Inhibition of corrosion and hydrogen permeation into carbon steel in solutions containing hydrogen sulphide and carbon dioxide

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Abstract

The efficiency of ethoxy higher aliphatic amines (EOAs) against carbon dioxide and hydrogen sulphide corrosion and hydrogen permeation into carbon steel in acid solutions has been studied. The influence of the number of ethoxy groups (2, 5 and 14), the length of the hydrocarbon radical ($R = C_{10}-C_{13}$ and $R = C_{17}-C_{20}$), medium acidity (0.005−0.05 M HCl), and electrode potential was investigated. Concurrently, the influence of higher aliphatic amine bottoms (emulgin) that are a mixture of primary and secondary aliphatic amines was studied. The protective efficiency of EOAs reaches 95−99.9%, hydrogen permeation decreases both at the corrosion potential and under conditions of anodic and cathodic polarization of the steel electrode. The inhibiting effect of emulgin is 96−97%.

Introduction

Development of composite inhibitors and, specifically, inhibitors against general, hydrogen sulphide and carbon dioxide corrosion and hydrogen permeation into steel will enable a considerable reduction of the too broad assortment of inhibitors [1−10], thus improving the economical efficiency of inhibiting protection and solving a wide range of ecological problems in both production and application. With that end in view, the multifunctional properties of a mixture of homologous ethoxy amines (EOAs) and, in addition, of higher aliphatic amines bottoms that are a mixture of primary and secondary aliphatic amines (emulgin) were studied. The practical insolubility in aqueous media in molecular forms, which increases upon protonation, is common to both EOAs and emulgin.

Experimental

HCl solutions (0.005 to 0.05 M) were used as background. H_2S was introduced by saturating the background solutions with gaseous hydrogen sulphide. The concentration of

the latter was checked by iodometric titration. In a number of cases, the working solutions were saturated with CO_2 (1.7 g/L) using gravimetric control.

Corrosion tests of steel samples sized $20 \times 15 \times 3$ mm and treated up to surface finish rating 6 followed by acetone degreasing were conducted in cells with ground-in plugs (6 to 72 hours). Potentiostatic polarization measurements were performed in a three-electrode cell (pyrex) with divided anode and cathode spaces. The electrophysical properties of the steel surface were studied using the photoelectric polarization method (PEP) [11]. The impedance measurements were carried out on a total impedance meter (VM 507).

The solid-phase diffusion rate of hydrogen (i_H) was evaluated at E_{cor} or under cathodic ($\Delta E_c = E_{cor} - E_c$) and anodic ($\Delta E_a = E_a - E_{cor}$) polarization of the working side of the membrane (MB) in an electrochemical hydrogen permeation cell (pyrex) which was similar to that used by Devanathan [12]. The procedure is described in detail in [13].

The efficiency of EOAs and emulgin (averaged $M = 320$ g/mole) at concentrations of 25 to 200 mg/L (Table 1) was studied.

Table 1. Products investigated as inhibitors against corrosion and hydrogen permeation into St3 steel.

EOAs Number	Formula	R	$n = x + y$
I		$C_{10} - C_{13}$	2
II		$C_{10} - C_{13}$	5
III	$R - N \begin{smallmatrix} (CH_2CH_2O)_x H \\ (CH_2CH_2O)_y H \end{smallmatrix}$	$C_{10} - C_{13}$	14
IV		$C_{17} - C_{20}$	5
V		$C_{17} - C_{20}$	14
Emulgin	$R - NH_2$	$C_{10} - C_{15}, C_{16} - C_{20}$	–
	$R - NH - R$	$C_{10} - C_{15}, C_{16} - C_{20}$	–

The protective effect of the inhibitors was calculated according to the equation:

$$Z, \% = (K_0 - K_i) \cdot 100 / K_0,$$

where K_0 and K_i are the steel corrosion rates in uninhibited and inhibited solutions, respectively. The hydrogen diffusion depression coefficient γ was calculated according to the formula:

$$\gamma = i_H^0 / i_H,$$

where i_H^0 and i_H are hydrogen diffusion flux in the solutions without and with inhibitors, respectively.

Results

1. The influence of EOAs on steel corrosion. In 0.005 M solutions of HCl without or with CO_2, the Z_{EOAs} values are not high (Table 2). The highest efficiency is characteristic of the amines with R = C_{17}−C_{20}. The presence of H_2S increases Z. The growth of n_{EOAs} (in the presence of CO_2 and H_2S) with R = C_{10}−C_{13} decreases Z, whereas the opposite dependence is observed for the amines with R = C_{17}−C_{20}. In the presence of both H_2S and CO_2, Z_{EOAs} increases. The growth of C_{HCl} also influences Z. The presence of CO_2 (1.7 g/L) decreases Z.

Table 2. Steel corrosion rate (K, g/(m²h)) and protective effect (Z, %) of inhibitors (100 mg/L) in 0.005 M (numerator) and 0.05 M HCl (denominator) solutions containing 80 mg/L H_2S and/or 1.7 g/L CO_2. 293 K, tests duration is 18 hours.

Inhibitor	Additive							
	−		**H_2S**		**CO_2**		**$H_2S + CO_2$**	
	K	*Z*	*K*	*Z*	*K*	*Z*	*K*	*Z*
none	$\frac{0.28}{1.27}$	−	$\frac{0.41}{3.38}$	−	$\frac{0.09}{0.09}$	−	$\frac{0.36}{1.30}$	−
I	$\frac{0.17}{0.12}$	$\frac{39}{91}$	$\frac{0.07}{0.06}$	$\frac{76}{98}$	$\frac{0.06}{0.07}$	$\frac{36}{21}$	$\frac{0.07}{0.06}$	$\frac{81}{96}$
II	$\frac{0.20}{0.10}$	$\frac{27}{92}$	$\frac{0.14}{0.08}$	$\frac{66}{98}$	$\frac{0.20}{0.10}$	$\frac{27}{18}$	$\frac{0.20}{0.10}$	$\frac{84}{96}$
III	$\frac{0.14}{0.13}$	$\frac{50}{90}$	$\frac{0.13}{0.10}$	$\frac{67}{97}$	$\frac{0.06}{0.07}$	$\frac{34}{25}$	$\frac{0.05}{0.06}$	$\frac{85}{96}$
IV	$\frac{0.13}{0.12}$	$\frac{53}{90}$	$\frac{0.12}{0.10}$	$\frac{69}{97}$	$\frac{0.055}{0.07}$	$\frac{38}{26}$	$\frac{0.07}{0.05}$	$\frac{81}{97}$
V	$\frac{0.15}{0.26}$	$\frac{45}{80}$	$\frac{0.08}{0.14}$	$\frac{80}{96}$	$\frac{0.05}{0.10}$	$\frac{45}{0}$	$\frac{0.04}{0.06}$	$\frac{89}{95}$

2. The influence of EOAs on the kinetics of partial electrode reactions (PERs). According to the nature of influence on kinetics of PERs in 0.005 M solutions of HCl, the EOAs under study can be divided into three groups (Fig. 1):

   – those that practically do not change the kinetic characteristics of PERs (product II), $E_{cor}^{II} = E_{cor}^{0}$, where the upper index is the product number and 0 is its absence;

   – those that only inhibit anodic reactions without substantial influence on the cathodic process in the kinetic area (product I, $E_{cor}^{I} > E_{cor}^{0}$);

– those that retard H_3O^+ reduction and stimulate the anodic process (products III, IV and V, $E_{cor} < E_{cor}^0$) with the first effect prevailing. For these, the following sequence is observed: III > IV > V.

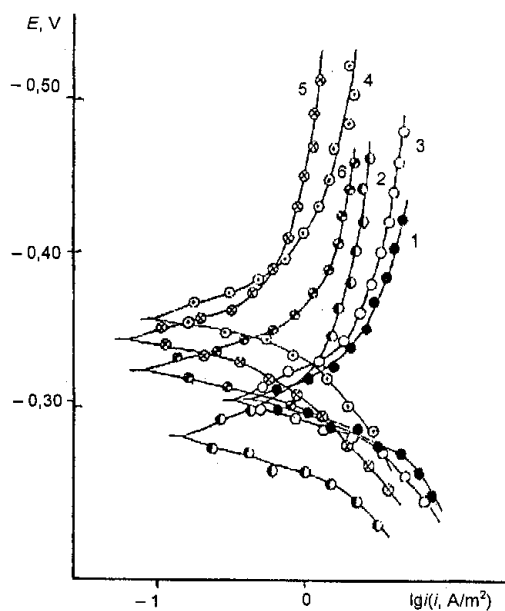**Figure 1.** Potentiostatic polarization curves measured on steel in 0.005 M HCl. Inhibitor (100 mg/L): *1* – none, *2* – I, *3* – II, *4* – III, *5* – IV, *6* – V. 293 K. Stationary electrode.
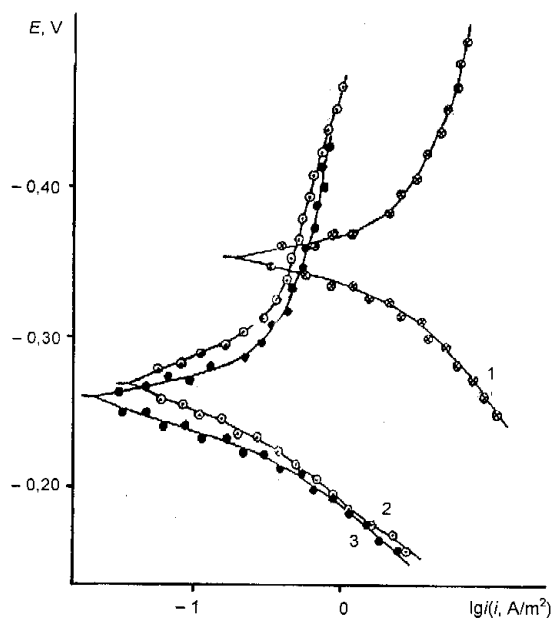

Figure 2. Potentiostatic polarization curves measured on steel in 0.005 M HCl in the presence of H_2S (80 mg/L) and CO_2 (1.7 g/L). Inhibitor (100 mg/L): *1* – none, *2* – I, *3* – II.

In general, the substances with smaller R retard the anodic reaction or have no influence on the kinetics of PERs. The greatest effect is achieved where *n* is small. An increase in R length stimulates the anodic ionization of steel and depresses the cathodic reaction; the effect is intensified as *n* grows. The limiting cathodic current in the presence of additives decreases in the sequence: II>I>V>III>IV.

In the presence of H_2S and CO_2, the situation changes drastically: I and II essentially retard metal ionization (Fig. 2) and stimulate the cathodic reaction. The values of b_a and b_c actually do not change. The former effect prevails, because the corrosion rate decreases by an order according to polarization measurements.

In 0.005 M HCl solutions, the initial signal of negative-sign photoelectric polarization E_{PEP} decreases to zero during the first 5 minutes and reaches a nearly constant value in 5 min after polarity reversal (Fig. 3). In the presence of H_2S, inversion of the signal sign is also observed, but its time τ_{inv} decreases considerably (Fig. 3). In comparison with the background solution, resistance R_p decreases and the capacitance slightly increases.

The influence of CO_2 in the absence of H_2S is qualitatively similar and τ_{inv} decreases to a greater extent. In the presence of both H_2S and CO_2, τ_{inv}, R_p and E_{PEP} acquire intermediate values (Table 2, Fig. 3). In 0.005 M HCl containing H_2S or H_2S+CO_2, injection of inhibiting additives increases the stationary amplitude of the positive signal (Fig. 3). Moreover, this effect is stronger in case of homologues with smaller R. At the same time, they decrease the resistance and, in a number of cases, increase the capacitance (Table 2). The plot $E_{PEP}=F(C_{EOAs})$ goes through the maximum, as shown for I as an example (Fig. 3).

3. The influence of EOAs on the hydrogen diffusion flux through a steel membrane. In 0.005 M HCl, the EOAs under study increase the hydrogen diffusion flux through the membrane (MB) at E_{cor} (Table 3), and the amines with R = C_{17}–C_{20} have the maximum effect, which is intensified as the number of ethoxy groups grows. An increase in *n* of compounds with R = $C_{10}-C_{13}$ causes a reverse effect. In the presence of CO_2, the influence of I to V on i_H is expressed insignificantly (Table 3). In 0.005 M HCl solutions containing hydrogen sulfide, the amines decrease i_H. Compound II is the most effective. In co-presence of H_2S and CO_2, the latter weakens the retardation of hydrogen permeation.

Under anodic polarization of MB in 0.005 M HCl solution, the dependence of i_H on ΔE_a goes through a maximum (0.05 V, Fig. 4) and γ does not exceed 1 in the entire range of potentials studied. A stimulating effect is observed in the intervals $\Delta E_a<0.1$ V and $\Delta E_a>0.2$ V. A plot with a maximum is also observed for the other media studied, in correlation with literature data, and is evidently common to all media. In the presence of CO_2, the influence of I, II and IV is qualitatively the same. Only in the presence of H_2S, II and especially I decrease i_H in the entire area of the investigated anodic potentials (Fig. 4). The presence of CO_2 together with H_2S weakens the effect, and only product I remains an inhibitor of hydrogen permeation (HP).
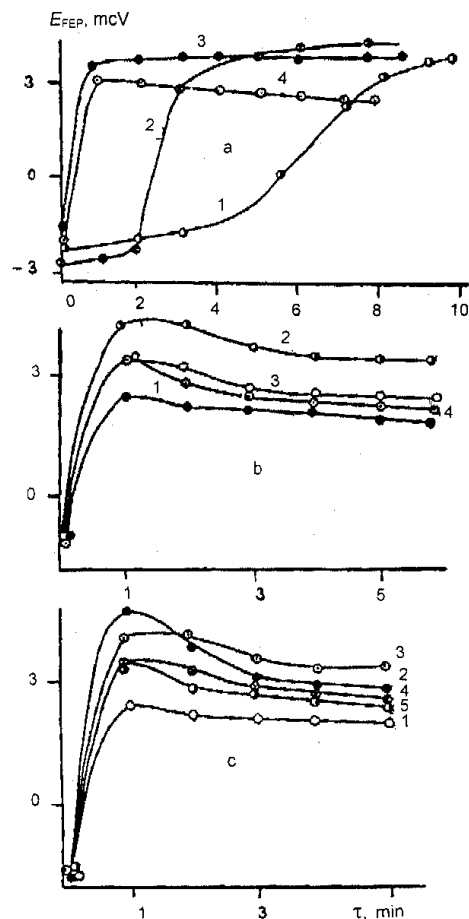
Figure 3. Dependence of E_{PEP} of steel on the presence of hydrogen permeation stimulators (*a*), the nature of EOAs (*b*) and concentration of I (*c*) in 0.005 M HCl. *a* – additives: *1* – none, *2* – 1.7 g/L CO_2, *3* – 80 mg/L H_2S, *4* – 1.7 g/L CO_2+80 mg/L H_2S. *b* – EOAs (50 mg/L): *1* – none, *2* – I, *3* – III, *4* – V, all in the presence of 1.7 g/L CO_2 and 80 mg/L H_2S. *c* – *C* (mg/l) of product I in the presence of 1.7 g/L CO_2 and 80 mg/L H_2S: *1* – none, *2* – 25, *3* – 50, *4* – 100, *5* – 200; 293 K.

Table 3. Influence of EOAs (100 mg/l) on the hydrogen diffusion flux through a steel membrane (i_H, A/m^2) and the γ coefficient at E_{cor} in 0.005 M HCl solution. The temperature is 293K.

Inhibitor	Additive							
	–		CO_2		H_2S		$H_2S + CO_2$	
	i_H	γ	i_H	γ	i_H	γ	i_H	γ
I	0.35	0.4	0.24	1.0	0.14	2.7	0.28	1.2
II	0.21	0.7	0.06	3.8	0.00	T*	0.06	5.6
III	0.43	0.4	0.32	0.7	0.15	2.4	0.31	1.1
IV	0.45	0.3	0.32	0.7	0.19	1.9	0.31	1.1
V	0.49	0.3	0.29	0.8	0.24	1.6	0.32	1.1

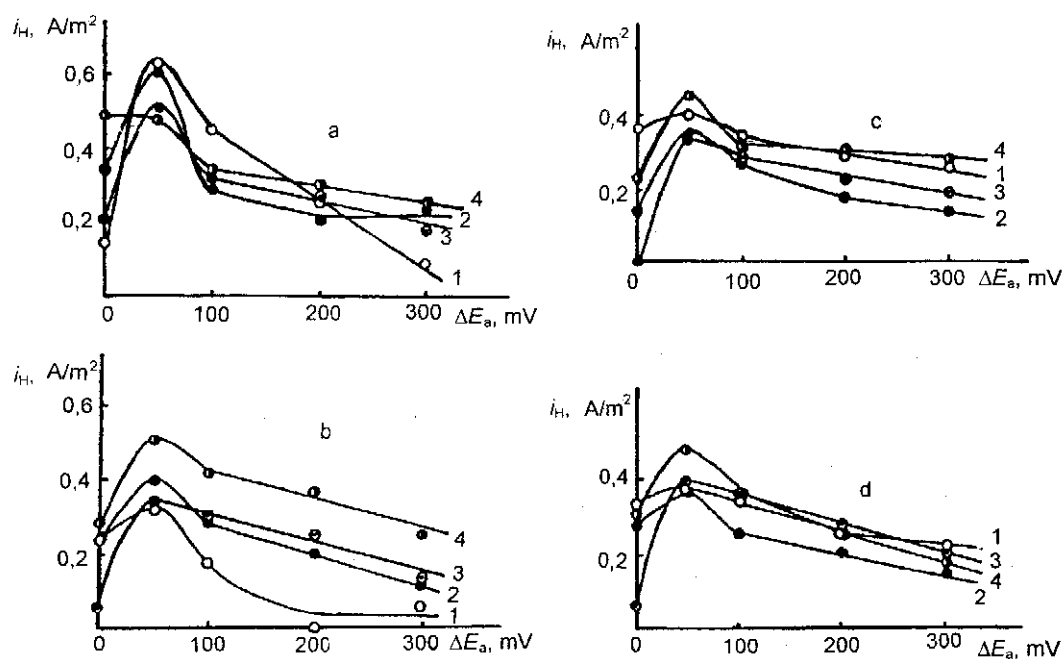T* - total protection.

Figure 4. Dependence of i_H on ΔE_a in 0.05 M HCl containing EOAs (100 mg/l): *1* – none, *2* – I, *3* – II, *4* – IV in the absence (*a*) and presence of 1,7 g/L CO_2 (*b*, *d*) and 80 mg/L H_2S (*c*, *d*). Duration is 2 hours, 293 K.

Under cathodic polarization, the $i_H = F(\Delta E_c)$ plot also has a maximum, especially in the presence of amines where pH =2.3 to 3 (pH grows due to EOA protonation). In 0.005 M HCl, all the EOAs under investigation stimulate HP, but only IV remains a stimulator if CO_2 is injected. When CO_2 is replaced by H_2S, the amines slow down HP. The same is observed in the co-presence of H_2S and CO_2.

4. The influence of emulgin on steel corrosion and PERs kinetics. In 0.005 M HCl background solutions, emulgin shows a considerable protective effect (*Z* is up to 62%) already at a concentration of 25 mg/L. An increase in its concentration to 200 mg/L leads to a *Z* increase (80%). In the presence of CO_2, estimation becomes complicated. Firstly, CO_2 itself exhibits an inhibiting action in such media (*Z* up to 40%). Secondly, *Z* can be calculated in relation to K_0 in a solution either containing CO_2 or not. In the former case, the *Z* value is appreciably lower. Hydrogen sulfide injected together with CO_2 essentially increases *Z* (up to 90%), as was repeatedly observed for amines. In the presence of 200 mg/L H_2S and with a simultaneous 2- or 10-fold increase in C_{HCl}, *Z* reaches 97% but decreases slightly in the presence of CO_2 (Table 4).

In 0.05 M solutions of HCl containing 200 mg/L H_2S and 1.7 g/L CO_2, emulgin slows down the anodic reaction with $d\lg i_a/d\lg C_{em}$ close to -0.6 (i_a – steel anodic ionization rate)

and accelerates the cathodic process. Steel dissolves anodically in the inhibited solutions being in active state with a Tafel slope of $b_a = 55$ mV. The Tafel sections of the cathodic polarization curve are not long and have a slope less than 120 mV due to their closeness to the limiting cathodic current ($i_{c,lim}$). The inhibitor retards the anodic reaction rather than accelerates the cathodic process.

Table 4. Influence of emulgin and HCl concentration on the inhibitor protective effect (Z, %) with respect to St3 corrosion in the presence of H_2S (200 mg/L) and CO_2 (1.7g /L).

C_{HCl}, mole/L	$C_{inh} \cdot 10^3$, mole/L	Corrosion stimulator		
		CO_2	H_2S	$CO_2 + H_2S$
0.005	0.625	72	89	90
0.010	0.625	87	86	92
0.050	0.078	86	94[c]	90[c]
	0.156	75	95[s]	95[s]
	0.312	87	97[i]	96[i]
	0.625	81	97	96

Note. Pitting formation: c − considerable; s − small; i − isolated; none in all other cases.

If C_{HCl} is increased by an order, the pattern remains qualitatively the same in the presence of H_2S ($d\lg i_a/d\lg C_{em} = -0.4$). The i_a inhibition predominates again, although $d\lg i_c/d\lg C_{em} > 0$ and $\Delta E_{cor} > 0$.

5. Steel hydrogen permeation in the presence of emulgin. The i_H increases essentially at E_{cor} potential upon injection of CO_2 and especially H_2S, which correlates with other data [14−16]. The ρ value is used to define the fraction of adsorbed hydrogen diffusing into the metal with respect to its total amount on the cathode including the gaseous phase (rate i_ρ). The following equality is obvious:

$$i_{gen} = i_\rho + i_H$$

A tenfold increase in the background solution acidity, the presence of 1.7 g/L CO_2 or 200 mg/L H_2S in it separately or together decrease ρ 1.8, 2.2, 3.6, and 2.9-fold, respectively. In the background solution and in the same solution containing CO_2, emulgin stimulates steel hydrogen permeation, thus increasing both i_H ($\gamma > 1$) and its contribution to i_{gen} ($\rho_{inh}/\rho_{n/inh} > 1$).

At a concentration of 200 mg/L, emulgin arrests hydrogen permeation almost completely, even in 0.05 M HCl solution containing CO_2 or H_2S separately. With an increase in temperature up to 353 K, the efficiency of hydrogen permeation depression increases essentially, especially in media containing hydrogen sulfide.

Discussion

The following reaction occurs in an acidic medium in the presence of EOAs or emulgin:

$$R_iN + H_3O^+ \rightarrow R_iNH^+ + H_2O, \tag{1}$$
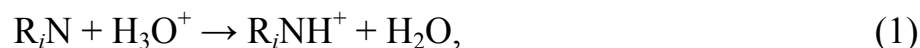
where R stands for all the fragments in the corresponding molecules apart from the nitrogen atom. We failed to find any basicity constants for R_iN in other studies. From general considerations, nevertheless, it may be presumed that the degree of protonation is high enough because their basicity grows due to the induction effect of alkyl radicals and charge localization in the presence of substitutes is weakened by the interaction between a solvent and protonated amine, thus lowering cation acidity and stabilizing it.

The discharge stage is delayed on iron in HCl solutions [17].

$$H_3O^+ + e \rightarrow H_{ads} + H_2O, \tag{2}$$

whereas H_{ads} removal occurs in the quick chemical recombination stage

$$H_{ads} + H_{ads} \rightarrow H_2 \tag{3}$$

and also due to its absorption by the metal

$$H_{ads} \rightarrow H_{abs}, \tag{4}$$

which stipulates steel hydrogen permeation. The acceleration of the cathodic reaction at potentials corresponding to the Tafel sections of the polarization curves is evidently related to the promotion of organic cations reduction compared to (2).

$$R_iNH^+ + e \rightarrow H_{ads} + R_iN \tag{5}$$

Possibly, adsorption of amines on steel results in formation of a polymolecular film, H_3O^+ mass transfer through which determines $i_{c,lim}$. This explains the kinetic regularities of the cathodic process in 0.005 M HCl solutions containing H_2S and CO_2. The situation practically does not differ from the one observed in the background solution. The only difference is that at pH=2−3, the dissociation of the weak acids H_2S and H_2CO_3 is suppressed and together with (1) and (5), only reactions (6) and (7) can proceed concurrently, thus increasing the overall rate of the cathodic process.

$$H_2S + e \rightarrow HS^- + H_{ads} \tag{6}$$

$$H_2CO_3 + e \rightarrow HCO_3^- + H_{ads} \tag{7}$$

Based on photoelectric polarization data (Fig. 3), we will examine the origin of anodic reaction retardation by EOAs. According to the theory of the method [11], Cl^- anions of the background solution interact with the lattice of the surface oxide (SO) by the mechanism of oxygen substitution and exhibit electron donor properties. A decrease in τ_{inv} in the presence of H_2S is evidently related to a more active interaction of H_2S and the products of its dissociative adsorption with the SO lattice. Hydrogen sulfide acts as an electron donor, hence R_p decreases. HS^- or S^{2-} anions can substitute the O^{2-} ion in the SO

lattice. Additive states with a positive effective charge (negative charge deficiency) that arise upon substitution act as centers for recombination of unbalanced electrons leading to E_{PEP} sign inversion. The negative charge deficiency is compensated, proceeding from the conditions of oxide electric neutrality, by the reaction $Fe^{3+} + e \rightarrow Fe^{2+}$. The reaction products (Fe^{2+}) are the 'active centers' of preferable adsorption and dissolution of metal covered with a non-stoichiometric oxide film of *n*-type. A growth in their concentration leads to an increase in corrosion rate. After E_{PEP} inversion, some of the states arising upon oxygen substitution participate in the exchange of electrons with the valent zone. Being below the Fermi level, they are able to trap electrons, thus increasing the concentration of holes and lowering the resistance.

The influence of CO_2 is analogous, but τ_{inv} is slightly smaller (Fig. 3). Carbon dioxide is also an electron donor, however the mechanism of its interaction with iron oxide is evidently different because its substitution or incorporation into the SO are improbable. Most likely, CO_2 forms a surface adsorption complex (SAC) and, being in its composition and transferring electrons to the conduction zone, forms CO_2^+. The field of the arising cation retards Fe^{2+} release into the solution, thus slightly inhibiting corrosion ($Z = 40\%$). As a result, R_p becomes greater than in the solution with H_2S, whereas the capacitance decreases.

Concurrent presence of H_2S and CO_2 leads to intermediate values of τ_{inv}, E_{PEP} and R_p. Addition of I, III, or V decreases R_p and τ_{inv} with a general tendency of increasing the amplitude of E_{PEP}. The large size of protonated amine molecules does not allow them to penetrate into or substitute in the SO lattice. Like in the case of CO_2, a SAC is formed at the expense of an unshared electron pair of nitrogen atom in molecules from the layer of amines closest to the metal, on the one hand, and the d-orbital of iron atoms, on the other hand. A positively charged film is formed that hinders the transfer of metal cations into the solution, thus decreasing the corrosion rate.

Conclusion

EOAs and emulgin inhibit the corrosion of carbon steel in dilute hydrochloric acid solution containing H_2S with a protective efficiency Z of up to 95−99.9% and prevent the local destruction of the metal. Z increases with increasing H_2S concentration. Under certain conditions, these inhibitors are capable of suppressing hydrogen diffusion into the steel almost completely; this is promoted by acidity increase, presence of H_2S, and increase in temperature (emulgin). The hydrogen permeation inhibition is obviously caused by a decrease in surface coverage by H_{ads} because of decreasing hydrogen portion of total H_{ads} diffusing into the metal.

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