Quantitative Evaluation of the Efficiency of Two Component Inhibitors based on Polyelectrolytes

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Abstract--- *This paper considers the results of gravimetric determination of the degree of protection of two-component corrosion inhibitors based on polyelectrolytes and phosphorous-containing organic compounds synthesized by us and gives a quantitative assessment of their effectiveness. The paper investigated the influence of various factors on the effectiveness of inhibitors and found that two-component inhibitors effectively protect carbon steels from corrosion at high temperatures and exhibit a chemisorption mechanism of action.*

Keywords--- *Metal Corrosion, Corrosion Protection, Corrosion Inhibitor, Sodium Carboxymethyl Cellulose (SCC), Hydrolyzed Polyacrylonitrile (HYPAN), Uniflok, Piperidin1-yl-methylene Phosphonic Acid (PMFC), 3-Nitrophenyl Piperidin1-yl-methylene Phosphonic Acid (NPMP), 1-(phenyldiazo) 2,4-propargyl Resorcinol Ether (Sha-25).*

I. INTRODUCTION

In a world with a rapidly developing industry in various sectors of the economy, the prevention of metal corrosion and the creation of inhibiting systems and anti-corrosion coatings are of great theoretical and practical importance. In countries with developed chemical and petrochemical industries, metal corrosion causes great economic damage, so the development and practical use of highly effective corrosion inhibitors is even more important.

Today, the world pays special attention to the creation of new multifunctional inhibitors that prevent chemical, electrochemical, microbiological corrosion and salt deposition, while their environmental safety is important. In industrially developed countries, a number of multifunctional inhibitors based on phosphorus-containing compounds have been developed and used: derivatives of phosphoric and phosphonic acids and organophosphates and their compositions with polyelectrolytes and complexes with metal ions. Therefore, it is important to develop environmentally safe, low-toxic, multi-component, multifunctional inhibitors. Promising inhibitors of this kind are compositions containing compounds that can form self-organizing surface layers, but such modification of the metal surface by multicomponent inhibitors of the oligomeric and polymer types is a poorly studied area. At the same time, it can be argued that the main role in inhibition processes is played by surface complexation, so the most

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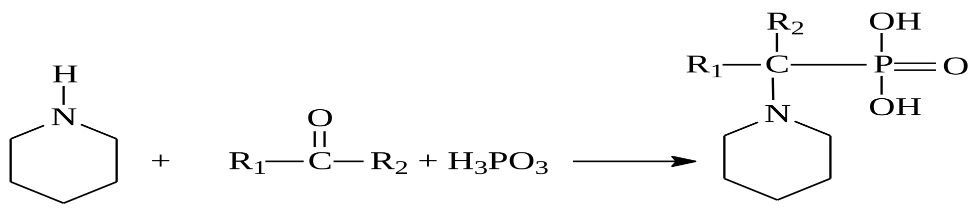
promising are chelating reagents [1]. The main place among them is occupied by derivatives based on phosphonic acids. These compounds have a number of unique properties, one of which is the possibility of formation under certain conditions of poorly soluble compounds with a polymer structure. Having both an amino group and a phosphonic acid residue in their composition, these compounds have wide possibilities of practical use as biologically active substances, complexons and multifunctional metal corrosion inhibitors[2].

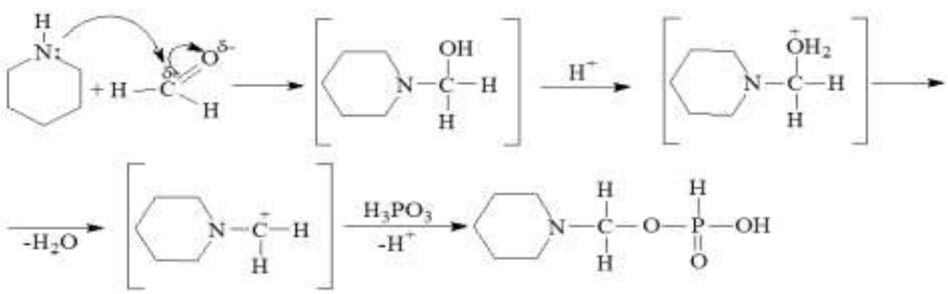
II. THE MAIN RESULTS AND FINDINGS

Formaldehyde and m-nitrobenzaldehyde were used as carbonyl compounds. The mechanism and speed of the reaction depend on the basicity of the amine and the nature of the carbonyl compound. [3].The reaction proceeds according to the scheme:

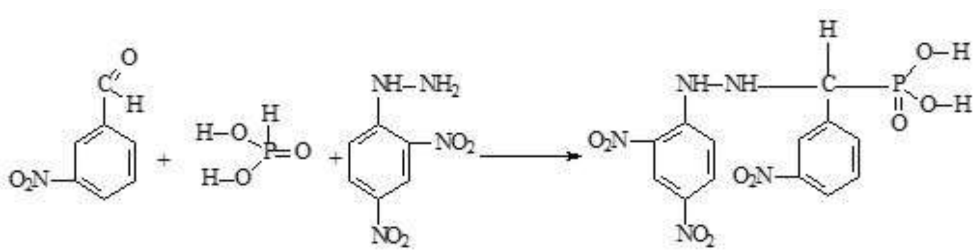


1) $R_1=R_2=H$; 2) $R_1=H$, $R_2=m\text{-}NO_2C_6H_4\text{-}$, 3) $R_1=R_2=CH_3$

There are various opinions of researchers about the reaction mechanism. The reaction of orthophosphoric acid with formaldehyde proceeds with a high yield and the Mannich reaction mechanism is considered the most likely, although other mechanisms are not excluded.



The difference in mechanisms can be explained from the point of view of hard and soft acids and bases (HSAB).According to this concept; hard acids (aliphatic aldehydes and ketones) react quickly with hard bases. [4]. Soft bases-phosphites preferably interact with soft acids (aromatic carbonyl compounds). From this point of view, it can be assumed that the reaction of 2,4-dinitrophenylhydrazine with m-nitrobenzaldehyde proceeds by a mechanism that can be represented by the following scheme:



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The structure of the synthesized substances was confirmed by IR spectroscopy, mass spectrometry and x-ray diffraction analysis.

Research Method

In this work, two-component type inhibitors based on polyelectrolytes and phosphorus-containing compounds were studied [5,6]. Studies were conducted in the background solutions of the composition: 5% Na_2SO_4+ 3% H_2SO_4 (Φ-1) and in a neutral environment (Φ-2). The electrodes are made of St.3 compositions %: 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.B gravimetric experiments used steel samples in the form of plates with the size of: 3.0 × 3.0 × 0.1 cm, treated with SIC abrasive paper of 320, 400 and 600 grades, respectively. The objects of the study were sodium carboxymethyl cellulose (SCC), hydrolyzed polyacrylonitrile (HYPAN), uniflok and their mixtures with PMFC (piperidin-1-ilmethylenphosphonic acid), NPMP (3-nitrophenyl piperidin 1-yl methylene phosphonic acid), 1-(phenyl diazo) 2,4-propargyl ether of resorcinol (SHA-25). Experimental work was carried out to determine the rate of corrosion of the working electrode in salt media in the presence of the studied inhibitors at their different concentrations and ratios in a certain temperature range by gravimetric method. To get an average result, each experiment was performed three times to get an accurate result. [5] The braking coefficient and the degree of protection (%) were calculated using the equations:

$$\gamma = \frac{i_c}{i_c^{`}} \qquad (1);$$

$$Z = \frac{i_c - i_c^{`}}{i_c} * 100\% \qquad (2)$$

where i_c and $i_c^{`}$ –are corrosion currents, respectively, in the absence and presence of an inhibitor. The corrosion rate (ic) was determined by the following equation:

$$i_c = \frac{P * n * 26,8}{S * \tau * A} \; ; \Gamma * \frac{\text{А}}{\text{см2}} \qquad (3)$$

n - metal valence; 26,8-Faraday number; P-decrease in the mass of the electrode, gr

S-the area of the electrode, cm2; τ-the test time, h; A - the atomic mass of the metal.

Table 1 shows the results of determining the corrosion rate, deceleration coefficient, and degree of protection of SCC steel with heterocyclic derivatives at various background solutions, depending on the concentration of the inhibitor. The table shows that inhibitors based on heterocyclic derivatives exhibit a slightly greater inhibitory ability. With an increase in the concentration of inhibitors, their protective ability increases to a concentration of 30 mg/l, and then changes slightly. With an increase in the medium temperature, the inhibiting ability of SCC and heterocyclic derivatives also increases, which indicates an increase in chemosorption processes. Inhibitors of SCC and its mixtures with PMFC, NPMP, and sHA 25were used at concentrations from 10 mg/l to 30 mg/l. The studied

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mixtures according to ten-day tests show high protective properties from 82.64% to 88.21 % at a temperature of 20^0C (Table 1).

Table 1: Results of Gravimetric Determination of the Degree of Protection of Steel Samples with St3 Inhibitors SCC -PMFC, SCC-NPMFC, SCC -sHA 25at a Temperature of 20^0C and Various Concentrations

Inhibitor	C, m/l	K, (gr/m^2*сут)	γ	Z, %
SCC – PMFC	0	123,71	-	-
	10	29,48	4,19	**76,17**
	15	28,06	4,40	77,31
	20	22,89	5,40	81,49
	25	21,62	5,72	82,52
	30	21,47	5,76	82,64
SCC – NPMFC	0	141,98		
	10	34,95	4,06	**75,38**
	15	31,19	4,55	78,03
	20	21,73	6,53	84,69
	25	21,35	6,65	84,96
	30	20,13	7,05	85,82
SCC – sHA 25	0	158,13	1	
	10	24,53	6,44	**84,48**
	15	22,71	6,96	85,63
	20	19,31	8,18	87,78
	25	19,08	8,28	87,93
	30	18,64	8,48	88,21

The results of gravimetric studies and calculations of the values of the corrosion rate, the braking coefficient and the degree of protection of heterocyclic compounds with polyelectrolytes at different temperatures are shown in table 2.

With an increase in temperature (Table.2) the values of the inhibition coefficient and the degree of protection of two-component inhibitors based on heterocyclic compounds and polyelectrolytes in equimolar ratios, depending on the chemical nature of the second component, increase. For all the studied two-component systems with an increase in temperature, there is an increase in the values of the braking coefficient and the degree of protection, which indicates chemosorption processes.

Table 2: Comparative Table of Results of Gravimetric Determination of the Degree of Protection of St. 20 with two-Component Inhibitors in Equimolar ratios in Solutions Depending on Temperature (C=10mg)

Inhibitor	^{0}C	K, (g/m^2·сут)	γ	Z, %
Background	20	132,73	-	-
NPMFC -SCC		29.48	4.502	77.78
PMFC - SCC		29,65	4,477	77,66
sHA 25– SCC		24.54	5.409	**81.51**
Background	40	148,44	-	-
NPMFC - SCC		27.7	5.36	81.33
PMFC -SCC		54.12	4.74	73,54
SHA 25– SCC		16.85	8.81	**88,65**
Background	60	162,83	-	-
NPMFC - SCC		15.76	10.33	89,98
PMFC - SCC		58.6	2.78	73, 71
sHA 25– SCC		11.1	14.7	**93,12**

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These compounds have a number of unique properties, one of which is the possibility of formation under certain conditions of poorly soluble compounds with a polymer structure. Having both an amino group and a phosphonic acid residue in their composition, these compounds have wide possibilities of practical use as complexons and analytical reagents. According to experimental data, the greatest effect among individual inhibitors on the rate of steel corrosion at 20^0C b is shown by the sHA 25 inhibitor, but the studied individual inhibitors are not effective, the highest protective effect of which reaches up to 81.51% at 20^0C and 93.12% at 60^0C (Table 2).

These results allow us to conclude that these inhibitors interact chemically with the steel surface and a process of chemical adsorption is observed, which indicates an increase in the degree of protection when the temperature increases.

Quantitative evaluation of the effectiveness of a mixed inhibitor compared with individual components was carried out on the basis of calculations of their mutual influence coefficient:

$$\chi^{\Sigma}=\gamma^{\Sigma}/\Pi\gamma_i=\Pi\chi_i, \qquad (4)$$

where $\gamma^{\Sigma}=K_o/K^{\Sigma}$ и $\gamma_i=K_0/K_i$– inhibitor of steel corrosion inhibitor; K^{Σ} -corrosion rate in the presence of a mixed inhibitor, K_i-the rate of corrosion in the presence of only one of its components. [4]. Studies have shown that at 20^0C and pH=8, PAMBFC–HYPAN compositions were most effective at an equimolar ratio (Table 3). For the PAMBFC-HYPAN and PAMBFC-SCC systems, a high synergistic effect is also observed at the equimolar ratio, but somewhat lower than in the first case [5].

Table 3: Values of the Inhibition Coefficient and the Coefficient of Mutual Influence of Components of Multicomponent Inhibitors (pH=8, T=20^0C and SYNG.=10 mg/l)

Inhibitor	Theratioofcomponents	γ^{Σ}	$\sum \gamma_i$	χ^{Σ}
PUBCHEM CID–UNIFLOK	1:3	10,79	11,56	0,93
	1:2	13,27	11,56	1,14
	1:1	17,81	11,56	**1,54**
	2:1	16,03	11,56	1,38
	3:1	11,74	11,56	1,02
PUBCHEM CID–HYPAN	1:3	10,23	13,18	0,77
	1:2	16,73	13,18	1,27
	1:1	36,27	13,18	**2,75**
	2:1	14,25	13,18	1,08
	3:1	9,06	13,18	0,69
PUBCHEM CID–SCC	1:3	9,25	11,27	0,81
	1:2	12,47	11,27	1,10
	1:1	26,81	11,27	**2,38**
	2:1	18,12	11,27	1,61
	3:1	8,53	11,27	0,75

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III. CONCLUSION

Comparison of the obtained data shows that the efficiency of the developed two-component systems based on aminomethylenephosphonic acid derivatives slightly exceeds the efficiency of systems based on polyphosphates and exhibit chemosorption properties.

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