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INHIBITING THE ACIDIC CORROSSION OF METALS: SURFACE AND BULK EFFECTS

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The usage of inhibitors is an efficient technological method of concurrently mitigating the summary loss of a metal, its hydrogenation, and local damage during the treatment and operation of metallic structures and parts in corrosive environments. By Antropov, the first tentative estimation of the protective effects of an inhibitor on a metal surface can be restricted to two basic mechanisms of the inhibitor action, namely, the "blockading" and "energetic" aspects [1]. In this case, the electrochemical corrosion rate in the presence of inhibitors can be given by the following relation [2]:

 $i_{\theta} = i_0 (1 - \theta) \exp(-K\theta),$ (1)

It is obvious that $i \to 0$ at $\theta \to 1$. In fact, at the ultimately high coverage, the electrochemical reaction rate has a finite value. Therefore, as was proposed in [3], it is reasonable to involve the reaction rate at the full coverage $i_0 = 1$ in Eq. (1):

 $i_{\Theta} = i_{O} (1 - \theta) \exp(-K \theta) + i_{\Theta=1} \theta$. (2) Among the reasons for the adsorption of inhibitor particles at the metal-

electrolyte boundary, people usually distinguish the following:

(1) a hydrophobic interaction between nonpolar fragments of their molecules and water [4];

(2) their salting-out from the interion electrolyte spaces as of particles with a low dielectric constant [5J;

(3) an electrostatic interaction between ions or dipoles of the inhibitor and a charged metal surface; and

(4) a donor-acceptor interaction between them.

The dispersion constituent of the metal-inhibitor interaction is usually neglected because of its small value [4].

Surfaces of the most of solids, including metals, are structurally and energetically nonuniform [6]. There fore, the surface concentration of an inhibitor A_{inh} , depends on the character of interaction between its molecules and the surface. In particular, molecules with the adsorption activity determined by factors (1)

through (3) only, i.e., those which adsorb at the outer Helmholtz plane, cannot blockade all of the adsorption centers even at the unit coverage. Chemisorbable inhibitor molecules or ions interact directly with the surface point or linear defects of various energetics, sorbing in either "on top" or "bridge" positions [7]. Different mechanisms of adsorption and interaction between inhibitors and the surface of a real defective polycrystalline metal should seemingly result in different experimental adsorption isotherms. In particular, a large scope of experimental data on the adsorption of organic and inorganic compounds on iron was analyzed in [8]. As was shown, the energetic nonuniformity of a metal does not reveal itself during the adsorption of amines and ammonium or phosphonium cations. At the same time, an iron surface behaves as energetically nonuniform in the adsorption of nucleophilic particles, such as inorganic anions, sulfur-containing compounds, and substances with multiple bonds. It is worth noting that the adsorption of particles, which can be chemically transformed, and the subsequent chemisorption of the products at the surface of corroding iron are described with Temkin's isotherm. It was clearly shown during the investigation of the inhibition and adsorption properties of sulphonium and arsonium salts [9. 10].

Thus, the adsorption of inhibitors of various nature on metal surfaces results in the adsorption layers formed at different distances from the surface atoms of a metal. Therefore, the surface coverage μ experimentally measured in impedance tests is insufficient for unambiguously judging the actual coverage of the adsorption sites, at a corroding metal surface, with the inhibitor [11].

The adsorption of inhibitors on a metal surface results not only in a decrease in the cathodic or anodic reaction rate. In most cases, linear Tafel segments of the cathodic and anodic branches of polarization curves are substantially distorted; the kinetic parameters of cathodic (i_c), anodic (i_a), and corrosion (i_{cor}) processes, such as *d* log i_c/dpH , *d* log i_a/dpH , and *d* log i_{cor}/dpH , corresponding to one or another mechanism of the cathodic or anodic reaction, are also changed [2,12, 13].

Computer modeling has shown that the limiting cathodic currents in the polarization curves can be caused by a high degree of the surface coverage μ with an inhibitor, which increases according to the known $\theta = f(E)$ dependence in terms of the Frumkin and Damaskin adsorption theory [14] in the case when the cathodic reaction of the process is limited by discharge, while the anodic reaction proceeds according to the Bockris mechanism [15]. Taking into account the dependence of the surface coverage on the pH and the potential value, as well as the theory of the effect of surface active substances on the kinetics of electrode processes [16], the $d\log_i_0/dpH$ and $d\log_i_a/dpH$ parameters measured at various pH values of the

electrolyte are shown to provide an insufficient information for determining the mechanism of a particular electrode reaction in the presence of inhibitors [3,17]. The calculated polarization curves with the aforementioned limiting cathodic currents and ceasing anodic Tafel slope given in [3] are experimentally observed in inhibited acid solutions [18-20]. For clarifying the reasons for the deceleration of the acidic corrosion of metals with inhibitors of various nature, one should analyze the regularities of adsorption on a metal surface and the related changes in the kinetics of both cathodic and anodic processes [2].

The acidic corrosion of metals involves the cathodic evolution of hydrogen

$$H_{3}O^{+} + e^{-} \rightarrow \frac{1}{2}H_{2} + HOH$$
(3)

and the anodic dissolution of the metal

$$Fe \rightarrow Fe^{2+}+2e^{-}.$$
 (4)

Reaction (3) implies three successive stages: the hydronium transport from the bulk of solution to the metal;

the discharge itself (irrespective of the mechanism, which is discussed below); and the removal of reduced hydrogen.

Reaction (4) is also multistage [21]:

the exposure of a metal atom;

its transfer in the ionic form through the phase boundary; and

the solvation of the ion.

One can inhibit the corrosion by impeding any stage listed.

Let us analyze the peculiarities of the cathodic (Eq. (3)) and anodic (Eq. (4)) processes of the acidic corrosion of iron in more detail. Taking into account the anomalously high mobility of protons, we can state that the transport stage does not control the cathodic reaction (3) in solutions in the pH range from 0 to 3. There are various hypotheses about the mechanism of the cathodic electroreduction of hydrogen on iron. As noted in reviews [2] and [22], the discharge, the electrochemical desorption, and the recombination of atomic hydrogen are considered as the rate-determining stages. The mechanisms proposed by Tamm [23-26] and Tsionskii [27, 28] involve the stages of water adsorption, which can be accompanied by the dissociation, but the rate-determining stage is always the electrochemical reaction itself. The recombination stage seems to play an insubstantial role in the hydrogen electroreduction on iron. Thus, independently of a particular mechanism proposed, the process of the cathodic evolution of hydrogen on iron is controlled by the electrochemical stage.

According to the modern concept of the nature of an elementary reaction act,

the reorganization energy of the solvent is one of the most important physical characteristics, which predetermines the kinetics of the charge transfer in a polar medium [29]. By Marcus [30], the activation energy of an elementary act can be written as follows:

$$E_{act} = N_A(\Delta e)^2 \left(\frac{1}{\varepsilon_0} - \frac{1}{\varepsilon_s}\right) \left(\frac{1}{2a} - \frac{1}{4R}\right),$$
(5)

where N_A is Avogadro's number; Δe is the charge transferred; e_0 and e_s are the optical and static dielectric constants; a is the radius of an ion; and R is the distance between the center of the depolarizer ion and the surface.

Taking into account Eq. (5), we can state that the adsorption of an inhibitor can change the conditions of the electroreduction of hydrogen ions via the changes in

 ε_s during the adsorption of polar inhibitor molecules;

a depending on the structure and composition of the coordination shell of protons (obviously, a value differs in $H_9O_4^+$ and $[H_7O_3Inh]^+$ protonated complexes); and

R depending on the discharge conditions of a depolarizer ion, which can either be in the inner or outer Helmholtz layer.

Having thoroughly analyzed Eq. (5) in the case of the hydrogen ion discharge, Krishtalik showed [31] that the discharge of a proton from a relatively large (in size) complexes requires a small reorganization energy. It means that as the degree of proton hydration decreases in a series:

$$H_9O_4^+ \xrightarrow[-HOH]{} H_7O_3^+ \xrightarrow[-HOH]{} H_5O_2^+ \xrightarrow[-HOH]{} H_3O^+$$

which may be particularly caused by an inhibitor, the activation energy of the discharge noticeably increases.

The way the data on the anodic dissolution of iron is treated (which is widely adopted in literature after the works of Frumkin and coworkers [32]) implies the construction of a scheme involving the adsorption of nucleophilic particles N (water, background anions, inhibitor molecules or ions) and their participation in the stages of successive detachment of one electron in each electrochemical stage:

$$Fe + N \longrightarrow FeN^{r^{+}} + e^{-}, \qquad (6)$$

$$FeN \longrightarrow Fe^{2r^{+}} + N + e^{-}, \qquad (7)$$

Bearing in mind that stages (6) and (7) are written for the metal atoms at the "active surface sites" and obey the regularities of the slow discharge theory, the authors wrote the kinetic equation as follows:

$$i_a = k_a[N] \exp\left[\frac{(n\alpha+1)F}{RT}E_a\right],$$
 (8)

where n and k_a are constants; [N] is the concentration of a nucleophilic component that participates in the reaction; a is the transfer coefficient (typically equal to 0.5); and E_a is the electrode potential vs. the reference electrode.

However, the physicochemical essence of the anodic dissolution of metals cannot be reproduced in terms of the aforementioned approaches for some principal reasons.

By [7], the anodic dissolution of metals can be considered as a first-kind phase transition accompanied by a charge transfer between the solid and liquid phases. Equations (6) and (7) are valid for the metals which can form aquacomplexes or complexes with other ligands at the oxidation degree of +1 (e.g., Cu⁺). The detachment of the first and second electrons, which belong to the collective Fermi level of iron, from an iron atom does not require an activation energy to overcome a barrier. The discharge itself (the depolarization of the anode as a cooperative atomic system with the Fermi level constrainedly lowered by polarization) is a transfer of the iron ion to the surface electrolyte layer:

 $Fe_{s} \xrightarrow{2^{+}} (Fe_{solv})_{v}^{2^{+}}$ (9)

This is confirmed by the fact that the k_a value estimated in the experiment [33] is higher by four to six exponents than a similar value for the cathodic reaction [18].

Taking into account that the ions at half-crystalline surface positions (at kinks) of the metal detach from the matrix most easily, and the lifetime of an ion at a kink is substantially smaller than the characteristic adsorption time of a nucleophilic particle (water molecule or anion), Khaldeev [7] and Lazorenko-Manevich [34] supposed that these particles do not participate in the elementary stages of the anodic process.

On the basis of the above discussion, we can say that the adsorption of nucleophilic particles affects the rate of the anodic process, because the nucleophilic molecules (ions) adsorbed at terraces

increase the electron density of the Fermi level and, in this way, decrease the polarization of the anode;

decelerate the motion of the dissolution steps;

change the mobility and concentration of water molecules in the layer near the electrode; and promote the reconstruction of the surface layer of metal atoms, which results in the change in the electron work function and the exchange current.

The peculiarities listed in combination with the possibility of iron ions to detach from some surface sites other than kinks provoked the construction of the dissolution model of a hydrophilic metal with the spatially separated dissolution and passivation processes (SSDP) [34, 35]. The statistical phenomenology of SSDP allowed suggesting a new explanation for the role of the adsorption of water [34, 35] and halide ions [36] in the anodic dissolution of iron. Being a doubtless step ahead from the formal kinetic models of the anodic dissolution, the SSDP model does not provide an interpretation for the deviations of the anodic polarization curves from Tafel slopes and for the experimentally measured limiting currents [37, 38].

It means that the known distinguishing between the blockading and electricdouble-layer inhibitors should be supplied, in the case of acidic corrosion, by thoroughly distinguishing their effects on the cathodic hydrogen evolution and the anodic metal dissolution.

Technical inhibitors of the acidic corrosion are typically mixtures of compounds of various nature [2, 39], and it is expedient to study the mechanisms of the effect the components of the mixtures produce by considering some model compounds. In this work, we investigated the derivatives of tetraalkyl(aryl)ammonium, phosphonium, arsonium, and trialkylsulphonium as the models of cation-active inhibitors; dibenzylsulfoxide as a non-ionogenic one; while phenylarsonic acid and halide ions were taken as anion-active model substances.

Antropov drew attention to the so-called "energetic" mechanism of the effect of cation-active inhibitors of acid corrosion [1]. An attractiveness of this idea became the main reason for explaining the effect of sulfur-containing compounds on its basis [40]. The model simulations of Afanas'ef [41, 42] snowed that the noticeable repulsive interaction between the adsorbed depolarizer cations and an inhibitor takes place only at high degrees of coverage. As a result, the maximum possible deceleration of the electrolytic hydrogen evolution on iron by tetrabutylammonium cations should be observed at $\theta \rightarrow 1$. It is known that at the adsorption of tetrabutylammonium on bismuth, $\theta = 1$ is attained at $c = 5 \times 10^{-4}$ mol/1. An improvement of the protective action at the higher degrees of coverage is related in [43-46] to the structuring of water in the electrolyte layers near the surface and to the change in the conditions of the relay-race proton transfer. Furthermore, under these conditions, the degree of proton hydration may decrease in a layer near the electrode, which should lead to an increase in the activation energy due to an increase in the reorganization energy of the solvent [31]. Note that symmetric quaternary ammonium cations (similarly to tetraphenylphosphonium cations [47]) can seemingly undergo two-dimensional condensation upon the adsorption on the metal surface. Asymmetric dimethylphenylpropylammonium and dimethylphenylallylammonium cations reveal much lower adsorption inhibiting

effect [48]. Quaternary tetraalkylammonium salts are not chemically changed on the metal surface during the cathodic reaction [49], which means that they are inert with respect to the corrosion processes proceeding. Therefore, the so-called secondary inhibition is not typical of them. Among the nitrogen organic onium derivatives, quinolinium salts can produce the secondary inhibition effect [50].

Amines protonated in acid solutions, as well as quaternary ammonium salts, inhibit the anodic dissolution of iron usually stronger than the cathodic evolution of hydrogen [51-54]. The nature of the phenomenon is not clarified, but seems to be related to the aforementioned differences in the ways the anodic and cathodic reactions are depolarized. The formal kinetic description of the anodic processes with the participation of the background anions, water, its surface dissociation products, and inhibitor particles implied that the inhibitors can compete for the unoccupied metal surface sites. In connection with this, one should assume that the surface deprotonation of amines [55] and anilines [56] is possible even in strongly acidic solutions or that tetraalky-lammonium cations, revealing no nucleophilic properties, can participate in the elementary stages of metal dissolution [2], Quaternary ammonium cations and protonated amines adsorbed due to the electrostatic and hydrophobic effects can decelerate the described anodic dissolution of hydrophilic metals either by creating a positive adsorption III_1 , potential or by hampering the translation motion of water molecules [57], which increases the potential hydration barrier of the ion transferred to the liquid phase.

Thus, quaternary ammonium salts, which are unable to block the active surface sites of the metal (typically, surface defects), inhibit the cathodic and anodic reactions primarily due to the changes in the structure of water near the electrode. Insofar as the changes are not restricted to a monolayer, but involve some bulk of electrolyte near the phase boundary, such an inhibiting effect can conditionally be referred to as "bulk."

Onium compounds of the elements of the third and fourth periods of the V and VI groups also inhibit the acidic corrosion of metals. However, along with the considered ways of the deceleration of the electrode reactions typical of ammonium salts, phosphonium, arsonium, and sulfonium compounds can be cathodi-cally split [58]:

$$[R_4X]^+ + H^+ + 2e^- \rightarrow R_3X + HR, \qquad (10)$$

$$X = P, As,$$

$$[R_3S]^+ + H^+ + 2e^- \rightarrow R_2S + HR. \qquad (11)$$

Being split concurrently with the hydrogen reduction (3), phosphonium, arsonium, and sulfonium cations act as additional cathodic depolarizers. Besides

that, the surface products of reactions (10) and (11) are much more hydrophobic than the original cations and can specifically adsorb on the metal due to the electron-donor properties of the central atoms. As a result, both cathodic and anodic processes are decelerated due to the adsorption of the original (or primary, following Horner [50]) inhibitor and the newly formed secondary inhibitor. As was shown in independent tests, dialkylsulfides and ternary phosphines and arsines reveal strong inhibiting ability [59, 60]. Being very weak bases, dialkylsulfides are not protonated in dilute acid solutions [61]. Ternary phosphines and arsines can be protonated under the similar conditions and can work not only as inhibitors, but also as additional cathodic depolarizers [62]:

$$\mathbf{R}_{3}\mathbf{P} + \mathbf{H}_{3}\mathbf{O}^{\dagger} \longrightarrow \mathbf{R}_{3}\mathbf{P}\mathbf{H}^{\dagger} + \mathbf{H}_{2}\mathbf{O}, \qquad (12)$$

$$R_3 P H^+ + e^- \longrightarrow R_3 P + \frac{1}{2} H_2$$
(13)

The secondary inhibition was confirmed in various experiments, namely, in chemical [50], electrochemical [63], and XPS [49, 64] studies.

The inhibition of anodic dissolution with sulfonium, phosphonium, and arsonium ions is particularly related to the ability of their chemisorbed split products to hamper the motion of dissolution steps.

Being nonionogenic inhibitors, organic sulfoxides can also be chemically transformed at the metal surfaces. Dibenzylsulfoxide protonated in the bulk of acid solution is reduced to dibenzylsulfide [65-67]. Phenilarsonic acid, which does not practically dissociate in mineral acid solutions, can reduce at an iron surface [68], strongly decelerating the corrosion process.

Thus, organic compounds, which can be cathodically reduced on a metal surface, can affect the surface not only in their original state, but also via their transformation products, which may either decelerate or catalyze the electrode processes.

In addition to all the facts considered, one should take into account that inhibitors can react purely chemically with the metal surface or its corrosion products in the bulk of solution. Troqet and Pagetti have found that tetraphenylphosphonium bromide forms a difficultly soluble binary salt with zinc ions $[Ph_4P]_2 Zn Cl_4$, which can lead, on the one hand, to an improvement of the protective effect, and, on the other hand, to the deposition of the inhibitor and a decrease in its volume concentration [69]. Phenylarsonic acid decelerates the corrosion of titanium through the formation of the surface titanium complex compounds rather than through the products of its cathodic reduction [70].

During the adsorption of inhibitors, not only the adsorbate, but also an

adsorbent changes. A wide usage of tunnel scanning microscopy allowed people to reveal the reconstruction of the metal surface upon the adsorption of nucleophilic particles [71, 72]. Therefore, one should not neglect the effect of chemisorbed inhibitor particles on the corrosion reactions of a metal via the reconstruction of the surface as well. This peculiarity may probably predetermine the similarity of the effect of CO and I⁻ on the cathodic hydrogen evolution and the anodic iron dissolution [73, 74]. The problem of the reconstruction of the metal surface caused by the adsorption of nucleophilic particles (water molecules, its dissociation products, anions, etc.) requires special investigation, but it is already obvious that this phenomenon cannot be neglected in interpreting the effect of inhibitors on the corrosion of metals. The restructuring during annealing [75], hydrogenation [76], or mechanical treatment [77, 78] affects the kinetics of the anodic dissolution of iron.

Thus, analyzing the mechanism of the protective effect of inhibitors, one should differentially take into account their electrode and near-electrode effects.

The near-electrode effects involve

changes in the structure of a solvent near the electrode and the resulting change in the conditions of proton transfer;

changes in the parameters of the translation motion of the solvent molecules near the electrode; and

changes in the composition of the first coordination shell of the depolarizer.

Besides adsorption, the electrode effects involve

changes in the chemical nature of the inhibitor during the corrosionelectrochemical process;

a change in the Fermi level of a metal due to the adsorption of nucleophilic inhibitors; and

a reconstruction of the metal surface upon the adsorption of inhibitors.

We hope that the electrode and near-electrode effects of inhibitors considered in this paper can assist in formulation of a deeper and more thorough concept of the nature of blockading and energetic effects introduced by Antropov [1].

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