Peculiarities of protective efficiency of nitrogen containing inhibitors of steel corrosion

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Abstract

The protective efficiency of a number of nitrogen containing inhibitors against steel hydrosulfide corrosion and their effect on the kinetics of partial electrode reactions have been studied by gravimetrical corrosion tests, polarization resistance and impedance spectroscopy methods. The bactericidal efficiency of the inhibitors with respect to sulfate reducing bacteria (SRB) has been estimated as a function of their nature and concentration.

Key words: *inhibition, corrosion, protective effect, polarization resistance, impedance spectroscopy, bactericidal action.*

Introduction

The protective efficiency of inhibitors of hydrosulfide and carbon dioxide steel corrosion is generally studied in two model media:

1. Highly mineralized chloride media containing $30-150$ g/L NaCl with various concentrations of hydrogen sulfide ($10-1500$ mg/L) [1]. As a rule, such model solutions satisfactorily simulate metal corrosion under oil production conditions. Corrosive media containing carbon dioxide are prepared by CO_2 introduction to the solutions used in the laboratory studies.
2. The model environment recommended by the National Association of Corrosion Engineers of USA (NACE) contains 5 g/L NaCl and 0.25 g/L CH_3COOH and is saturated with hydrogen sulfide [2, 3].

The physicochemical characteristics of these media differ substantially. The acidity of highly mineralized chloride media is small. Their pH only depends on hydrogen sulfide concentration. This acid is weak: its first and second constants of electrolytic dissociation are $K_1 = 8.9 \cdot 10^{-8}$ and $K_2 = 1.3 \cdot 10^{-13}$. Therefore, the pH is $5.5-6.0$. Chloride ions are surface active with respect to carbon steel, therefore the kinetics of steel active anodic dissolution depends substantially on the anion concentration.

The NACE medium is characterized by $pH = 3.5 - 3.6$ because of a much higher electrolytic dissociation constant of CH_3COOH ($K = 1.74 \cdot 10^{-5}$). This fact can essentially change the nature and concentration of the protonated form of hydrosulfide corrosion inhibitors that frequently belong to nitrogen containing substances. Moreover, the kinetics of iron ionization is a function of solution pH and $d \log i_a / d\, pH \approx 1$ (where i_a is the anodic current density).

Acetic acid is present in NACE medium mainly in molecular form because its degree of dissociation is $\approx 6\%$. The surface activity of the acid in molecular form has not been studied sufficiently. Nevertheless, it is impossible to neglect its effect on metal anodic ionization. The rather small concentration of surface active chloride ions in the NACE medium favours the adsorption of acetate-containing species both in molecular and anionic forms.

The aim of this paper is to study the peculiarities of inhibitor efficiency depending on the nature of corrosive media and bactericidal action against SRB.

Experimental

The following inhibitors were used: I – a 10 mass% solution of higher aliphatic amines $C_{10} - C_{16}$ in a mixture of aprotic solvents; II – a mixture of imidazolines and amidoamines obtained in a reaction of polyethylene polyamine with oleic acid. Highly mineralized chloride media containing 50 g/L NaCl and NACE medium saturated by H_2S and CO_2 were used as the working solutions.

The protective efficiency of inhibitors against steel corrosion was studied by the following methods: gravimetrical corrosion tests [4], linear polarization resistance, and impedance spectroscopy. The steel had the following composition, mass%: C – 0.20; Mn – 0.50; Si – 0.15; P – 0.04; Cr – 0.30; Ni – 0.20; Cu – 0.20, Fe – balance. The protective effect (Z, %) of an inhibitor is calculated according to the formula:

$$Z\,(\%) = 10^2 \,(K_0 - K_i)/K_0,$$

where K_0 and K_i are the corrosion rates in the uninhibited and inhibited solution, respectively.

The linear polarization resistance (LPR) technique was used for instant monitoring of variations in corrosion rates in the inhibited and uninhibited solutions [5]. An "Expert-004" LPR device developed at A.N.Frumkin Institute of Physical Chemistry and Electrochemistry of the Russian Academy of Sciences [6] was used in this study.

Electrochemical impedance spectroscopy measurements (Solartron 1255 Frequency Response Analyzer and 1287 potentiostat) were carried out in the frequency range of 10 kHz – 50 mHz. Processing of the results was conducted using ZView 3.0 software [7].

The bactericidal properties of the inhibitors with respect to SRB were studied in the Postgate medium with the composition, g/L: NH_4Cl – 1.0; K_2HPO_4 – 0.5; $MgSO_4 \cdot 7H_2O$ – 2.0; Na_2SO_4 – 0.5; $CaCl_2$ – 0.1; calcium lactate – 3.5, yeast extract – 1 [8]. The *Luk* sulfate-reducing bacterium strain used in this study was phylogenetically similar (99% similarity

of 16S rRNA genes) to the *Desulfomicrobium apsheronum 1105^T* strain isolated from a petroleum reservoir [9]. The experiment duration (168 h) is determined by the SRB vital cycle [10]. The concentration of biogenic hydrogen sulfide was measured daily (iodometric titration).

Results and discussion

According to gravimetrical corrosion tests in NACE media containing 10 mg/L H_2S, the protective efficiency of inhibitor I (25 mg/L) is 77%. It increases to 87 or 90% upon a five- or tenfold increase in hydrogen sulfide concentration, respectively. A further growth in H_2S content to 200 mg/L does not change the Z value. A Z value of 88–91% is reached in the entire range of H_2S concentrations studied and at an inhibitor concentration of 100 mg/L. Inhibitor II is less efficient at a concentration of 25 mg/L but shows a protective efficiency equal to that of inhibitor I at a four times higher concentration. In the presence of both H_2S and CO_2 (1 atm.) simultaneously, the protective efficiency is smaller by 10%.

In highly mineralized chloride media (50 g/L NaCl), the presence of inhibitor I at 25 mg/L results in very small protective efficiency or even corrosion stimulation (Table 1). A fourfold growth in the inhibitor concentration nearly does not change the picture. Inhibitor II (25 mg/L) is more efficient under these conditions at C_{H2S} = 10 and 50 mg/L, but its Z decreases essentially with an increase in H_2S concentration to 100–200 mg/L (Table 1). A fourfold growth in its concentration results in a Z value of 87–90%. Addition of CO_2 (1 atm.) together with H_2S decreases the efficiency of inhibitor I but nearly does not change the efficiency of inhibitor II.

Table 1. Protective efficiency (Z, %) of inhibitors I (numerator) and II (denominator) in media containing 50 g/L NaCl and H_2S.

C_{Inh}, mg/L	Z, % at C_{H2S}, mg/L			
	10	**50**	**100**	**200**
25	8/85	S*/87	11/29	21/39
100	21/88	61/90	S*/87	S*/90

*S denotes stimulation

The corrosion rate of steel decreases in time in both uninhibited and inhibited solutions, but this decrease is more appreciable in the second case, as shown in [5]. This indicates the protective properties of the film corrosion products formed on the steel surface in uninhibited solutions or a combined effect of the film of corrosion products and inhibitor in inhibited solutions. Measurements of the instantaneous corrosion rate by the LPR method in the uninhibited and inhibited solutions for 24 h and the method described in [5] permit the calculation of the protective effect of the corrosion product film (Z_f), the total protective effect (Z_{total}) of the corrosion product film and inhibitor, and the inhibitor contribution (Z_{Inh}) to the total protective effect.

At small H_2S concentration (10 mg/L) in NACE medium, $Z_f << Z_{Inh}$ and the protective efficiency of the film increases with increasing test duration. However, the Z_{Inh} value remains practically constant, then it decreases 1.5-fold (Table 2). This is characteristic of both inhibitors. A qualitatively similar picture is observed with a four times higher inhibitor concentration. Furthermore, the Z_f / Z_{Inh} ratio increases essentially with a growth in test duration in the presence of the inhibitors (25 and 100 mg/L) and decreases with an increase in H_2S concentration up to 200 mg/L.

Table 2. Effect of H_2S concentration and exposure time of steel specimens in the solution on the contributions of the surface film (Z_f) and inhibitor I (25 mg/L) (Z_{Inh}) to the total protective effect (Z_{total}) (numerator, Z_i values in NACE solution; denominator, Z_i values in the solution with 50 g/L NaCl).

Time from the start of corrosion, h	Z_i at hydrogen sulfide concentration, mg/l								
	10			50			200		
	Z_f	Z_{Inh}	Z_{total}	Z_f	Z_{Inh}	Z_{total}	Z_f	Z_{Inh}	Z_{total}
0.15	−6/62	2/23	56/85	2/−5	70/18	72/12	−7/48	76/11	69/37
1.0	1/80	63/8	64/88	10/18	69/29	79/47	−3/59	80/1	77/60
2.0	3/81	63/8	66/89	14/36	66/24	80/60	11/63	68/1	79/64
4.0	29/87	36/4	65/91	18/69	62/−4	80/65	24/66	55/10	79/76
20.0	29/89	39/3	68/91	36/64	46/8	82/72	26/74	57/9	83/83

*The "−" sign denotes stimulation.

A different picture is observed in highly mineralized chloride media (50 g/L NaCl). In the presence of inhibitor I, the Z_f / Z_{Inh} ratio essentially exceeds 1. It decreases with an increase in H_2S concentration from 10 to 50 mg/L and then increases again with an increase in C_{H2S} to 100 or 200 mg/L (Table 2). The same results are observed in the presence of inhibitor II.

One can conclude that the regularities of polysulfide film growth on steel surface and inhibitor adsorption in NACE medium and in a highly mineralized chloride medium differ substantially. In the former case in the presence of 10 mg/L H_2S, the inhibitor is adsorbed quickly and the film is formed slowly. Then, with a growth in C_{H2S} to 50 or 100 mg/L, the film formation is accelerated and the effect of both inhibitors is identical. In the presence of 200 mg/L H_2S, the film structure evidently changes, inhibitor contribution increases substantially and becomes predominant irrespective of the inhibitor nature.

In highly mineralized chloride media, a film of corrosion products is quickly formed already in the presence of 10 and 50 mg/L H_2S and makes a major contribution to Z_{total}. The inhibitor is adsorbed on the film insignificantly and its contribution to Z_{total} varies from stimulation ($Z_{Inh} < 0$) to $Z_{Inh} \leq 33\%$. With H_2S content growth (100 mg/L) the inhibitor contribution increases, but the inequality $Z_{Inh} < Z_f$ remains true. However, at 200 mg/L H_2S,

Z_{Inh} substantially decreases again. With a fourfold growth in the inhibitor concentration, the picture remains qualitatively the same. Addition of CO_2 does not change the picture.

Let us consider some impedance spectroscopy data. The equivalent circuit shown in Fig. 1 [4] was used as a model of steel electrode impedance at E_{cor}. Addition of the inhibitors under study to the corrosive media results in an increase in the diameter of the semicircles in the Nyquist plots. This indicates that the total resistance of the system increases and the corrosion rate decreases. The diameters of the semicircles increase with an increase in experiment duration (Fig. 2), like in uninhibited solutions, which is caused by an increase in the protective efficiency of the surface coatings being formed in time. The charge transfer resistance in the anodic (R_1) and cathodic (R_2) reactions increases in the presence of inhibitors. This is particularly true for the anodic reaction. After exposure in NACE medium containing 100 mg/L H_2S for 24 h, the values of R_1 and R_2 are 1800 and 20 Ohm·cm^2, respectively, in the presence of 100 mg/L inhibitor I. The R_1/R_2 ratio amounts to 90. This indicates that the corrosion process occurs under anodic control. In highly mineralized chloride media, $R_1 = 1750$–1780 Ohm·cm^2 and R_2 decreases twofold, therefore $R_1/R_2 = 175 - 178$. Hence, inhibitor I weakly hinders the cathodic process but nearly does not affect the corrosion rate because, as before, the corrosion process occurs under anodic control.
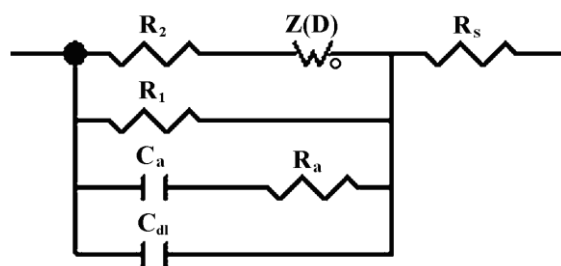

Fig. 1. Equivalent circuit of steel electrode at E_{cor}.

In the presence of inhibitor II in NACE medium, R_1 and R_2 are 380 and 20 Ohm·cm^2 and $R_1/R_2 = 19$ (other conditions being equal). Although this ratio is smaller than in the presence of inhibitor I, the corrosion process is still under anodic control.

Addition of the inhibitors to the solution causes a decrease in the double layer capacity C_{dl}. In NACE solution, C_{dl} decreases from 50 to 10 µF/cm^2 in the presence of 100 mg/L of inhibitor I ($C_{H2S} = 100$ mg/L). In the medium containing 50 g/L NaCl, it changes from 150 to 20 µF/cm^2.

The inhibitors under study show a bactericidal effect against SRB in the Postgate medium where bacteria grow under the most favorable conditions. Addition of 25 mg/L inhibitor I to Postgate medium suppresses their vital activity and decreases the concentration of biogenic H_2S from 300 mg/L to 200 mg/L (Fig. 3). A further four-fold growth in the inhibitor concentration decreases the H_2S content by an order of magnitude (to 30 mg/L). Inhibitor II shows similar efficiency. The higher the inhibitor concentration, the more considerably inhibiting compositions I and II decrease the quantity of sulfate-reducing bacteria in the Postgate medium (Fig. 4).
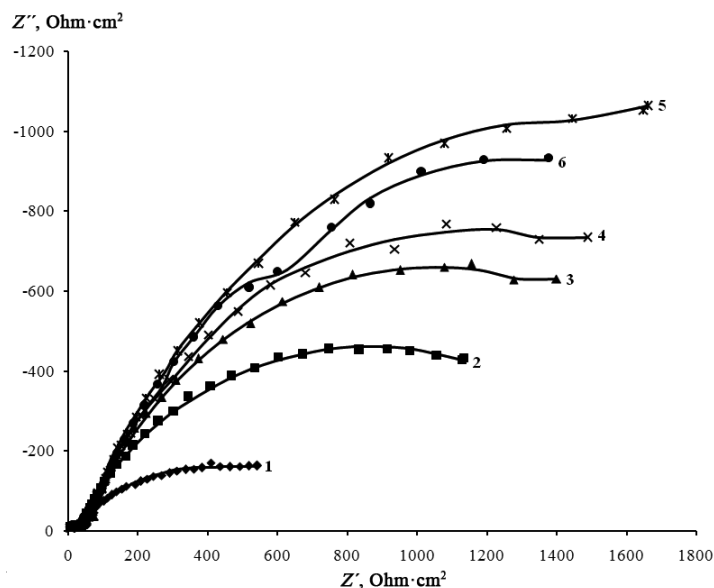
Fig. 2. Nyquist plot at E_{cor} in NACE medium saturated with H_2S (200 mg/L) and CO_2 (1 atm) in the presence of inhibitor II (200 mg/L). Test duration, h: *1*, 0.25; *2*, 2; *3*, 4; *4*, 6; *5*, 8; *6*, 24. (The dots correspond to the experimental data, whereas the solid line shows data calculated from the equivalent circuit).
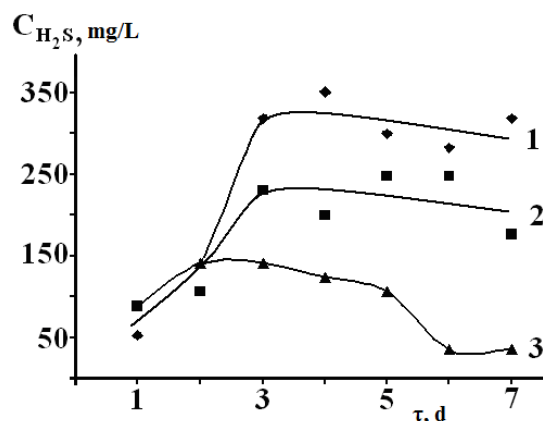

Fig. 3. Plot of H_2S concentration produced by SRB *versus* time (τ/d) of microorganism growth in the Postgate medium without an inhibitor (*1*) and with inhibitor I at concentrations of 25 (*2*) and 100 mg/L (*3*).

Conclusions

The inhibitors under study are versatile: they suppress the corrosion process both in the presence of hydrogen sulfide and in the presence of H_2S and CO_2 together. In addition, they are efficient as bactericides.

Inhibitor I hinders the anodic reaction of steel more efficiently than inhibitor II. However, both are anodic inhibitors in the presence of which the charge transfer resistance of the anodic reaction is many times higher than that of the cathodic reaction.

The nature of the corrosive medium substantially affects how inhibitor protective efficiency changes in time. In NACE medium in all studied range of H_2S concentration the

inhibitor adsorption is substantially faster than the formation of the film of corrosion products. In highly mineralized chloride media, an opposite picture is observed, so the film contribution to the total protective efficiency is larger than that of the inhibitor and essentially increases in time. The protective efficiency of "inhibitor/corrosion product film" system depends on hydrogen sulfide concentration.
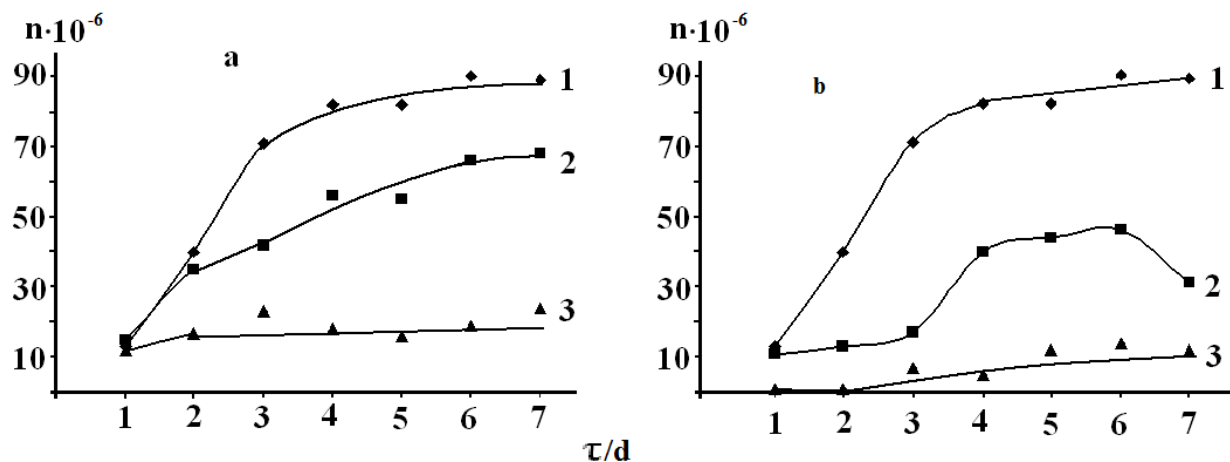
Fig. 4. SRB cell number (n/cm^3) (ordinate) is a function of time (τ/days) (abscissa) of microorganism growth in the Postgate medium without an inhibitor (*1*) and with inhibiting compositions I (*a*) and II (*b*) at concentration of 25 (*2*) and 100 mg/L (*3*).

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