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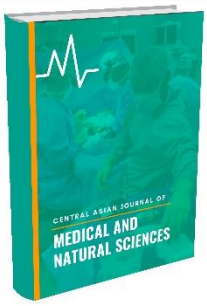

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QUANTITATIVE ASSESSMENT OF EFFICIENCY OF INHIBITORS, NITROGEN CONTAINING COMPOUNDS ON THE RESULTS OF ELECTROCHEMICAL AND GRAVIMETRIC RESEARCH

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ABSTRACT: Results of investigation of inhibition of metals corrosion inhibition by synthesized water- soluble oligomeric compounds are presented. Influence of oligomeric compounds on the corrosion behavior of steel -3 in phone solution has been investigated by the gravimetric methods. Influence of keeping time of steel samples of oligomeric inhibitors on their protective action has been investigated.

KEYWORDS: inhibitors, steel corrosion, mechanism of inhibition, urea, phosphate urea, phosphate tiourea, phosphate of dimethilolurea, phosphate dimethilolmelamin, dimethilolhexamethylendiamine, oligomer, heteroatom, adsorption, polarization curves, polarization resistance, hydropholical, synergism, IKM, OIKM.

INTRODUCTION

Every year 10% of metals are destructed in result of corrosion rising owing chemical and electrochemical interactions with environment what has caused to financial waste amounting by millions of sums. The material for mordent technologies – alloys on the base of iron in great degree undergo to corrosion under action of air's oxygen, moisture and exide's of sulfur, nitrogen and other chemically- active compounds.

Carrying out of purpose investigation by increasing of quality of metals and their effective using is important in all world and at this special attention is devoted to following tasks: using of water-soluble oligomeric and polymeric inhibitors; fighting with salt-deposits, determination of optimal conditions as of inhibition of metals corrosion, synthesis of water-soluble inhibitors on the base of nitrogen and

phosphorous- containing compounds effectively protecting black and non-ferrous metals from corrosion in deferent mediums, investigation of mechanisms of their action, determination of different physico-chemical particulates. Investigation by protection properties abovementioned inhibitors in results of their adsorption interaction with surface of metallic equipment at different temperatures and studying of mechanisms of their action are at presence time actual tasks [1].

Dozens of individual substances and mixtures based on them are known as effective corrosion inhibitors. The film-forming inhibitors exhibit a mixed nature of the protective effect, forming films on both the cathodic and anodic sections of the micro galvanic corrosion elements functioning on the metal surface. These signs of film-forming inhibitors are possessed by various substances of organic and inorganic origin [2].

To elaboration of inhibitors of corrosion are devoted investigations both forming and native sciences. At present time the most elaborated are physic- chemical, electro-chemical and some others method in investigation of inhibitors of corrosion, but with development of technologies demands to study mechanism of inhibitoral action of organic compounds on processes of corrosion and of steel have been increased. Question about inhibition by organic and phosphate compounds of last process are remain interesting and didn't investigated. It is necessary to carried to carried out complexes investigation based on new achievements of experimental technics what has allowed to synthesis high-effective inhibitoral composition [3].

Objects investigationare nitrogen and phosphorous-containing adducts (phosphate of thioures, phosphate of urea, phosphate of melamine, phosphate of hexamethylendiamine) and inhibitors of oligomeric type on base nitrogen-containing organic compounds and phosphorous acid (phosphate of dimethilolhexamethylendiamine, dimethilol of urea, dimethilol melamine, phosphate of dimethilol urea, phosphate of dimethilol melamine) and also steel and some metals.

METHODS

In work methods of polarization curves, polarization resistance, chronopotentiometry, gravimetrical, criaskopiya and also quant-chemical, microscopically methods and IR-spectroscopy have been used.

RESULTS

Nitrogen and phosphorus-containing salts, inhibitor of metals corrosion (IKM); oligomeric inhibitor of metals corrosion (OIKM) are objects of this investigation which are presented in table-1.

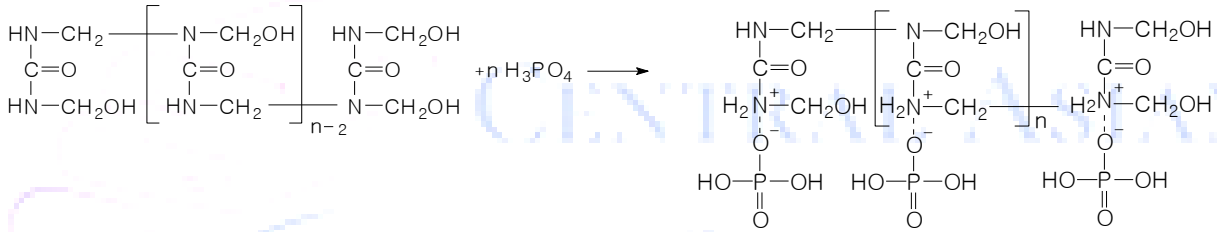
Table-1. Characteristics of organical and oligomerical inhibitors

№	Inhibitor	Molecular mass	Name of inhibitor
1	IKM-1	174	phosphate of thiourea
2	IKM-2	158	phosphate of urea
3	IKM-3	224	phosphate of melamine
4	IKM-4	213	phosphate of hexamethylendiamine
5	OIKM-5	2200	Phosphate dimethilolhexamethylendiamine
6	OIKM-6	814	dimethilol urea

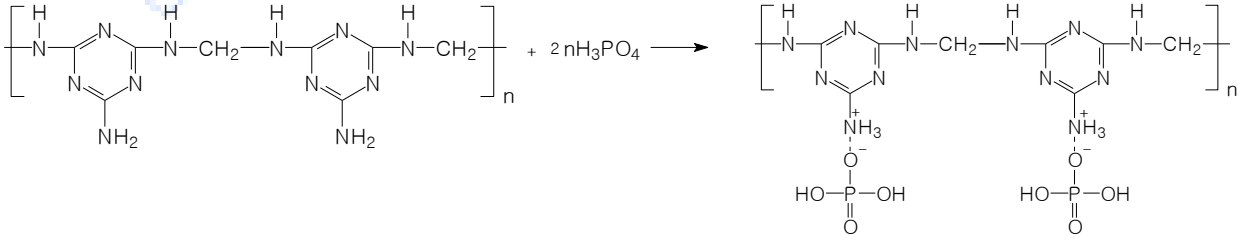
7	OIKM-7	1860	dimethilol melamine
8	OIKM-8	1900	phosphate of dimethilolurea
9	OIKM-9	3300	phosphate of dimethilolmelamin

Investigations of corrosion behavior of steel (St.3) were carried out on samples in form of plates. Effectivity of inhibitors was determined by methods of polarization resistance on device P-5035 I, polarization curves using potenciastate PI-50.1.1 with programator PR-8 and gravimetric by decreasing of sample mass after corrosion tests. Investigations were carried out in phone solutions of composition 5%Na_2SO_4+3%H_2SO_4 (Ph-1), in neutral medium (Ph-2), 3%NaCl+5%$NaCO_3$ (Ph-3). Solutions were prepared from reagents of mark «ch.p» an distillate. Electrodes were prepared from St.3 of composition %: Fe=98,36; C=0,20; Mn=0,50; Si=0,15; P=0,04; S=0,05; Cr=0,30; Ni=0,20; Cu=0,20.

New oligomer derivatives synthesized on the base of urea and formaldehyde with phosphoric acid phosphates dimethylolureadelute solutions in neutral, weak-acid and weak-base mediums at usual temperatures have linear structure with polymerization degree from 8 to 13; thus they are oligomers with molecular mass 1400-2400. Synthesis of phosphates of dimethylolurea can be presented by following scheme:



Effective oligomeric inhibitors of metals corrosion were synthesized on the base of melamine,phormaldehydeand ortophosphoric acid. Melamine-formaldehyde oligomers with phosphoric acid have formed compounds of type phosphate dimethylolamine which are soluble in water. Synthesis of water–soluble melamine–formaldehyde oligomers, containing in there composition phosphoric acid can be presented by following scheme:



where: n=6-11; thus they are oligomers with molecular mass 2650-4300.Investigates the molecular - dynamical and quant-chemical characteristics of synthesized organicallyoligomeric compounds have allowed to obtain information about their structures and by this reason characteristic have a self – depended interest from the point of view of physical chemistry. Also knowledge of geometry of molecules is necessary for calculations the heats of formation, heat effects and energy of activation of reactions. By this reason electronic densities and distribution of charges in molecular of compounds presented in table 1 and also their structures were determined by semiemperical quanta–chemical method MNDO. As example results of investigation of electronic structure and also structure of inhibitor OIKM–8.

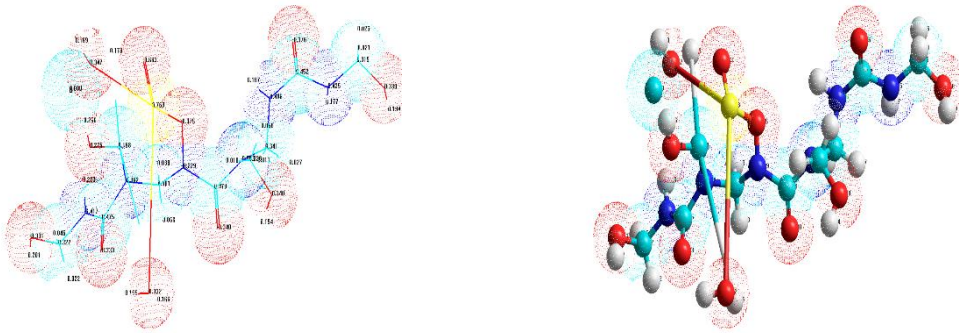


Fig.1. Distribution of electronic density in molecule OIKM-8 and it's ball-pivotal model

These molecules have possessed by acid properties and at dissociation have formed protons and complex anions which at corrosion on metallic surface have formed compounds with positive charged atoms of metals (in base with iron atoms). Also owing to large volume these molecules have covered some surface of metallic constructions. Above-mentioned factors have caused inhibition properties of this type of inhibitors at acid corrosion of metallic surfaces [4].

From literature it is known that urea and thiourea have possessed by weak inhibition effect in acid and neutral mediums. At their using jointly with KJ degree of protection has increased in acid medium before 60% and in neutral medium before 72% but with increasing of temperature protective properties of these compounds have decreased. Also it is necessary to note deterioration of metal plasticity at using of these inhibitors.

Table-2. Influence of duration of corrosion tests on protection effectiveness of St-3 in phone solution Ph-2 at pH=6,4 and temperature 25°C

Inhibitor	C_{ing}, mg/l	360 hours		720 hours	
		K, g/(m^2/ 24 hours)	Z, %	K, g/(m^2/ 24hours)	Z, %
Phone	20	34,50	-	56,67	-
Thiourea		10,75	68,84	18,71	66,98
Urea		11,72	66,02	17,63	68,92
GMDA		10,78	68,75	16,69	70,54
Melamine		10,54	69,44	17,01	69,98

For comparison with literature data [5] initial compounds: thiourea, urea, hexamethylendiamine and melamine have been investigated in neutral medium by gravimetrical methods and obtained results are presented in table-2. Inhibitors in neutral medium at 25°C and durations 360 and 720 hours of tests have shown low protective effect what is conformed with literature data. In accordance with this adducts and oligomers of above-mentioned inhibitors have been synthesized. In process of corrosion potentials of cathode and anodic parts on the steel surface aren't constant; the polarization was appeared owing to which approach of potentials of cathode and anodic parts was carried out and also the corrosion current decreased. On the fig. 2 (*a,b*) results of investigation of kinetics of electrode processes and polarization of measurements of corrosion process of steel electrode at different temperatures are presented from which shown that value of stationary potential of corrosion. Is constant relatedly of normal electrode in the phone

solution and is equal -0,780 V at 50°C.At addition of inhibitor IKM-4 in phone electrolyte the value of the corrosion potential has increased to -0,620 V and also it was noted displacement of polarization curves on 160 mV and in case of inhibitor OIKM-9 on 260 mV in side of more positive values. Such effect can be explained by formation on the surface of steel of wine adsorption lager from phosphate of hexamethylendiamine, salts of phosphate of dimethylolhexamethylendiamine, phosphate of dimethylol urea and salts of phosphate-melaminformaldehyde oligomers which have blockade of steel surface and have decreased rate of its corrosion destruction. Simultaneously with changing of corrosion current the mixed mechanism of action in inhibitors was determined. Results of calculations of values of stationary potential (E_{st}), corrosion current (i_c), coefficient of braking (γ), protection degree (Z) and relative stationary deviation at different temperatures are presented in table 3. It was shown that solutions of oligomeric inhibitors OIKM-8 and OIKM-9 in small concentrations are effective and have the protection degree from 99,56 to 99,64% and 99,61 to 99,76 %, C=20 and 30 mg/l. About state of surface of samples it is possible to judge by value of the electrode potential. From investigated compounds inhibitor OIKM-7 has a bower protection effect 87,23% and 89,47% at it's concentration 20 and 30 mg/l at temperature 80°C in phone solution Ph-1.

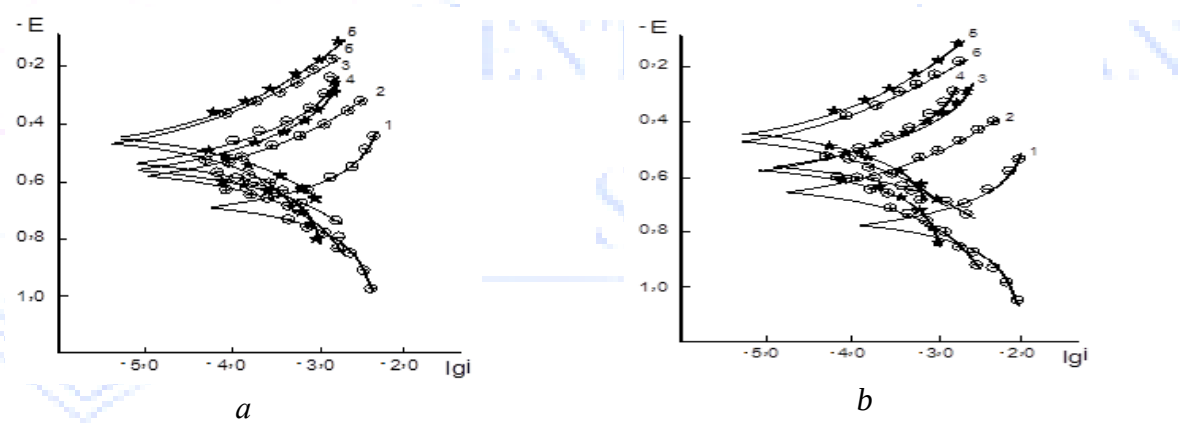


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Fig. 2 Polarization curves of the steel electrode in phone solution ph-1 (1) and also in the presence of solutions of oligomer inhibitors (C_{inh}=20; 30 mg/l.): IKM-4 (2); OIKM-5 (3); OIKM-6 (4); OIKM-8 (5); OIKM-9 (6) at 25 (a) and 50°C (b).

It is necessary to note that by it self increasing of corrosion rate with increasing of temperature can't be proof that during of experiments part of active of metal surface was increased. High rates of corrosion have observed in some cases also from passive state. Information about state of steel surface during corrosion tests is very importance because passivators are effective only in case of low rates of corrosion from passive state. With increasing temperature its inhibition effect has increased and chemo sorption bonds between its molecules and metal surface also have been increased.

Table 3. Results of electrochemical determination of degree of protective action of oligomer inhibitors (T=80°C) in phone solution Ph-1 (pH=5,3) at their different concentrations

Inhibitors	C_{inh}, мg/l	$-E_{st}$, B	i_c, мА/см^2	γ	Z, %

Ph-1	0	0,820	607,53	–	–
IKM-1	20	0,740	75,76	8,02	87,53
IKM-2		0,730	61,12	9,94	89,94
IKM-3		0,730	63,91	9,51	89,48
IKM-4		0,610	26,00	23,36	95,72
OIKM-5		0,570	17,38	34,97	97,14
OIKM-6		0,580	13,24	45,87	97,82
OIKM-7		0,610	77,58	7,82	87,23
OIKM-8		0,520	2,67	227,27	99,56
OIKM-9		0,490	2,19	277,78	99,64
IKM-1	30	0,750	38,21	15,90	93,71
IKM-2		0,730	30,62	19,84	94,96
IKM-3		0,740	33,60	18,08	94,47
IKM-4		0,630	25,33	23,98	95,83
OIKM-5		0,560	15,07	40,32	97,52
OIKM-6		0,570	10,69	56,82	98,24
OIKM-7		0,620	63,94	9,50	89,47
OIKM-8		0,530	2,37	256,41	99,61
OIKM-9		0,530	1,46	416,67	99,76
NALKO	20	0,530	52,44	7,73	87,06

Influence of oligomers and their compositions on the rate of steel corrosion was determined by method of polarization resistance. Results of measuring of the polarization resistance of steel zond in weak-acid medium (Ph-1) and also in the presence of such inhibitors as IKM-2; IKM-3 and oligomer inhibitors OIKM-8 and OIKM-9 are presented in fig.3 as example.

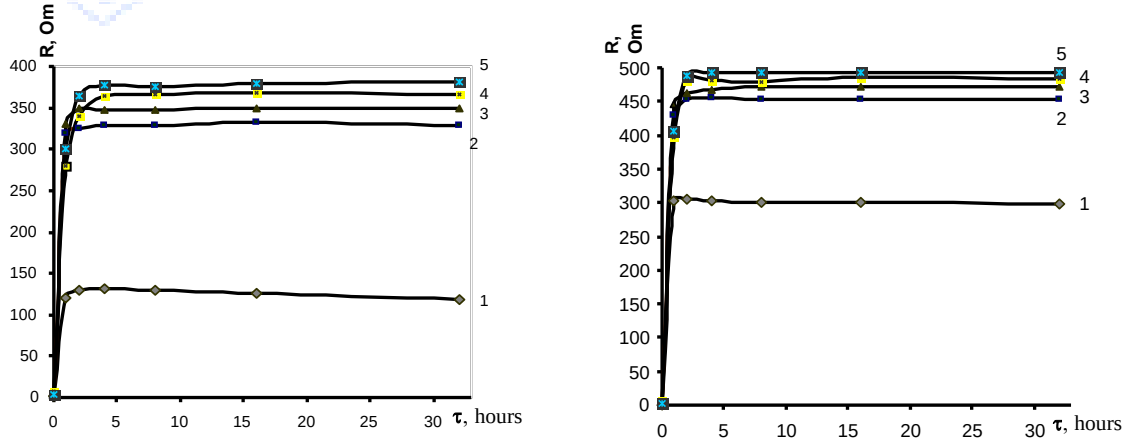

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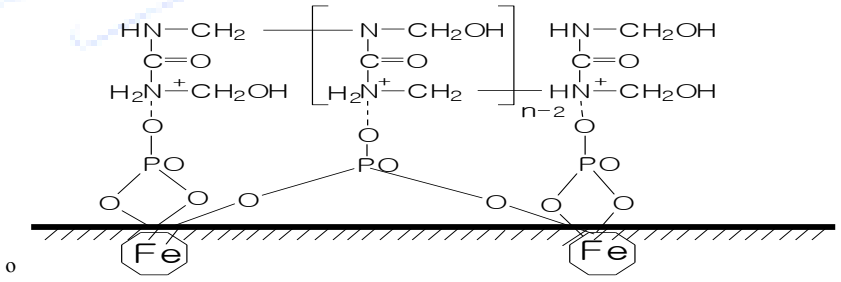
Fig.3. Curves of the polarization resistance of steel electrode in phone solution (1) and also in the presence of inhibitors (C_{inh}=20 mg/l): IKM-2 (2); IKM-3 (3); OIKM-8 (4); OIKM-9 (5); at temperature 25°C; Ph-1 (a) and Ph-3 (b).

It is shown from the fig.3 that introduction in phone solution of individual inhibitors has increased the polarization resistance and at introduction of oligomer inhibitors it's value has increased in more degree. Such results have indicated on the shape brick of the electro-chemical process and have allowed to obtain preliminary information about effectively of investigated inhibitors.

In solution of phone Ph-1 and Ph-3 (Fig-3, curve 1, *a* and *b*) the integral value of the polarization resistance (R) during experiment has been equaled 120 and 302 Om/sm^2. In phone solution in the presence inhibitor OIKM-8 R=367 and 493 Om/sm^2 at temperature 25^{o}C correspondently. Thus it is possible to affirm that participation on the steel surface the protective film consisting from nitrogen- and phosphorous-containing complexes in the presence of investigated inhibitors has carried out under action of corrosion processes and has correlated with intensity of corrosion what has caused by higher effectivety of above-mentioned inhibitors. Synergetic effect of some organic compounds is bounded with formation of destruction products one of which is an organically cation and other-anion. Main point of this effect is caused by introduction in inhibitor molecule one or two functional groups with heteroatom differing by value and sigh of charge from atom presented in inhibitor molecule. This one group can be considered as cation and other - anions. Substances containing –NH_2 and –OH; –NH_2 and –H_2PO_3; –NH_2 and –COOH groups can be examples of such type of inhibitors. At adsorption of these inhibitors part of their molecules has adsorbited by one type of group (for example, by amino - group) and other part –by other type of group (for example, by oxy- group). Owing to this decreasing of forces of repulsion and formation of more film of inhibitor on the surface of steel has been observed. By such mechanism inhibitor phosphate dimethylolurea has acted and at this its high effectivity also is caused by inn molecular synergism [6;7].

Phosphates of dimethylolurea are inhibitors and they have broken anodic process of dissolution steel owing to formation of protective films consisting from hard-soluble products formed owing to interaction of inhibitors molecules with ions of metal in solution. The structure of such films can be presented by following scheme:



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The method of x-ray structural analysis was carried out and the wavelength of x-ray radiation and the distances between atoms or their groups in the crystal lattice of a substance of the same order were determined, the crystal lattice is a diffraction lattice for x-rays. The size and shape of the cell is determined by the size, shape and relative position of its constituent particles. The geometry of the crystal is described by the size of the unit cell, characterized by the length of its three non-parallel edges (a0, b0, c0) in nanometers and the angles between them (α, β, γ).

Table 4. Unit cell parameters for dimethylolurea

a	*b*	*c*	α	β	γ	V	Структура
5,6	5,6	4,7	90	90	90	149	4/m(t-c) tetragonal

Interpretation of the results of x-ray studies at small angles is different. Detected when shooting at large angles should be part of a large period detected by shooting at small angles and shows the following structure:

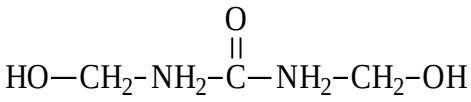
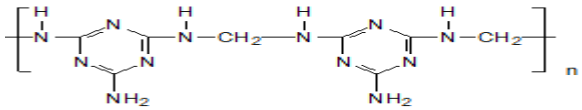


Table 5. Unit cell parameters for dimethylolmelamines

a	*b*	*c*	α	β	γ	V	Структура
7,29	7,45	10,34	90	108,5	90	533; 65/68	1s15m monoclinic P(33); 95,6%

Thus, a necessary task is the creation of new oligomeric inhibitors that could provide a high protective effect in a wide range of conditions of use, or improve the quality of existing compositions.



At addition of inhibitor OIKM-9 the rate of corrosion of steel has decreased in 107,53 time and at this the degree of protection was 99,07%. In result of carrying out investigation the most effective inhibitors OIKM-8 and OIKM-9 were determined. Introduction of them has allowed to decrease a corrosions aggressive of Ph-2 and to protect steel St-3 from corrosion destruction on 98-99%. The optimal concentration of these inhibitors was equaled 20 mg/l (table-6). Role of phosphor-containing organic and oligomer compounds can be explained by fact that they have formed on surface of metal thin layers. Effectively of action of inhibitors is depended in great degree on temperature and their composition, for example inhibitor OIKM-7 at 50 and 80ºC has a protection degree 90,06 and 92,36% correspondently. It's protection properties are displayed in more degree at higher temperatures owing to adsorption interactions with metal and at this it has acted by chemo sorption mechanism and has formed especially strength protection layers. Molecules of inhibitor chemisorbed owing to non-coupling electrons of heteroatom's and effect of synergism at this is are responsible for explained by formation of covalent bonds. At adsorption of cations and anions electrostatic forces of attraction between them are formed what has carried out to condense of forming layers. The obtained patterns of the inhibitory effect of water-soluble inhibitor in corrosive waters and the effect of pH, temperature and concentration of aggressive anions of the solution on it [8].The tendency to complexation in a solution and the high dispersing ability of oligomers, on the contrary, can adversely affect the corrosion resistance of iron in their solutions, since it facilitates the removal of metal corrosion products from its surface [9].

Table 6. Results of the gravimetrical determination (St-3) of protective degree of different inhibitors ($C_{inh.}$=20 mg/l) in phone solution 3%NaCl+5%Na_2CO_3 (pH=8,6) at different temperatures

Inhibitors	Temperature, ºC	360 hours			720 hours		
		K, g/(m^2/ 24hours)	γ	Z, %	K, g/(m^2/ 24hours)	γ	Z, %

Phone	50	131,73	-	-	103,07	-	-
IKM-1		8,81	14,95	93,31	3,92	26,32	96,20
IKM-2		16,93	7,78	87,15	11,10	9,29	89,23
IKM-3		9,55	13,79	92,75	6,60	15,63	93,60
IKM-4		6,28	20,96	95,23	4,14	24,88	95,98
OIKM-5		4,24	31,06	96,78	3,09	33,33	97,00
OIKM-6		3,65	36,10	97,23	1,52	68,03	98,53
OIKM-7		13,04	10,10	90,10	10,25	10,06	90,06
OIKM-8		5,01	26,32	96,20	2,44	42,19	97,63
OIKM-9		1,53	86,21	98,84	0,96	107,53	99,07
NALKO		12,81	9,23	89,16	12,53	9,43	89,40
Phone	80	272,43	-	-	243,72	-	-
IKM-1		14,98	18,18	94,50	13,31	18,32	94,54
IKM-2		38,11	7,15	86,01	39,92	6,11	83,62
IKM-3		29,50	9,23	89,17	44,65	5,46	81,68
IKM-4		12,91	21,10	95,26	9,75	25,00	96,00
OIKM-5		5,97	45,66	97,81	4,27	57,14	98,25
OIKM-6		7,36	37,04	97,30	6,17	39,53	97,47
OIKM-7		18,88	14,43	93,07	18,62	13,09	92,36
OIKM-8		3,51	77,52	98,71	2,27	107,53	99,07
OIKM-9		2,89	94,34	98,94	1,39	175,44	99,43
NALKO		38,93	6,99	85,71	30,27	8,05	87,58

It was shown that in process of electro chemical corrosion with participation low-molecular and oligomeric inhibitors in result of interaction with metal surface the outer surface of adsorption layer is charged negatively and inner surface-positively. Equinity of the adsorbed compound dated to unit of surface has depended on temperature of medium and concentration of adsorbate in liquid phase. At this it is counted that adsorbited of organic as also inorganic inhibitors according to literature data [10] a fully are took out from sphere of anodic reaction the part of surface of metal which is occupied by inhibitor. These suppositions were used at calculation of degree of filling of metal surface at caring out of electro-chemical process of corrosion. Obtained data by dependent of adsorption oligomer inhibitors an their concentration in solution on steel in range of high degree of filling are described by isotherm which is characterized for formation of monolayer. On figures 4 *a*, *b* dependence on filling degree of steel surface from inhibitor concentration at different phones is presented from which it is shown that values θ, obtained on the base of volumetrically measuring at inhibitor concentration 20 mg/l are wery similar between themselves, but values obtained at inhibitor concentration 10 mg/l have differed in high degree.

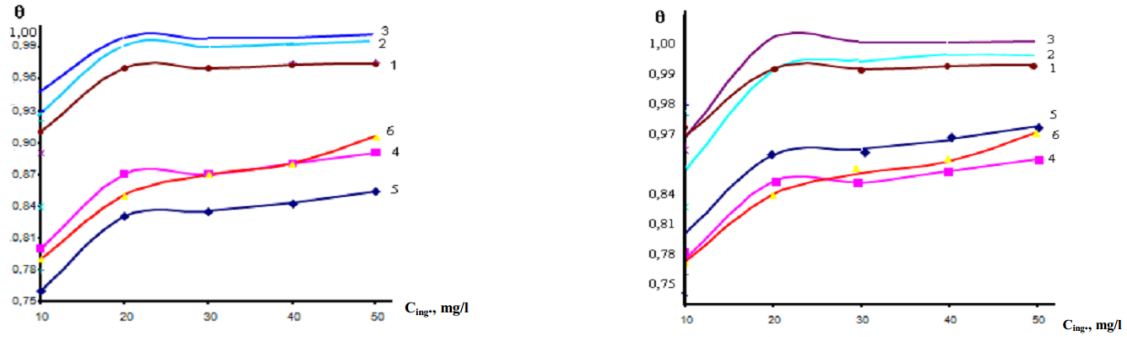


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Fig 4. Dependence on the degree of filling of steel surface from concentration of different investigation inhibitors:OIKM-6 (1); OIKM-8 (2); OIKM-9 (3); IKM-2 (4); IKM-1 (5); IKM-3 (6) at pH=6,4 (a) and pH=8,6 (b); T=80°C.

By type of adsorption isotherm, it is possible to about adsorption characteristics of inhibitors. By method of straightening of plots $\theta=f(C_{inh})$ with using corresponding functional nets in the first concentration range of additions it was determined that adsorption of inhibitors has described by isotherm typical for homogeneous surface of adsorbent (fig. 4).

On the base of data by degree of filling of metallic surface by inhibitors isotherm of adsorption was determined character of which has allowed to obtain information about properties of adsorbited compounds. From table 7 it is shown that degree of filling of metallic surface by inhibitor OIKM-7 has increased from 0,90 to 0,92; the constant of adsorption equilibrium has changed from 0,45 to 0,58. At adsorption of amino-containing compounds the strangest of repulsion are prevailed what has carried out to decreasing of values of the constant of the adsorption equilibrium in comparison with nitrogen and phosphorous-containing inhibitors.

So it is possible to wait the electro-donoral molecules with low potential of ionization, high negative charge on nitrogen atom of active center and more positive charge on hydrogen atom in puritanical form must be the best inhibitors owing to formation of strength coordinated or hydrogen bonds with metallic surface. The high protection properties of oligomer inhibitors can be explained by formation of hard-soluble compounds on corrosiated surface and preceding stage-adsorption of oligomeric molecules of inhibitors on metallic surface. These results have been confirmed by above-shown mechanism of protection action of these inhibitors. Possible reasons for the decrease in the anticorrosive efficiency of the inhibitor may be, firstly, its weak ability to compete with aggressive ions upon adsorption, and secondly, that with an increase in temperature at the initial stage, the corrosion rate significantly exceeds the rate of formation of protective layers, as a result of which heterogeneous coatings with weaker protective properties [11].

Gravimetrical investigations have shown (table 7) that rate of corrosion (K) of steel electrode has a lowest values in the presence of nitrogen and phosphorous-containing oligomer inhibitors at their concentration 20 mg/l. At phosphorous-containing oligomer inhibitors values of degree of filling of electrode surface by monomolecular layer the highest what has been confirmed also by calculations of the constant of adsorption equilibrium (B) in dependence on an chemical structure of inhibitors which in 3-5 time has prevailed its value obtained at other concentration of inhibitors.

Table 7. Values of the filling degree and the constant of adsorption equilibrium of different inhibitors in phone solution Ph-3 ($C_{inh.}$=20 mg/l)

Inhibitor	Temperature, °C	K	Θ	B
IKM-1	50	3,92	0,96	1,20
IKM-2		11,10	0,89	0,40
IKM-3		6,60	0,94	0,78
IKM-4		4,14	0,96	1,20
OIKM-5		3,09	0,97	1,62
OIKM-6		1,52	0,99	4,95
OIKM-7		10,25	0,90	0,45
OIKM-8		2,44	0,98	2,45
OIKM-9		0,96	0,99	4,95
IKM-1	80	13,31	0,95	0,95
IKM-2		39,92	0,84	0,26
IKM-3		44,65	0,82	0,23
IKM-4		9,75	0,96	1,20
OIKM-5		4,27	0,98	2,45
OIKM-6		6,17	0,97	1,62
OIKM-7		18,62	0,92	0,58
OIKM-8		2,27	0,99	4,95
OIKM-9		1,39	0,99	4,95

It is necessary to note that at all changing's of parameters in choose range of experiments oligomeric inhibitor OIKM-8 has preserved high protection properties. Energy of activation is connected with degree of screening of electrode surface and has given information about mechanism of protection action of inhibitors and kinetics of corrosion process. Obtained results have shown that adsorption of oligomeric inhibitors has changed rate constant of reaction and also charge of surface. Difference in degree of filling of surface by phosphorous-containing oligomeric inhibitors calculated from kinetics characteristics and by data measures are connected with process of adsorption. Also on value of coefficient of braking has descended not only temperature and concentration of inhibitor and also its composition [12;13]. Comparative results of investigation of inhibitors properties salts of phosphate tiourea and phosphate urea with oligomeric compounds have shown that their protectional effect has caused by formation of adsorption layers on surface of metal. On the surface of steel samples at their protection by inhibitors IKM-1 and IKM-2 in water systems the protective film has formed consisting from complexes with cations of iron. Important factor influencing on the effectively of inhibitors is their surface configuration molecules determining the area of inhibited surface of steel. Protection of metals from corrosion by inhibitors has bonded by chemical adsorption of their molecules including the changing of charge of adsorbing compounds and also by transfer of it from one phase to other. By this reason the special importance is an molecular structure of

inhibitors molecules. IR-spectroscopic investigation was carried out synthesized nitrogen and phosphorous-containing low-molecular and oligomer inhibitors [14;15].

Hydrocarbon radical having by hydropholical properties are oriented in side of aggressive medium have water molecules and corrosion-active particles from surface of metal and also in addition have scented and increased block of metal surface. Role of phosphates can be explaining by formation on surface thin layers in composition of which there are ions of protective metal.

Oligomer phosphorous-containing inhibitors are more effective owing to formation of don't soluble complexes [19;20]. Addition in water of organic inhibitors has decreased corrosion of metals and tendency of water to scum-formation. It is proposed that inhibition action by relation to some metals has the most degree for inhibitors containing such functional groups as $-NH_2$, =NH, CN, N=O. In case inhibitor adsorption phosphate thiocarbamide (IKM-1) is possible through amino-groups having no divided electronic pairs. In process of inhibition also no reduced molecules of thiocarbamide have participated forming adsorbed film on the surface of steel owing to formation of bonds between atoms of sulfur and iron [16;17].

Thus activity of molecules of these inhibitors of corrosion is caused by presence of two adsorption-active centers and also by adsorption of products of their destruction. IR- spectrums have shown that length of chain of alkyl radical in structure of inhibitors has an important influence on their protective action and important role in phase at formation of protective film what has conformed with rule of adsorption dissolution of compound in water has decreased with increasing of its chain length.In circulating systems for fight with corrosion it is possible to use oligomer inhibitors, which have promoted to deposit of different crystalical lagers and have averted appearance of ulcerous corrosion. Value of pH it is necessary to support on level 6,5-7,0 or several lower. On the base of obtained data of corrosion tests it was determined that in water with increasing salts containing not only concentration of aggressive anions such as (ClO^-, SO_4^{2-}) but also cations Ca^{2+} and Mg^{2+} promoting to formation on the surface of steel a protective films and decreasing of the corrosion aggressively has carried out [18].

Inner-molecular synergism and high effectively of two component inhibitors OIKM-7+KH_2PO_4 can be explain by presence of such functional groups as $–NH_2$ and –OH, $-NH_2$ and $–H_2PO_3^-$, $-NH_2$ and –COOH. It was shown that two-component inhibitors have a high effectivity by breaking of process of dissolution of metals in different systems [21;22]. By this reason mixture of dimethylol-melamine with KH_2PO_4 can be used also as inhibitor of scale formation. Anticorrosion protection by such inhibitors consists in formation of low-soluble compounds which are entered in composition of corrosion deposits what has caused their condensation and low-permeability for corrosion active reagents. Then adsorption processes have carried out which have caused to slowing of growing of phosphate layers owing to which it became less porous, more thin and its protection properties were increased.

From table 8 it is shown that dimethilolmelamine with KH_2PO_4 in weak acid mediums has a degree of protection from 93,26 to 99,54%. With increasing of inhibitor concentration, it became more effective. Its molecules have adsorbed on metal surface what has carried out to decreasing of forces of repulsion between molecules on surface and promote to formation of more compact film from inhibitor molecules.

Table 8. Influence of duration of corrosion tests on the effectivity of St-3 protection by inhibitor OIKM-7+KH_2PO_4 in phone solution Ph-1 pH=5,3 temperature 25°C

	360 hours	720 hours

C_{inh}, mg/l	K, g/(m^2 24 h)	Z, %	K, g/(m^2 24 h)	Z, %
0	216,09	-	172,64	-
10	10,61	94,18	10,58	93,26
20	5,97	97,81	4,29	98,27
30	2,84	98,64	1,38	99,54
40	5,21	98,29	3,07	99,15
50	3,52	98,71	2,29	99,06

Thus if at metal surface at its protection by two-component inhibitors in water solutions the protective film is formed consisting from complexes with cations of Fe. As shown from table 8, solutions of two-components inhibitor OIKM-7+KH_2PO_4 at temperatures 25^{o}C are effective for protection of St.3 and its degree of protection equaled 99,54%.

Effectively of action of this inhibitor is depended on temperature. With increasing temperature from 50 to 80^{o}C using of this inhibitor in combination with KH_2PO_4 that is two-component inhibitor it's protection properties were increased with increasing temperature. Investigations by determination of combined action inhibitors and finding of their more effective mixtures have been carried. Second component of inhibitor KH_2PO_4 has promoted formation of insoluble compounds which are stable in weak acid and neutral mediums and with increasing of tests duration more high protective effects have been observed. Advanced of second component KH_2PO_4 consists in fact that it has provided protection properties at corrosion of metals in different aggressive mediums. Oligomer compounds in combination with KH_2PO_4were tested as two component inhibitors and if was founded that they are neutral, weak-acid and weak-base mediums.

DISCUSSION

On inhibitors of corrosion of different metals (steel-3, copper, aluminum, brass) in circulating waters and in systems of cooling waters were obtained from acts of testing Becabod metallurgical combination, AJ «Navoiyazot», UDP «Fergana NPZ».

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 by investigation of mechanism of protection action of nitrogen and phosphorous inhibitors on the base of H_3PO_4 and also oligomers and phosphorous-containing adducts hae been presented. Phosphorous-containing oligomers as inhibitors of metals corrosion have able to provide effective protection in different aggressive mediums. Results of visual observations have shown that at absence of nitrogen and phosphorous – containing adducts and oligomeric salts steel has been undergone to corrosion locally. Already through 20-24 hours after placing samples of steel in solution on their surface separate seats of corrosion as spots have been appeaded. In presence of additions of oligomeric inhibitors on the surface of steel samples formation of devise films has not been observed. Investigated inhibitor IKM-1 at is concentration 20 mg/l according to tests during 15 sutoks in neutral medium has displayed the high protection properties 94,07% and in case of using inhibitor IKM-3 degree of protection was equaled 94,05% (table 9). Gravimetrical investigations

have shown that in stationary conditions addition of solution OIKM-7 has carried out to decreasing of corrosion rate of steal in comparison with phone in 6–8 times what was corresponded to degree of protection from 84,06 to 87,53%.

Effectively of complex-formatting properties of reagent was investigated by modelation of laboratorial conditions of process of salts formation hardness and optimizing compositions of inhibitors of scum-formation in dependence on chemical composition circulating water. On the base of results of carrying out investigations expediency of using compositions complex – formatting reagents and oligomers was based [23;24].

Table 9. Degree of protection St.3 by elaborated inhibitors in neutral medium at temperature 80°C

Inhibitor	C_{inh}, mg/l	K, g/(m^2 24 h)	γ	Z, %
Phone (pH=6,4)	-	0,5500	-	-
IKM-1	10	0,0757	7,26	86,23
IKM-2		0,0851	6,46	84,52
IKM-3		0,0692	7,94	87,41
IKM-4		0,1310	4,20	76,18
OIKM-5		0,1125	4,89	79,54
OIKM-6		0,1037	5,31	81,15
OIKM-7		0,0877	6,27	84,06
OIKM-8		0,0275	20,00	95,00
OIKM-9		0,0254	21,65	95,38
IKM-1	20	0,0326	16,86	94,07
IKM-2		0,0327	16,81	94,05
IKM-3		0,0327	16,81	94,05
IKM-4		0,0337	16,31	93,87
OIKM-5		0,0524	10,50	90,48
OIKM-6		0,0541	10,16	90,16
OIKM-7		0,0686	8,02	87,53
OIKM-8		0,0273	20,12	95,03
OIKM-9		0,0249	22,08	95,47

In practical aim obtained results will be used at elaboration compositions of inhibitors of scum–formation for complex protection in circulating waters in some concrete industrial conditions. Analysis of

data of table 10 obtained by method rentgenophluorescental spectrometry on the device «Niton Xl 3t 900», has shown that chemical composition of different metals has corresponded to demands.

Table 10. Results of rentgenophluorescental spectrometrical determination of chemical composition of different metals before and after corrosion tests in the presence of inhibitor OIKM-8

Content of elements, mass %									
	C	Si	Mn	P	Zn	Ni	Cu	Fe	Al
Steel-3	0,20	0,15	0,50	0,04	-	0,20	0,20	98,60	-
Steel-3+OIKM-8	0,75	0,15	0,47	0,45	-	0,20	0,21	97,62	-
Aluminum	-	6,8	0,12	-	0,04	0,01	2,30	0,28	90,14
Aluminum+OIKM-8	0,73	6,06	0,04	0,58	0,19	0,012	2,23	1,07	88,92
Copper	-	-	0,02	-	-	0,03	99,51	0,08	-
Copper+OIKM-8	0,28	-	0,02	0,18	-	0,03	99,24	0,06	-
Brass	-	0,78	-	-	37,01	-	61,62	-	-
Brass+OIKM-8	-	0,52	-	17,54	25,22	-	55,69	0,06	-

Results of tests have shown that in the presence of oligomer inhibitor OIKM-8 composition of investigated metals was changed owing to adsorption of this inhibitor on their surface. Composition of metal has enriched by phosphorous. In result of adsorption of inhibitor the rate of corrosion has decreased in 30-40 times [25;27].

Investigation phosphorous-containing oligomeric inhibitors has shown high effectively of decreasing of progress of steel dissolution in weak–acid and neutral mediums. Distinctive properties of these inhibitors are their low optimal concentration, cheapeners, universal and albescence of toxically [31].

They also have provided maintenance of busicality which in necessary for protection of metals from corrosion and have preserved of protected layers on steal in circulating system [26;28]. Tests were carried out and obtain results were comparison with data of gravimetrical method which has shown that in stationary conditions addition of solution of oligomerical inhibitors OIKM-6 and OIKM-7 was carried out to decreasing of rate corrosion of steel what corresponded to degree of protection 88,2 and 80,84%. Oligomer inhibitors of corrosion OIKM-8 and OIKM-9 at their concentration 30 mg/l have higher protective properties degree of protection 92,66 and 98,61% correspondently.

In result of carrying out investigation the most effective inhibitor OIKM-9 has been revealed. It’s using has allowed to decrease corrosion aggressively of water and to protect metal from corrosion destructions. Optimal concentration of this inhibitor was equaled 30 mg/l and at this sufficient protective effect was reached [29;30].

Table 11. Degree of St-3 protection by elaborated inhibitors at temperature 25°C

Inhibitor	C_{inh}, mg/l	K, g/(m^2 24 h)	γ	Z, %
Phone(Ph-2)	-	1,43	-	-
OIKM-6	30	0,16	11,8	88,2
OIKM-7		0,27	19,16	80,84
OIKM-8		0,10	7,34	92,66
OIKM-9		0,02	1,39	98,61

Laboratorial investigations of elaborated inhibitors were carried out in «Fergana» NPZ and also act of introduction of results of tests phosphorous-containing oligomer inhibitors of metals corrosion in systems circulating water supply has been obtained.

CONCLUSIONS

Number of nitrogen and phosphorous –containing adducts on the base of phosphates of thiourea, urea, melamine and hexamethylendiamine and also inhibitors of oligomeric type on the base of nitrogen containing organic compounds and phosphoric acid have been synthesized. Molecular dynamical and quantum chemical characteristics of synthesized compounds were determined, mechanism of inhibition by oligomeric compounds was exposed and general regularities inheriting to such inhibitors were determined what will to promoted elaboration of new approaches to purposeful synthesis of such inhibitors.

It was shown that such oligomeric compounds as phosphate of dimethilourea (OIKM-8) have displayed effect of inner molecular synergism owing to presence of different functional groups and mechanism of their adsorption is differed by fact of formation of more compact layers of inhibitors on the metal surf are of and correspondely they possessed higherinhibition effect. On the base of kinetics and thermodynamicalle investigation it was shown that adsorption properties of inhibitors of oligomeric and low-molecular type are different about what high values of filling degree of electrode surface and constants of adsorption equilibrium are witnessed. Constant of equilibrium in 4 time is higher it's value for low-molecular inhibitors. Systematical investigation of two component inhibitors on the base of dihydrophosphate of potassium was carried out and it was found that addition of second component has increased their inhibitional action; from obtained results conclusion have been mode about passible mechanism of their protective action which has included formation of thin layers of complex composition preventing appearance of ulcerous corrosion. Effectively of inhibitor dimetilolmelamin in aggressive mediums with increasing temperature has increased before achieving definite temperature after which it didn't changed what has indicated on chemo-sorption mechanisms of action of this inhibitor forming strong protective layers on the surface of protective metal.

Phosphates dimethilolurea and dimethilolmelamine in mediums with different values of pH have formed on the steal surface protective layers which differed by composition and structure from initial samples, it was determined that these compounds were acted as anionical inhibitors with braking of anodic process.

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