

PHYSICO-CHEMICAL PROPERTIES OF CORROSION INHIBITION OF St.3 AND St.12 AND THE FORMATION OF MINERAL SALT DEPOSITS.

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Currently, the Republic of Uzbekistan deservedly pays attention to the introduction of inhibitors to protect equipment from corrosion and scaling in production. The use of inhibitors allows several times to increase the service life of expensive equipment. In this regard, the most effective inhibitors of neutral and slightly alkaline media are nitrogen, amine and oxygen-containing organic compounds [1-3] as well as zinc organophosphonic acids, which effectively prevent corrosion and deposits of mineral salts on the surface of equipment.

The republic's demand for such types of inhibitors is more than 5.0 thousand tons per year. Due to the lack of production of these products in the republic, they have recently been brought from other foreign countries for a fee [4]. Therefore, the development of new import -substituting, export-oriented inhibitors of corrosion and mineral salt deposition based on local raw materials and production wastes, and the study of their physicochemical, as well as inhibitory properties, is a very urgent task. Results and its discussion. Experimental data on the study of the polarity curves of inhibitors, their relationship from concentration and temperature to the degree of anti-corrosion protection of a sample of steel grades St.3 and St.12 in the presence of inhibitors and without them showed that the applied composite inhibitors synthesized on the basis of nitrogen, amine and phosphorus-containing local raw materials and production wastes have a degree of protection at 25°C 88.5÷94.4%, and at 40÷50°C this indicator will be in the range of 89.0÷99.7%. If the process temperature rises to 70°C, then the degree of anti-corrosion protection begins to decrease somewhat to the interval, values of 99.3÷90.4% of polarization. With the introduction of nitrogen-, amine- and phosphorus-containing inhibitors into the solution, the value of the electrode potential changes in a positive direction, which indicates a slowdown in the anodic reaction. This state indicates that a thin protective film is formed on the metal surface, consisting of such protective substances as nitrogen, amide and phosphate, which are part of the introduced inhibitors. With a change in the corrosion potential, the value of the corrosion current simultaneously changes, which indicates the effect of the inhibitor on the corrosion process of the metal by a mixed mechanism. Samples of metals (St.3 and St.12) were placed in various aggressive acidic hydrogen sulfide media in order to protect against corrosion, and the inhibition properties of amines, which contain various radicals and monomers, were studied.

Gravimetric method for time, temperature, inhibitor concentration and other indicators found that when the process is carried out in aqueous, acidic and neutral environments, the corrosion rate of the metal alloy grades St.3 and St.12 at a temperature of 25÷70°C for 360 and 720 hours for inhibitors with solutions of 0.1% concentration, the degree of anticorrosion protection was equal to 95.8÷99.6%. With an increase in the concentration of inhibitors from 0.1% to 1.0%, the corrosion protection index will be equal to 96.2÷99.8%. The degree of anti-corrosion protection of the Nalco brand inhibitor imported into our Republic is 87.6% at a temperature of 80°C. Based on the calculated data, the thermodynamic properties in the phases of acid, hydrogen sulfide solutions and the dependence of inhibition on temperature with the participation of inhibitors in the process of metal corrosion were established. At the same time, an increase in temperature has very little effect on the corrosion process, so with an increase in temperature, the adsorption of the metal surface remains almost unchanged. It was found that an increase in the concentration of inhibitors in both cases affects the effectiveness of corrosion inhibition. In all aggressive media studied, inhibitors have an energetic effect on completely filled surfaces. To calculate the activity (E_{act}), a graph of the dependence of $IgK -1/T$ was drawn, and the energy of effective activity (E_{act}) was calculated using the tangent of the slope ($E_{act}=2.3 \cdot R \cdot tg\alpha$). It was found that with an increase in the temperature of the corrosion process, the energy efficiency index is equal to 28.5÷47 kJ/mol.

Established indicators of E_{act} , ΔH and ΔS multicomponent composite inhibitors containing nitrogen, amide and phosphorus, in environments of strong acids are given in table -1.

Table 1

Thermodynamic values of corrosion in 3% Na₂S solutions with 3% H₂SO₄ and H₂S metal sample St. 3

Metal sample	Inhibition background	E_{act} , kJ/mole	ΔN , J/mol	ΔS J/mol
St. 3	3% H ₂ SO ₄	39.88	37.48	70.49
St. 12		76.54	-41.82	48.64
St. 3	H ₂ S with 3% Na ₂ S	37.48	38.25	69.75
St. 12		59.56	-70.04	39.51

From the results obtained, it was found that in the process of corrosion of the metal sample St.3 under conditions with inhibitors placed and not placed in an acidic environment, the indicators E_{act} and ΔH were almost close to each other. The results obtained provide a good explanation for the fact that, according to the Langmuir isotherm, a high degree of filling of the metal surface is directly proportional to the dependence of the adsorption process with the concentration of nitrogen, amine, and phosphorus-containing composite inhibitors. Also, that the rate of dissolution (K) of metal samples depends on the content of inhibitors and, even if the inhibitor is at a low concentration, the anti-corrosion will be 96-99.6%. When a composite inhibitor is introduced into the medium of a 3% H₂SO₄ solution of a steel sample St.3 St.12, the change in ΔG_{ads} in the temperature range 298÷343K from -48.24 kJ/mole⁻¹ to -42.52 kJ/mole⁻¹ on the effect of different kind of adsorption on the surface of the steel sample St.3 St.12 this inhibitor is adsorbed as a result of physical and chemical sorption. The thermodynamic properties of the metal surface adsorption process in the alkaline-salty medium of the composite inhibitor were calculated (Table 2), and the Langmuir adsorption isotherms of the composite inhibitor in the alkaline-salty medium were also studied. The relationship between the process temperature along the directions of the Langmuir adsorption isotherm in alkaline-salty aggressive media was found out. Steel samples St.3 and St.12 that is at different temperatures (between 298÷343K) nitrogen, amine and phosphorus-containing inhibitor has a different degree of anti-corrosion protection of metal samples.

Table 2

Thermodynamic values of surface adsorption of metal samples in a 3% NaOH + 3% NaCl solution of a composite inhibitor St.3

Temperature, K	K_{ads} mole ⁻¹	ΔG_{ads} , kJ/mole	ΔH_{ads} , J/mole	ΔS_{ads} , J/mole * K
298	$7.4 \cdot 10^5$	-50.94	-79.25	97.54
313	$7.8 \cdot 10^5$	-49.58	-79.56	96.98
323	$5.4 \cdot 10^5$	-48.86	-78.49	96.31
343	$3.2 \cdot 10^5$	-46.78	-78.80	96.44

Synthesized composite corrosion inhibitors with the participation of zinc oxide, glycerin, caustic soda, sodium hydroxide and the bottom residue of methyl ethyl ammonium reagents based on hydroxyethylidene diphosphonic acid, the composite inhibitor was tested on the equipment and

pipelines of the Shurtan gas chemical complex for anti-corrosion , including prevention formation of deposits of mineral salts, comparing the performance of inhibitors brands " Option " and Nalco, supplied from abroad. Based on the results of the tests, it was found that the applied composite inhibitor reduces the formation of deposits of mineral salts, and also, in comparison with the inhibitor used in industry, reduces corrosion to $4.8 \div 7.6\%$.

Table 3

Indicators of the degree of protection against corrosion of nitrogen, amino phosphorus-containing inhibitors

Compositions of inhibitors	Corrosion inhibition efficiency, %	Efficiency from the formation of mineral salts, %
1	97.8	94.8
2	96.8	95.2
3	98.4	97.7
4	93.3	92.5
5	91.5	88.6
Inhibitor brand "Option"	96.6	90.1

Conclusion. On the basis of the conducted studies, the prospects for the use of nitrogen, amine and phosphorus-containing inhibitors based on local raw materials and industrial wastes of the republic are shown. Optimal concentrations of inhibitors have been established to protect metals from corrosion and prevent the formation of deposits of mineral fields in acidic and hydrogen sulfide media. It is shown that the rate of coating on the surface of a steel sample (St.3 and St.12) of composite inhibitors passes in the same plane and is realized according to the Langmuir law with the formation of a layer that prevents corrosion of the metal, and the activation energy in these media of steels St.3 and St. is determined. 12 with the use of inhibitors. Based on the thermodynamic functions (ΔH , ΔS , ΔG) it is found that the Gibbs energy has a high negative value (ΔG_{ads}). The applied composite inhibitors increase the efficiency of inhibiting the accumulation of mineral salts by 2-6% and increase the degree of protection of metals against corrosion up to 98.4%.

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