AMINOOXOETHYLPYRIDINIUM CHLORIDES AS INHIBITORS OF MILD STEEL ACID CORROSION

*Olena Bondar[1], Viktoria Vorobyova[2], Iryna Kurmakova[1, *], Olena Chygyrynets[2]*

Abstract. Aminooxoethylpyridinium chlorides under the St3ps steel corrosion in acid hydrochloric and sulfuric solutions demonstrate the inhibition efficiency at 98 %. The compound with hydrazinocarbonyl and 2,3-dimethylphenyl fragments turns out to be the most effective within the interval 293–333 K. This inhibitor is also characterized by a significant aftereffect due to the chemisorption on the steel surface.

Keywords: aminooxoethylpyridinium chlorides, inhibitors, acid corrosion, mild steel.

1. Introduction

Acid mediums are widely used in a variety of chemical industry processes, particularly for the acid rinse of technological equipment, metal chemical milling, *etc*. Corrosion inhibitors are used in such processes to protect the metal fund. The inhibitors efficiency provides the technical and economic characteristics of the process. Despite the wide range of acid corrosion inhibitors [1], the search of new chemical agents which decelerate steel corrosion is still important. Pyridinium derivatives [2-4] as corrosion inhibitors in hydrochloric and sulfuric mediums are of a particular interest for the researchers. The interest in these compounds is connected with their ability of chemical adsorption on the metal surface with the help of unpaired electrons of nitrogen atom of pyridinium cycle, providing high inhibition efficiency. A higher inhibition effect can be expected from the quaternary pyridinium salts, which are cationic active substances. The presence of the amides, amide fragments, and aroma cycles, which can act as additional adsorption-reaction centers, in the structure of the mentioned above derivatives, can ensure not only a considerable inhibition efficiency level, but also a considerable inhibition aftereffect.

[1] Chernihiv National T.G. Shevchenko Pedagogical University,
53, Hetmana Polubotka St., 14013 Chernihiv, Ukraine
[2] National Technical University of Ukraine
"Igor Sikorsky Kyiv Polytechnic Institute",
37, Peremogy Ave., 03056 Kyiv, Ukraine
* *i.kurmakova@gmail.com*

The aim of this paper is to study the inhibition efficiency of aminooxoethylpyridinium chlorides under the mild steel acid corrosion and establish its mechanism.

2. Experimental

Aminooxoethylpyridinium chlorides were studied as corrosion inhibitors (Fig. 1). They were produced by the alkylation of substituted pyridines with *a*-chloroacetanilides [5]. The structure of the compounds was confirmed by H NMR spectroscopy (Bruker-300). The purity of the compounds was confirmed by combined gas chromatography (LC/MSD) method on the Agilent 1200 device with mass-spectrometry detector Mass Quad G1956B (Agilent Technologies Inc.).

The corrosion tests were performed with the help of gravimetric and electrochemical methods. The mild steel St3ps plates (surface area 0.002 m^2), polished to the 4-5 class of accuracy, were used for the gravimetric testing. Before being placed in the corrosive medium, the steel samples were cleaned with acetone, and weighed with analytical scales accurate to $5 \cdot 10^{-5}$ g.

Corrosion rate with or without the inhibitors was calculated with the help of the formula: $k_m = \Delta m/(S \times t)$, where Δm – weight loss, g; S – area, m^2; t – exposure time, h.

Corrosion inhibition rate coefficient was calculated with the help of the formula: $\gamma_m = k_m/k_m'$, where k_m, k_m' is the corrosion rate with and without the inhibitor, respectively.

The inhibition efficiency was calculated using the equation: $IE = (1 - 1/\gamma_m) \cdot 100$ %.

0.1M and 1M solution of HCl and 1M solution of H$_2$SO$_4$ were used as a testing corrosive medium. Samples soaking time was 24 h at 293 K and 1 h at 303 and 333 K. Inhibitor concentration was 0.1; 0.25 and 0.5 g/l. The existence of the aftereffect was established during the testing of steel samples, previously soaked in solutions with inhibitors (24 h at 293 K), in solutions without inhibitors. The inhibition efficiency due to the aftereffect was calculated ($IE_{a.f.}$, %).
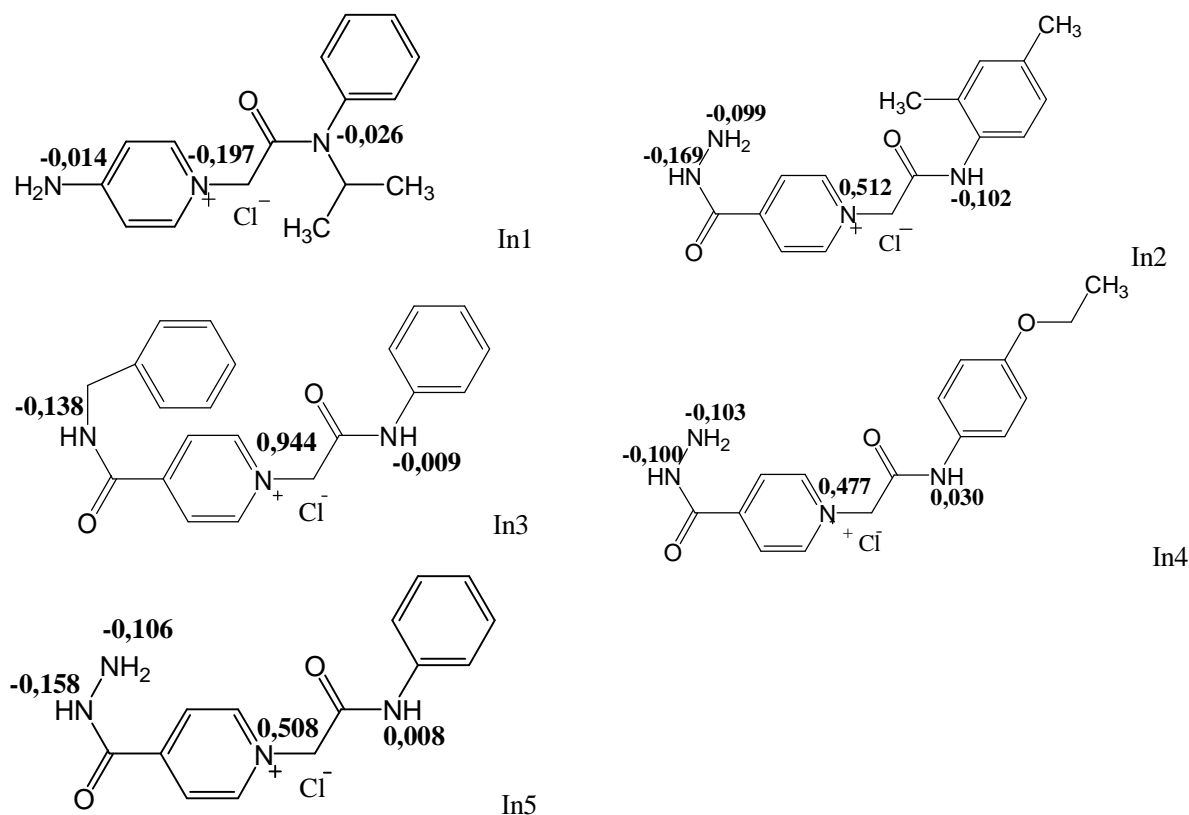
Fig. 1. Formulas of the studied aminooxoethylpyridinium chlorides

Electrochemical tests were performed with the help of a potentiostate PI-50-1.1 and programmer PR-8. In this test a cylindrical steel electrode made of St3ps steel had been molded into Teflon casing. The preparation of the electrode surface to the testing included polishing, washing with distilled water and with the studied solution. Three-electrode cell with the separated cathode and anode scope was used. Polarization curves were measured from the potential of free corrosion to 0.7 V and from –0.7 to 0 V. Chloride silver electrode ($E = 0.29$ V) was used as a comparison electrode, which was conducted to the steel electrode with the help of electrolytic bridge and Lugin capillary. The extra electrode was a platinum one. The electrode potentials, provided in the paper, were recalculated in accordance with the common hydrogen electrode. The results are presented as data curves of the correlation between the voltage (E, V) and current density logarithm ($\lg i$, (i, A/cm^2)). The calculated data were: potential and current of free electrochemical corrosion (E_{corr}, i_{corr}), cathode (E_k, i_k) and anode (E_a, i_a) partial processes, inhibition rate coefficients g_c, g_k, g_a ($g = i/i'$, where i, i' – corrosion current without and with the inhibitor, respectively).

The steel samples surface morphology after the mechanical treatment and exposure to 0.1M HCl solution, inhibited with In1 and In2, was examined using FEIE-SEM XL 30. With the help of electron microscope, the picture was taken in the mode of functioning in secondary electrons. Maximum residual pressure in the microscope pillar was no more than $6.7 \cdot 10^{-4}$ Pa under the gun current of 76 mA.

Infrared spectrum of corrosion products formed on the steel surface after 72 h of exposure to 0.1M HCl solution and with the corrosion inhibitor, was registered by the infrared Fourier spectrometer Jasco FT/IR–4000. The research conditions were the following: spectrum registration scope 4000–400 cm^{-1}; resolution 4 cm^{-1}; scan number – automatic; scanning speed 1 mm/s; scanning mode – in transmitted light; detector – TGS.

The calculations of the molecule atoms charge (Fig. 1) and their energetic characteristics were performed using the computer software Chem3D 9.0 (Cambrige Soft). The order of molecule protonation in the solutions with the different pH was established with the help of software package ACDLabs 6.0. (ACD/Log D, Advanced Chemistry Development Inc.).

Statistical analysis of experimental data (the corrosion rate) for the reliability level of 95 % was conducted with the help of Microsoft Excel. The experiment was conducted three times.

3. Results and Discussion

The studied aminooxoethylpyridinium chlorides show high inhibition efficiency under the St3ps steel corrosion in 1M solutions of sulfuric and hydrochloric acids (Table 1). The inhibition efficiency in hydrochloric acid is higher by 4.4–63.0 % in comparison with sulfuric acid. The compound In2, containing hydrazinocarbonyl (R_1) and 2,3-dimethyl-phenyl (R_2) fragment, was found to be the most effective corrosion inhibitor (93.3 % efficiency in 1M H_2SO_4 and 98.2 % in 1M HCl at 293 K). The introduction of an extra benzene rings to the structure of R_1 (In3) substituent or the substitution of R_2 in the structure of In2 for the ethoxyphenyl (In4) or phenyl radical (In5) lead to the decrease of inhibition efficiency. Compound In1, containing amides (R_1) and unsubstituted phenyl radical (R_2), proved to be less effective, particularly in sulfuric acid solution.

In 1M HCl all the studied quaternary salts showed the inhibition aftereffect (Table 1) of 12.0–85.5 %. This fact indicates the chemisorption of aminooxoethylpyridinium chlorides on the samples surface during the inhibition process of steel dissolution in corrosive medium.

The indicated effect is most vividly expressed with In2 and also appears when sulfuric acid solution is used as corrosive medium. The inhibition aftereffect is absent with In1 and In3 in 1M H_2SO_4 solution. This indicates the primarily electrostatic interaction of these inhibitors and the steel surface in sulfuric solution.

With the temperature increase to 313 K the inhibition level of In1, In3, In4, and In5 in hydrochloric medium decreases (by 28.1–73.9 %). This indicates that the created surface compounds fail to provide the dense inhibition layer. The least decrease of inhibition effect (by 13.9 %) can be observed with In2, which is characterized by the high inhibition aftereffect. This fact suggests that a dense inhibition biofilm is formed on the steel surface under the chemisorption of the stated inhibitor. With the further increase of the temperature to 333 K the inhibition efficiency of all the compounds increases. The most effective is In2.

The correlation between the corrosion inhibition rate coefficient and the inhibitor concentration for the compounds In1, In2 and In5 is demonstrated in Fig. 2. The correlation varies for different compounds. The following rule can be observed: the higher the inhibition aftereffect, the lower the inhibitor concentration.

The study of the acid medium influence on the compound inhibition efficiency (Table 2) showed that their effectiveness in 0.1M HCl solution is higher by 1.9–22.3 % compared to 1M HCl. At the same time, the increase of efficiency for In2 is the smallest, which means that the inhibition efficiency level of this inhibitor practically does not depend on the corrosive medium pH balance. It also indicates that the inhibition efficiency of this quaternary salt is caused by its chemisorption on the steel surface.

Table 1

Aminooxoethylpyridinium chlorides efficiency under St3ps steel corrosion in acid mediums ($C_{In} = 0.5$ g/l) according to the data of gravimetric method

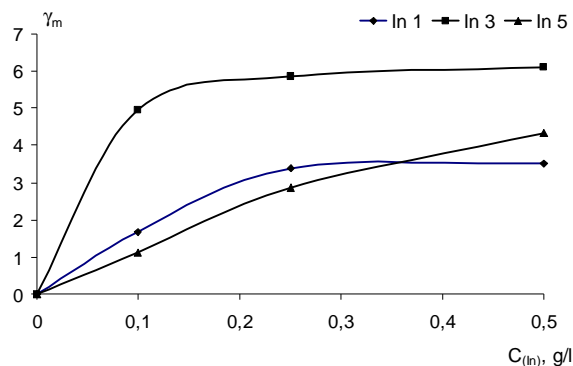| In	1M H_2SO_4		1M HCl			
	293 K		293 K		313 K	333 K
	IE, %	*IE_{a.f}*, %	*IE*, %	*IE_{a.f}*, %	*IE*, %	*IE_{a.f}*, %
1	76.2	–	96.1	39.9	40.0	81.1
2	93.3	79.1	98.2	85.5	84.3	92.4
3	85.1	–	89.5	12.0	61.4	87.9
4	70.1	3.6	82.5	30.5	8.6	71.2
5	13.9	25.1	76.9	19.5	38.6	90.3

Fig. 2. The correlation between the inhibition rate coefficient and the inhibitor concentration under St3ps steel corrosion in 1M HCl

Table 2

**Aminooxoethylpyridinium chlorides efficiency under St3ps steel corrosion
in acid mediums with different pH ($C_{In} = 0.1$ g/l) according to the data of gravimetric method**

In	$k_m \cdot 10^2$, g/(m²·h)	g_m	IE, %	$k_m \cdot 10^2$, g/(m²·h)	g_m	IE, %
		1 M HCl			0.1 M HCl	
–	80.2	–	–	68.2	–	–
1	22.9	3.5	71.4	6.9	9.9	89.9
2	11.8	6.8	85.3	8.7	7.8	87.2
3	16.0	5.0	80.0	10.3	6.6	84.8
4	26.7	3	66.7	12.9	5.3	81.1
5	44.6	1.8	44.4	22.7	3.0	66.7

Table 3

The energy characteristics of aminooxoethylpyridinium chlorides

In	E_{HOMO}, eV	E_{LUMO}, eV	ΔE, eV
1	−8.47938	−2.64637	5.83301
2	−8.50043	−1.80711	6.69332
3	−8.06596	−0.82165	7.24431
4	−8.49243	−2.07060	6.42183
5	−8.86401	−1.82062	7.04339

a)   b)   c)
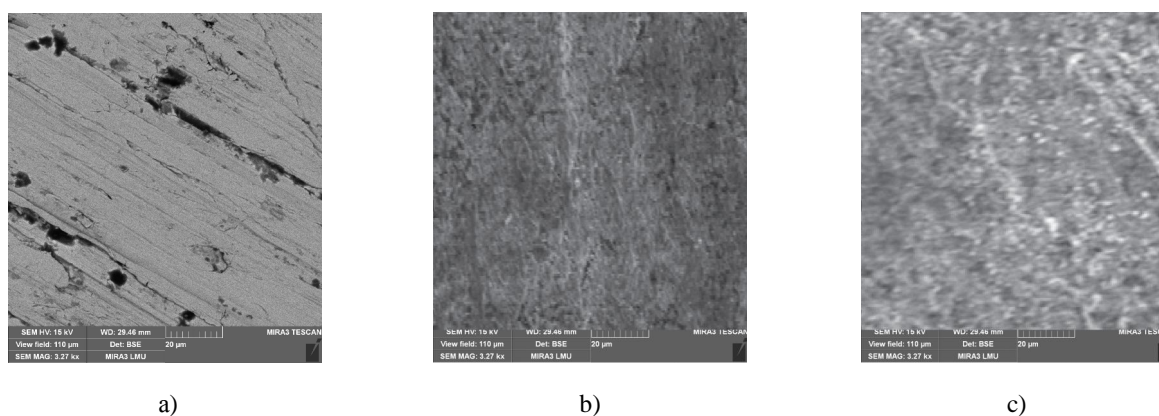
Fig. 3. Samples surface morphology: after mechanical treatment (a); after 24-hour exposure to 0.1M HCl
solution with inhibitors In1 (b) and In2 (c)

The atoms with increased electron density (Fig. 1) can serve as absorption-reaction centers of aminooxoethylpyridinium chlorides under their chemisorption. According to the calculations, In1 atoms of nitrogen can be characterized by comparatively low negative charges, the highest electron density is concentrated on pyridinium nitrogen. In the In2 molecule three atoms of nitrogen have increased electron density, while the nitrogen atom of the pyridinium circle is positively charged. In the molecules of In3, In4 and In5 there are only 2 possible absorption-reaction centers, able to create bonds by transferring electron density to the iron free orbitals. The regression analysis showed that there is no correlation between the inhibition indices and the charges on the certain absorption-reaction centers or molecules energy indicators. This could be due to the considerable effect of the conformational factor. At the same time, the energy gap parameters (ΔE) indicate the sufficient chemical activity of the studied compounds (Table 3).

The samples surface morphology was examined with FEIE-SEM XL 30 after the mechanical treatment and after the exposure to the inhibited solutions to prove the steel chemisorption ability of the studied compounds. For this purpose, In1, different from the other studied quaternary salts by the nature of its R_1 and R_2 substituents, and In2 were chosen. These quaternary salts are characterized by the highest inhibition efficiency rate in 0.1M hydrochloric acid solution (Table 2). Moreover, In2 with 0.5 g/l demonstrates better inhibition characteristics in 0.1M hydrochloric acid solution and the highest aftereffect (Table 1).

It has been established that only a few scratches from the metal mechanical treatment could be observed on the surface before the exposure to 0.1M hydrochloric acid solution (Fig. 3a). After the 24-hour exposure to the inhibitor solution an inhibition film was formed on the steel samples surface (Fig. 3b, c). The morphology of different films looks different. The films, formed on the steel surface from the In 1 inhibited solution, have a more "loose" structure if compared to the films from the In2 inhibited solution. This fact agrees with the results of gravimetric tests, provided in Tables 1 and 2. It has been determined that with the increase in time of inhibition film formation to 72 h the formed film becomes smoother and denser. The infrared attenuation spectra of the film, formed on the steel surface after 72 h of exposure to 0.1M hydrochloric acid solution with In1 and In2, are demonstrated in Fig. 4. The peak typical of the C–Cl bond at 705.97 cm^{-1}, which is characteristic of corrosion products in 0.1M HCl solution with the inhibitors, is shifted to 569.02 cm^{-1}. With In2 the peak, typical of the C–H bond at keeping the wave length at 862.21 cm^{-1}, is

shifted to 669.32 cm^{-1}. The peak, typical of valence C=C bond at 1637 cm^{-1} is shifted to 1649.19 cm^{-1}. Retention at 2926 cm^{-1}, typical of C–H bond, is shifted to 2928.1 cm^{-1}. After the steel samples exposure to solutions with In2 a film is formed on their surface, which demonstrates the following infrared spectra vibrations:

– in the range of 3400–3500 cm^{-1}, corresponding to stretching vibrations of N–H group;

– in the range of 3340 cm^{-1}, corresponding to stretching vibrations of NH_2 group bond;

– 1140, 2880–2890, 2960 cm^{-1}, corresponding to stretching vibrations of CH_2-, –CH and CH_3 groups.

With In1, the peaks are less intensive, compared to In2. Thus, the obtained results prove that in the inhibition solution the molecules of inhibitors (In1 and In2) undergo chemisorption on the steel surface, leading to the surface blocking.

The study of the samples surface morphology, when defining the aftereffect presence in 0.1M HCl, shows that the inhibition film retains despite the inhibitor absence in the solution (Fig. 5).
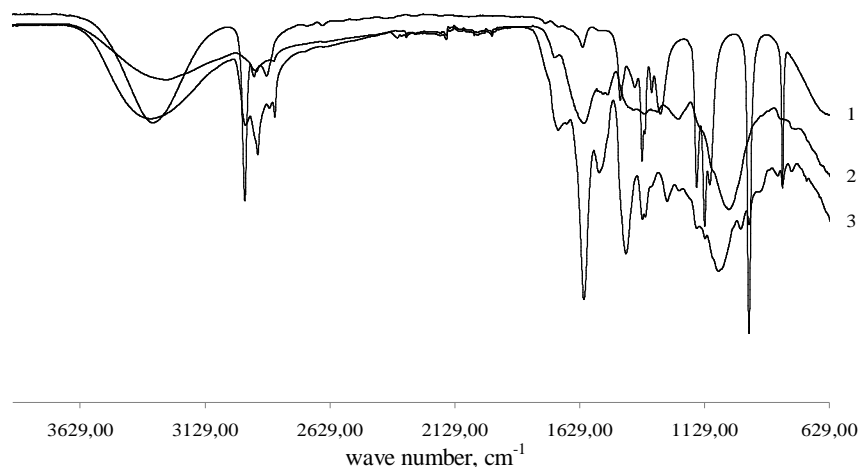

Fig. 4. Infrared attenuation spectra of corrosion products, obtained in 0.1M HCl solution without the inhibitors (1) and corrosion products, obtained after St3ps steel samples exposure to 0.1M HCl with In1 (2) and In2 (3)
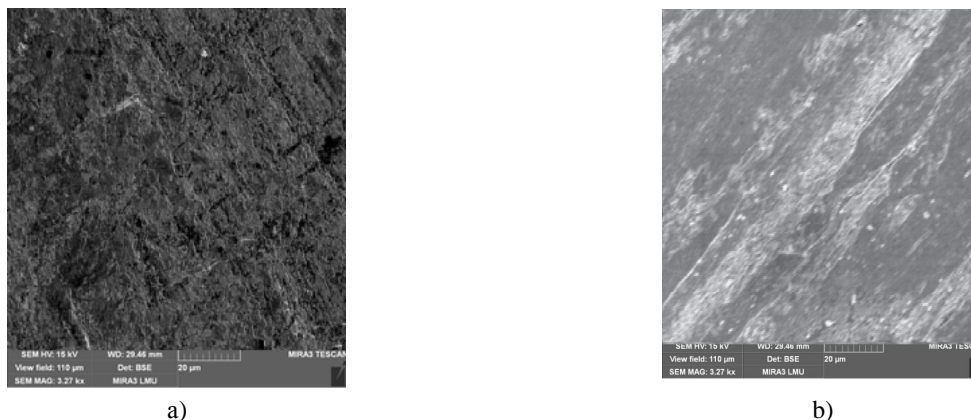

a)   b)

Fig. 5. Surface morphology after the study of aftereffect in 0.1M HCl for the samples with In1 (a) and In2 (b)

For In2 the film morphology is similar to the film formed on the surface if the stated inhibitor is used. On the surface of the sample with In1 corrosion products can be observed. This fact is in agreement with the data from Table 2, namely the indices of inhibition aftereffect.

The results of polarized measurements (Figs. 6, 7) show that In1 and In2 act as the inhibitors of the mixed type corrosion, which means they inhibit both cathode and anode reactions of the corrosion process.

In 0.1M HCl the potential of the free electrochemical corrosion in the inhibited media is shifted to the positive indices by 0.02–0.03 V (Fig. 6), meaning the metal dissolution is inhibited predominantly. In 1M HCl solution the potential of the free electrochemical corrosion for the media with and without the inhibitors

has practically no difference (Fig. 7), which means that without the electrode polarization cathode and anode processes are inhibited equally.

The studied quaternary salts do not change the slope of cathode and anode polarization curves, *i.e.* do not affect the mechanisms of cathode and anode steel corrosion reactions at 293 K. In2 ensures higher cathode and anode electrode polarization compared to In1, and, therefore, has higher inhibition efficiency. This agrees with the results of gravimetric method (Tables 1, 2). The indices of cathode and anode polarization with In2 in 0.1M solution are 0.11 and 0.23 V, respectively. For cathode process ($E_k = -0.470$ V) inhibition coefficients are 2.54 and 4.47, whereas for anode process ($E_a = -0.200$ V) – 2.53 and 3.55, under In1 and In2, respectively.
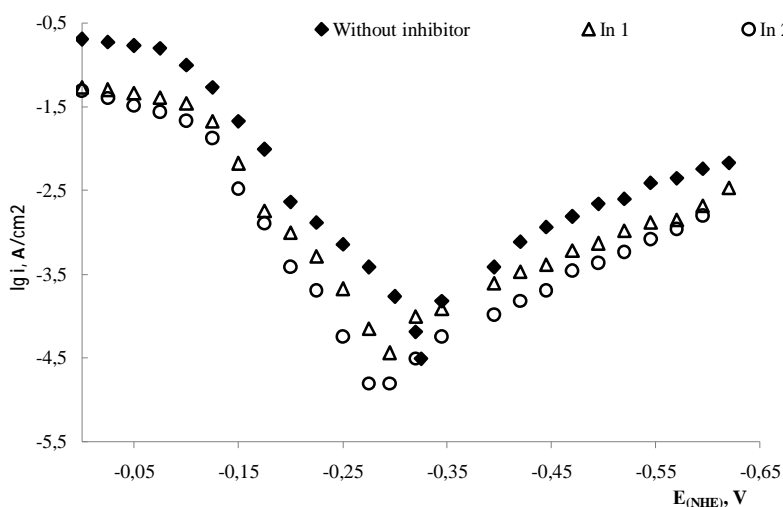

Fig. 6. Polarized cathode and anode curves on St3ps steel in 0.1M HCl solution with and without the inhibitors In1 and In2
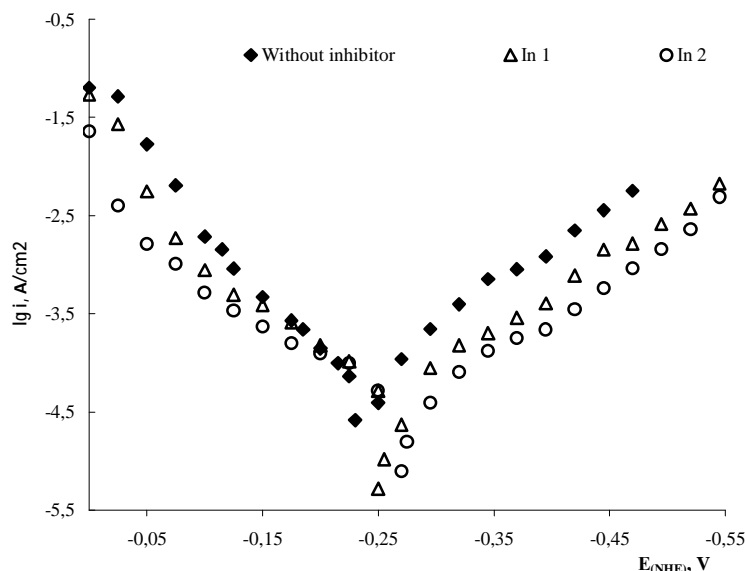

Fig. 7. Polarized anode and cathode curves on St3 steel in 1M HCl solution with and without the inhibitors In1 and In2

In 1M hydrochloric acid solution the cathode process ($E_k = -0.395$ V) is inhibited by In1 by 3.01 times, and by In2 – by 5.57 times. The anode process ($E_a = -0.100$ V) is inhibited by In1 and In2 by 2.18 and 3.72 times, respectively.

The increase of cathode process inhibition coefficient with the decrease of medium pH, more expressed for In2, can be explained with the change in molecule protonation order, which occurs at pH = 1. In 1M HCl solution In 2 is protonated with 2 atoms of nitrogen – the one of the pyridinium circle and the one of amides, while In1 – only with 1 atom of nitrogen.

Therefore, the obtained data from the electrochemical tests prove that the studied aminooxoethylpyridinium chlorides act as the inhibitors of cathode-anode type.

4. Conclusions

Aminooxoethylpyridinium chlorides are the effective inhibitors of cathode-anode type under the mild steel corrosion in acid hydrochloric and sulfuric mediums. The highest inhibition efficiency (93.3 % inhibition efficiency in 1M H$_2$SO$_4$ and 84.3–98.2 % in 1M HCl in the temperature range of 293–333 K) and the presence of high aftereffect (up to 85.5 %) was established for In2 due to its chemisorption on the steel surface with creating a dense inhibition film.

References

[1] Pogrebova I.: Ingibitory Korozii Metaliv. Hai-Tek Pres, Kyiv 2012.
[2] Karthik R., Vimaladevi G., Shen-Ming Chen *et al.*: Int. J. Electrochem. Sci., 2015, **10**, 4666.
[3] Abd El-Maksoud S., Fouda A.: Mat. Chem. Phys., 2005, **93**, 84. https://doi.org/10.1016/j.matchemphys.2005.02.020
[4] Ansari K., Quraishi M., Ambrish Singh: Measurement, 2015, **76**, 136. https://doi.org/10.1016/j.measurement.2015.08.028
[5] Polevichenko C., Bondar O., Kurmakova I., Demchenko A.: XXIV Ukr. konf. z organichnoi khimii, Ukraine, Poltava 2016, 158.

ХЛОРИДИ АМІНООКСИЕТИЛПІРИДИНІЮ ЯК ІНГІБІТОРИ КИСЛОТНОЇ КОРОЗІЇ МАЛОВУГЛЕЦЕВОЇ СТАЛІ

Анотація. Хлориди амінооксиетилпіридинію при корозії сталі Ст3пс в кислих хлоридних та сульфатних розчинах виявляють захисну дію до 98 %. Найбільш ефективною в інтервалі 293–333 K є сполука з гідразинокарбонільним та 2,3-диметил-фенільним фрагментами. Для цього інгібітора також характерний значний ефект післядії, що зумовлено хемосорбцією на поверхні сталі.

Ключові слова: хлориди амінооксиетилпіридинію, інгібітори, кислотна корозія, маловуглецева сталь.