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INFLUENCE OF SOME DERIVATIVES OF XANTHIC ACID ON CORROSION AND ELECTROCHEMICAL PARAMETERS OF ST-20

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By various methods, namely: by removing of the polarization curves and electrochemical impedance spectroscopy it has been investigated the influence of some derivatives xanthic acid (DXA) with total formula $R-O-C(S)-S-R^1$ (where $R = -C_2H_5$, $i-C_3H_7$, $n-C_4H_9$; $R^1 = -CH_2-CH(OH)-CH_2-N(C_2H_5)_2$, $-CH_2-CH_2-O-C(O)-R^*$, R^* - radical of naphthene acid) on corrosion and electrochemical parameters of St-20 in the system 0.1 N aqueous solution HCl. It has been established that the investigated compounds along with previously detected useful properties possess also inhibiting properties in this system. Under influence of these compounds the Ecor value is displaced to the positive side, b_a , b_c , R_p , R_c values grow and icor, $C_{d,l}$ values are decreased. It has been shown that these compounds are referred to the mixed inhibitors. The existing regularities of interrelation "Chemical structure of the investigated compounds – protective effect" have been detected. It has been also established that the corrosion and electrochemical characteristics of St-20 are very close to characteristics St-3

Key words: *corrosion inhibitors, xanthic acid, polarization curves, electrochemical impedance spectroscopy, Nyquist diagram*

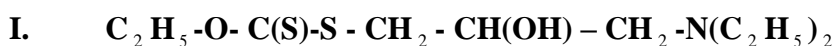
In spite of the fact that a question of interrelation "Chemical structure of the compounds – protective effect" is discussed in literature comparatively long and in this field the numerous regularities have been prepared [1-5], but unambiguous solution of this problem has not yet been achieved. However, a necessity in the development of theoretical bases of selection of inhibitors requires further improvement of theory of corrosion inhibitors with new theoretical and modern experimental developments on regularities of adsorption of SAS over metals, their influence on kinetics of electrochemical reactions proceeding at the border of metal-solution and also by expansion of investigations on study of interrelation "Chemical structure of the compounds – protective effect". Taking into account this circumstance we have previously synthesized some derivatives of xanthic acid (DXA) with total formulas $R-O-C(S)-S-R^1$, $R^{11}-C(S)-S-R^1$ and by gravimetric method investigated as steel corrosion inhibitors St-3 in the systems: 3% aqueous solution NaCl –kerosene, 0.04% aqueous solution CH_3COOH – kerosene and 0.1 N aqueous solution HCl [6-8].

It has been established that the investigated compounds in that or other degree inhibit a steel corrosion process St-3 in the indicated systems, though an efficiency of these compounds in

the neutral system is larger than in the acidic system (in the systems of 3% aqueous solution NaCl –kerosene these compounds show 96-98% protective effect). It has been also established a dependence of inhibiting action on nature of radicals R, R^1, R^{11} [6-8].

This paper has been devoted to the study of influence of some from above-mentioned DXAs with total formulas $R-O-C(S)-S-R^1$ (where $R = -C_2H_5, i-C_3H_7, n-C_4H_9$; $R^1 = -CH_2-CH(OH)-CH_2-N(C_2H_5)_2, -CH_2-CH_2-O-C(O)-R^*$, R^* - radical of naphthene acid) on corrosion and electrochemical parameters of St-20 in the system 0.1 N aqueous solution HCl by electrochemical methods and on their basis to make an attempt to reveal the existing regularities of interrelation “Chemical structure of the investigated compounds – protective effect”.

Chemical formula, full and abbreviated names (FN and AN) of the investigated compounds are presented below.



FN: 2-hydroxy-3-diethylamine propyl ether-ethyl of xanthic acid

AN: 2-H-3-DEAPE-EXA



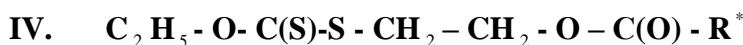
FN: hydroxy-3-diethylamine propyl ether –isopropyl of xanthic acid

AN: 2 – H – 3 – DEAPE – i – PXA



FN: 2- hydroxy-3-diethylamine propyl ether – n.-butyl of xanthic acid.

AN: 2-H-3-DEAPE –n.- BXA



FN: Acyloxyethyl ether - ethyl of xanthic acid

AN: AOEE-EXA

Experimental procedure

The investigations were carried out by the following electrochemical methods: method of removing of polarization curves (MRPC) and electrochemical impedance spectroscopy (MEIS) on apparatus AUTO LAB POTENTIOSTAT GALVANOSTAT of mark «PGSTAT-30». In removing of the polarization curves three-electrode cell consisting of working electrode (St-20), platinum auxiliary electrode and reference electrode (saturated chlorine – silver electrode) has been used. Value change rate of potentials was $2mB \cdot c^{-1}$. The impedance measurements were carried out at potential of open chain (ICC), in this case a frequency of alternating current changed from 10^4 to 1 Hz, and amplitude of voltage was 10mV. The capacity values of double electric layer ($C_{d,l}$) have been calculated by the following equation:

$$f(-Z_{i_{max}}) = \frac{1}{2\pi C_{d,l} R C}$$

where $f(-Z_{i_{max}})$ - current frequency values (Hz), corresponding to maximum impedance value; C_{d-l} - capacity values of double electric layer at the border of metal-solution (F), R_c – capacitance values (Om).

The values of protective effect of the investigated compounds have been calculated:

1) on polarization data

$$\eta_p = \left[\frac{i^0_{cor-icor}}{i^0_{cor}} \right] \cdot 100(\%)$$

2) on impedance data

$$\eta_c = \left[\frac{C^0_{d-l} - C_{d-l}}{C^0_{d-l}} \right] \cdot 100(\%)$$

where i^0_{cor} – density value of corrosion current in the absence of inhibitor ($A \cdot sm^{-2}$), $icor$ – the same in the presence of inhibitor ($A \cdot sm^{-2}$); C^0_{d-l} - capacity value of double electrical layer in the absence of inhibitor (F), C_{d-l} - the same in the presence of inhibitor (F).

Aggressive (working) solution (0,1N HCl) is made with use of the concentrated solution of HCl of high purity (E MEQCK) and double distilled water. For computed treatment of the prepared polarization and impedance data there have been correspondingly used the special programs «GPES» and «FRA» [9-11].

Procedure of carrying out of experiment and treatment of the obtained data has been in detail described in [9-15].

2. RESULTS AND DISCUSSION.

2.1.POLARIZATION MEASUREMENTS

In Fig 1-4 the anode and cathode polarization curves of St-20 in the system 0.1N aqueous solution HCl without inhibitors and with inhibitors ($200 \text{ mg} \cdot l^{-1}$) I, II,III and IV are presented and in Table 1 the results of computer treatment of these curves on program «GPES» are presented.

It is seen from polarization curves and also data of Table that these DXAs although are not on a level of neutral system but still in some degree possess inhibiting properties and at corrosion of St-20 in the system 0.1N aqueous solution HCl. Under influence of these compounds a value of corrosion or stationary potential (E_{cor}) is displaced in some degree (45-82Mv) to the positive side. This fact evidences about that the inhibitors of I, II,III and IV in this system decelerate a process of anode dissolution of metal. However, since these compounds considerably increase the slopes of both anode and cathode Tafel sites of the polarization curves (ba and bc), they can be classified as mixed inhibitors. It is also seen from data of Table 1 that under action of inhibitors I, II,III and IV the polarization resistance value of Rp St-20, i.e. resistance values of charge transfer process through border of electrode – solution is increased in 2.66, 26.3, 2.96 and 3.80 times, respectively.

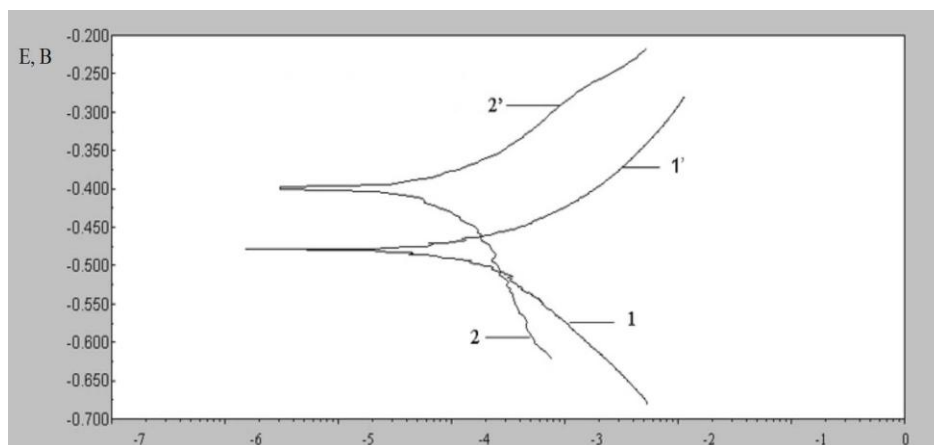


Fig.1 Cathode (1,2) and anode (1¹,2¹) polarization curves of St-20 in the system 0.1N aqueous solution HCl. 1-1¹- without inhibitor; 2-2¹ in the presence of (200 mg · l⁻¹) inhibitor I (2 – H – 3 DEAPE-EXA)

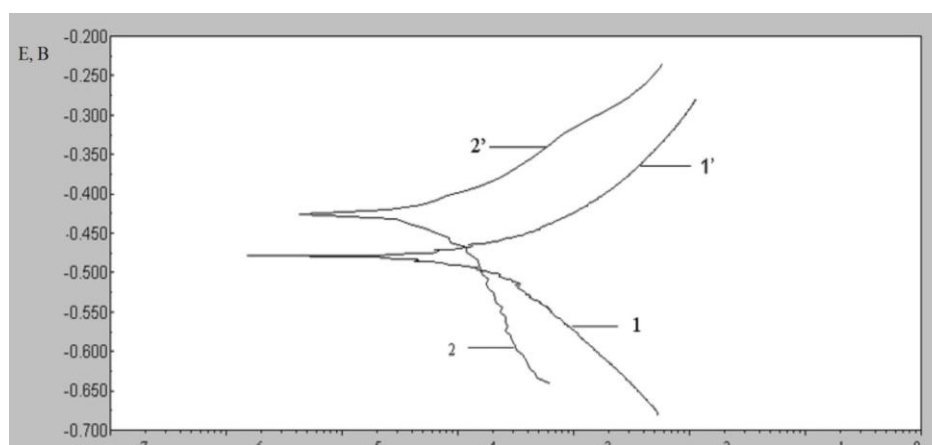


Fig.2. Cathode (1,2) and anode (1¹,2¹) polarization curves of St-20 in the system 0.1N aqueous solution HCl. 1-1¹- without inhibitor; 2-2¹ in the presence of (200 mg · l⁻¹) inhibitor II (2 – H – 3 DEAPE- i – PXA)

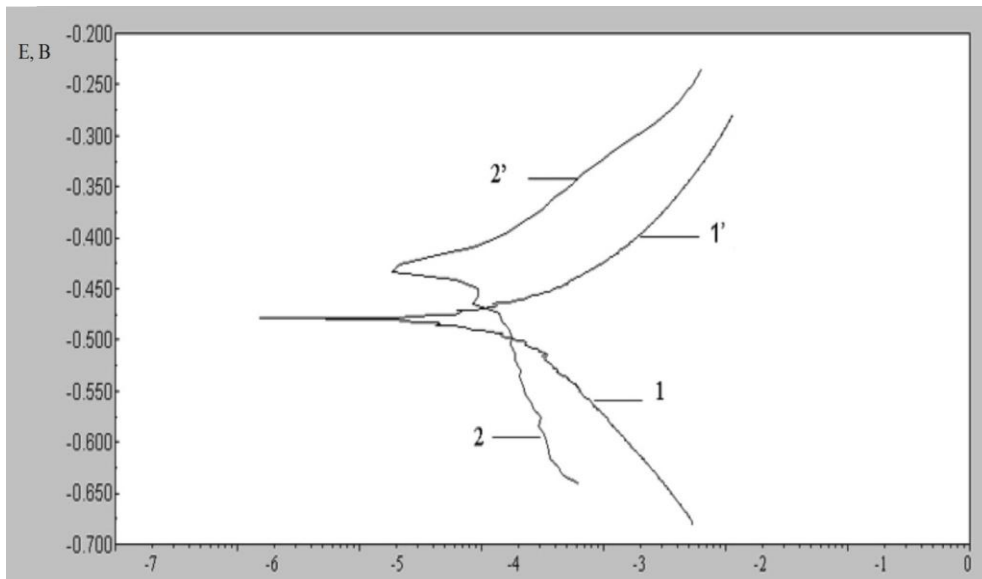


Fig.3. Cathode (1,2) and anode (1¹,2¹) polarization curves of St-20 in the system 0.1N aqueous solution HCl. 1-1¹ - without inhibitor; 2-2¹ in the presence of (200 mg · l⁻¹) inhibitor III (2 – H – 3 DEAPE- n – BXA)

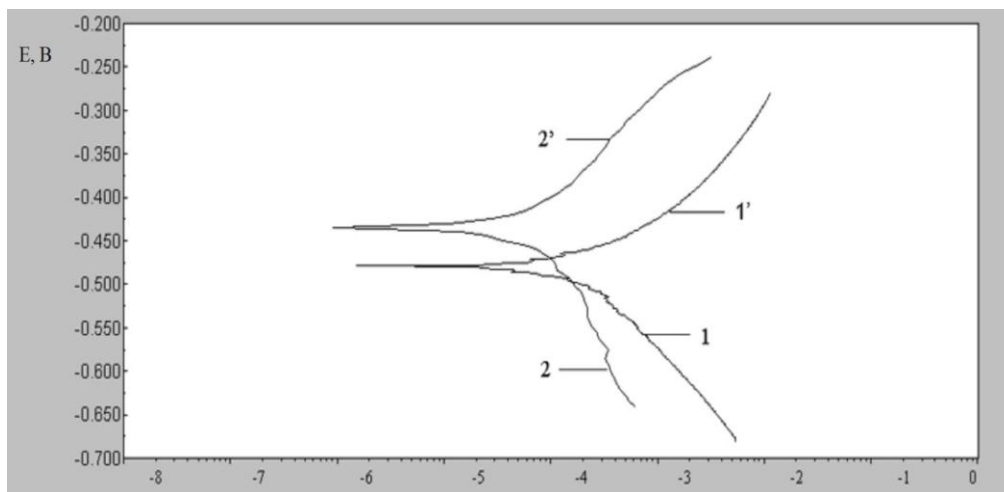


Fig.4. Cathode (1,2) and anode (1¹, 2¹) polarization curves of St-20 in the system 0,1N aqueous solution of HCl. 1-1¹ - without inhibitor; 2-2¹ in the presence of (200 mg · l⁻¹) inhibitor IV (AOEE – EXA)

Table 1. Results of computer treatment of the polarization curves of St-20 in the system 0.1N aqueous solution HCl without inhibitor and in the presence of inhibitors ($200 \text{ mg} \cdot \text{l}^{-1}$)

Inhibitor	Ecor,B	Rp,Om	ba, B	bc, B	$\dot{I}_{\text{cor.}}$, $A \cdot \text{cm}^{-2}$	Corrosion rate, $\text{Mm} \cdot \text{year}^{-1}$	η_p , %
Without inhibitor	-0.480	97.3	0.086	0.169	$1.49 \cdot 10^{-4}$	1.74	-
I (2 – H – 3 DEAPE-EXA)	-0.398	259.2	0.104	0.380	$5.189 \cdot 10^{-5}$	0.42	65.17
II (2 – H – 3 DEAPE- i – PXA)	-0.427	256	0.108	0.347	$5.49 \cdot 10^{-5}$	0.46	63.15
III (2 – H – 3 DEAPE- n – BXA)	-0.434	288	0.128	0.513	$4.649 \cdot 10^{-5}$	0.39	68.80
IV (AOEE – EXA)	-0.435	369.3	0.178	0.277	$4.42 \cdot 10^{-5}$	0.37	70.34

As a result of all these ones a total corrosion rate, i.e. corrosion current (\dot{I}_{cor}) is subjected to the considerable decrease (in 2.87, 2.71, 3.20 and 3.37 times, respectively).

So, in the presence of inhibitors I, II, III and IV a corrosion current is decreased from $1.49 \cdot 10^{-4} A \cdot \text{cm}^{-2}$ to $5.189 \cdot 10^{-5} A \cdot \text{cm}^{-2}$, $5.49 \cdot 10^{-5} A \cdot \text{cm}^{-2}$, $4.649 \cdot 10^{-5} A \cdot \text{cm}^{-2}$ and $4.42 \cdot 10^{-5} A \cdot \text{cm}^{-2}$ respectively.

Comparing data referring to the various DXA, one can note that at the same concentration and efficiency of these compounds although are not strongly differed from each other, but still it is seen that according to the efficiency these compounds in the indicated system are located in the following order:

$$\text{IV} > \text{III} > \text{I} > \text{II}$$

It has been shown in literature [3] an efficiency of inhibitors essentially depends on length of hydrocarbon radical and on its branching. However, in connection with these problems there are many contradictions. So, in opinion some researchers a transition from isocompounds to normals leads to strengthening of protective properties and in others opinion – vice versa. The first group of researchers confirms that an availability of the branched radicals prevents the dense packing of the adsorbed molecules and the interweaving of their hydrocarbon chains.

The experimental data prepared by us correspond to the last theses. So, as follows from corresponding formulas, a difference between compounds I and II is the fact that if in compound I $R = -C_2H_5$, then in compound II $R = i-C_3H_7$, i.e. in transition from compound I to compound II it takes place a branching of radical R. As follows from Table 1, this leads to the decrease of efficiency II in comparison with I. In transition from compound I to compound III it takes place

an elongation of radical R ($R = n-C_4H_9$). And this leads to the increase of efficiency of III in comparison with compound I.

Comparing data referring to the compounds I and IV, one can detect that a compound IV according to the efficiency exceeds a compound I. As follows from corresponding chemical formulas, a difference between compounds I and IV is that if in IV $R^1 = -CH_2 - CH_2 - O-C(O) - R^*$, i.e. in transition from compound I to compound IV it takes place a substitution of nitrogen-containing fragment with analogous oxygen-containing fragment combined with radical of naphthene acid. This indicates that a fragment $-CH_2 - CH_2 - O-C(O) - R^*$ more strongly favors compounds to adsorption on metal surface than a primary fragment.

2.2. IMPEDANCE MEASUREMENTS

In Figs.4-7, and also in Table 2 the results of investigations carried out by the methods of EIS i.e., Nyquist diagrams for St-20 in the system 0,1N aqueous solution HCl in the absence and in the presence of inhibitors I, II, III and IV, and in Table 2 the results of computer treatment of these diagrams on program FRA are presented [9-11].

As follows from these diagrams and also from data of Table 2 under influence of the investigated DXA a capacitance value (R_c) is considerably increased, but capacity value of double electrical layer ($C_{d,l}$), formed at the border of metal-solution is decreased. So, if without participation of inhibitors a value $C_{d,l}$ in the indicated system is $5.00 \cdot 10^{-5} F$, then at participation of these compounds ($200 mg \cdot l^{-1}$), $C_{d,l}$ value is decreased to $1.22 \cdot 10^{-5} F$ (in 4,1 times for I), to $1.31 \cdot 10^{-5} F$ (in 3.82 times for II), to $1.12 \cdot 10^{-5} F$ (in 4,46 times for III) and to $1.06 \cdot 10^{-5} F$ (in 4.72 times for IV). A protective effect calculated on these values is 75.60%, 73.80%, 77.60% and 78.80%.

The detected facts again evidence about that the molecules of the investigated DXAs adsorbing on metal surface in the corrosion – aggressive system form a protective film on them, isolate it from environmental system and thereby prevent proceeding of the electrochemical processes at the border of metal-solution. As is seen, an availability of various functional groups and heteroatoms in molecules of the investigated DXAs give them properties of propensity for adsorption on metal surface.

In comparison of data of Table 1 and Table 2. one can detect that an efficiency of the investigated DXAs calculated according to the impedance data is slightly higher in comparison with efficiency calculated according to the polarization data.

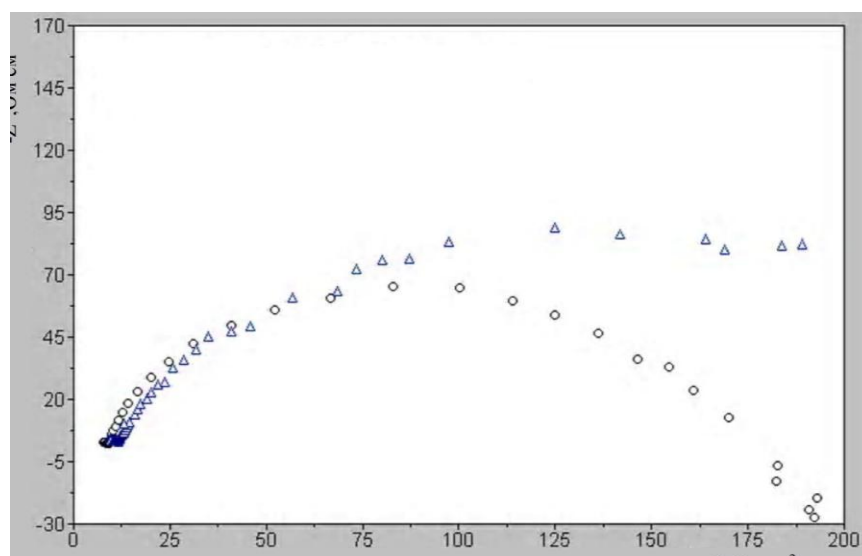


Fig.5 Nyquist diagram for St-20 in the system 0.1N aqueous solution HCl. o - in the absence and in ∇ - in the presence of $(200 \text{ mg} \cdot \text{l}^{-1})$ inhibitor I (2-H – 3 DEAPE-EXA)

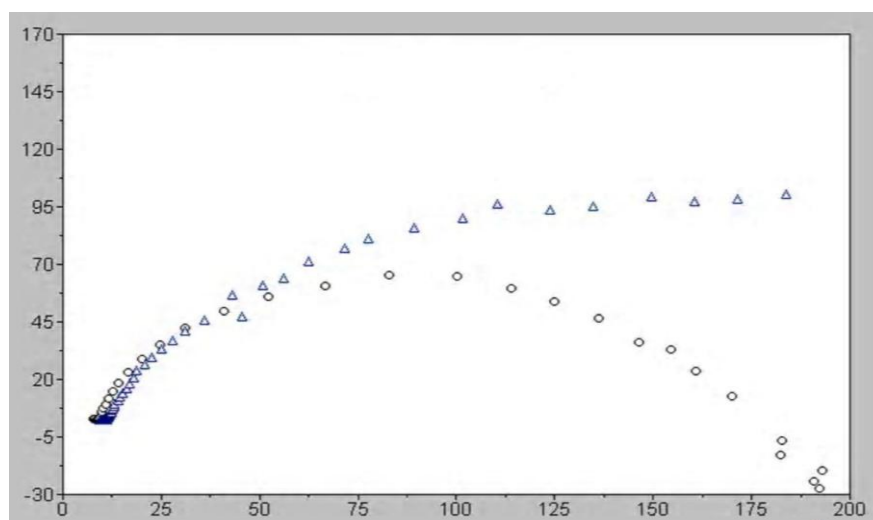


Fig.6. Nyquist diagram for St-20 in the system 0.1N aqueous solution HCl. o-in the absence and ∇ - in the presence of $(200 \text{ mg} \cdot \text{l}^{-1})$ inhibitor II (2 – H – 3 DEAPE- i – PXA)

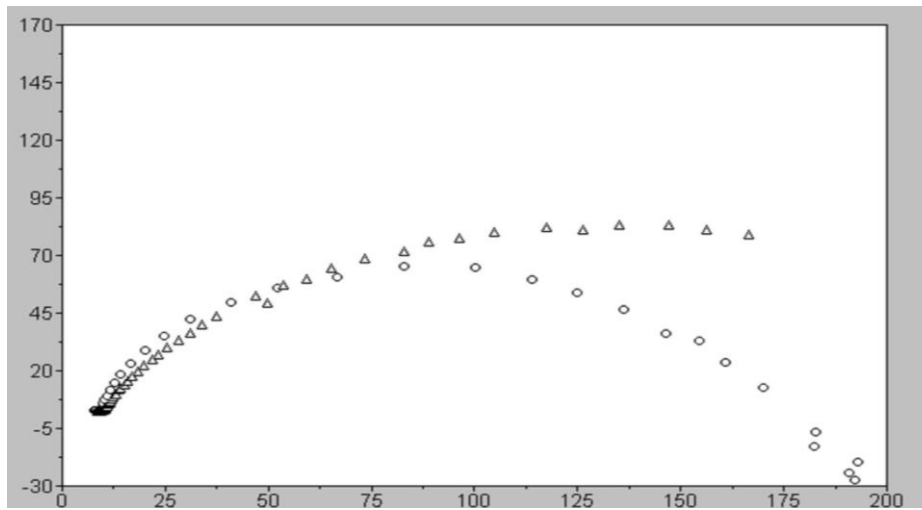


Fig.7. Nyquist diagram for St-20 in the system 0.1N aqueous solution HCl. o-in the absence and ▽ - in the presence of ($200 \text{ mg} \cdot \text{l}^{-1}$) inhibitor III (2 - H - 3 DEAPE- n - BXA)

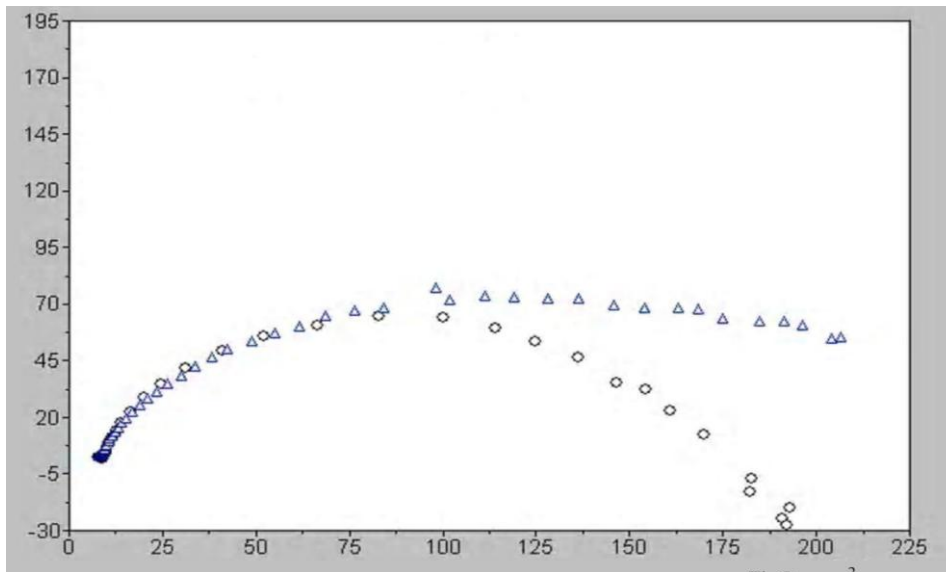


Fig.8. Nyquist diagram for St-20 in the system 0.1N aqueous solution HCl. o-in the absence and ▽ -in the presence of ($200 \text{ mg} \cdot \text{l}^{-1}$) inhibitor IV - (AOEE -EXA)

Table 2. Results of computer treatment of the polarization curves of St-20 in the system 0.1N aqueous solution HCl without inhibitor and in the presence of ($200 \text{ mg} \cdot \text{l}^{-1}$) DXA on the program «FRA».

Inhibitor	$C_{inh}, \text{mg} \cdot \text{l}^{-1}$	Rc, Ом	C_{dl}, F	$\eta_c, \%$
Without inhibitor	0,00	162.8	$5.00 \cdot 10^{-5}$	-
I (2 – H – 3 DEAPE-EXA)	200	247.7	$1.22 \cdot 10^{-5}$	75.60
II (2 – H – 3 DEAPE- i – PXA)	200	242.9	$1.31 \cdot 10^{-5}$	73.80
III (2 – H – 3 DEAPE- n – BXA)	200	250.6	$1.12 \cdot 10^{-5}$	77.60
IV (AOEE – EXA)	200	256.4	$1.06 \cdot 10^{-5}$	78.80

However, firstly, this difference is not so great, and secondly, the detected sequence of location of inhibitors on efficiency in both methods are the same.

This evidences that the results of polarization and impedance measurements are well agreed with each other.

Thus, one can conclude from above-mentioned ones that the investigated DXAs along with previously revealed useful properties at corrosion of St-3 [6–8], possess also inhibiting properties in the system 0.1N aqueous solution HCl and at corrosion of St-20. In our opinion, the use of these inhibitors in the various fields of industry, including gas and oil-extracting industry will allow to increase a reliability of work of various steel constructions used in this branch of industry. In addition, the established interrelations “Chemical structure of DXA – protective effect” can be used in improvement of theoretical bases of selection of inhibitors.

CONCLUSIONS

1. By the methods of SEC and EIS the influence of four DXAs on corrosion of St-20 in the system 0.1N aqueous solution HCl has been investigated. It has been established that these compounds along with previously detected useful properties possess also inhibiting properties in this system.

2. It has been revealed that under influence of the investigated DXAs a value E_k is displaced to the positive side, values b_a , b_c , R_p , R_c grow, and values E_{cor} and C_{oc} - are decreased. It has been shown that these inhibitors are referred to the mixed inhibitors.

3. It has been established by the both methods that according to the efficiency the investigated DXAs are located in the following order.

AOEE – EXA (IV) > 2 – H – 3 DEAPE- n – BXA (III) > 2 – H – 3 DEAPE -EXA (I) > II 2 – H – 3 DEAPE - i – PXA (II).

4. It has been suggested that the use of these DXAs in the various branches of industry, including gas and oil-extracting industry will allow to increase a reliability of work of steel equipments of this branch of industry. In addition, the established interrelations "Chemical structure of DXA – protective effect" - can be used in improvement of theoretical bases of selection of inhibitors.

5. It has been established that the corrosion and electrochemical characteristics of St-20 are very close to the characteristics of St-3.

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