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Electrochemical and Gravimetrical Investigation Inhibirors on the Base Organic Compounds

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Abstract:

In article the results of electrochemical and gravimetrical investigations by the influence of new elaborated oligomeric salts on the base of some organic compounds on the corrosion behavior of steel samples (St.3, 45) in different mediums are presented. It was shown that protective effect of investigated oligomeric salts has been increased with increasing their molecular mass and hydrocarbon radicals. The influence of the experiments duration and also some other factors on the protective effect of the investigated oligomers have been discussed.

Keywords: inhibitors, steel corrosion, mechanism of inhibition, adsorption, polarization curves, polarization resistance, hydropholical, synergism, electrodonoral, acetamide, formamide, aminoethanol, melamine phosphate, phosphate dimethylolhexamethylenediamine.

Introduction. The materials for mordent technologies – alloys on the base of iron in great degree undergo to corrosion under action of air's oxygen, moisture and oxides of sulfur, nitrogen and other chemically- active compounds [1]. The high pollution of environment and hard regimes of exploitation of the technological equipment of oil-gaseous branch have caused great damage from the corrosion which in industrial development contrives has achieved about 10% of the combined profit. At the exploitation of cooling systems of circulating water-supply in without through high regime the brevity of using of circulating waters has increased what caused the increasing of their mineralization. Aliphatic, aromatic and heterocyclic amides, amines, hinolines and some other compounds are the most investigated in this plane. In spite of the wide spectrum of investigations in this field some questions have remain practically not enough investigated. Anodic protection by the passivating inhibitors has based on the fact that in process of the reduction the current has appeared which enough to transition metals in passive state. Some salts of Fe^{3+} – nitrates, dichromate's and some others can be used as inhibitors. Application of such inhibitors has allowed to protect metals in hard accessible places – cracks and clearances; it is necessary to note that their short ate is a contamination of technological medium [2]. The study of corrosion processes and the elaboration of methods for protection metals are among current scientific and technical problems. One of the common methods of protection is the use of inhibitors to reduce the rate of corrosion of metals and alloys that come into contact with an aggressive medium in industrial conditions [3]. This is due to the fact that at low temperatures, inhibitor molecules are physically adsorbed on the metal surface, and with increasing temperature chemical adsorption occurs. Decreasing of the inhibitory effect with a further increasing of temperature is associated with desorption of the inhibitor from the surface of the corroding metal. The inhibition mechanism is based on the inhibition of cathode and anodic corrosion processes under the influence of the surface activity of the inhibitory composition, which corresponded to meet the following requirements: combination a high degree of protection along with low economic cost; complex protective effect against various aggressive mediums; safety for the environment, people and equipment; low cost and simplicity of their synthesis [4]. The objects of study are nitrogen- and phosphorus-containing low-molecular organic compounds such as acetamide, formamide, aminoethanol and also synthesized salts of melamine phosphate, melamine glycerate phosphate and phosphate dimethylolhexamethylenediamine.

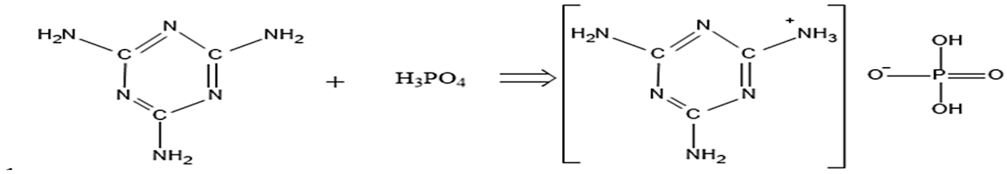
Methods. Electrochemical (Corrtest: Potentiostat/Galvanostat), gravimetrical IR-spectroscopic (IR-spectrometer EN 1407) and X-ray phase analysis methods (X-ray diffractometer DRON-05) were used in this investigation.

Results. The objects of the study were nitrogen- and phosphorus-containing organic compounds. Investigation of the corrosion behavior of steel (St. 3, St. 45) was carried out on samples in the form of plates. The effect of salts, medium and inhibitors on the corrosion behavior of steel samples was determined by electrochemical and gravimetricall methods by the loss of sample mass after corrosion tests.

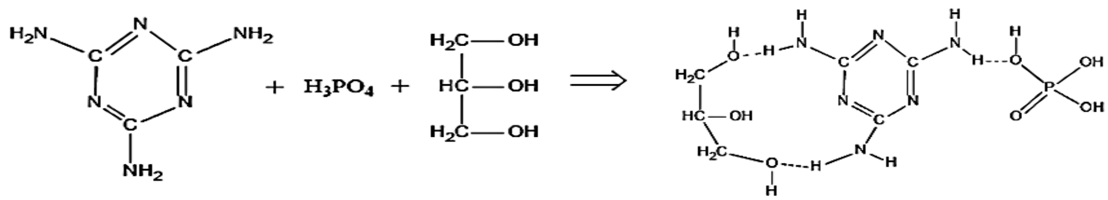
Table-1. Used organic and oligomeric inhibitors

№	Inhibitor	Molecular mass	Name of inhibitors
1	AKI-1	59,07	Acetamide
2	AKI-2	45,04	Formamide
3	AKI-3	61,08	2-Aminoethanol
4	AKI-4	224	Melamine phosphate
5	AKI-5	814	Melamine phosphate glycerate
6	AKI-6	213	Phosphate hexamethylenediamine
7	AKI-7	1700	Dimethylolhexamethylenediamine
8	AKI-8	2200	Phosphate dimethylol hexamethylenediamine

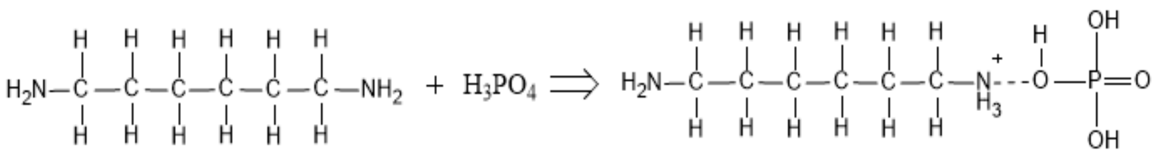
Corrosion inhibitor (AKI-4): based on melamine and phosphoric acid. Melamine (0.1 M) and phosphoric acid (0.1M) are loaded into a round-bottomed flask equipped with a mechanical stirrer and mixed until completely dissolved and a homogeneous mass is obtained. Then the temperature has rised been to 60-70°C, the reaction is carried out until the sediment is completely separated, which is dried in the open air. The synthesis of water-soluble melamine phosphate adduct is described by the following scheme:



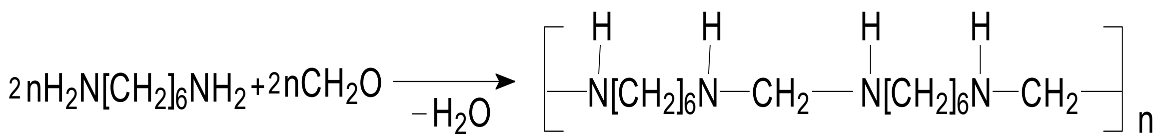
Corrosion inhibitor (AKI-5): based on melamine, phosphoric acid and glycerin: 0,1M solutions of melamine and phosphoric acid with glycerin were poured into a 250 ml round-bottom flask equipped with mechanical stirrer. Next a mechanical stirrer was turned on and the reaction mixture was heated to 70ºC. The resulting salt has a light purple color and is a crystalline powder. Melamine phosphate glyceride salt is highly soluble in water and has the following structure:



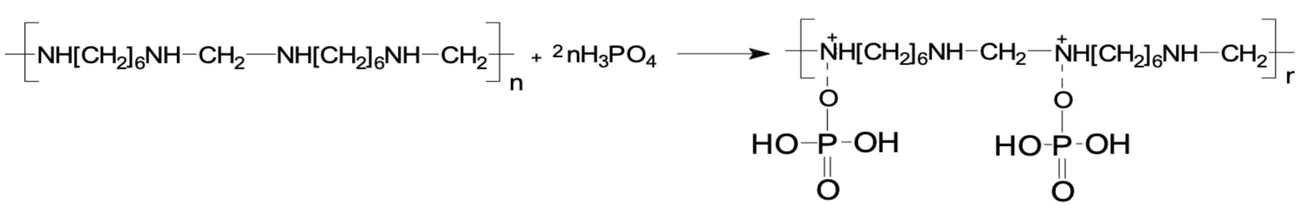
Corrosion inhibitor (AKI-6): based on hexamethylenediamine adduct phosphate: HMDA (0,1M) and phosphoric acid (0,1M) were loaded into three-neck flask equipped with mechanical stirrer and mixed until completely dissolution with obtaining homogeneous mass. Then the temperature was raised to 70-90°C, the reaction was carried out until the precipitate is completely separated, which than is dried in the open air:



Corrosion inhibitor (AKI-7): based on formaldehyde and hexamethylenediamine: formalin was poured into a 250 ml round-bottom flask equipped with a mechanical stirrer and was neutralized by 25% aqueous ammonia solution to pH=7 (universal indicator). Next, a mechanical stirrer was turned on, hexamethylenediamine was added and the reaction mixture was heated to 60°C. The reaction mixture was kept at this temperature 40-60 min. and then cooled to 40-45°C. The cooled mass was poured into a device for distillation under vacuum, and the water was distilled off at a residual pressure of 60 mmHg. and temperature 60°C. The resulting porous mass was dried in a vacuum at 40°C until a solid product was formed, the yield of which was 87-92% from theoretical. The synthesis of hexamethylenediamine with formaldehyde can be described by the following scheme:



Corrosion inhibitor (AKI-8): based on formaldehyde and hexamethylenediamine with phosphoric acid: formalin was poured into 250 ml round-bottom flask equipped with a mechanical stirrer and neutralized with 25% aqueous ammonia solution to pH=7 (universal indicator). Next a mechanical stirrer was turned on, hexamethylenediamine was added and the reaction mixture was heated to 60°C, gradually mixing with phosphoric acid. The resulting mass was dried in a vacuum oven at 40°C, the resulting salt has a light pink color. The synthesis of oligomers on the base of hexamethylenediamine, formaldehyde and orthophosphoric acid can be described by the following scheme:



Dimethylolhexamethylenediamine phosphates in dilute solutions in neutral, slightly acidic and slightly alkaline mediums at ordinary temperatures have a linear structure with a degree of polymerization from 7 to 14, i.e. they are oligomers with a molecular mass about 1750-3500. The size and shape of a cell are determined by the size, shape and relative position of it is constituent particles. The geometry of the crystal is described by the dimensions of the unit cell, characterized by the length of it is three non-parallel edges (a0, b0, c0) in nanometers and the angles between them (α, β, γ). The X-ray structural analysis method has been applied to collagen research in two ways: 1) high-angle study and 2) low-angle study. Both methods are based on the same principle - diffraction and interference of X-rays reflected from internal planes in the crystal. It is known, that crystal is built from a more or less complex groups of atoms - a motif unit, which is regularly repeated in three dimensions by linear transfers and translations.

Table 2. Changes in melamine phosphate parameters in unit cells

K	β (rad)	2θ(deg)	θ(rad)	d, nm	$\bar{d}$, nm
0,9	0,32290	17,2350	0,15041	24,6015	29,0586
0,9	0,23610	25,9776	0,22669	33,6459	
0,9	0,27460	16,8703	0,14715	28,9285	

These complications in the interpretation of X-ray diffraction patterns of polymers are obviously due to the difference in structure and structure of the latter from low molecular mass of crystalline substances. $\lambda=2d\sin\theta$ where λ is the wavelength of X-rays; d-distance between planes; θ is the “angle of reflection” of X-rays. Regarding continuous diffuse scattering near the central spot, there are indications without a detailed analysis of this phenomenon.

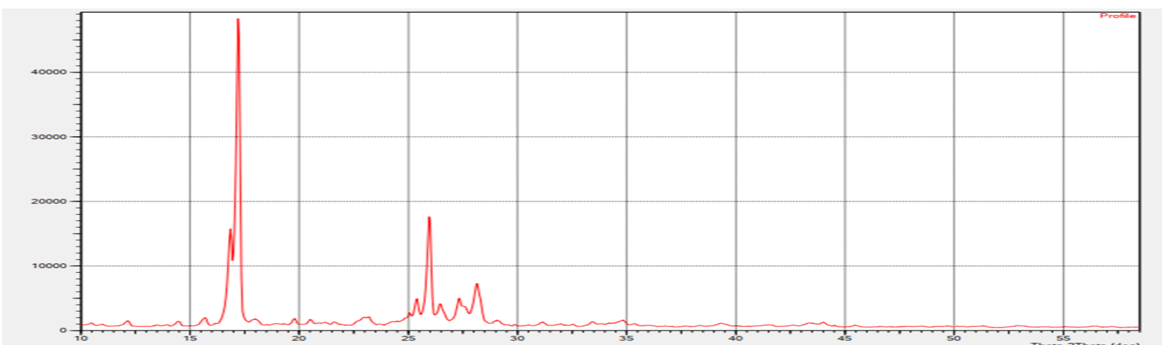


Fig.1. X-ray diffraction pattern of melamine phosphate (AKI-4), λ=0,15406 nm

Basically, almost all works are devoted to discrete scattering at small angles. These atomic groups, representing lattice sites, are capable of scattering X-ray radiation incident on them only under certain conditions.

Table 3. Changes in parameters of melamine phosphate glycerate in unit cells (AKI-5)

K	β (rad)	2θ(deg)	θ(rad)	d, nm	$\bar{d}$, nm
0,9	0,05749	22,2971	0,194579	2,4108	2,6716
0,9	0,006318	11,1106	0,096958	2,1945	
0,9	0,004065	19,7573	0,172414	3,4096	

In the process of performing X-ray analysis of compounds, the greatest difficulties arise in interpreting obtained data.

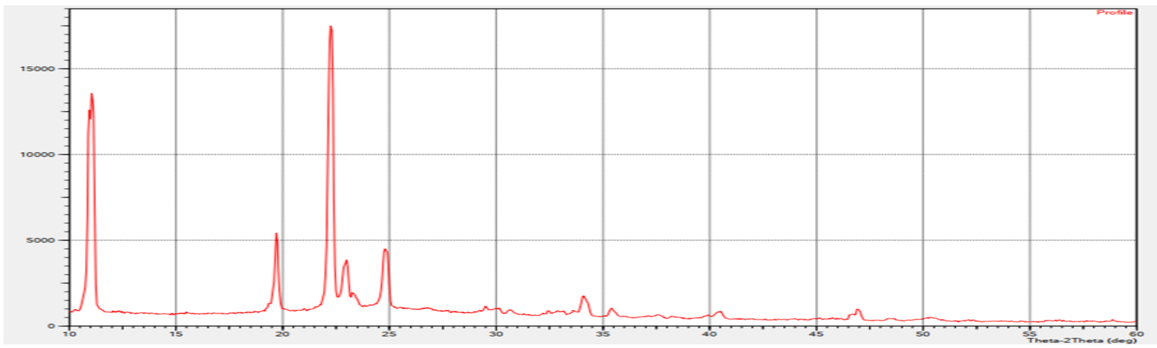


Fig.2. X-ray diffraction pattern of melamine phosphate glycerate (AKI-5), λ=0,15406 nm

If a parallel monochromatic beam of X-rays is passed through a crystal, then the rays emerging from it will have diffraction maxima at angles.

Table 4. Changes in the parameters of phosphate hexamethylenediamine (AKI-6) in unit cells

K	β (rad)	2θ(deg)	θ(rad)	d, nm	$\overline{d}$, nm
0,9	0,0173	17,9043	0,1562	4,95021	8,149436
0,9	0,0154	24,2718	0,2118	3,66406	
0,9	0,0186	20,9601	0,1829	4,23490	

Atoms in a crystal are interconnected by characteristic symmetry relationships, according to which these crystals are divided into classes.

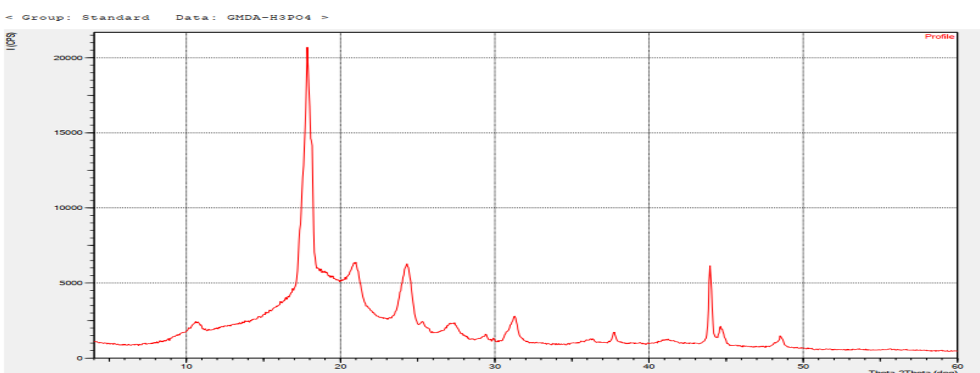


Fig.3. X-ray diffraction pattern of phosphate hexamethylenediamine (AKI-6), λ=0,15406 nm

The interpretation of the results obtained from radiographic examination at small angles is different. IR spectrums of the obtained salts and comparison of inhibitory connection properties. Comparative results of a study of the inhibitory properties of melamine phosphate, HMDA phosphate, melamine phosphate glycerate, hexamethylenediamine formaldehyde are presented, which showed that their protective effect is due by formation of an adsorption layers on the metal surface.

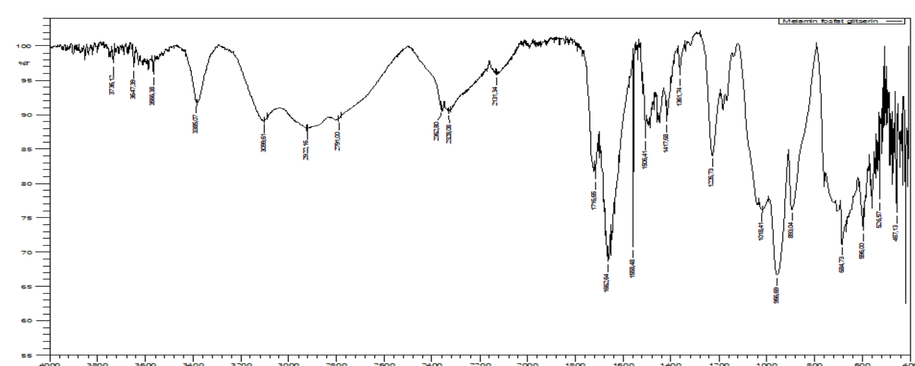


Fig. 4. IR spectrum of melamine phosphate glycerate (AKI-5)

At protection by inhibitors in aqueous systems, a protective film is formed on the surface of low-carbon steel, mainly consisting of complexes with iron cations [5]. Inhibitors have connected to the metal surface with NH_2 groups. In the IR spectrum of the synthesized compound melamine phosphate glycerate there are new peaks belonging to aminogroups in the region 3373 cm-1; $-CH_2$-groups give asymmetric and symmetric broad vibrations in the regions 2941-2885 cm^{-1}; stretching vibrationsof–C-O groups are observedin the region of 1725-1671 cm^{-1}; vibrations indicating the location of P-O-P groups are located in the region 976-927 cm^{-1}; CH groups appeared in the range 775-713 and 680 cm^{-1} and in range 579-509 cm^{-1} was observed maximum corresponding to the -NNN bond.

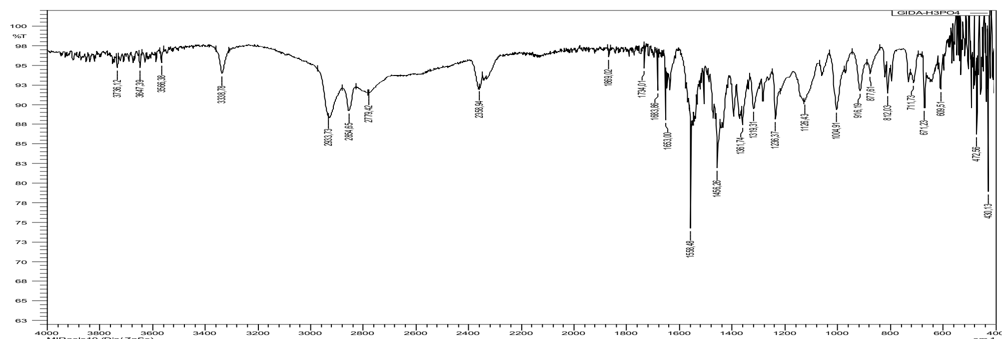


Fig. 5. IR spectrum of phosphate hexamethylenediamine (AKI-6)

In the IR spectrum of phosphate hexamethylenediamine there are 609,51, 671,23, 812,03, 877,61 and 916,19 cm^{-1} frequencies with average intensity related to non-plane deformation vibrations corresponding to torsional $-CH_2$ group bands which are quite characteristic to this functional group. Absorption caused by hydrogen bonding with polar solvents such as amines also occurs in this region; 1558-1683 cm^{-1} $-NH_2$ plane bending vibrations corresponding to scissor vibrations like $-CH_2$; bands 1004-1126 refer to $R-NH_2$; in the region 1236 cm^{-1} there are flat band of average height, belonging to the -OH group; the bands in range 1361-1319 cm^{-1} are attributed to the –P-O group. Hydrocarbon radicals with hydrophobic properties, oriented towards the aggressive medium by repel water molecules and corrosive particles from the metal surface, also additionally screen and thereby have enhanced blocking of steel surface. The pH value should be maintained at 6.5-7.0 or even slightly lower. Based on the data obtained from corrosion experiments, it was established that in circulating waters with a high salt content there are not only aggressive anions (ClO^-, SO_4^{2-}) but also calcium and magnesium ions, participated in the formation of protective films on the metal surface and decreasing corrosion aggressiveness. The protective film of the inhibitor on the surface of steel consists of a single component, what indicates on complete involvement of the phosphonate groups of the inhibitor in formation during its adsorption protective film on the metal surface. The strongest interactions occur with the molecules containing P-O-P; P-O-C; P-H; P-C; P=O groups and similar strong effect is observed in case of using two-component systems [6]. Results obtained by electrochemical methods on figure is shows the results of study of the open circuit potential for St.45 in a background solution (pH=8,9) of 3%NaCl+5%Na_2CO_3 in the absence and presence of corrosion inhibitor at concentration 30 mg/l are presented. In general, open-circuit potentials shifted toward more negative values in the presence of the inhibitor. This is due to the orientation of adsorption and the structure of the inhibitor molecule. At the same time AKI-5 and AKI-7 are more stable, have the greatest negative value in comparison with other inhibitors, they form an insoluble and protective thin films on the metal surface in a background solution, while the potential above the OCP (open circuit potential) is considered thermodynamic unstable and susceptible to corrosion.

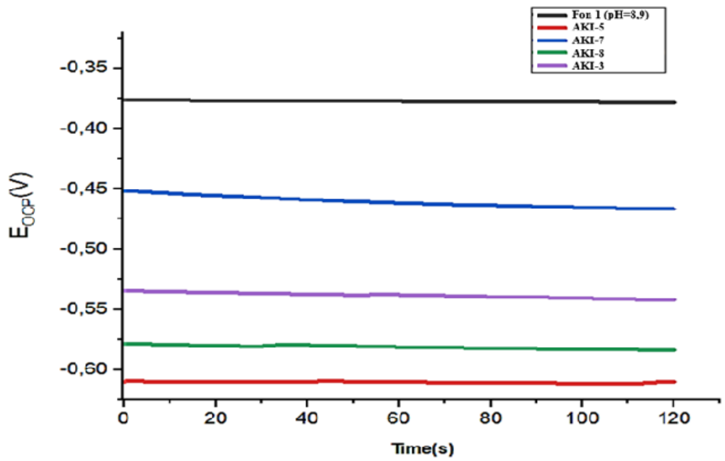


Fig. 6. Open Circuit Potential (OCP) measurements in background solution (Fon-1) pH=8,9 (3%NaCl +5%Na_2CO_3) with various inhibitors 30 mg/l fon-1 (1); AKI-5 (2) AKI-7 (3) AKI-8 (4); AKI-3 (5).

Measuring corrosion rate by methods polarization curves. With cathode polarization the rate of hydrogen evolution increases but the rate of metal dissolution decreases. Thus, with the help of cathode polarization it is possible to protect the metal from corrosion. Based on the data of polarization measurements near a stationary potential, using linear electroporation of the obtained curves, the corrosion current and the slope angle of the polarization curves of hydrogen evolution and metal dissolution were determined. Sufficiently high corrosion rates were observed in some cases from passive state [7].

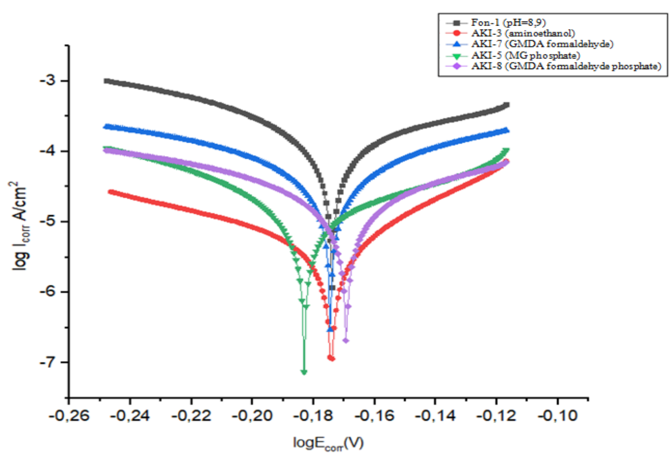


Fig. 7. Polarization curves of a steel electrode in a background solution (Fon-1) pH=8,9 (3%NaCl+5%Na_2CO_3) (1), in presence 30 mg/l solutions of various inhibitors AKI-3 (2); AKI-7 (3); AKI-5 (4); AKI-8 (5).

The state of the surface of the samples can be unambiguously judged by the value of the electrode potential. In order to clarify the effect of additions of various organic inhibitors on the stability and depth of the passive state of St.45 in the background solution, measurements of the electrode potential were carried out every 5 min. during 25 min. of exposure of the sample in an aggressive medium. In the presence of an inhibitor in background solution pH=7 the best results were shown for inhibitors AKI-3, AKI-8 and AKI-7 with a concentration of 30 mg/l.

Table 5. The effectiveness of inhibitors was determined by the method of polarization curves in solution (Fon-1) pH=8,9 (3%NaCl + 5%Na_2CO_3) at a temperature 25°C

Inhibitors	**C,**	*i*, (mA/sm^2)	*i*	**Θ**	**B_c**	**B**

	(mg/l)					
Fon-1 (3%NaCI+5%Na_2CO_3)	30	0,72	–	–	–	–
AKI-3		0,41	0,56	0,82	4,55	0,15
AKI-7		0,38	0,52	0,86	6,14	0,20
AKI-5		0,35	0,48	0,90	9,0	0,30
AKI-8		0,30	0,41	0,97	32,3	1,07

The addition of inhibitors has reduced the polarization of the working electrode and has blocked anodic and cathode corrosion [8]. With change of the corrosion current, it is possible to determine the degree of metal surface (θ) and the adsorption equilibrium constant (B_c) from the influence of concentration. Results obtained from gravimetric tests: experiments were carried out to determine the corrosion rate of a steel electrode in the presence of the investigated inhibitors at their various ratios in a certain temperature range. After holding the samples during 360 and 720 hours the corrosion products were removed by a scalpel and the corrosion rate and corrosion losses related to a blank corrosion experiment without an inhibitors were determined gravimetrically.

Table 6. Results of gravimetric determination of the protection of St.45 grade metals from corrosion with nitrogen and phosphorus-containing inhibitors (C=30 mg/l) concentrations at pH=8,9 and 25°C

Inhibitors	**result 15 days**				**result 30 days**			
	K, g/(m^2day)	П (permeability/ corrosion depth) mm/day	γ	Z, %	K, g/(m^2day)	п (permeability/ corrosion depth) mm/day	γ	Z, %
F-1 (pH=8,9)	4,897	$9,38\cdot10^{-7}$	-	-	4,954	$18,88\cdot10^{-7}$	-	-
AKI-1 (acetamide)	2,345	$4,49\cdot10^{-7}$	2,08	62,11	1,127	$2,16\cdot10^{-7}$	4,39	77,25
AKI -2 (formamide)	0,338	$6,48\cdot10^{-8}$	14,48	72,09	0,357	$6,84\cdot10^{-8}$	13,86	73,78
AKI -3 (2-aminoethanol)	1,980	$3,79\cdot10^{-7}$	2,47	72,56	1,724	$3,3\cdot10^{-7}$	2,87	75,01
AKI-4 (melamine phosphate)	1,105	$2,11\cdot10^{-7}$	4,43	82,43	0,752	$1,4\cdot10^{-6}$	6,58	84,80
AKI-5 (melamine phosphate glycerate)	0,147	$2,83\cdot10^{-8}$	10,27	90,26	0,204	$3,92\cdot10^{-8}$	24,18	95,86
AKI-6 (hexamethylene diamine phosphate)	1,138	$2,18\cdot10^{-7}$	4,30	96,98	0,101	$1,91\cdot10^{-8}$	49,54	97,98
AKI-7 (dimethylolhexa methylenediamin)	1,104	$2,00\cdot10^{-7}$	10,28	90,56	0,263	$5,05\cdot10^{-8}$	18,79	94,67

AKI–8 (phosphate dimethylol hexamethylenediamine)	0,0295	$5,5\cdot10^{-9}$	18,86	92,40	0,059	$1,1\cdot10^{-8}$	83,96	96,82

Conclusions. Presence in products of corrosion-active compounds is created the actual problem of protection of metals from inner corrosion. Anticorrosion treatment transporting product by inhibitors is important tasks of protection of steel and metallic pipes of different purpose from inner corrosion. Results of visual observations have shown that at absence of nitrogen and phosphorous – containing adducts and oligomer salts steel has been undergone to corrosion locally. Investigation phosphorous-containing oligomer inhibitors has shown their high effectivety in decreasing of steel corrosion in weak–acid and neutral mediums.

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