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**The Inhibition of Corrosion and Hydrogen Permeation of Steel  
in Media, Containing H<sub>2</sub>S and CO<sub>2</sub>**

**L.E. Tsygankova, V.I. Vigdorovitch, S.E. Siniutina**

*Department of non-organic and physical chemistry,  
Tambov State University after G.R. Derzhavin*

*Represented by a member of Editorial Board Professor V.I. Konovalov*

**Key words and phrases:** corrosion; diffusion; ethoxy amines; inhibitor; hydrogen permeation.

**Abstract:** The efficiency of ethoxy higher aliphatic amines as composite inhibitors of carbonic-acid and hydrogen-sulfide corrosion and hydrogen diffusion into carbonaceous steel in acid solutions were studied. The influence of the number of ethoxy groups (2, 5 and 14), the length of the hydrocarbon radical (R=C<sub>10</sub>–C<sub>13</sub> and R=C<sub>17</sub>–C<sub>20</sub>), medium acidity (0.005 – 0.05 M HCl) and electrode potential was investigated.

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### Introduction

Development of composite inhibitors and, specifically, general, hydrogen sulfide and carbonic-acid corrosion and hydrogen permeation of steel will enable to reduce the expanded nomenclature of inhibitors to a great extent, heighten the economical efficiency of inhibiting protection and solve a wide range of ecological problems in both production and application. With that end in view, the multifunctional properties of homologous ethoxy amines (EOAs) mixture and, in addition, higher aliphatic amines bottoms that are a mixture of primary and secondary aliphatic amines (emulgin) were studied. Practical insolubility in aqueous media in molecular modes, that is increased as a result of protonation, is common to both EOAs and emulgin.

### Experimental

0.005 to 0.05 M solutions of HCl were used as background. H<sub>2</sub>S was injected through saturating the background solutions with gaseous hydrogen sulfide which concentration was checked by iodine-metric titration. In a number of cases, the working solutions were saturated with CO<sub>2</sub> (1.7 g/l) under gravimeter checking.

Corrosion tests of the steel samples sized 20×15×3 mm and processed up to surface-finish rating 6 after acetone degreasing were conducted in the cells with the plugs ground in (6 to 72 hours). Polarization potentiostatic measurements were performed in the three-electrode cell (pyrex) with a divided anode and cathode space. The electro-physical properties of the steel surface were studied using a photo-electrical polarization

method (PEP) [1]. The impedance measurements were carried out on a full-impedance meter (VM 507).

The hard-phase diffusion rate of H ( $i_H$ ) was evaluated under  $E_{cor}$ , 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 the electrochemical hydrogen permeation cell (pyrex) which was similar to that used by Devanathan. The procedure is described in detail in [2].

The EOAs and emulgin (averaged  $M=320$  g/mole) efficiency with the concentration being 25 to 200 mg/l (Table 1) was studied.

Table 1

**Products investigated as inhibitors of corrosion and hydrogen permeation of the St.3 steel**

EOAs Number	Formula	R	$n = x + y$
I	$R - N \begin{cases} (CH_2CH_2O)_x H \\ (CH_2CH_2O)_y H \end{cases}$	$C_{10} - C_{13}$	2
II		$C_{10} - C_{13}$	5
III		$C_{10} - C_{13}$	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 action of the inhibitors was calculated according to equation

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

where  $K_0$  and  $K_i$  are steel corrosion rates in uninhibited and inhibited solutions. The hydrogen diffusion depressing coefficient  $\tilde{a}$  was calculated according to equation

$$y = i_H^0 / i_H$$

where  $i_H^0$  and  $i_H$  are flows of hard-phase diffusion in solutions without and with inhibitors respectively.

## Results

**1. The influence of EOAs on steel corrosion.** In 0.005 M solutions of HCl or in addition containing  $CO_2$ ,  $Z_{EOAs}$  is not high (Table 2). Most efficient are the amines with  $R=C_{17}-C_{20}$ . The presence of  $H_2S$  heightens  $Z$ . The growth of  $n_{EOAs}$  (in the presence of  $CO_2$  and  $H_2S$ ) with  $R=C_{10}-C_{13}$  decreases  $Z$  and, for the amines with  $R=C_{17}-C_{20}$ , the dependence is reverse. The simultaneous presence of  $H_2S$  and  $CO_2$  heightens  $Z_{EOAs}$ . Also, the growth of  $C_{HCL}$  influences  $Z$ . The presence of  $CO_2$  (1.7 g/l) decreases  $Z$ .

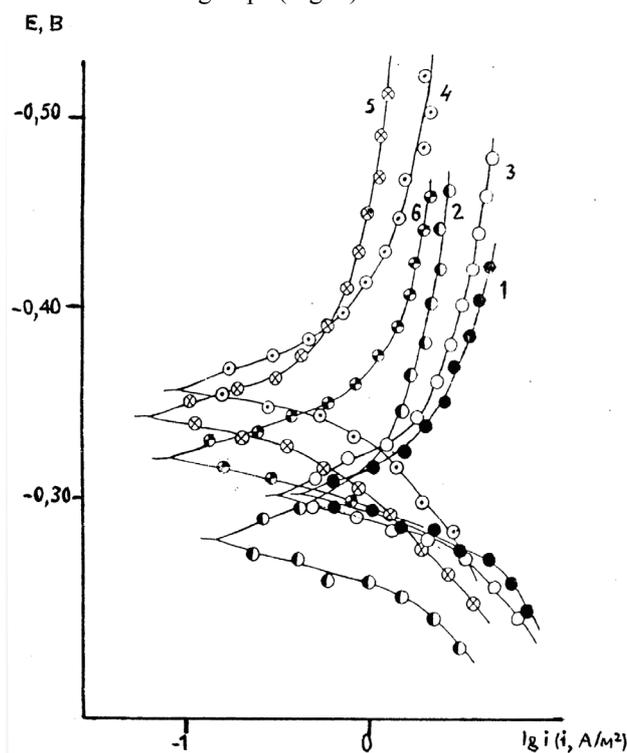
Table 2

**Steel corrosion rate (K, g/m<sup>2</sup>h) and protective action (Z, %) of inhibitors (100 mg/l) in 0,005 M (numerator) and 0,05 M HCl (denominator) solutions containing 80 mg/l H<sub>2</sub>S, 1.7 g/l CO<sub>2</sub>. 293 K, tests duration 18 hours**

Inhibitor	Additive							
	–		H <sub>2</sub> S		CO <sub>2</sub>		H <sub>2</sub> S + CO <sub>2</sub>	
	K	Z	K	Z	K	Z	K	Z
absent	$\frac{0,28}{1,27}$	–	$\frac{0,41}{3,38}$	–	$\frac{0,09}{0,09}$	–	$\frac{0,36}{1,30}$	–
I	$\frac{0,17}{0,12}$	$\frac{39}{91}$	$\frac{0,07}{0,06}$	$\frac{83}{98}$	$\frac{0,06}{0,07}$	$\frac{33}{22}$	$\frac{0,07}{0,06}$	$\frac{81}{95}$
II	$\frac{0,20}{0,10}$	$\frac{29}{92}$	$\frac{0,14}{0,08}$	$\frac{66}{98}$	$\frac{0,06}{0,08}$	$\frac{33}{11}$	$\frac{0,06}{0,05}$	$\frac{83}{96}$
III	$\frac{0,14}{0,13}$	$\frac{50}{90}$	$\frac{0,13}{0,10}$	$\frac{68}{97}$	$\frac{0,06}{0,07}$	$\frac{33}{22}$	$\frac{0,05}{0,06}$	$\frac{86}{95}$
IV	$\frac{0,13}{0,12}$	$\frac{54}{91}$	$\frac{0,12}{0,10}$	$\frac{70}{97}$	$\frac{0,05}{0,07}$	$\frac{44}{22}$	$\frac{0,07}{0,05}$	$\frac{81}{96}$
V	$\frac{0,15}{0,26}$	$\frac{46}{80}$	$\frac{0,08}{0,14}$	$\frac{80}{96}$	$\frac{0,05}{0,10}$	$\frac{44}{0}$	$\frac{0,04}{0,06}$	$\frac{89}{95}$

**2. The influence of EOAs on the kinetics of partial electrode reactions (PERs).**

According to the nature of influence on PERs in 0.005 M solutions of HCl, the studied EOAs can be divided into three groups (Fig. 1):



**Fig. 1 Potentiostatic polarization curves of steel in 0.005 M HCl. Inhibitor (100 mg/l): 1 – absent, 2 – I, 3 – II, 4 – III, 5 – IV, 6 – V. 293 K. Stationary electrode**

- those that equally change the kinetic characteristics of PERs (product II),  $E_{cor}''=E_{cor}^{\circ}$ , in which the upper index is 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,  $E_{cor}'>E_{cor}^{\circ}$ );
- those that retard  $H_3O^+$  reduction and stimulate the anodic process (products III, IV and V,  $E_{cor}'<E_{cor}^{\circ}$ ) with the first effect prevailing. For them, this sequence holds true:  $III>IV>V$ . In general, substances with a lesser R retard the anodic reaction or in like measure influence on the kinetics of PERs. The greatest effect is achieved when n is small. An increase of R length stimulates the anodic ionization of steel and depresses the cathode reaction; the effect being intensified by growing n. The limiting cathodic current, when injecting additives, is reduced as 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 stimulates the cathodic reaction. The quantities of  $b_a$  and  $b_c$  actually do not change. The first effect prevails as corrosion rate, according to the polarization measurements, decreases by an order.

In the 0,005 M solutions of HCl, the initial signal of negative-sign photoelectric polarization  $E_{PEP}$  falls off to zero during the first 5 minutes and in 5 minutes after polarity reversal practically reaches a constant value (Fig. 3). In the presence of  $H_2S$ , signal sign inversion is also observed whereas its time  $\tau_{inv}$  reduces considerably (Fig. 3). In comparison with the background solution, the quantity of resistance  $R_p$  decreases and the capacity slightly increases.

The influence of  $CO_2$ , in the absence of  $H_2S$ , is qualitatively analogous and  $\tau_{inv}$  reduces to a greater extent. In the mutual presence of  $H_2S$  and  $CO_2$ , the quantities of  $\tau_{inv}$ ,

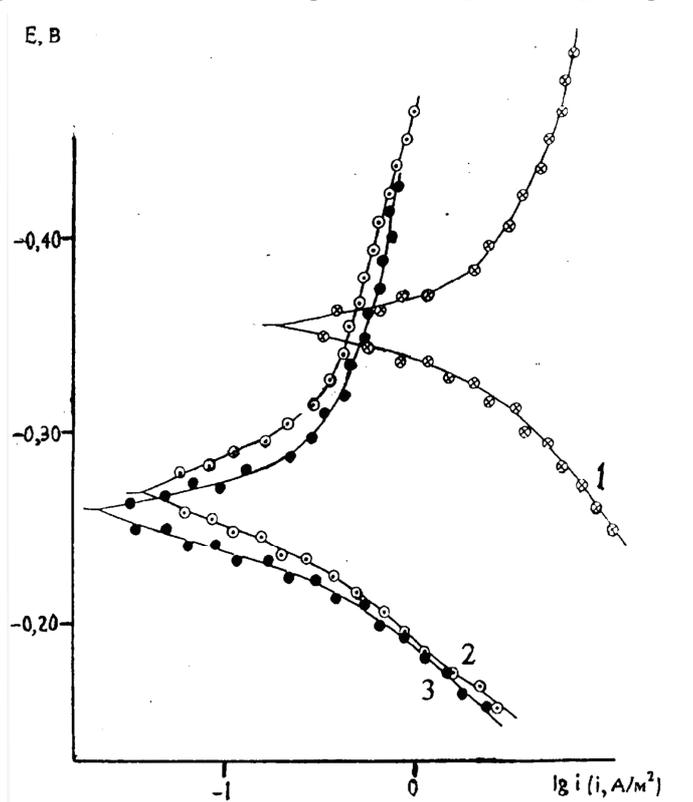
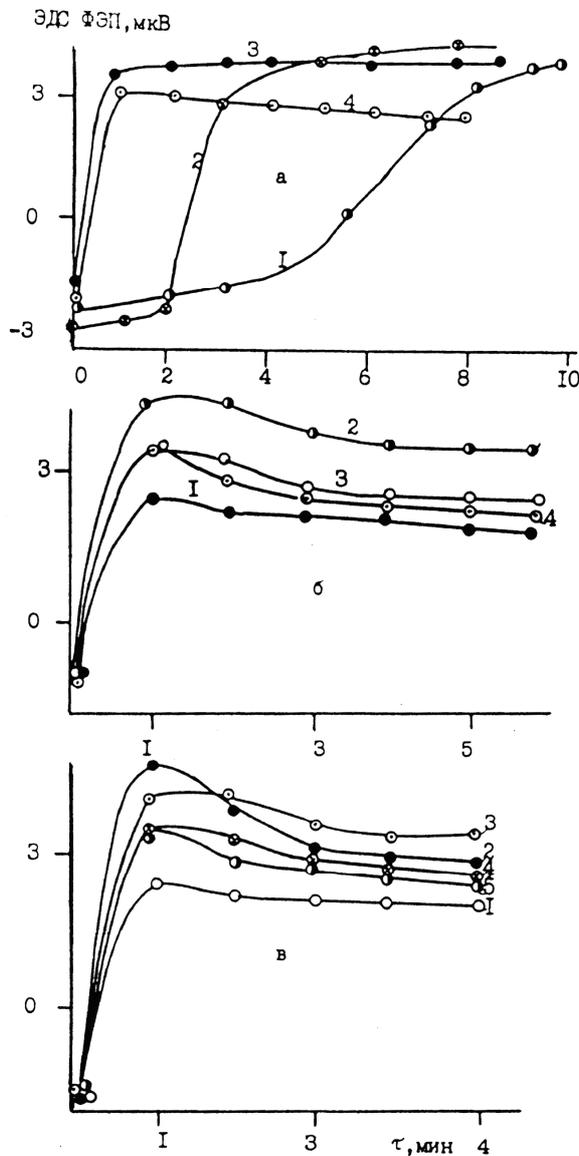


Fig. 2 Potentiostatic polarization curves of steel in 0.005 M HCl in the presence of  $H_2S$  (80 mg/l) and  $CO_2$  (1.7 g/l). Inhibitor (100 mg/l): 1 – absent, 2 – I, 3 – II

$R_p$  and  $E_{PEP}$  acquire an intermediate value (Table 2, Fig. 3). In 0,005 M HCl containing  $H_2S$  or  $H_2S+CO_2$ , the injection of inhibiting additives increases the stationary amplitude of the positive signal (Fig. 3). Moreover, to a greater extent, this effect is caused by homologues with a lesser R. At the same time, they decrease the resistance and, in a number of cases, increase the capacity (Table 2). The dependence  $E_{PEP} = F(C_{EOAs})$  goes through the maximum, which is shown in example of I (Fig. 3).



**Fig. 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 – absent, 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 – absent, 2 – I, 3 – III, 4 – V.

All in the presence 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 – absent, 2 – 25, 3 – 50, 4 – 100, 5 – 200. 293 K

**3. The influence of EOAs on the flow of hydrogen diffusion through a steel membrane.** In 0,005 M HCl, the studied EOAs increase the flow of hydrogen diffusion through a membrane (MB) at  $E_{cor}$  (Table 3), and amines with  $R=C_{17}-C_{20}$  - to the maximum; their effect is intensified with a growing number of ethoxy groups. 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, III - V on  $i_H$  is poorly pronounced (Table 3). II considerably suppress hydrogen permeation. In the 0,005 M HCl solutions containing hydrogen sulfide, amines decrease  $i_H$ . II is the most effective. In the co-presence of  $H_2S$  and  $CO_2$ , the latter weakens the retardation of hydrogen permeation.

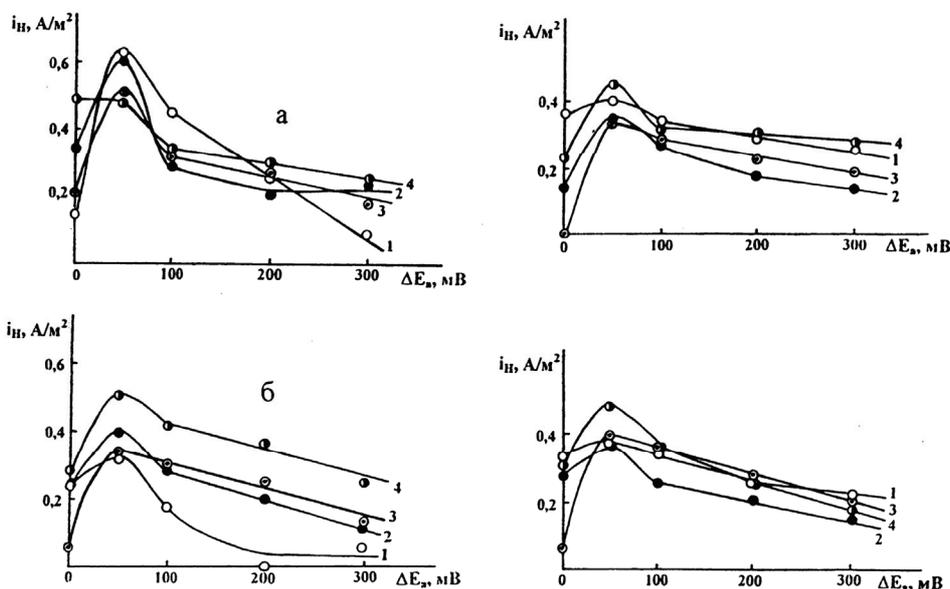
Table 3

**Influence of EOAs (100 mg/l) on the rate of hydrogen diffusion through a steel membrane ( $i_H, A/m^2$ ) and the  $\gamma$  coefficient under  $E_{cor}$  in 0,005 M HCl solution. Temperature 293K**

Inhibitor	Additive							
	-		$H_2S$		$CO_2$		$H_2S + CO_2$	
	$i$	$\gamma$	$i$	$\gamma$	$i$	$\gamma$	$i$	$\gamma$
I	0,35	0,4	0,14	2,6	0,24	1,0	0,28	1,2
II	0,21	0,7	0,00	T*	0,006	4,0	0,06	5,7
III	0,43	0,4	0,15	2,5	0,32	0,8	0,31	1,1
IV	0,45	0,3	0,19	2,0	0,32	0,8	0,31	1,1
V	0,49	0,3	0,24	1,5	0,29	0,8	0,32	1,1

T\* – total protection

Under MB anode polarization in 0,005 M HCl solution, the dependence of  $i_H$  on  $\Delta E_a$  goes through the maximum (0.05 B, Fig. 4) and  $\gamma$  close to 1 in the interval of



**Fig. 4 Dependence of  $i_H$  on  $\Delta E_a$  in 0.05 M HCl containing EOAs (100 mg/l):**  
 1 – absent, 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 2 hours, 293 K

potentials  $\Delta E_a=0...0.2$  B. A stimulating effect is observed then  $\Delta E_a>0.2$  B. Dependence with the maximum is also characteristic of other studied media, which correlates with literature data and is, evidently, common to all. In the presence of  $\text{CO}_2$ , the influence of I, II and IV is qualitatively the same. It is only when injecting  $\text{H}_2\text{S}$  in the whole area of the investigated anodic potentials that II and, especially, I decrease  $i_H$  (Fig. 4). The presence of  $\text{CO}_2$  together with  $\text{H}_2\text{S}$  weakens the effect and I only remains as an inhibitor of hydrogen permeation (HP).

Under cathodic polarization, the dependence  $i_H=F(\Delta E_c)$ , especially in the presence of amines when pH 2, 3... 3 (pH grows due to EOA protonation), is also with the maximum. In 0,005 M HCl, all EOAs under investigation stimulate HP and IV only remains stimulating when  $\text{CO}_2$  is injected. When  $\text{CO}_2$  is changed into  $\text{H}_2\text{S}$ , amines retard HP. It is also characteristic of the co-presence of  $\text{H}_2\text{S}$  and  $\text{CO}_2$ .

**4. The influence of emulgin on steel corrosion and PERs kinetics.** In 0.005 M background solutions of HCl, emulgin creates a considerable protective effect (Z up to 62 %) already in the concentration 25 mg/l. Its concentration increase of 200 mg/l leads to Z increase of 80 %. In the presence of  $\text{CO}_2$ , estimation becomes complicated. Firstly,  $\text{CO}_2$  itself exhibits inhibiting action in such media (Z up to 40 %). Secondly, Z can be calculated in relation to  $K_o$  in the solution either containing  $\text{CO}_2$  or not. In the first case, the quantity Z is appreciably lower. The  $\text{H}_2\text{S}$  injected together with  $\text{CO}_2$  essentially increases Z (up to 90 %) which was repeatedly observed for amines. In the presence of 200 mg/l  $\text{H}_2\text{S}$  and with the simultaneous  $C_{\text{HCl}}$  increase of 2 and 10 times, Z comes to 97 % but slightly decreases in the presence of  $\text{CO}_2$  (Table 4).

In 0,005 M solutions of HCl containing 200 mg/l  $\text{H}_2\text{S}$  and  $\text{CO}_2$  (1.7 g/l), emulgin slows down the anode 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 inhibited solutions being active with the Tafel slope  $b_a=55$  mV. Tafel sections of the cathodic polarization curve are not long and have a slope less than 120 mV, which is stipulated by their closeness to the limiting cathodic current ( $i_{c,lim}$ ). The inhibitor rather retards the anodic reaction than accelerates the cathodic process.

Table 4

**Influence of emulgin and HCl concentration on an inhibitor's protective action with respect to St3 corrosion in the presence of  $\text{H}_2\text{S}$  (200 mg/l) and  $\text{CO}_2$  (1,7g/l)**

$C_{\text{HCl}}$	$C_{inh} \cdot 10^3$	Corrosion stimulator		
		$\text{CO}_2$	$\text{H}_2\text{S}$	$\text{CO}_2 + \text{H}_2\text{S}$
mole/l				
0,005	0,625	72	89	90
0,010	0,625	87	86	92
0,050	0,078	86	94 <sup>c</sup>	90 <sup>c</sup>
	0,156	75	95 <sup>s</sup>	95 <sup>s</sup>
	0,312	87	97 <sup>i</sup>	96 <sup>i</sup>
	0,625	81	97	96

Note. Pitting formation: c – considerable, s – small, i – isolated, absent in other cases.

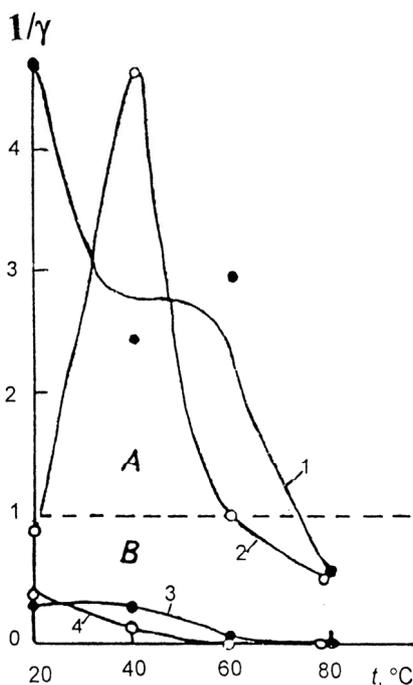
When  $C_{\text{HCl}}$  is increased by an order, the pattern qualitatively remains in the presence of  $\text{H}_2\text{S}$  ( $d\lg i_a/d\lg C_{em}=-0,4$ ).  $i_a$  retardation prevails again, although  $d\lg i_c/d\lg C_{em}>0$  and  $\Delta E_{cor}>0$ .

**5. Steel hydrogen permeation in the presence of emulgin.** The  $i_H$  essentially increases under  $E_{cor}$  potential when injecting  $CO_2$  and, especially,  $H_2S$ , which correlates with other data [3 – 5]. The quantity  $\tilde{n}$  is used to define the fraction of the adsorbed hydrogen diffusing into the metal in its general discharge from the cathode including the gaseous phase (rate  $i_p$ ). The following equality is obvious:

$$i_{gen} = i_p + i_H$$

The increase of the acidity of solution, containing 1.7 g/l  $CO_2$  or 200 mg/l  $H_2S$  in it separately or the co-presence decrease  $\rho$  1.8, 2.2, 3.6 and 2.9 times respectively. In the background solution and that containing  $CO_2$ , emulgin stimulates steel hydrogen permeation, thus heightening both  $i_H(\gamma > 1)$  and its contribution to  $i_{gen}(\rho_{inh}/\rho_{n/inh} > 1)$ .

In the concentration 200 mg/l, emulgin practically arrests hydrogen permeation completely, even in 0.05 M solution of HCl that contains  $CO_2$  and  $H_2S$  simultaneously. With an increase in temperature up to 353 K, the efficiency of hydrogen permeation depression increases essentially, especially in media containing hydrogen sulfide (fig. 5).



**Fig. 5 Influence of temperature in 0.05 M HCl solution on  $1/\gamma$ . Emulgin concentration 200 mg/l.  $CO_2$ : 1 and 3 – 0, 2 and 4 – 1.7 g/l.  $H_2S$ , mg/l: 1 and 2 – 0, 3 and 4 – 200**

Table 5

**Influence of emulgin concentration on steel hydrogen permeation ( $i_H$ ,  $A/m^2$ ) in HCl solutions ( $T = 293$  K,  $C_{CO_2} = 1,7$  g/l, two-hour experiments)**

Stimulator nature and concentration, mg·l	$C_{CHI}$ , mole/l	$i_H$ , $A/m^2$	$1/\gamma$	$\rho$	$-E_{cor}$ , V	25 mg/l emulgin		200 mg/l emulgin		$-E_{cor}^*$ , V
						$i_H$	$1/\gamma$	$\rho$	$-E_{cor}^*$ , V	
1	2	3	4	5	6	7	8	9	10	
Absent	0,005	0,21	3,72	0,86	0,29	0,12	2,12	~1	0,28	
$CO_2$		0,34	2,56	~1	0,30	0,12	0,89	0,86	0,35	
50 $H_2S$		0,09	0,50	-	0,35	0,11	0,64	-	0,35	
200 $H_2S$		0,09	0,40	0,53	0,35	0,07	0,29	0,50	0,35	
50 $H_2S+CO_2$		0,07	0,58	-	0,36	0	0	0	0,34	
200 $H_2S+CO_2$		0,09	0,50	0,43	0,36	0,06	0,37	0,32	0,34	
Absent	0,050	-	-	-	-	0,02	0,20	0,32	0,34	
$CO_2$		-	-	-	-	0,06	0,20	0,10	0,29	
50 $H_2S$		-	-	-	-	0	0	0	0,32	
100 $H_2S$		-	-	-	-	0	0	0	0,29	



Continued Table 5

1	2	3	4	5	6	7	8	9	10
150 H <sub>2</sub> S		-	-	-	-	0,01	0,02	-	0,30
200 H <sub>2</sub> S		-	-	-	-	0,02	0,04	0,10	0,30
200 H <sub>2</sub> S+CO <sub>2</sub>		-	-	-	-	0	0	0	0,32

Note.  $E_{cor}^*$  – corrosion potential of the reaction side of a membrane.

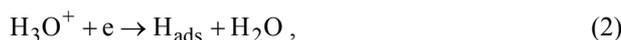
### Discussion

When injecting EOAs and emulgin, in an acidic medium proceeds the reaction



in which R stands for all the fragments of corresponding molecules, apart from the atom of nitrogen. We failed to find out any basicity constants for  $R_iN$  in other works. From general considerations, nevertheless, it may be presumed that the degree of protonation is high enough because their basicity grows being influenced by the induction effect of alkyl radicals and charge localization in the presence of substitutes is weakened by the interaction between solvent and protonated amine, thus lowering cation acidity and stabilizing it.

The discharge stage is delayed on iron in HCl solutions [6].



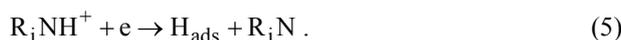
whereas  $H_{ads}$  removal proceeds in the quick stage of chemical recombination



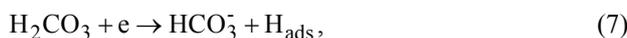
and also at the expense of its absorption by metal



which stipulates steel hydrogen permeation. The acceleration of the cathode reaction at the potentials correspond to the Tafel sections of the polarization curves, is evidently connected with the promotion of organic cations' reduction compared to (2).



Possibly, amines adsorption on steel results in polymolecular film formation, through which  $H_3O^+$  mass transfer determines  $i_{c,lim}$ . This explains the kinetic regularities of the cathode process in 0,005 M HCl solutions containing H<sub>2</sub>S and CO<sub>2</sub>. The situation practically does not differ from the one observed in the background solution. The only difference is that under pH=2 - 3, the dissociation of the weak acids H<sub>2</sub>S and H<sub>2</sub>CO<sub>3</sub> is depressed and together with (1) and (5), there can only proceed concurrently grand (7) thus increasing the summary rate of the cathode process.



In view of photoelectric polarization (Fig. 3), we will examine the origin of anodic reaction retardation by EOAs. According to the theory of method [1], Cl<sup>-</sup> anions of the background solution interact with the lattice of surface oxide (SO) by the mechanism of oxygen substitution and exhibit electron donor properties. A decrease in  $\tau_{inv}$  in the presence of H<sub>2</sub>S is evidently connected with a more active interaction of H<sub>2</sub>S and the prod-

ucts of its dissociation adsorption with the lattice of SO. Hydrogen sulfide acts as donor for electrons, owing to which  $R_p$  decreases. Anion  $HS^-$  or  $S^{2-}$  can substitute ion  $O^{2-}$  in the lattice of SO. Additive states with a positive effective charge (negative charge deficiency) that arise under substitution act as centers for recombination of unbalanced electrons leading to  $E_{PEP}$  sign inversion. The negative charge deficiency is compensated for, proceeding from the conditions of oxide electric neutrality, by the reaction  $Fe^{3+} + e \rightarrow Fe^{2+}$ . The products of the reaction  $Fe^{2+}$  are 'active centers' of preferable adsorption and dissolving of metal covered non-stoichiometric oxide film of n-type. Their concentration growth leads to an increase in corrosion rate. After  $E_{PEP}$  inversion, some of the states arising under oxygen substitution participate in the exchange of electrons with a valent zone. Being below the Fermi level, they are able to catch electrons, thus increasing the concentration of holes and lowering resistance.

The influence of  $CO_2$  is analogous, but  $\tau_{inv}$  is slightly decreased (Fig. 3). Carbon oxide (IV) is also a donor for electrons, however the mechanism of its interaction with iron oxide is evidently different, because its substitution or introduction into SO is improbable. Most likely  $CO_2$  forms a surface adsorption complex (SAC) and, being in its composition and transferring electrons to the zone of conduction, forms  $CO_2^+$ . The arising cation field retards  $Fe^{2+}$  output 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 capacity decreases.

The simultaneous presence of  $H_2S$  and  $CO_2$  leads to intermediate values of  $\tau_{inv}$ ,  $E_{PEP}$  and  $R_p$ . The injection of I, III and V decreases  $R_p$  and  $\delta_{inv}$  under the general tendency of increasing the amplitude of  $E_{PEP}$  (Fig. 5). The large size of protonated molecules of amines 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 the undivided electron pair of nitrogen atom in molecules from the layer of amines that is closest to the metal and d-orbital of iron atoms. A positively-charged coverage is formed that hinders the transfer of metal cations into the solution, which decreases corrosion rate.

## Conclusion

EOAs and emulgin inhibit corrosion of carbonaceous steel in dilute hydrochloric acid solution containing  $H_2S$  with their protective efficiency  $Z$  up to 95-99,9% and remove the local destruction of metal.  $Z$  increases with increasing  $H_2S$  concentration. Under some conditions these inhibitors are capable to suppress hydrogen diffusion into the steel almost completely what is promoted by the acidity increase,  $H_2S$  presence and the temperature increase (emulgin). The hydrogen permeation inhibition is obviously caused by decrease of surface coverage by  $H_{ads}$  because of decreasing hydrogen portion of total  $H_{ads}$  diffusing into the metal.

## References

1. Ye. K. Oshe, I. L. Rosenfeld. Itogi nauki i tekhniki. Corrosion and protection against corrosion. VINITI. Moscow (1978).
2. V. I. Vigdorovitch, Protection of Metal (Rus), **31**, 541, (2000).
3. I. L. Rosenfeld. Inhibitors of Corrosion. Khimiya, Moscow (1977).
4. J. I. Bregman. Corrosion Inhibitors. Khimiya. Moscow (1966).
5. M. V. Loskutova, A. V. Boldyrev. Vestnik Tambovskogo Universiteta. **2**, 41 (1997).
6. V. I. Vigdorovitch, T. P. Dyachkova, O. L. Pupkova, L. E. Tsygankova. Electrochemistry (Rus), **37**, 1437 (2001).

## **Ингибирование коррозии и водородопроницаемости стали в средах, содержащих H<sub>2</sub>S и CO<sub>2</sub>**

**Цыганкова Л.Е., Вигдорович В.И., Синютина С.Е.**

**Ключевые слова и фразы:** коррозия; диффузия; оксиэтилированные амины; ингибитор; водородопроницаемость.

**Аннотация:** Изучена эффективность оксиэтилированных высших алифатических аминов в качестве комплексных ингибиторов углекислотной коррозии и наводороживания углеродистой стали в кислых растворах. Исследовано влияние числа оксиэтильных групп (2, 5 и 14), длины углеводородного радикала ( $R=C_{10}-C_{13}$  и  $R=C_{17}-C_{20}$ ), кислотности среды (0.005 – 0.05 М HCl) и потенциала электрода.

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## **Inhibierung der Korrosion und der Wasserstoffdurchdringungsfähigkeit des Stahls in den H<sub>2</sub>S und CO<sub>2</sub> enthaltenen Mitteln**

**Zusammenfassung:** Es ist die Effektivität von ethoxy höchsten aliphatic Aminen als Komplexeinhibitoren der Kohlensäurekorrosion in Sauerlösungen erlernt. Es ist der Einfluß der Zahl von Ethoxygruppen (2, 5 und 14), der Länge des Kohlenstoffradikals ( $R=C_{10}-C_{13}$  und  $R=C_{17}-C_{20}$ ), der Mediumsauerkeit (0.005 – 0.05 М HCl) und des Elektrodenpotentials untersucht.

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## **Inhibition de la corrosion et de l'étanchéité de l'acier dans les milieux contenant H<sub>2</sub>S et CO<sub>2</sub>**

**Résumé:** On a étudié l'efficacité des amines oxyéthylées primaires aliphatiques en qualité d'inhibiteurs complexes de la corrosion carbonique-acide et de l'hydrogénation de l'acier dans les solutions acides. On a étudié l'influence du nombre de groupes oxyéthylés (2, 5 et 14), de la longueur du radical hydrocarbonique ( $R=C_{10}-C_{13}$  et  $R=C_{17}-C_{20}$ ), du milieu acide (0.005 – 0.05 М HCl) et du potentiel de l'électrode.

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