FORMAL THEORY OF ORGANIC CORROSION INHIBITORS

L. I. Antropov

UDC 620.197.3

Various possible modes are discussed in which organic inhibitors can affect the processes of metal corrosion by oxygen, equations are analyzed which describe the mechanism of inhibition according to various concepts about it, the feasibility is demonstrated of using simplified relations for describing the inhibition effect, results of electrocapillary measurements are used for calculating the retardation factors, and the role of synergism in the inhibition process is emphasized.

Upon the addition of an inhibitor, one usually notes a drop in the corrosion rate from i_c to i_c' with a shift of the corrosion potential ε_c up or down to a new level ε_c' and also a change in several physicochemical as well as mechanical properties of the metal.* The question is what causes this?

The first possible explanation is based on the proposition that a part of the metal surface θ becomes shielded by a solid film of inhibitor and thus completely excluded from the corrosion process, while this process continues at the initial rate on the exposed part of the surface $(1-\theta)$. Then

$$i_c'=i_c(1-\theta) \tag{1}$$

and the retardation (inhibition) factor

$$\gamma=\frac{i_c}{i_c'}=\frac{1}{1-\theta}, \tag{2}$$

where

$$\theta=1-\frac{1}{\gamma}=1-\frac{i_c'}{i_c}, \tag{3}$$

i.e., the corrosion rate and the retardation factor can be calculated from the degree of coverage, and vice versa.† Such a simple explanation does not, however, agree with most experimental evidence and has been confirmed in rare cases only. For instance, during diffusive corrosion (e.g., with oxygenic depolarization) the corrosion rate at a given coverage θ has decreased less than it should according to relation (1). For reconciling this relation with experimental evidence, one may suggest that a lateral feed of depolarizer [2] causes the diffusion to occur over a regional area equal not to $(1-\theta)$ but to some function of it $f(1-\theta) > (1-\theta)$ so that the true corrosion current is, indeed, larger than i_c' according to relation (1). The effect of an inhibitor may not be apparent up to nearly full coverage, although the actual degree of coverage increases with increasing inhibitor concentration [3]. Furthermore, Eq. (1) does not reflect the change in the corrosion potential which usually occurs upon addition of an inhibitor and even assuming a lateral feed of depolarizer

*The lowering of mechanical (strength) characteristics is usually related to a penetration of hydrogen into the metal as well as to an increasing nonuniformity of the metal surface relief (appearance of weak sites) during corrosive breakdown.

†The other often used quantitative characteristic of inhibitor effectiveness, viz., the degree of protection P, is related to θ in an even simpler manner:

$$P=(i_c-i_c')/i_c=1-(1/\gamma)=\theta. \tag{4}$$

Kiev Polytechnic Institute. Translated from Zashchita Metallov, Vol. 13, No. 4, pp. 387-399, July-August, 1977. Original article submitted January 17, 1976.

TABLE 1. Directions of Increase of Quantities Characterizing Certain Anisotropic Properties of Metals [10-13]

Characteristic quantity	Type of face (011) (001) (111)
Packing density	→
Hydrogen overvoltage	→
Metal overvoltage	→
Exchange currents	←
Corrosion rate	←
Neutral point on metal (positive value)	→ (+)
Charge at a given potential (negative value)	→ (−)

will not correct this disparity. It would be logical then to suggest, as has been done by several authors [4-7], that the corrosion process continues also on the part of surface covered by an inhibitor, but at a slower rate. In other words, that an inhibitor film does not insulate a metal completely as does an enamel coating, for example. Then instead of relation (1) we have the relation

$$i_c'=i_c'(1-\theta)+i_c''\theta.* \quad (5)$$

In the case of a kinetically limited corrosion process such as, e.g., one with hydrogenic depolarization, the process rate decreases more than according to relation (1) at a given degree of coverage.† It must be assumed, therefore, that in the presence of an inhibitor the corrosion rate varies over the entire metal surface, remaining equal to zero in regions where the inhibitor has built up into clusters. Then

$$i_c'=i_c'''(1-\theta). \quad (6)$$

If corrosion at a certain rate i_c'' is possible in regions covered with an inhibitor, however, then the relation

$$i_c'=i_c'''(1-\theta)+i_c''\theta \quad (7)$$

rather than relation (6) will apply.

It must be remembered, however, that the actual surface of a corroding metal is energetically nonuniform even in the absence of chemical or phase inhomogeneities and that pure metal dissolves. The energetical nonuniformity of a pure polycrystalline metal is due particularly to an egress of various types of crystal faces with much differing characteristics [10-13], as shown in Table 1.

The packing density of crystal faces in fcc lattices increases in the order (011) < (001) < (111). With an increase in the packing density, both the hydrogen and the metal overvoltages also increase, while the exchange current and the corrosion rate decrease. The neutral point ε_N shifts regularly in the positive direction by an amount which, according to Table 2 [14-24], may reach a few tenths of a volt.

Meanwhile, corrosion processes as well as many other electrochemical processes are usually completed on an almost equipotential metal surface. Inasmuch as the charge is, to the first approximation, determined by the φ-potential on the reference scale [25-29]

$$\varphi=\varepsilon-\varepsilon_N, \quad (8)$$

and ε_N depends on the type of the crystal face, charges on different faces will be different at the same potential ε_c‡ This arising charge "anisotropy" leads to an adsorption anisotropy and, consequently, to an inhibiting action by organic substances so that the corrosion distribution can become either less or more uniform.

Faces with different indices not only carry different amounts of charge but also have different numbers of defects [30, 31] with different densities; in other words, they differ in the concentration of sites most ac-

*Here and everywhere i_c' denotes the corrosion current in the presence of an inhibitor; naturally, depending on the selected model, its theoretical magnitude can vary within certain limits and differs from its measured magnitude.

†As has been shown in [9], e.g., in the $Fe^{III}-Fe^{II}$ system, doubling the degree of coverage of a platinum electrode surface with an inhibitor reduces the maximum current by less than half (only 1.2-1.4 times) and the exchange current by more than half (4-5 times).

‡The difference in charge densities at the same electrode potential may be related to the different capacitances of faces of different reticular densities.

TABLE 2. Neutral Points on Faces in Several Metallic Single Crystals [14-24]

Metal	Neutral points (V, on the hydrogen scale) on the faces			Metal	Neutral points (V, on the hydrogen scale) on the faces	
	(011)	(001)	(111)		(011)	(001)
Ag	−0,77	−0,67	−0,45	Zn	−0,68	−0,60
Ag	−0,59	−0,52	−0,45		(0101)	(0001)
Ag	−0,77	−0,65	−0,50	Zn	−0,92	−0,77
Au	+0,19	+0,38	+0,50		(0101)	(0001)
Cu	−0,075	−0,050	−0,025			

tive with respect to adsorption and electrode reactions. Which of these nonuniformity effects predominate will depend mainly on the nature of the metal. When the neutral points on different faces are close, as in the case of a copper single crystal (Table 2) not the effect of charge but of defect density and dislocation density [32, 33] may predominate. In the case of silver, with very different ε_N values on different crystal faces, the situation may be reversed. Whatever it is, however, any nonuniformity on the metal surface must inevitably occur and give rise to regions with different degrees of coverage by the inhibitor and with different permeabilities. Therefore, Eq. (7) corresponds only to some averaged and simplified pattern.

Further complexity of the inhibitor effect on corrosion is associated with the possibility of direct participation of inhibitors in the corrosion process. It will be more expedient to consider this aspect later, after the equations for the partial electrode reactions have been established.

We now assume that corrosion proceeds with hydrogenic depolarization within the kinetic range and with the corrosion potential ε_C sufficiently far from the equilibrium potentials ε_H of the hydrogen electrode and ε_M of the metal electrode. Let the cathodic evolution of hydrogen and the anodic dissolution of metal be determined by the kinetics of charge transport. Then, disregarding the rates of reverse reactions, we can write [34]

$$\vec{i}_{M(\varepsilon=\varepsilon_C)} = nF \exp\left\{\frac{n\alpha_M - z_M}{RT} F\psi_2\right\} \vec{k}_M \vec{f}_M \exp\left\{\frac{1-\alpha_M}{RT} nF\varepsilon_C\right\} \tag{9}$$

for the anodic process and

$$\vec{i}_{H(\varepsilon=\varepsilon_C)} = nF \exp\left\{\frac{\alpha_H - z_H}{RT} F\psi_2\right\} \vec{k}_H \vec{f}_H \exp\left\{-\frac{\alpha_H}{RT} F\varepsilon_C\right\} \tag{10}$$

for the cathodic process, the rates of both being equal at $\varepsilon = \varepsilon_C$ and corresponding to the corrosion current

$$(i_M = i_H = i_C)_{\varepsilon=\varepsilon_C}. \tag{11}$$

In expressions (9) and (10) n denotes the number of electrons participating in a given reaction (during the slow stage), α_M and α_H are the transport coefficients of metal and hydrogen evolution, respectively, during these reactions, z_M and z_H are the charges on particles of metal and hydrogen sources, respectively, and ψ_2 is the potential at the outer surfaces of the Helmholtz layer.*

Upon addition of an inhibitor, a preferred adsorption of the latter at the energetically most favorable sites occurs and this effects a change in the reaction rate coefficients $\vec{k}_M$ of metal ionization and $\vec{k}_H$ of hydrogen evolution, not necessarily to the same extent.

Adsorption of the inhibitor may cause a dislodgment of anions participating in the dissolution of metal and a corresponding change in the nature as well as in the stoichiometry of the anodic reaction $\vec{f}_M$ [35].

The appearance of inhibitor particles on the metal surface will change the heat of adsorption of hydrogen atoms as well as their surface concentration, which may alter the slow stage of the hydrogen evolution process and the stoichiometry of the cathodic reaction $\vec{f}_H$ [36-38].

As a result of inhibitor adsorption, one should also expect changes in the structure of the electric double

*Strictly speaking, the ψ_2 potential here should be replaced with a quantity which corresponds to the location of ions at the instant of charge transfer: this quantity may not necessarily coincide with the potential of either the inner or the outer Helmholtz layer. We will assume here a ψ_2 potential equal to the adsorption potential, which in the case of mercury can be determined from the shift of the peak on the electrocapillarity curve.

layer and, particularly, in the adsorptional jump of potential ψ_2, especially when an inhibitor is distributed more or less uniformly over the metal surface.*

There is weighty evidence for the assertion [39-42] that almost all components of a solution can affect the dissolution of metal. By expelling from the interface those components of the solution which facilitate anodic ionization of the metal as hydroxyl ions, e.g., an inhibitor retards the anodic reaction and shifts the static potential in the positive direction.

When the inhibitor particles are capable of forming with the corroding metal soluble complexes and this reaction is easier than (or at least as easy as) dissolution of the metal in combination of any other components of the solvent, then adsorption of the inhibitor will accelerate the anodic dissolution of the metal. When the cathodic reaction is greatly retarded, on the other hand, then the corrosion rate will decrease. Inhibitors can accelerate also the cathodic reaction by acting like Brönsted bases and acids, e.g., while retarding the anodic reaction and thus the corrosion process more. Regardless of the acceleration of either partial reaction, therefore, the inhibiting effect of an organic (or other) substance can still be retained. Naturally, additional terms should appear in Eqs. (13) and (14) for each case accordingly.

Finally, dissolution of a metal by electrolytes including acids can proceed either electrochemically or chemically [40, 41] and this too must be taken into consideration in the analysis of the kinetics of the partial reactions. The effect of inhibitors on these two modes of dissolution is not the same and the equation for the corrosion rate in the presence of an inhibitor must include a term which represents chemical dissolution.

We will consider here only one of the simplest cases corresponding to Eq. (6). For the logarithm of the retardation factor (quantities changing upon addition of an inhibitor denoted by a dash) Eqs. (2), (9), and (10) yield

$$\ln\gamma=\ln\frac{i_M}{i_M'}=\frac{n\alpha_M-z_M}{RT}F(\psi_2-\psi_2')+\ln\frac{\overleftarrow{k}_M}{\overleftarrow{k}_M'}+\ln\frac{\vec{f}_M}{\vec{f}_M'}+\frac{1-\alpha_M}{RT}nF(\varepsilon_c-\varepsilon_c')-\ln(1-\theta) \tag{12}$$

or

$$\ln\gamma=\ln\frac{i_H}{i_H'}=\frac{\alpha_H-z_H}{RT}F(\psi_2-\psi_2')+\ln\frac{\vec{k}_H}{\vec{k}_H'}+\ln\frac{\vec{f}_H}{\vec{f}_H'}+\left(-\frac{\alpha_H}{RT}F\right)(\varepsilon_c-\varepsilon_c')-\ln(1-\theta). \tag{13}$$

According to relations (12) and (13), an inhibitor has even in this simple case an adsorptional or double-layer effect (first term on the right-hand side of these equations), a kinetic effect (second term), a chemical effect (third term), an electrochemical effect (fourth term), and a mechanical or blocking effect (last term) [44]. In reality these effects, or at least some of them, are functionally interdependent. These effects can superpose on one another, some of them predominant and others insignificant, depending on the specific conditions of the corrosion process as well as on the nature and the concentration of the inhibitor. The contribution of each effect is determined by the degree of coverage θ and by the manner in which it depends on the latter.

The coefficients of the reaction rates should vary with the degree of coverage, mainly because of the effect of the latter on the chemical component of the activation energy; the relative changes in $\overleftarrow{k}_M$ and $\vec{k}_H$ largely determine the magnitude and the direction of the shift of potential ε_c.

Equating (9) and (10), finding an expression for ε_c, and inserting the latter into any of these two equations, we obtain a single expression for the corrosion rate at $\varepsilon = \varepsilon_c$:

$$\ln i_c=\ln nF+\frac{n(1-\alpha_M)}{n(1-\alpha_M)+\alpha_H}\ln\vec{k}_H\vec{f}_H+\frac{\alpha_H}{n(1-\alpha_M)+\alpha_H}\ln\overleftarrow{k}_M\overleftarrow{f}_M+\frac{F}{RT}\frac{\alpha_H(n-z_M)-(1-\alpha_M)nz_H}{n(1-\alpha_M)+\alpha_H}\psi_2. \tag{14}$$

The equation for the corrosion rate in the presence of an inhibitor will differ from Eq. (14) in the value of $\vec{k}_H$, $\overleftarrow{k}_M$, $\vec{f}_H$, $\overleftarrow{f}_M$, ψ_2 and by the appearance of the additional term $\ln(1-\theta)$:

$$\ln i_c'=\ln nF+\frac{n(1-\alpha_M)}{n(1-\alpha_M)+\alpha_H}\ln\vec{k}_H'\vec{f}_H'+\frac{\alpha_H}{n(1-\alpha_M)+\alpha_H}\ln\overleftarrow{k}_M'\overleftarrow{f}_M'+\frac{F}{RT}\frac{\alpha_H(n-z_M)-(1-\alpha_M)nz_H}{n(1-\alpha_M)+\alpha_H}\psi_2'+\ln(1-\theta). \tag{15}$$

The retardation factor can now be determined from the equation

*An unconcentrated "open-work" distribution of inhibitor is promoted not only by energetical nonuniformity but also by forces of repulsion between particles (especially those carrying charges of the same polarity) of a given inhibitor over short distances.

$$\ln\gamma=\ln\frac{i_c}{i_c'}=\frac{1}{n(1-\alpha_M)+\alpha_H}\ln\left(\frac{\vec{k}_H}{\vec{k}_{H'}}\right)^{n(1-\alpha_M)}\left(\frac{\overleftarrow{k}_M}{\overleftarrow{k}_{M'}}\right)^{\alpha_H}+$$
$$+\frac{1}{n(1-\alpha_M)+\alpha_H}\ln\left(\frac{\vec{f}_H}{\vec{f}_{H'}}\right)^{n(1-\alpha_M)}\left(\frac{\overleftarrow{f}_M}{\overleftarrow{f}_{M'}}\right)^{\alpha_H}+\frac{F}{RT}\frac{\alpha_H(n-z_M)-(1-\alpha_M)n_H^2}{n(1-\alpha_M)+\alpha_H}\psi_2'-\ln(1-\theta). \quad (16)$$

Here instead of the five effects in Eqs. (12) or (13) we have only four: the kinetic, the chemical, the adsorptional (double-layer), and the blocking one.

The change in the reaction rate coefficients has to do mainly with the dependence of the chemical component of the activation energy on the surface concentration of inhibitor. Assuming that the activation energy varies linearly with the degree of coverage, it seems that the kinetic effect should also be a linear function of θ, albeit probably a more intricate one. The chemical effect is not a single-valued function of θ and even more difficult to establish, especially when considering that during adsorption of the inhibitor the mechanism of hydrogen evolution or metal dissolution may change. The adsorptional effect should, within certain limits, vary linearly with the degree of coverage θ whenever the inhibitor particles are charged or carry a dipole moment and are adsorbed with a definite orientation.* The blocking effect varies with the degree of coverage according to relation (2). The value of α is usually close to 0.5, while n and z_M are most often, depending on the nature of the metal and the mechanism of the process, equal to 1 and 2, respectively, and $z_H = 1$ in acidic media. Instead of Eq. (16), we can then write

$$\lg\gamma=0.5\lg\frac{\vec{k}_H\overleftarrow{k}_M}{\vec{k}_{H'}\overleftarrow{k}_{M'}}+0.5\lg\frac{\vec{f}_H\overleftarrow{f}_M}{\vec{f}_{H'}\overleftarrow{f}_{M'}}+8.4(\psi_2'-\psi_2)-\lg(1-\theta) \quad (17)$$

for $\alpha_M = \alpha_H = 0.5$ and $n = z_M = z_H = 1$,

$$\lg\gamma=0.67\lg\left(\frac{\vec{k}_H}{\vec{k}_{H'}}\right)\left(\frac{\overleftarrow{k}_M}{\overleftarrow{k}_{M'}}\right)^{0.5}+0.67\lg\left(\frac{\vec{f}_H}{\vec{f}_{H'}}\right)\left(\frac{\overleftarrow{f}_M}{\overleftarrow{f}_{M'}}\right)+5.5(\psi_2'-\psi_2)-\lg(1-\theta) \quad (18)$$

for $\alpha_M = \alpha_H = 0.5$, $n = 2$ and $z_M = z_H = 1$, or

$$\lg\gamma=0.67\lg\left(\frac{\vec{k}_H}{\vec{k}_{H'}}\right)\left(\frac{\overleftarrow{k}_M}{\overleftarrow{k}_{M'}}\right)^{0.5}+0.67\lg\left(\frac{\vec{f}_H}{\vec{f}_{H'}}\right)\left(\frac{\overleftarrow{f}_M}{\overleftarrow{f}_{M'}}\right)^{0.5}+11.1(\psi_2'-\psi_2)-\lg(1-\theta) \quad (19)$$

for $\alpha_M = \alpha_H = 0.5$, $n = 2$, $z_M = 2$ and $z_H = 1$.

It follows from Eqs. (17)-(19) that even in the case of a linear decrease in the activation energy of partial corrosion reactions with increasing degree of coverage,† the contribution of the first two terms to the retardation factor should be smaller than that of the third term at low and intermediate degrees of coverage and smaller than that of the fourth term at high degrees of coverage.

One may, therefore, assume that, to the first approximation, the simplified equations for the retardation factor

$$\lg\gamma=k\Delta\psi_2-\lg(1-\theta)=k\Delta\psi_2+\lg\frac{1}{1-\theta} \quad (20)$$

or

$$\gamma=\gamma_a\gamma_b, \quad (21)$$

where

$$\gamma_a=10^{k\Delta\psi_2}, \quad (22)$$

and

$$\gamma_b=\frac{1}{1-\theta} \quad (23)$$

hold true over almost the entire range of coverage and thus over a wide range of inhibitor concentration under conditions of corrosion with hydrogenic depolarization.

The foregoing analysis, its formal character notwithstanding, provides a certain basis for making judg-

*As the degree of orientation changes, there is possible either partial or complete change in orientation of the adsorbed inhibitor particles. Quite common is, evidently, "oblique" adsorption of particles at some angle to the interface [45].

†In reality, this relation is probably more intricate and weaker.

TABLE 3. Effect of Pyridine on the Potential of an Uncharged Mercury Surface ($_{Hg}\varepsilon_{q=0}$) and the Corrosion of Iron in 0.5 M H_2SO_4 at 20°C [46, 55]

Concn., M	$\Delta\psi_2 = \Delta_{Hg}\varepsilon_{q=0}$, V	γ_r	γ_a accord. to relation (22) with k equal to		
			5,5	8,4	11,1
0,00256	0,015	1,4	1,2	1,3	1,5
0,0064	0,022	2,1	1,3	1,5	1,8
0,01 *	0,025	1,2 *	1,4	1,6	1,9
0,016	0,032	2,4	1,5	1,9	2,3
0,02 *	0,036	1,3 *	1,6	2,0	2,5
0,04	0,042	2,5	1,7	2,3	2,9
0,05 *	0,056	1,4 *	2,0	3,0	4,2
0,1	0,075	3,3	2,6	4,2	6,8
0,1 *	0,075	1,7 *	2,6	4,2	6,8
0,2 *	0,090	2,3 *	3,1	5,7	10,0
0,5 *	0,110	3,0 *	4,0	8,4	16,7

*[55].

ments about the mechanism of inhibition and in many cases not only renders an interpretation of experimental data but also reveals the probable trend of inhibitor action; the validity of these propositions will be subsequently demonstrated, essentially on the basis of relation (20).

The quantities $\Delta\psi_2$ and θ are most easily determined from electrocapillary and the capacitive measurements on a mercury electrode. Obtaining such data directly on the corroding metal is much more difficult and sometimes impossible.* In view of this, we will consider what can be measured on the reference or φ scale of potentials, especially since many conclusions on this basis have been experimentally confirmed [48-50]. One cannot conclude from this, however, that the surface concentrations of the same substance on different electrodes are equal, even when the φ potentials are equal [45, 46]. Naturally, $\Delta\psi_2$ and θ determined on mercury can be different on other metals. For various reasons, which we will not delve into here, they are usually lower on other metals than on mercury. Consequently, in the general case coefficient k will not be equal to the coefficients in Eqs. (17)-(19) but smaller. At the same time, the first term in Eq. (20) may contain both the kinetic and the chemical effects, which should make coefficient k larger than its theoretical value. Measured values of coefficient k can, therefore, deviate in either direction from the values given here earlier and, as a special case, be the same. Furthermore, at low and intermediate degrees of coverage the contribution of γ_a to the resultant value of γ is larger than that of γ_b, with the difference increasing as $\Delta\psi_2$ becomes more positive. Inhibitors with which these conditions prevail should, therefore, retard corrosion with hydrogenic depolarization (in this kinetically limited case all the effects come into play, or both effects according to the simplified equation) matchlessly more effectively than corrosion with oxygenic depolarization [in this diffusionally limited case only the blocking effect comes into play and according to relation (5)]. From this we can deduce at least three corollaries. First of all, in the presence of such inhibitors the relative amount of oxygenic depolarization should increase and the probability of hydrogenation of the metal should correspondingly decrease [46, 51-54]. Secondly, such inhibitors cannot suppress corrosion completely (there still remains metal breakdown due to the attendant reaction of reduction of diffused oxygen). Thirdly, measurements in the presence of such inhibitors should deviate from calculations, inasmuch as during hybrid depolarization the retardation factor is determined not by the reaction of hydrogen evolution alone

$$\gamma_H = \frac{i_H}{i'_H}, \tag{24}$$

as when serving as the basis for all the derived equations, but by two reactions: hydrogen evolution and oxygen reduction [45, 46]

$$\gamma_0 = \frac{i_H + i_0}{i_H' + i'_0}. \tag{25}$$

Comparing calculations with measurements, especially in the case of effective inhibitors, makes sense only when both refer to conditions of largely predominating hydrogenic depolarization, i.e., to sufficiently acidic media, deaerated solutions, inert atmospheres, etc. Some results of such a comparison for three different inhibitors are given in Tables 3-5.

It follows from the data in Table 3 that in the case of pyridine, which covers the surface of mercury to a very small degree, considering only the first term in Eq. (2), i.e., calculating according to the relation

*The procedure used earlier for estimating $\Delta\psi_2$ [46, 47] cannot always be regarded as sufficiently reliable.

TABLE 4. Effect of Decyl-Pyridine Chloride on the Potential of an Uncharged Mercury Surface ($_{Hg}\varepsilon_{q=0}$) and the Corrosion of Iron at 20°C [56, 57]

Concn., M	$\Delta\psi_2 = \Delta_{Hg}\varepsilon_{q=0}$ (0,5 M H_2SO_4), V	γ_r		γ_a	γ_b
		0,5 M H_2SO_4	1,5 M H_2SO_4, H_2 — atm	with $k=5,5$	
0,000256	0,020	1,6			
0,00064	0,100	2,7	5,8	3,5	1,7
0,0016	0,225	8,0	11,6	17,3	0,6
0,004	0,250	8,7	28,0	23,7	1,18
0,01	0,275	14,6	32,0	32,5	0,98

TABLE 5. Effect of Decyl-Trioxypyridine Chloride on the Potential of an Uncharged Mercury Surface ($_{Hg}\varepsilon_{q=0}$) and the Corrosion of Iron at 20°C [56, 57]*

Concn., M	$\Delta\psi_2 = \Delta_{Hg}\varepsilon_{q=0}$ (0,5 M H_2SO_4), V	γ_r		γ_a	γ_b	θ_{cal}, accord. to relation (23)	θ [58]
		0,5 M H_2SO_4	1,5 M H_2SO_4, H_2 — atm	with $k=5,5$			
0,000256	0,03	3,3					
0,00064	0,12	6,8	6,7	4,6	1,5	0,34	
0,0016	0,23	10,2	37,5	18,4	1,6	0,37	0,4
0,004	0,27	13,9	62,0	30,6	2,0	0,50	
0,01	0,30	15,5	110,0	44,7	2,4	0,68	0,5

*It is to be noted that the agreement between the two sets of θ values could be accidental. The degree of coverage determined from capacitance and electrocapillarity curves (whether on the basis of dislodgment of hydrogen, or slowdown of diffusion, or slowdown of charge transport) may not at all be the same, inasmuch as adsorption layers have different "permeabilities" with respect to different processes. Thus, a close packing of inhibitor molecules, which in purely capacitive measurements corresponds to a degree of coverage equal to unity and to the formation of a solid monolayer, may be permeable with respect to transport of charge. The latter will occur through clearances due to the configuration of adsorbed particles or even through the particles themselves: through the interstices between molecular rings [8], etc. These data, therefore, pertain to degree of coverage smaller than unity.

$$\gamma_r = \gamma_a = 10^{k\Delta\psi_2},$$

with k = 5.5 yields values of γ lying between two sets of test values and with k > 5.5 yields values definitely too high. For this reason, k = 5.5 is used here and will be in subsequent evaluation of the effectiveness of inhibitors in the same class with respect to corrosion of iron in sulfuric acid.

It follows from the data in Table 4 that, according to the assumptions made, the effectiveness of the cationically active inhibitor decyl-pyridine chloride is lower in a more diluted solution of acid containing oxygen and higher in a more concentrated deaerated solution. In this case the calculated values agree with the second set of γ_r values.

Analogous data for decyl-trioxypyridine chloride, a compound which only differs from decyl-pyridine chloride by the presence of the oxy-group carrying a weak negative charge, are given in Table 5. A comparison with the data in Table 4 indicates that at approximately equal magnitudes of $\Delta\psi_2$ in 0.5 M H_2SO_4, where oxygenic depolarization superposes on hydrogenic depolarization, the retardation factor is much larger in the presence of decyl-trioxypyridine chloride than in the presence of decyl-pyridine chloride. This is most probably attributable to the blocking mechanism. A transition to a more concentrated acid solution and to an inert atmosphere results in a larger γ_r factor. The values of γ_b calculated from γ_r and γ_a according to Eq. (21) yield the degree of coverage θ according to Eq. (23); they are rather close to the values obtained by the independent method in [58] (last two columns in Table 5). The emergence of the blocking mechanism in the case of decyl-trioxypyridine chloride must be associated with the possibility of intramolecular synergism

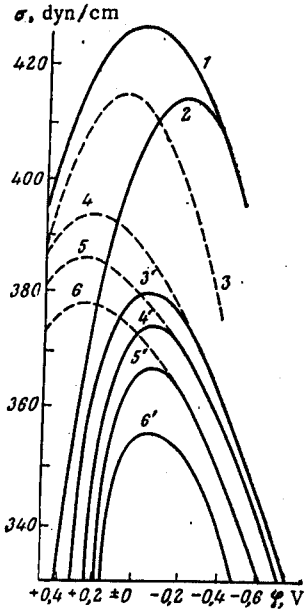

Fig. 1. Electrocapillarity curves plotted on mercury in 0.5 M H_2SO_4 at 20°C (curve 1), with addition of 0.03 M KI (curve 2), with addition of decyl-trioxypyridine chloride (curves 3-6), with addition of 0.03 M KI + decyl-trioxypyridine chloride (curves 3'-6'); concentration of decyl-trioxypyridine chloride: 3,3') 0.00064 M, 4,4') 0.016 M, 5,5') 0.004 M, 6,6') 0.01 M.

[44, 59, 60]. Intermolecular synergism [61-65] is possible with either decyl-pyridine chloride or decyl-trioxypyridine chloride, inasmuch as surface-active cations (decyl-pyridine or decyl-trioxypyridine) enter the solution together with surface-active anions (chlorine ions). The surface activity of chlorine anions is, especially within the given range of inhibitor concentrations, so weak as not to ensure any noticeable synergetic effect. For synergism in the case of decyl-trioxypyridine chloride is mainly the adsorption of some of its molecules by nitrogen atoms and of others by oxygen atoms, which weakens the forces of repulsion between particles on the surface and facilitates the formation of a more dense inhibitor film. However, according to the data in Table 5, in this case too the degrees of coverage remain rather small and this is explained by the weak adsorptivity of decyl-trioxypyridine chloride molecules by the $-\overset{\|}{C}-OH$ group. Better protective characteristics of an inhibitor can be ensured, therefore, by a stronger intramolecular or intermolecular synergism. A high degree of protection against corrosion can be attained in either case, mainly due to a stronger blocking effect. This can be easily ascertained in a typical case such as the decyl-trioxypyridine chloride + potassium iodide system, where surface-active cations (decyl-trioxypyridine) and anions (iodide) exist. The effect of decyl-trioxypyridine chloride has already been characterized. The graph in Fig. 1 [66] indicates how, with an increasing concentration of decyl-trioxypyridine chloride, the peak of the electrocapillarity curve shifts more and more in the positive direction. In the presence of this inhibitor (Table 5) the corrosion rate decreases mainly owing to the additional positive adsorption potential. Upon addition of potassium iodide to the acid solution, the peak of the electrocapillarity curve shifts to the right, which indicates an additional negative adsorption potential here. This, according to Eq. (20), should accelerate the corrosion. Its actual retardation observed in the experiment, is attributable either to the other effects represented in Eq. (16) and included in the expression for γ_a or to surface blocking.

On the basis of the second assumption, a calculation of γ_b according to Eq. (21) yields for it ≈25 (see Table 6 containing data for corrosion of zinc in 0.5 M H_2SO_4). Upon addition of increasing amounts of decyl-trioxypyridine chloride to a solution containing 0.03 M KI, the potential $_{Hg}\varepsilon_{q=0}$ shifts toward more positive values and the surface tension decreases sharply (Fig. 1).

The corrosion rate of zinc decreases here not proportionally to the potential shift $\Delta\psi_2$ in the positive direction but much faster. Here the blocking effect plays the decisive role already, as the data in Table 6 indicate. It must be emphasized that for solutions containing only an addition of decyl-trioxypyridine chloride calculations with k = 7.0 agree almost perfectly with the experiment, while the degree of coverage is found to be zero and there appears almost no blocking effect at all ($\gamma_b \approx 1$). For solutions containing both additives (KI + decyl-trioxypyridine chloride), on the contrary, calculations yield a predominant blocking effect ($\gamma_b \gg \gamma_a$) and almost complete coverage ($\theta > 0.95$) of the surface by the inhibitor mixture regardless of k (5.5 or 7.0). Such inhibitor combinations ensure a high degree of protection under conditions of hydrogenic, oxygenic, or hybrid depolarization.

TABLE 6. Effect of KI and Decyl-Trioxypyridine Chloride and Their Mixtures on the Magnitude of $Hg^{\varepsilon}_{q=0}$ and on the Corrosion of Zinc in 0.5 M H_2SO_4 at 20°C [66]

Compound, M	$\Delta\psi_2 = \Delta_{Hg^{\varepsilon}_{q=0}}$	γ_I	γ_a with k		γ_b with k		θ_{cal} with k	
			5,5	7,0	5,5	7,0	5,5	7,0
decyl-trioxy-pyridine chloride								
0,00064	0,12	7,5	4,6	8,7	1,6	0,88	0,38	−0,13
0,0016	0,23	39,0	18,4	40,7	2,1	0,96	0,52	−0,04
0,004	0,27	80,0	30,6	77,8	2,6	1,03	0,62	+0,03
0,01	0,30	120,0	44,7	126,0	2,7	0,95	0,63	−0,04
0.03 M KI	−0,20	2,0	0,08	0,04	25	50	0,96	0,98
0.03 M KI+ decyl-trioxy-pyridine chloride								
0,00064	−0,04	326	0,61	0,53	534	603	0,998	0,998
0,0016	±0,00	400	1,00	1,00	400	400	0,998	0,998
0,004	+0,02	1000	1,3	1,4	769	714	0,999	0,999
0,01	+0,03	1100	1,5	1,6	753	733	0,999	0,999

CONCLUSIONS

1. The inhibiting action of organic substances cannot be interpreted as a simple mechanical shielding of the surface, but it involves several effects associated with changes in the structure of the electric double layer, in the kinetics of the cathodic reaction and the anodic reaction, also in the conditions under which the cathodic reactants and the solution components are adsorbed.

2. Despite the complexity of the mechanism by which organic substances inhibit acidic corrosion, it can in many cases be formally described by an equation including only two effects: the double-layer (adsorptive or energetical) effect and the blocking (mechanical) effect. Satisfactory agreement with test values can be obtained, if one uses results of electrocapillary measurements on mercury and a coefficient which is a function of the kinetic parameters of both cathodic and anodic reactions. The numerical values of the coefficients in the equations are found here within the limits set by the kinetics of partial electrode reactions.

3. The formal theory explains such experimentally established trends as the dependence of the inhibitor effect on the atmosphere above the corrosive medium, on the acidity of the solution, and on the metal; it also explains the larger relative amount of oxygenic depolarization in the presence of inhibitors such as tetra-substituted ammonium, amines, pyridine, etc.

4. According to the formal theory, replacement of individual monofunctional substances (especially cationic ones) with mixtures or bifunctional substances (of the cation–anion kind) results in a different mechanism of inhibitor action and in a sharply increased effectiveness of inhibitors.

LITERATURE CITED

1. A. Sieverts and P. Lueg, Z. Anorg. Chem., 126, 192 (1923).
2. N. D. Tomashov, Corrosion of Metals with Oxygenic Depolarization [in Russian], Izd. Akad. Nauk SSSR, Moscow (1947).
3. L. I. Antropov, Zashch. Met., 11, 260 (1975).
4. J. Weber, J. Koutecky, and J. Koryto, J. Electrochem. Soc., 63, 583 (1957).
5. R. W. Schmid and C. N. Reilley, J. Am. Chem. Soc., 80, 2087 (1958).
6. J. Kuta and J. Smoller, Z. Elektrochem., 64, 285 (1960).
7. O. L. Riggs and R. M. Hurd, Corrosion, 23, 252 (1967).
8. N. Hackerman and R. M. Hurd, First International Congress on Metal Corrosion, London, Butterworth, Nat. (1962), p. 166.
9. L. I. Antropov and M. A. Marinich, Elektrokhimiya, 13, (1977).
10. G. B. Bokii, Crystallochemistry [in Russian], Moscow State Univ., Moscow (1960), p. 74.
11. R. Piontelli, B. L. Peraldi, and A. la Vecchia, Atti Acad. Nat. Lincei U. Sci. Fiz., Math., 28, 277 (1960).
12. R. Piontelli, Electrochim. Metall., 1, 5 (1966).
13. L. I. Bachmann and K. J. Vetter, Z. Phys. Chem., N. F., 51, 98 (1966).
14. G. Valette and A. Hamelin, C. R. C272, 602 (1971).
15. G. Valette and A. Hamelin, J. Electroanal. Chem., 45, 301 (1973).

16. É. R. Sevast'yanov, T. Vitanov, E. Budevskii, and A. Popov, Elektrokhimiya, 8, 412 (1972).
17. A. Hamelin and G. Valette, C. R., C269, 1020 (1969).
18. E. Budevskii, T. Vitanov, S. Sevast'yanov, and A. Popov, Elektrokhimiya, 5, 90 (1969).
19. A. Hamelin and J. Lecouer, Coll., 36, 714 (1971).
20. J. Clavilier, A. Hamelin, and G. Valette, C. R., C265, 221 (1967).
21. G. M. Schmid and N. Hackerman, J. Electrochem. Soc., 109, 243 (1962).
22. L. M. Novosel'skii, N. I. Maksimyuk, and L. Ya. Egorov, Elektrokhimiya, 9, 1578 (1973).
23. B. S. Krasikov and V. V. Sysoeva, Dokl. Akad. Nauk SSSR, 114, 826 (1957).
24. V. V. Batrakov, B. B. Damaskin, and Yu. P. Ipatov, Elektrokhimiya, 10, 144 (1974).
25. L. I. Antropov, Tr. Erevan. Politekh. Inst., 2, 97 (1940).
26. L. I. Antropov, Zh. Fiz. Khim., 25, 1494 (1951).
27. L. I. Antropov, Ukr. Khim. Zh., 29, 555 (1963).
28. L. I. Antropov, Reference or φ Scale of Potentials [in Russian], Znanie, Leningrad (1965).
29. L. I. Antropov, Khim. Tekhnol., 17, 75 (1971).
30. R. C. Rein, C. M. Sliepcevich, and R. D. Daniels, J. Electrochem. Soc., 112, 739 (1965).
31. B. B. Damaskin, O. A. Petrii, and V. V. Batrakov, Adsorption of Organic Substances by Electrodes [in Russian], Nauka, Moscow (1968).
32. S. M. Mayanna and T. U. V. Setty, Corrosion Sci., 14, 651 (1974).
33. S. M. Mayanna and T. U. V. Setty, Corrosion Sci., 15, 627 (1975).
34. P. Delahay, Double Layer and Electrode Kinetics, Wiley (1965).
35. H. Kaesche, Corrosion of Metals [in German], Springer-Verlag, Berlin (1966), p. 129.
36. H. Kaesche, Z. Elektrochem., 63, 492 (1959).
37. M. Breiter and R. Clamroth, Z. Elektrochem., 58, 493 (1954).
38. L. I. Antropov and A. T. Petrenko, Zh. Prikl. Khim., 31, 1849 (1958).
39. Ya. M. Kolotyrkin, Usp. Khim., 31, 332 (1962).
40. Ya. M. Kolotyrkin, Zashch. Met., 3, 131 (1967).
41. Ya. M. Kolotyrkin, Zh. Vses. Khim. O-Va., 20, 59 (1975).
42. Ya. M. Kolotyrkin and G. M. Florianovich, Science and Engineering Abstracts: Corrosion and Corrosion Protection [in Russian], Vol. 4, All-Union Institute of Scientific-Technical Information (VNIITI), Moscow (1975), p. 5.
43. L. I. Antropov, Corrosion Sci., 7, 707 (1967).
44. L. I. Antropov, Izv. Sev.-Kavkask. Nauch. Tsentra, Vysshaya Shkola, 2, 3 (1974).
45. L. I. Antropov and I. S. Pogrebova, Science and Engineering Abstracts: Corrosion and Corrosion Protection [in Russian], Vol. 2, All-Union Institute of Scientific-Technical Information (VNIITI), Moscow (1973), p. 27.
46. L. I. Antropov, Zashch. Met., 2, 279 (1966).
47. L. I. Antropov, I. S. Pogrebova, and G. I. Dremova, in: Inhibitors of Corrosion during Electrodeposition of Metals [in Russian], Dnepropetrovsk (1971), p. 10.
48. A. N. Frumkin, B. B. Damaskin, N. B. Grigor'ev, and T. A. Bagotskaya, Electrochim. Acta, 19, 69 (1974).
49. V. V. Batrakov, B. B. Damaskin, and Yu. P. Ipatov, Elektrokhimiya, 10, 144 (1974).
50. L. I. Antropov, Zh. Fiz. Khim., 37, 965 (1963).
51. I. P. Anoschenko, Tr. Novacherk. Politekh. Inst., 25/39, 43 (1954).
52. I. P. Anoshchenko, in: Corrosion Inhibitors [in Russian], Vol. 2, Moscow (1957), p. 45.
53. A. I. Podobaev and F. N. Kurbanov, Teploenergetika, 4, 73 (1964).
54. L. I. Antropov and Yu. A. Savgira, Proceedings of the Third International Congress on Corrosion of Metals [in Russian], Vol. 2, Mir, Moscow (1968), p. 54.
55. R. N. Ride, J. Electrochem. Soc., 103, 48 (1956).
56. L. I. Antropov, I. S. Pogrebova, and G. I. Dremova, Zashch. Met., 7, 3 (1971).
57. I. S. Pogrebova, G. I. Dremova, and L. I. Antropov, Ref. Inf. Zakonch. Rabot. Vuzakh Ukr. SSR, Khim. Promyshl., 17, 77 (1976).
58. M. A. Marinich, Candidate's Dissertation, Kiev Polytech. Inst. (1973).
59. L. I. Antropov, G. I. Dremova, and I. S. Pogrebova, Ref. Inf. Zakonch. Rabot. Vuzakh Ukr. SSR, Khim. Promyshl., 16, 70 (1975).
60. I. S. Pogrebova and G. I. Dremova, Second International Scientific-Technical Conference on CMEA Problems: "Development of measures for protecting metals against corrosion," Prague, Czechoslovakia (1975), p. 1860.

61. Z. A. Iofa, E. I. Lyakhovetskaya, and K. Sharifov, Dokl. Akad. Nauk SSSR, 84, 543 (1952).
62. I. N. Putilova, S. A. Balezin, and V. P. Barannik, Inhibitors of Metal Corrosion [in Russian], Goskhimizdat, Moscow (1958).
63. T. Murakawa, S. Naguara, and N. Hackerman, Corrosion Sci., 7, 79 (1967).
64. Z. Scklowska-Smialowska, Inhibitors of Metal Corrosion [in Polish], Warsaw, N. T. (1971).
65. M. G. Fontana and R. W. Staehle (editors), Advances in Corrosion Science and Technology, Vol. 1, Plenum Publ., New York (1970).
66. L. I. Antropov, I. S. Pogrebova, and G. I. Dremova, Elektrokhimiya, 8, 108 (1972).

CHOICE OF THE STANDARD CORROSIVE MEDIUM FOR PLOTTING A POTENTIODYNAMIC CURVE OF ANODIC POLARIZATION FOR STEELS 18-10

L. A. Medvedeva, V. M. Knyazheva, Ya. M. Kolotyrkin, and S. G. Babich

UDC 620.193.01

As a result of much search, an electrolyte on the basis of $HClO_4$ + NaCl is proposed which at room temperature yields a well-reproducible potentiodynamic curve of anodic polarization for steels 18-10, with the active-to-passive transition range and the stable passive state distinctly evident.

The use of potentiostatic and potentiodynamic anodic polarization curves for characterizing the corrosive properties of stainless steels 18-10 [1] is often encumbered by the fact that these steels usually undergo self-passivation in dilute H_2SO_4 solutions selected for this purpose [1-4]. Regarding the problem, it was the object of this study to develop an electrolyte which at room temperature would ensure a stable corrosion potential (φ_{cor}) of steel in the active state and would yield a complete anodic polarization curve so as to distinctly reveal the Tafel segment within the active range and with a stable passive state also retained. Accordingly, we studied the effect of certain activating additives (thiourea and CNS^-, F^-, Cl^- anions) and their concentration on the potentiodynamic anode curve for quenched stainless steels 18-10 in solutions of sulfuric acid as well as of perchloric acid.

Method of the Experiment

Grade 08Kh18N10T steel (GOST 5632-72) in the quenched state was used in this study.

Prior to testing, the specimens (plates 50 × 20 × 2 mm in size) had been cleaned with emery paper of various grain sizes and repeatedly degreased with sulfuric ether. With the aid of special tools [5], the active surface was separated in the shape of a circle 1 cm^2 in area by insulating the rest of the surface with a 1:2 mixture of rosin and paraffin.

The solutions were prepared in water bidistillate. Sulfuric acid and perchloric acid were distilled twice, the salts were twice recrystallized. The electrode potential was measured relative to a mercury sulfate (in 1 N H_2SO_4) reference electrode and then converted to the potential relative to a normal hydrogen electrode. The measurements were performed at room temperature in a three-electrode cell in a nitrogen atmosphere pure of oxygen traces; in some tests the measurements were made in aerated solutions.

Prior to electrochemical measurements, a specimen had been activated with a cathode current of 10 mA/cm^2 density for 5 min, whereupon the cathodic polarization curve up to φ_{cor} and the potentiodynamic

L. Ya. Karpov Physicochemical Scientific-Research Institute. Translated from Zashchita Metallov, Vol. 13, No. 4, pp. 400-405, July-August, 1977. Original article submitted May 5, 1976.