EFFECT OF HYDROGEN SULFIDE ON IRON CORROSION AND ON INHIBITOR ADSORPTION IN ACIDIC SOLUTIONS

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UDC 620.193.01

Corrosion of pure iron by hydrogen sulfide in acidic solutions and protection from this corrosion by inhibitors have been studied under conditions such that the reactions were not complicated by the formation of films at the metal surface.

Mechanism for the Effect of Hydrogen Sulfide on the Cathodic and Anodic Reactions

In solutions of sufficiently high conductivity, the corrosion of a metal is described most simply by the equations of electrochemical kinetics. At a steady potential φ_{ct} in a deaerated solution, the rate i_c of the cathodic evolution of hydrogen is equal to that i_a of the anodic ionization of the metal and to the corrison rate: $i_{cor} = i_c = i_a$.

The potential dependences of the hydrogen evolution rate and the metal ionization rate can be found from polarization curves. Extrapolation of a plot of φ vs log i along the log i axis yields log i_{cor}. The i_{cor} values thus obtained agree with the corrosion rate determined from the sample weight loss.

All the results are for 20°C, and the potentials are expressed with respect to the hydrogen electrode in the same acidic solution (φ_r). Curves 1, 1' and 3, 3' in Fig. 1 show that addition of Na_2S to 1 N H_2SO_4 causes a slight acceleration of the cathodic process, and a greater acceleration of the anodic process.

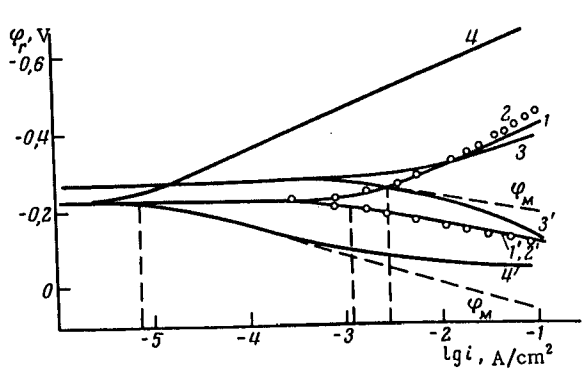

Fig. 1

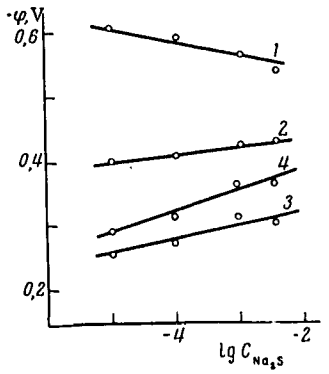

Fig. 2

Fig. 1. Cathodic and anodic polarization curves for zone-refined iron. 1) 1 N H_2SO_4; 2) +0.001 M $N(C_6H_5CH_2)_3$; 3) $+10^{-4}$ N Na_2S; 4) $+10^{-4}$ N Na_2S + 0.001 M N $(C_6H_5CH_2)_3$. The dashed curves were obtained by an oscillographic method.

Fig. 2. Dependences on log [Na_2S] of:1) φ_c; 2) φ_{ct}; 3) φ_a; 4) φ_M.

M. V. Lomonosov Moscow State University. Translated from Zashchita Metallov, Vol. 6, No. 5, pp. 491-498, September-October, 1970. Original article submitted June 16, 1969.

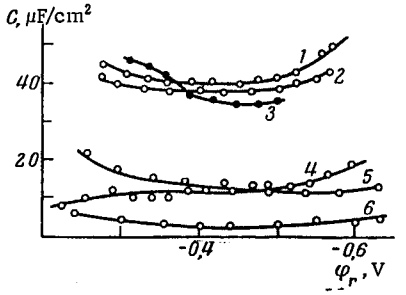

Fig. 3

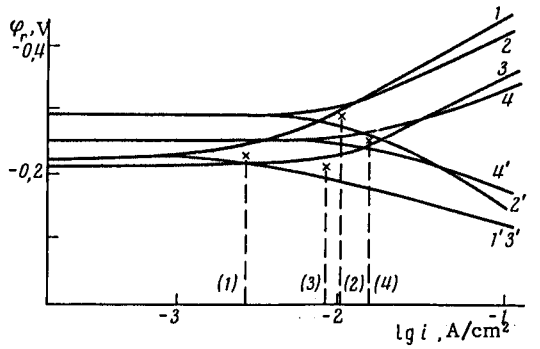

Fig. 4

Fig. 3. Differential capacitance of iron. 1) 1 N H_2SO_4; 2) $+10^{-4}$ M N $(C_6H_5CH_2)_3$; 3) $+10^{-4}$ N Na_2S; 4) $+10^{-4}$ N Na_2S + 10^{-4} M N$(C_6H_5CH_2)_3$; 5) $+8\cdot10^{-2}$ g/liter catapin; 6) $+8\cdot10^{-2}$ g/liter catapin + 10^{-4} N Na_2S. Frequency: 800 Hz.

Fig. 4. Cathodic and anodic polarization curves for zone-refined iron. 1) In 1 N H_2SO_4; 2) + 0.0001 N Na_2S; 3) 0.01 M sulfosalicyclic acid; 4) + 0.01 M sulfosalicylic acid + 0.0001 N Na_2S.

TABLE 1. Corrosion–Retardation Coefficients for Armco Iron in 1 N H_2SO_4 in the Presence of Certain Organic Substances and Hydrogen Sulfide

No.	Organic compound	Concentration, M	γ in 1 N H_2SO_4	γ in 1 N H_2SO_4 + 0.001 N Na_2S
1	None	—	1	0,22
2	$C_6H_{13}OH$	Sat.	1,3	0,05
3	$C_5H_{11}COOH$	Sat.	1,2	0,05
4	$CH_3(CH_2)_3COOH$	0,05	1,1	0,22
5	CH_3CHO	0,1	7,8	0,30
6	CH_3CH_2CHO	0,1	7,6	0,14
7	$C_6H_{13}SO_3Na$	0,01	0,3	0,05
8	$C_{12}H_{25}SO_3Na$	0,001	0,5	0,06
9	$C_{18}H_{37}SO_3Na$	Sat.	2,1	0,06
10	$C_6H_5SO_3Na$	0,01	0,5	0,27
11	CH_2NH_2COOH	0,005	1,0	0,20
12	Phenyl-β-alanine	0,005	1,3	0,28

The acceleration of the cathodic process is evidently associated with adsorption of HS^- anions; however, the mechanism for the effect of hydrogen sulfide on the cathodic discharge of hydrogen ions is not yet understood. Anions adsorbed on the metal may accelerate the discharge of hydrogen ions because of the arisal of a negative adsorption ψ_1-potential; they may retard it because of a reduction in the binding energy between hydrogen and the metal [1, 2]:

$$i_c = k[H^+]\exp\left\{-\frac{F}{RT}[\alpha(\varphi-\psi_1+\Delta W_{M-H})-\psi_1]\right\}, \quad (1)$$

$$\varphi_c = k-\frac{RT}{\alpha F}\ln i+\frac{RT}{\alpha F}\ln[H^+]-\frac{1-\alpha}{\alpha}\psi_1-f(\Delta W_{M-H}), \quad (1a)$$

where ψ_1 is the potential which arises during ion or inhibitor adsorption, $f(\Delta W_{M-H})$ is a function which describes the reduction of the hydrogen–metal binding energy, and α is a constant near 0.5. For a metal with a high hydrogen overvoltage and a low M-H binding energy, e.g., during the adsorption of halide anions on mercury, the ψ_1-potential is found to accelerate the adsorption. For a metal with a high M-H binding energy, e.g., iron, the reduction ΔW_{M-H} of the binding energy is dominant, and the hydrogen–ion discharge is retarded. The HS^- ions, like the halide ions, are chemisorbed on iron, but their effects are different. Halide ions reduce the differential capacitance of the iron and increase the hydrogen overvoltage, while HS^- ions have almost no effect on the capacitance (Fig. 3) and lower the hydrogen overvoltage, although they probably also reduce the M-H binding energy, since they form a tight bond with the metal. The reasons for these differences are unclear.

The accelerated ionization of iron in the presence of hydrogen sulfide, similar to that which results from a pH change [3, 4], is probably due to the formation of a surface catalyst. Although the structure of this catalyst is unknown, the knowledge that H_2S can adsorb cationic inhibitors in acidic solutions, leads one to expect H_2S to form an ionic or dipole compound on the iron surface. The catalyst formation and its effect on the iron ionization can be described by the following equations: *

$$Fe + H_2S + H_2O = (FeHS^-)_{ads} + H_3O^+ \quad (2)$$

$$[FeHS^-]_{ads} = K[H_2S] / [H_3O^+] \quad (3)$$

*We neglect the possible effects of other anions on the kinetics of the anodic reaction [6].

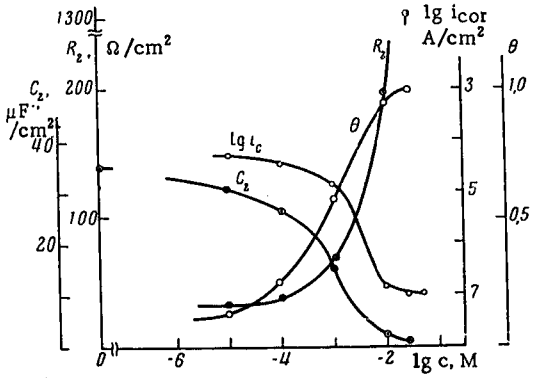

Fig. 5. Dependence of: 1) C_2; 2) θ; 3) R_2; and 4) log i_c on the logarithm of the dibutylsulfoxide concentration in 1 N H_2SO_4.

$$(FeHS^-)_{ads} \rightarrow FeHS^+ + 2e \quad (4)$$

$$FeHS^+ + H_3O^+ \rightarrow Fe^{2+} + H_2S + H_2O \quad (5)$$

$$i = k'[FeHS^-]_{ads} \exp(2\beta\varphi F/RT) \quad (6)$$

$$i = k''[H_2S]/[H_3O^+] \exp(2\beta\varphi F/RT) \quad (7)$$

$$\varphi_a = k + \frac{RT}{2\beta F}\{\ln[H_3O^+] - \ln[H_2S] + \ln i_a\}^* \quad (8)$$

Figure 1 shows that the slope of the anodic curve increases with increasing i_a for the acidic solution with Na_2S, and that the curve approaches that for the pure acidic solution. This is apparently due to the removal of the catalyst $(FeHS)_{ads}$ into the solution, along with the surface iron atoms which have dissolved, and to the inadequate rate of hydrogen sulfide adsorption. The φ_M vs log i dependence (dashed curve in Fig. 1) obeys a Tafel equation. For this curve, the φM values were determined from the point of the characteristic break on oscillograms showing the application of a constant-density anodic current [5].

The values of φ_k, φ_{ct}, φ_a, and φ_M depend linearly on the logarithm of the H_2S concentration for log i = –1 in 0.1 N H_2SO_4 [7] (Fig. 2).*

From Eq. (8), the order of the reaction is found to be $\Delta \log i/\Delta \log [H_2S] = -1$. From experiments, we have $\Delta\varphi_M/\Delta \log [H_2S] = -45$ mV and $\Delta\varphi_M/\Delta \log i_a = 55$ mV, yielding a reaction order of –0.81. The disagreement with Eq. (8) may occur because the equilibrium required by Eq. (2) is not established during the recording of the φ_M, t curves. The H_2S effects become less apparent as the acid concentration is increased, in agreement with (8), and the difference between φ_a and φ_M decreases. Equilibrium (2) shifts to the left as the H_3O^+ concentration increases, and the catalyst concentration decreases.

It should also be noted that corrosion in the presence of hydrogen sulfide is accompanied by penetration of hydrogen and sulfur into metal, by more than 1.5 μ for the sulfur [8].

Adsorption and Effects of Inhibitors in the Presence of Hydrogen Sulfide

Organic nitrogen compounds (amides, tetralkylammonium bases, pyridine salts, etc.) are usually used to inhibit acidic corrosion of iron and steel. As was shown earlier [9], these cationic compounds are adsorbed poorly from solutions of oxygenous acids, since the steady-state corrosion potential for iron is more positive than the iron zero charge potential. It has also been shown [10] that inhibitors are adsorbed well and become effective in the presence of halide anions.

These inhibitors also have a strong retarding effect in the presence of small concentrations of hydrogen sulfide. Figure 1 shows the combined effects of tribenzylamine (TBA) and H_2S. Curve 2 for the TBA almost coincides with the curve for the pure 1 N H_2SO_4. Addition of H_2S retards the cathodic and anodic reactions and reduces i_{cor} (curve 4). The slope of the anodic curve decreases with increasing i_a, and approaches the curve for the pure acid. This is due to removal of inhibitor into the solution along with the dissolved iron, and to the inadequate inhibitor-adsorption rate. The φ_M vs log i curve (dashed curve), found from the maxima of current-application recordings, is a Tafel line [5]. We can conclude from the experiments of [11, 12] that very small H_2S concentrations (10^{-6} M, greatly intensify the effects of cationic inhibitors, and that very small inhibitor concentrations (10^{-6} M TBA) suppress this intensifying effect of the H_2S. The maximum effect is observed at a definite ratio of H_2S and inhibitor concentrations [12].

A tracer study [8] has shown that HS^- ions bind more tightly with surface iron atoms than do iodine ions, so the latter are screened by hydrogen sulfide. The retarding effect of KI is reduced when Na_2S is added to an acidic solution containing KI, while addition of KI to a $H_2SO_4 + Na_2S$ solution has essentially no effect on the adsorption or on the stimulating effect of the hydrogen sulfide. However, the combined addition of Na_2S + KI to an inhibitor solution, e.g., TBA, reduces the corrosion rate significantly more than does either of the salts by itself [8].

*According to thermodynamic data for the equilibrium $FeS + 2H^{+2} + 2e = Fe + H_2S$, the equilibrium potential is $E = -0.334 - 0.0591\ pH - (0.0295) \log a_{H_2S}$. Here and below, it is assumed that Na_2S converts into H_2S when it interacts with H_2SO_4 in solution.

The degree of inhibitor adsorption can be determined from the drop in the differential double-layer capacitance C. From the C vs φ curves in Fig. 3, calculated for a parallel connection of a resistance and a capacitance, we see that $\Delta C = 1.0\text{-}1.5$ $\mu F/cm^2$ in 1 N H_2SO_4 + TBA, $\Delta C = 2$ $\mu F/cm^2$ in 1 N H_2SO_4 + Na_2S, and $\Delta C = 30$ $\mu F/cm^2$ for combined TBA and Na_2S. The inhibiting effect of the catapin (a chloride salt of methylbenzylpyridine*) is largely due to the chloride ions (curve 5 in Fig. 3), but the addition of Na_2S significantly increases its adsorption (curve 6 in Fig. 3), while the corrosion suppresion coefficient γ increases ($\gamma = \rho_0/\rho_i$, where ρ_0 and ρ_i are the corrosion rates in the solution without and with the inhibitor, respectively). With a catapin concentration of 2.5 g/liter in 1 N H_2SO_4, for example, we find $\gamma = 110$; after addition of 0.001 N Na_2S, we find $\gamma = 700$; and at a catapin concentration of 0.25 g/liter, we find $\gamma = 18$. A significant inhibiting effect can be obtained after the addition of 10^{-5} N Na_2S, for which $\gamma = 175$.

The mechanism for the effect on the cathodic process of inhibitors in the presence of hydrogen sulfide can be explained in the following manner. Adsorbed HS^- ions form dipoles whose negative ends, toward the solution, aid adsorption of cationic inhibitors. The positive ψ_1^- potential which is set up leads to a retardation of the cathodic reaction, as follows from Eq. (1). Adsorbed HS^- anions thus act as a connecting bridge between the metal atoms and the inhibitor cations. The retarding effect on the anodic reaction is due to a blocking of the operation of the surface catalyst by adsorbed inhibitor cations. The positive adsorption ψ_1^- potential which arises retards the escape of Fe ions from the metal.

It should also be noted that hydrogen brittleness and stratification bubbles of iron and steels are to a large extent suppressed in the presence of an adsorption inhibitor of the cationic type [7, 11].

Iron Corrosion During the Joint Adsorption of Hydrogen Sulfide, Alcohols, Organic Acids, Aldehydes, and Sulfo Acids

Organic acids and alcohols are adsorbed slightly from sulfuric acid solutions, apparently because of the hydrophilic nature of the iron surface; accordingly, they have essentially no effect on the iron corrosion rate [5].

Aldehydes of the aliphatic series are adsorbed on the iron surface and inhibit its corrosion,† particularly during a joint adsorption with halide ions [11].

During the acidic corrosion of iron, the aldehydes are reduced to alcohols, in a process which consumes some of the hydrogen evolved during corrosion.

The anions of the sulfo acids are adsorbed well on a positively charged iron surface, but tend to accelerate iron corrosion because of the arisal of a negative adsorption potential.‡

Hydrogen sulfide intensifies the stimulating effect of the sulfo acids. Differential-capacitance curves show that the addition of 10^{-2} M sulfosalicylic acid to 1 N H_2SO_4 leads to $\Delta C = 5.1$ $\mu F/cm^2$; its addition along with 10^{-3} N Na_2S leads to $\Delta C = 9\,\mu F/cm^2$, i.e., greater than the sum of the ΔC values from sulfosalicylic acid and Na_2S separately. The curves in Fig. 4 show that the corrosion rate when sulfosalicylic acid and Na_2S are both present in the solution is higher than would follow from the individual effects of these substances.

Organic acids and alcohols whose molecular weights are not too high also intensify the stimulating effect of hydrogen sulfide, as can be seen from Table 1.

Addition of the negative –COOH group to an amine molecule causes a reduction in the inhibiting effect of an amino acid. The closer the –COOH group is to the nitrogen in the amine, the more this group repels electrons from the positive nitrogen atom, the lower the ability of the latter to connect hydrogen ions, and thus the weaker the retarding effect of the amino acid on the electrochemical reactions and the iron corrosion. During joint adsorption with nitrogen sulfide, the stimulating effect of the latter is obtained.

*The corresponding commercial product is catapin A.

† The aldehydes are apparently of a slightly onium nature [13].

‡ The sulfo acids should be well purified, since a very small impurity of a high-molecular weight substance of an onium nature will retard corrosion. The high-molecular weight sulfo acids act as inhibitors, because of the screening effect of the long hydrocarbon chain, but they nevertheless stimulate the effect of hydrogen sulfide.

Inhibiting Effect of Organic Compounds of Sulfur

Many organic compounds containing sulfur (thiourea and its derivatives, sulfoxides, thiocyanates, sulfoamides, etc.) are good inhibitors of iron corrosion in acidic solutions. Their effects are usually due to the appearance of hydrogen sulfide, and depend on the concentration and nature of the compound, the acid concentration, the agitation, and the temperature. It has been established in tracer studies [14, 15] that thiourea and its derivatives, as well as several other organic compounds of sulfur, are reduced, and hydrogen sulfide is formed, during the acidic corrosion of iron [12, 16]. Thiourea is probably reduced according to the scheme

$$(NH_2)_2CS + 6e + 8H^+ \rightarrow H_2S + CH_3NH_3^+ + NH_4^+ \qquad (9)$$

In the case of the sulfoxides, the corresponding sulfides are formed [17]. The thiocyanate reduction involves an intermediate formation of thiourea [12]. Hydrogen is required to reduce the thiourea; from the amount required, one can calculate the extent of the decomposition. Experiments showed that during a 16-h corrosion of 8 cm^2 of iron in 50 ml of a 0.1 M thiourea solution in 1 N H_2SO_4, a few tenths of a percent decomposes; in a 0.001 M solution, about 1% of the thiourea decomposes; i.e., a H_2S concentration of 10^{-4} N is accumulated in the first case, and 10^{-5} N in the second case.

The molecules of the organic compounds of sulfur which do not decompose, like the nitrogen compounds, are of an onium nature; i.e., they connect hydrogen ions to their own molecules in acidic solutions, and convert into the corresponding cations [18]; the scheme is

$$R_3X + H^+ \rightarrow [R_3XH]^+$$
$$R_2SO + H^+ \rightarrow [R_2SOH]^+$$
$$R_3AsO + H^+ \rightarrow [R_3AsOH]^+$$
$$RHN{-}\overset{\overset{S}{\|}}{C}{-}NHR + H^+ \rightarrow [RHN{-}\overset{\overset{SH}{|}}{C}{-}NHR]^+$$

where R is the radical, and X is N, P, or As.

The hydrogen sulfide anions which appear during the reduction of the sulfur compounds aid the adsorption of the cations of the undecomposed molecules of the onium compounds. A reduction of these compounds amounting to only a few per cent, occurring right at the surface of the corroding iron, is nevertheless capable of providing the hydrogen sulfide required to form a monolayer of chemisorbed HS^- ions. When large H_2S concentrations appear, however, the iron corrosion is stimulated. A 0.1 M solution of thiourea, for example, stimulates the corrosion, while a 0.001 M solution inhibits it. In the case of KCNS in 0.0001 and 0.001 N concentrations, the corrosion is stimulated; on the other hand, a 0.1 N concentration inhibits it, because some thiourea and HS^- ions are formed during the reduction of the thiocyanate (see [12]). In low concentrations, the HS^- ions aid amine adsorption and intensify their inhibiting effect.

The inhibiting effect of the sulfoxides is due primarily to an increase in the hydrogen overvoltage; they have a weaker effect on the anodic ionization of iron. In addition, the retarding effect falls off sharply with decreasing sulfoxide concentration. It has been found that the differential capacitance falls off sharply at moderate concentrations (the case of dibutylsulfoxide is shown in Fig. 5), and reaches an extremely low value ($\sim \mu F/cm^2$) at large concentrations (the C_2 vs log c curves). As the capacitance is reduced, the surface coverage by the inhibitor (the θ vs log c curves) increases, and the corrosion rate falls off (the log i_{cor} vs log c curves). The reaction impedance also increases sharply with increasing $(C_4H_9)_2SO$ concentration, and reaches 1300 Ω/cm at 3.10^{-2} (the R vs log c curves). This latter effect indicates that the electrode becomes covered with a high-resistivity film as the limiting surface coverage is approached; the high hydrogen overvoltage and the strong inhibiting effect of the sulfoxides are due to the appearance of this film.

The high-molecular weight, relatively insoluble derivatives of thiourea, and the sulfoxides also inhibit iron corrosion. Addition of a small amount of hydrogen sulfide intensifies the inhibiting effect in several cases; addition of a large amount tends to reduce this effect. It was assumed in [16, 17] that the molecules in the thiourea derivates could be adsorbed because of the large dipole moment of the sulfhydryl group, and also because of the interaction of their sulfur, which has two free electrons, with the surface iron atoms, which have unfilled d-shells [16]. However, several factors, which we mentioned and described in [14], show that relatively insoluble thiourea derivatives also are partially reduced during iron corrosion in acid solutions, and that the hydrogen sulfide ions formed affect the adsorption.

CONCLUSIONS

The mechanism by which hydrogen sulfide stimulates iron corrosion has been examined. The stimulating effect is apparently due to acceleration of the anodic ionization of iron because of the catalyst $(FeHS^-)(FeHS^-)_{ads}$, which is adsorbed on the surface.

Small hydrogen sulfide concentrations greatly intensify adsorption and the inhibiting effect of organic compounds of an onium nature because of the formation of anionic bridges of adsorbed HS^- ions. Joint adsorption of hydrogen sulfide with sulfo acids, alcohols, organic acids, and aldehydes tends to stimulate the corrosion of iron in acidic solutions.

The inhibiting effect of the series of sulfur compounds is due to their onium nature and to the appearance of hydrogen sulfide or sulfides during the partial reduction of these compounds during the acidic corrosion of iron.

LITERATURE CITED

1. A. N. Frumkin and A. I. Shlygin, Izv. Akad. Nauk SSSR, Ser. Khim., 773 (1936); A. N. Frumkin, Usp. Khim., 24, 933 (1955).
2. L. A. Medvedeva and Ya. M. Kolotyrkin, Zh. Fiz. Khim., 31, 2668 (1957).
3. K. Heusler, Z. Elektrochem., 63, 582 (1958).
4. H. Jamaoka and H. Fischer, Electrochem. Acta, 10, 679 (1965).
5. Z. A. Iofa, V. V. Batrakov, and Ho Ngok Ba, Zashchita Metal., 1, 55 (1965).
6. Ya. M. Kolotyrkin, Zashchita Metal., 3, 131 (1967).
7. Z. A. Iofa, Proceedings of the All-Union Scientific Conference on Combatting Corrosion [in Russian], Gostoptekhizdat, Moscow (1962), p. 335.
8. Z. A. Iofa, Dokl. Akad. Nauk SSSR, 119, 971 (1958).
9. Z. A. Iofa, Vestn. MGU, No. 2, 139 (1956).
10. Z. Iofa, E. Lyakhovetskaya, and K. Sharifov, Dokl. Akad. Nauk SSSR, 85, 543 (1952).
11. Z. A. Iofa and G. T. Tomashova, Zh. Fiz. Khim., 34, 1036 (1960); Z. A. Iofa and Wei Pao Ming, Liquid-Phase Catalytic Reactions [in Russian], Izd. KazakhSSR, Alma-Ata (1963), p. 197.
12. Z. A. Iofa, Ho Ngok Ba, and M. K. Vasil'eva, Zh. Fiz. Khim., 39, 2182 (1965).
13. O. A. Peutov, Theoretical Problems in Organic Chemistry [in Russian], Izd. MGU (1956), p. 228.
14. A. Makrides and N. Hackerman, Ind. Engng Chem., 47, 1773 (1955).
15. A. I. Fil'ko, Inhibitors of Metal Corrosion [in Russian], Izd. MGPI (1960), p. 62.
16. L. Felloni, 3 Congress de la Federat. Europ. de la corros., Brussels, 1963.
17. L. Covallaro, L. Felloni, G. Trabanelli, and F. Zucchi, 2 Sympos. Europ. sur les Inhibit. de corros., Ferrara, 1966; (1964), p. 417.
18. L. Harner and F. Rottger, Werkstoffe und Korrosion, 15, 125 (1964).