyridyl
- 3) Electrolyte + 5.7.10⁻⁴ µ 1,10- phenanthrolin
- 4) Electrolyte + 5.7·10⁻⁴ µ 4,4′- dipyridyl

$$Fe(OH)_{2 ads.} + 2\dot{A}^{-} \leftrightarrow FeA_{2} + 2 OH^{-} \qquad ...(9)$$

In other words, the addition of 2,2′ dipyridyl and 1,10-phenanthrolin into the solution in the concentration range under study does not lead to the destruction of FeOH_{ads} hydroxycomplex. The formation of dipyridyl and phenanthrolin complexes becomes possible after the destruction of the hydroxyl complex FeOH_{ads}, while the solution is colored red due to the reaction Fe²⁺ + 3 dipy \leftrightarrow Fe(dipy)₃²⁺ which is a qualitative reaction to iron (II). Similar processes are also characteristic of 1,10phenanthrolin.

Figure 4 shows cyclic voltammetric curves on an iron electrode in a solution of $0.3 \text{ M Na}_2\text{SO}_4$ at different concentrations of 4,4' -dipyridyl from $2 \cdot 10^{-5}$ to $1.4 \cdot 10^{-3}$ M. According to Fig. 4, in the presence of 4,4' -dipyridyl at C > $1.4 \cdot 10^{-3}$ M, the current maximum (A) on cathode curves is practically not observed. Under the same conditions, at an initial potential E = - 0.35 V, the ionization of the iron electrode does not occur.

Figure 5 shows cyclic voltammetric curves on an iron electrode in a solution of 0.3 M Na_2SO_4 in the presence of 2,2⁷ -dipyridyl, 1.10 -



Fig. 6. Cyclic voltammetric curves of iron electrode in solutions of (V=15mV/S):

- 1) Electrolyte 0.3 M Na₂SO₄
- 2) Electrolyte $3.3 \cdot 10^{-3} \mu$ 2,2- dipyridyl
- 4) Electrolyte 3.3·10⁻³ μ Fe(dipy)₃²⁺

phenanthrolin and 4,4' -dipyridyl at the same concentration $5.7 \cdot 10^{-4}$ M. From comparison presented in Fig. 5 volt-ampere curves, it follows that the greatest inhibitory effect has a 4.4' -dipiridil (Fig. 5, curve 4). The observed effect is evidently due to the higher adsorption of 4,4' -dipyridyl than to 2,2' -dipyridyl.

Adsorption studies of the above compounds on mercury were carried out in⁶⁻¹⁰. According to the experimental data8-11 adsorption energy gained when moving from a solution / air boundary to boundary solution / mercury determines the interaction energy of organic molecules with the uncharged electrode surface. (ΔG_a) for 2,2[']-dipyridyl is 10.94 kJ / mol, and for 4,4['] -dipyridyl this value is 12.57 kJ / mol^{8.9}, for pyridine the value of (is 3.81 kJ / mol11. It follows that the articulation of the dipyrine rings enhances their π -electron interaction with the surface of mercury, the greatest effect seen at 4,4' -dipiridyl. With a positive charge of mercury, when the role of the π -electron interaction increases, 4,4[/] -dipyridyl is more active at the solution / mercury boundary. The stronger π -electron interaction of 4,4[/] -dipyridyl suggests a more flat orientation of this isomer.

In amplification π -electron interaction is also indicated by the Gibbs adsorption isotherm equation (> by E) in the transition from 2,2'-dipyridyl to 4,4' -dipyridyl. This sequence reflects the change in the structure of these compounds. It should be borne in mind that such a strong effect of 4,4' dipyridyl, in contrast to 2,2' -dipyridyl, is apparently due to the fact that 4,4' -dipyridyl forms poorly soluble polynuclear compounds with iron ions in the form polymers¹², which are able to more effectively block the surface of the iron electrode. As a consequence of these processes, the ionization of the iron electrode, the degree of surface filling by the ionization products and the current value of maximum (A) on the cathode part of the currentvoltage curves are sharply reduced.

In the presence of 1,10-phenanthrolin, the ionization of iron proceeds more strongly than in a 0.3 M Na₂SO₄ solution containing 2,2' -dipyridyl. In this case, the value of the cathode current of the maximum (A) is less than in the presence of dipyridyl isomers.

Of certain interest is to establish the influence of complexes Fe $(dipy)_3^{2+}$ which should be considered as the product of corrosion processes of the iron electrode in the presence of 2.2' -dipyridyl. In Figure 6 shows cyclic voltammetric curves on an iron electrode in a 0.3 M Na₂SO₄ solution (curve 1) in the presence of $3.3 \cdot 10^{-3}$ M Fe $(dipy)_3^{2+}$ (curve 2) and $3.3 \cdot 10^{-3}$ M 2,2' -dipyridyl (curve 3). According to Fig. 6 (curve 3), the presence of $3.3 \cdot 10^{-3}$ Ì Fe $(dipy)_3^{2+}$ in the solution leads to an increase of the iron ionization and an increase of the current maximum (A) at E = -0.97 V.

Trisdipyridyl iron complexes Fe (dipy)₃²⁺ are chelate thermodynamically stable complexes Igâ₃ =17.45¹³. In terms of their kinetic characteristics, these complexes are inert, the period of halfexchange of dipyridyl with water molecules in the coordination sphere of Fe (II) is 5 hours¹⁴. At low concentrations of Fe (dipy)32+ in solution the effect of this complex on ionization of iron and the cathode maximum (A) is much like effect 2.2' dipyridyl at the same concentrations. However, in the case when the concentration of Fe (dipy),²⁺ reaches 3.3-10-3 M, the ionization of the iron electrode is sharply increased, and the current value of the maximum (A) does not decrease, as in the case of 2,2[/] dipyridyl, but increases substantially. It is not possible to explain such effect by shielding the electrode surface with adsorbed Fe (dipy)32+. The observed effect can be explained by the enhancement of the oxidizing ability of Fe (dipy),²⁺ in the Fe / Fe (dipy),²⁺ system.

CONCLUSION

Use of cyclic voltammetry of the iron electrode in solutions close to neutral pH 5.9, containing heterocyclic amines 2,2'-dipyridyl, 4,4'-dipyridyl and 1,10-phenanthrolin, as well Fe (dipy)₃²⁺ complexes in the investigated solutions allowed to establish the relationship between the ionization of the iron electrode and the appearance of a current maximum at the cathode part of the current-voltage curves.

It has been established that the enhancement of the surface activity of heterocyclic amines on a mercury electrode causes similar effect in the inhibition of corrosion processes at the iron electrode. Dipyridyl isomers having stronger π electron interaction with the surface of mercury during their adsorption on the iron electrode with a flat orientation of pyridine rings (4,4'-dipyridyl) lead to increased anticorrosive ability. It is established that an increase in the concentration of Fe (dipy)₃²⁺ corrosion products in the investigated solutions causes an increase in the corrosion processes. It is found that increasing the concentration of corrosion product Fe (dipy)₃²⁺ in the investigated solutions causes increased corrosion processes.

The observed change in the current maximum on the cathode curves in the presence of

corrosion inhibitors can be used to determine the optimum concentration of inhibitors that prevent corrosion processes.

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