

New α -Aminophosphonates as Corrosion Inhibitors for Oil and Gas Pipelines Protection

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Abstract

The problem of corrosion of metal equipment is one of the most actual problems in oil industry. One of the methods to solve this problem is the development of new low-toxic, accessible and effective corrosion inhibitors. For this purpose, we carried out the synthesis of the new α -aminophosphonates based on syntanyl phosphites, formalin and diethanolamine according to the Kabachnik-Fields reaction. The resulting products are characterized by ¹H, ³¹P, ¹³C NMR, IR and mass spectroscopy methods. The obtained compounds contain a long radical chain of industrial (poly) ethoxylated alcohol residue with different length of the hydroxyethyl fragment, as well as an active center containing O-P-C-N fragment, which impart them inhibitory properties toward corrosion processes. The anticorrosive activity of the new aminophosphonates was studied by gravimetric analysis method. In the article the effect of concentration, time and degree of ethoxylation of the hydrocarbon radical in alpha-aminophosphonates on the protective effect of inhibitors was studied. It was shown that the obtained aminophosphonates exhibit high values of the protective effect of steel in a highly mineralized medium containing 250 g/m³ CO₂ and 200 g/m³ H₂S. The high value of the protective effect (82-85%) at inhibitor concentration of 25 mg/l was found. The maximum protective effect at 50 mg/ml dosage of the inhibitor is 94.3%, while there is a decrease of the corrosion rate (less than 0.04 mm/year).

Keywords: Corrosion; Corrosion Inhibitor; α -Aminophosphonate; Synthanol; Protective Effect; Corrosion Rate.

1. Introduction

Corrosion is one of the most pressing problems of the oil and gas industry. Corrosive processes contribute to the deterioration of the mechanical properties of the equipment, which can lead to oil spill into the environment. The main corrosive agents in the oil and gas industry are H₂S and CO₂. Currently, there is a tendency to replace alloy equipment with materials that are more resistant to corrosion, but, unfortunately, this increases the cost of production.

One of the main solutions to this problem is the creation of new corrosion inhibitors that impede the process of damage to the material by creating a protective layer on the metal surface [1]. It can improve economic abilities of the industrial establishments and minimize different factors of the environment pollution [2]. In this case, molecule is adsorbed on the metal surface and causes a slowdown in either the anodic dissolution of the metal, or the cathodic reaction of hydrogen evolution, or both [3].

Considerable attention as inhibitors of metal corrosion was obtained by organic compounds, in particular, having a

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heteroatom and/or π -electrons in their composition, as they are adsorbed on the metal surface and form a protective layer that prevents the penetration of corrosive agents in aggressive environment to the surface metal [4]. Moreover, in comparison with inorganic inhibitors, they are less toxic for both humans and the environment [5].

Recently, there is the development of "green" corrosion inhibitors based on natural compounds [6]. This field requires more "green" ways for synthesis of inhibitors with minimum by-products generation that avoid the formation of toxic substances. Thus new strategies such as chemical synthesis under solvent free condition, use of solid supported reagents, mechanochemical mixing and implementation of non-conventional activation using microwave and ultrasound irradiations have been developed [7]. Thus, studies on the use of environmentally friendly natural polymers - chitosan and carboxymethylcellulose [8], compositions based on rice bran oil are described [9]. The use of surfactants [10, 11] as well as a synergistic inhibitory effect when two of them combined are described [12].

It is known that good corrosion inhibitor should be effective even in small concentrations. One of such effective and interesting corrosion inhibitors are phosphonates because of their low toxicity, activity in aqueous media and stability toward hydrolysis and microorganisms degradation [13]. Also different types of amines and their derivatives are effectively used as corrosion inhibitors for steel in various corrosive environments because of their sp^3 hybridised nitrogen atom, which can form three single bonds with another element or functional group and so increase inhibition effect [14]. Such phosphorus compounds as, for example, aminomethylene phosphonates [15], phosphonic acids [16], and also α -aminophosphonates [17], and nitrogen-containing compounds as imidazolines, amides, amines, amidoamines [18], and pyrazine derivatives [19] and many others are widely used as corrosion inhibitors.

The charge distribution, the interaction between the surface of metal and inhibitor molecules, the number of available active centers for adsorption are the main keys for the corrosion inhibition efficiency of molecules [13]. The anticorrosive activity of metal corrosion inhibitors is due to their adsorption capacity; it is the highest due to the presence of active phosphorus-, nitrogen- and sulfur- containing and other groups [20]. However, as a rule, one inhibitor cannot effectively inhibit metal corrosion. Fortunately, the synergistic effect of inhibition, which helps to improve the effectiveness of inhibition or reduce its dosage, is an effective way to solve this problem. We have proposed a method for obtaining new corrosion inhibitors by combining several active centers that enhance the anti-corrosion effect in a single molecule. Phosphorus in the composition of the phosphonate, nitrogen in the form of diethanolamine and the hydrophilic-hydrophobic part in the form of a non-ionic surfactant synthanol were chosen as active centers.

Today, the market for corrosion inhibitors consists mainly of expensive foreign products, the chemical composition of which is often unknown; the so-called process of import substitution takes place. Therefore, we offer in our work an affordable method for producing inhibitors based on available industrial starting materials with high anticorrosive activity, as a basis for creating commercial inhibitors.

2. Materials and Methods

The ^{31}P NMR spectra were recorded on a Bruker Avance-400 instrument (161.94 MHz for ^{31}P and 400.05 MHz for ^1H). The IR spectra were recorded on a Tenzor 27 spectrometer (Bruker, Germany) on KBr plates. Mass spectra were recorded on an AmazonX instrument, electrospray ionization. Elemental analysis performed on the instrument Carlo-Erba brand EA 1108.

Determination of the protective effect of the products was carried out by a gravimetric method, which consists in determining the mass loss of metal samples during their stay in non-inhibited and inhibited corrosive environments, on the IKK-1 research gravimetric complex. The standard model of oilfield water of the following composition (g/dm^3) was used as a corrosive medium: $\text{NaCl} - 163.0$; $\text{CaCl}_2 \cdot 2\text{H}_2\text{O} - 23.0$; $\text{MgCl}_2 \cdot 6\text{H}_2\text{O} - 17.0$; $\text{CaSO}_4 \cdot 2\text{H}_2\text{O} - 0.14$ and CO_2 content - $200 \text{ g}/\text{m}^3$, $\text{H}_2\text{S} - 20 \text{ g}/\text{m}^3$ in the first medium and CO_2 content - $250 \text{ g}/\text{m}^3$, $\text{H}_2\text{S} - 200 \text{ g}/\text{m}^3$ in the second medium. Metal samples with dimensions of $25 \times 20 \times 1 \text{ mm}$ were weighed on a laboratory analytical balance AND GR-202 with an accuracy of 0.01 mg. The tests were carried out for 6, 24, 72 and 168 hours with stirring at a stirring speed of 700 rpm. The dose of the inhibitor was 2.5-50 mg/l. The reagent, before entering into a corrosive environment, was dissolved in 1 ml of isopropanol.

The protective effect $Z(\%)$ was calculated by the Equation 1:

$$Z = 100 * (\Delta m_1 - \Delta m_2) / (\Delta m_1 - \Delta m_3) \quad (1)$$

The corrosion rate V (mm/g) was calculated by the Equation 2:

$$V = 1.13 * (\Delta m_1 - \Delta m_2 - \Delta m_3) / (\tau * S) \quad (2)$$

Where Δm_1 , Δm_2 is the mass loss of the sample after the test in non-inhibited and inhibited media, g.;

$-\Delta m_3$ is the mass loss of the sample after the treatment with an etching solution, g.

T is the exposure time of samples in a corrosive environment, h;

S is the sample area, m^2 ($0.00109 m^2$).

The two parallel tests on three samples for each test were conducted. The time for samples testing in the inhibited and non-inhibited test medium was the same. Before pouring the model water into the installation, it was flushed with inert argon gas. The sample surface was polished to a roughness of no more than $1.6 \mu m$ according to GOST 2789-73 and degreased with acetone.

After degreasing, subsequent operations with the samples were performed with tweezers. To activate the sample surface before testing, it was immersed for 1 min in a solution of 15 % hydrochloric acid, then thoroughly washed with running and distilled water, dried with filter paper, packed into it, kept in a desiccator with desiccant for 1 h and weighed on an analytical balance with an error of $0.00001 g$. The temperature fluctuations of the test medium did not exceed $\pm 2 ^\circ C$. The decrease of the medium volume due to evaporation did not exceed 1%.

At the end of the test, the samples were removed and dried with filter paper. Then, the treatment was carried out in the following sequence: the remnants of corrosive products were removed with a soft pencil eraser; poorly removed corrosion products were removed by etching for 15 seconds at room temperature in a solution of the following composition (g/dm^3): sulfuric acid - 84.0; ammonium citrate – 100.0; thiourea - 10.0; distilled water - up to $1 dm^3$.

The remains of the pickling solution were removed by washing in tap water, then in distilled water. The samples were dried with filter paper, degreased with acetone, packed into filter paper, kept in a desiccator with desiccant for 1 h and weighed on an analytical balance.

3. Synthesis and Physico-chemical Characteristics of Phosphonates 4-6

Diethanolamine (2.5 g, 24 mmol for **1**; 1.1 g, 10 mmol for **2** and 1 g, 10 mmol for **3**) and 30% formalin solution (2 g, 66 mmol for **1**, 1.5 g, 49 mmol for **2** and 1.1 g, 36 mmol for **3**) was added to a solution of phosphite 1 (5 g, 19 mmol) (5 g, 7 mmol for **2** and 5 g, 5 mmol for **3**). The reaction mixture was stirred at $80 ^\circ C$ for 6 hours under an inert atmosphere. Unreacted formalin was removed under reduced pressure. **4** and **5** are yellow liquid transparent products with yields of 5.1 g (84%) and 4.6 g (82%), respectively. **6** - orange liquid transparent product with a yield of 4 g (78%). The structures of the compounds obtained were proved by 1H , ^{31}P , ^{13}C , IR and mass spectroscopy, elemental analysis.

• Characteristic of Compound 4.

NMR $^{31}P\{^1H\}$ (^{31}P) spectrum (C_6H_6), δ_P , ppm: 18.48, 18.67, 18.83. NMR 1H spectrum ($CDCl_3$), δ , ppm (J, Hz): 2.78, 2.80, 2.82 s (2H, PCH_2N , $^3J_{HH}$ 20, $^2J_{PH}$ 717), 3.35-3.63 m (4H, $(OCH_2CH_2)_2$), 4.04-4.10 t (2H, OCH_2CH_3 , $^3J_{HH}$ 7 $^3J_{PH}$ 717), 4.07 s (2H, NCH_2OH). FT-IR spectrum (liquid film) ν , cm^{-1} : 3361 ($\nu_{as,s}$ OH), 2925, 2855 ($\nu_{as,s}$ CH_3 , $\nu_{as,s}$ CH_2), 1465 (δ_{as} CH_3), 1354 (δ_s CH_3), 1251 (ν P=O), 1118 (ν_{as} C-O-C), 975 (ν C-C-O), 882 (δ P-O-C). Mass-spectrum (ESI), m/z : 484.7 $[M + H]^+$. For $C_{23}H_{50}NO_7P$ calculated 483.6. EA: for $C_{23}H_{50}NO_7P$ calculated, %: C 57.2; H 10.4; N 2.9; P 6.4. Found, %: C 57.9; H 11.1; N 3.0; P 6.1.

• Characteristic of Compound 5.

NMR $^{31}P\{^1H\}$ (^{31}P) spectrum (C_6H_6), δ_P , ppm: 24.76, 24.94, 25.32. NMR 1H spectrum ($CDCl_3$), δ , ppm (J, Hz): 2.76, 2.78, 2.80 s (2H, PCH_2N , $^3J_{HH}$ 20, $^2J_{PH}$ 717), 3.63-3.69 m (4H, $(OCH_2CH_2)_7$), 3.78-3.80 t (2H, OCH_2CH_3 , $^3J_{HH}$ 7 $^3J_{PH}$ 717), 4.35 s (2H, NCH_2OH). FT-IR spectrum (liquid film) ν , cm^{-1} : 3382 ($\nu_{as,s}$ OH), 2925, 2857 ($\nu_{as,s}$ CH_3 , $\nu_{as,s}$ CH_2), 1460 (δ_{as} CH_3), 1352 (δ_s CH_3), 1249 (ν P=O), 1113 (ν_{as} C-O-C), 956 (ν C-C-O), 874 (δ P-O-C). Mass-spectrum (ESI), m/z : 705.0 $[M + H]^+$. For $C_{33}H_{70}NO_{12}P$ calculated 703.9. EA: for $C_{33}H_{70}NO_{12}P$ calculated, %: C 56.3; H 10.0; N 2.0; P 4.4. Found, %: C 57.1; H 10.7; N 1.9; P 4.1.

• Characteristic of Compound 6.

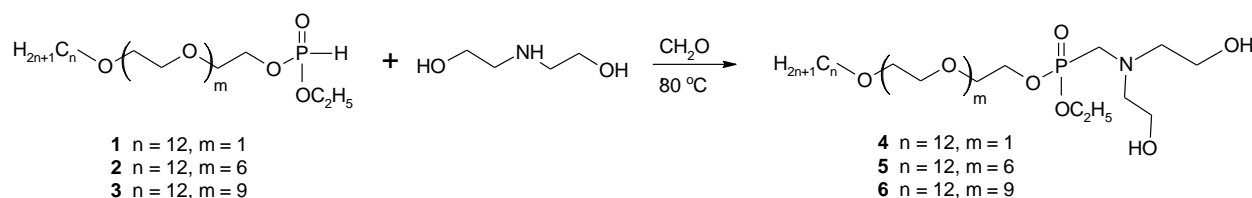
NMR $^{31}P\{^1H\}$ (^{31}P) spectrum (C_6H_6), δ_P , m.d.: 26.47, 26.89, 27.28. NMR 1H spectrum ($CDCl_3$), δ , ppm (J, Hz): 2.86, 2.90, 2.92 s (2H, PCH_2N , $^3J_{HH}$ 20, $^2J_{PH}$ 717), 3.59-3.66 m (4H, $(OCH_2CH_2)_7$), 3.82-3.84 t (2H, OCH_2CH_3 , $^3J_{HH}$ 7 $^3J_{PH}$ 717), 4.42 s (2H, NCH_2OH). FT-IR spectrum (liquid film) ν , cm^{-1} : 3376 ($\nu_{as,s}$ OH), 2924, 2856 ($\nu_{as,s}$ CH_3 , $\nu_{as,s}$ CH_2), 1457 (δ_{as} CH_3), 1352 (δ_s CH_3), 1249 (ν P=O), 1111 (ν_{as} C-O-C), 954 (ν C-C-O), 873 (δ P-O-C). Mass-spectrum (ESI), m/z : 837.1 $[M + H]^+$. For $C_{39}H_{82}NO_{15}P$ calculated 836.0. EA: for $C_{39}H_{82}NO_{15}P$ calculated, %: C 56.0; H 9.9; N 1.7; P 3.7. Found, %: C 56.8; H 10.3; N 1.7; P 3.4.

Table 1. Physico-chemical characteristics of compounds 4-6

No	NMR $^{31}\text{P}\{^1\text{H}\}$ δ_{P} , ppm	NMR ^1H PCH_2N		IR spectrum		Mass spectrum, m/z:	EA, %			
		δ , ppm	$^2\text{J}_{\text{PH}}$, Hz	$\nu \text{P=O}$	δ_{ROS}		C	H	N	P
4	24.32	2.78				483.6	57.9	11.1	3.0	6.1
	24.54	2.80	10.5	1251	882					
	24.91	2.82								
5	24.76	2.76				705.0	57.1	10.7	1.9	4.1
	24.94	2.78	10.5	1249	874					
	25.32	2.80								
6	26.47	2.86				837.1	56.8	10.3	1.7	3.4
	26.89	2.90	10.7	1249	873					
	27.28	2.92								

4. Results and Discussion

New corrosion inhibitors based on α -aminophosphonates were obtained under mild conditions by the method of amination of phosphites (Scheme 1).



Scheme 1. Scheme of the reaction of obtaining phosphonates 4-6

For this, phosphites 1–3 obtained by us earlier, which carry in their composition a fragment of industrial alcohol of the brand ALM (ALM-2, ALM-7 and ALM-10, where 2, 7 and 10 are the average number of ethoxy groups) were used in reactions of interaction with an excess of diethanolamine and 30% formalin solution at 80 °C for 6 hours.

A study of the inhibiting properties of 4-6 in carbon dioxide and hydrogen sulfide iron corrosion was carried out (content of CO_2 - 250 g/m^3 , H_2S -200 g/m^3). The main indicators for determining the effectiveness of a compound as a metal corrosion inhibitor are the determination of the protective effect of the metal and the corrosion rate in the presence of the inhibitor. The effect of inhibitors on the corrosion rate of low carbon steel and the protective effect were determined by the gravimetric method by the loss of mass of metal samples during their staying in inhibited and uninhibited corrosive environments [21]. The main advantage of the gravimetric method analysis is the high accuracy of determining the mass of a substance in the investigated sample. Also, the analysis does not require complex equipment. In addition, to work on the device, it is not necessary to calibrate it, to prepare a series of standard solutions. The main disadvantage of gravimetric method is the duration of the analysis and need to check the quality of the weight form. So, it should not contain any impurities, and its composition should be known reliably [22].

An increase in the length of the hydroxyethyl fragment leads to an increase in the stability of the inhibitors with respect to the residence time in the medium under study. When comparing the magnitude of the protective effect for 4-6 at low concentrations of phosphonates (10 and 25 mg/l , after 6 hours of incubation in the test medium), a decrease in the effectiveness of corrosion in this series is observed with increasing degree of oxyethylation (Figure 1). Probably, with an increase in the hydrophilic-lipophilic balance in phosphonate molecules, the process of their adsorption on the metal surface stops faster, which leads to a decrease in the protective effect. Presumably, in this case, the reverse process plays a large role - desorption of the molecule with an increase in its hydrophilicity as a result of an easier transfer of the inhibitor from the metal surface to the aqueous phase. Thus, the phosphonate with the shortest hydroxyethyl chain proved to be the most effective corrosion inhibitor.

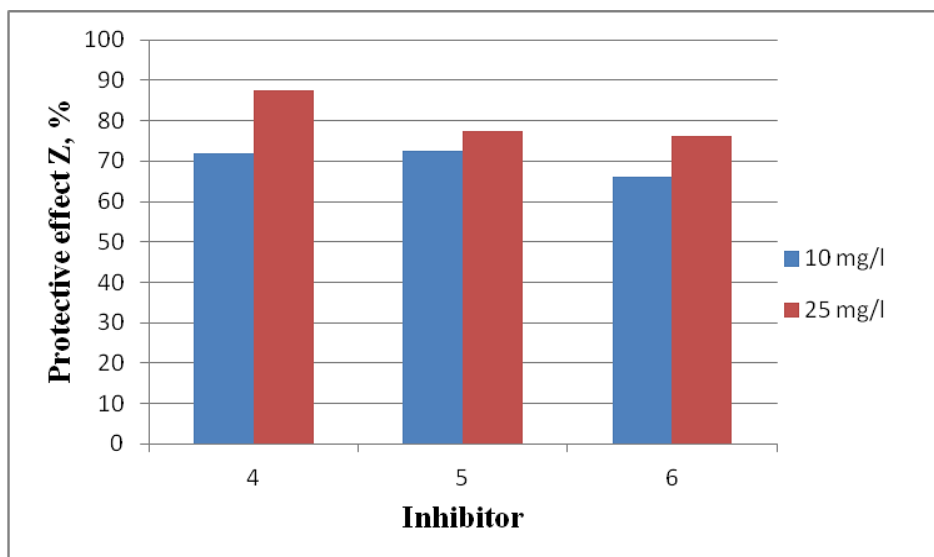


Figure 1. The protective effect of the composition 4-6 on the degree of radical ethoxylation at 10 and 25 mg/l after 6 hours of treatment in corrosive media

The study of the dependence of the protective effect on the residence time in the studied medium showed its decrease for all phosphonates.

The protective effect of inhibitor 6 was determined as a metal corrosion inhibitor by varying the phosphonate concentration after 6 hours of aging in the test medium (Figure 2). The experiment showed a protective effect of about 65% already at a low concentration (5 mg/l). With increasing concentration, the protective effect also increases and reaches its maximum (up to 94.3% at 50 mg/l). With a further increase of the 6 concentration to 100 mg/l, the protective effect decreases to 86.3%. Thus, to achieve a good indicator of the protective effect as a metal corrosion inhibitor does not require high concentrations in the case of phosphonate 6 (<100 mg/l).

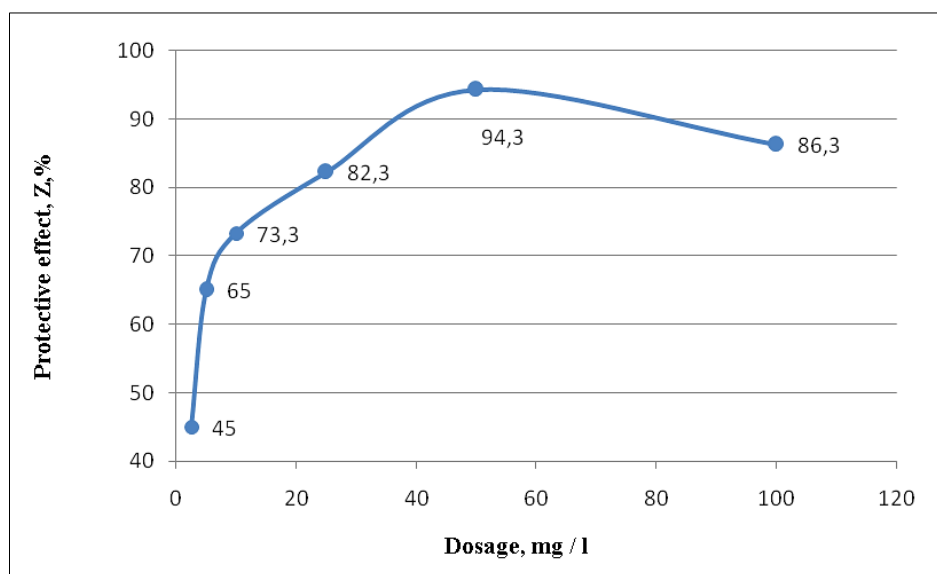


Figure 2. Dependence of the protective effect of compound 6 on concentration

Also, the studies were carried out at a concentration of CO₂ - 200 g/m³, H₂S-20 g/m³, the concentration of salts did not change. An increase in the protective effect was found compared to the results described above (in the test medium with a CO₂ concentration of 250 g/m³, H₂S - 200 g/m³) (Figure 3). The protective effect increased to 87.4 and 70.2%, 85.0 and 74.6%, 84.1 and 77.3% after 6 and 24 hours for 4-6, respectively. This can be explained by the increase in the rate of adsorption of the inhibitor on the metal surface when the environment changes to a less aggressive one.

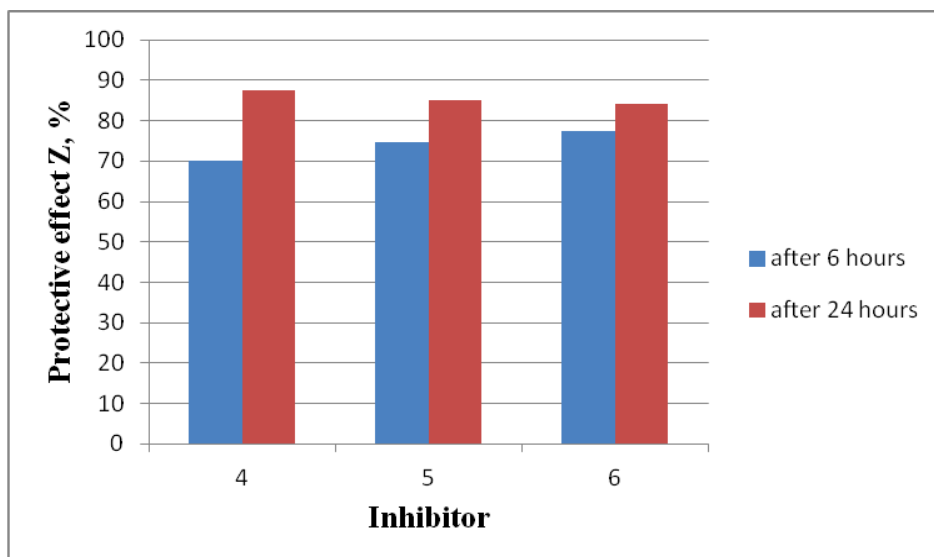


Figure 3. The protective effect of the composition 4-6 on after 6 and 24 hours after treatment in the corrosive media when corrosive media changed (CO₂ - 200 g/m³, H₂S-20 g/m³)

When testing inhibitors in model water without hydrogen sulfide, the protective effect also increases to 93.5 and 74.3%, 90.1 and 88.7 and 82.0% after 6 and 24 hours for 4-6, respectively (Figure 4).

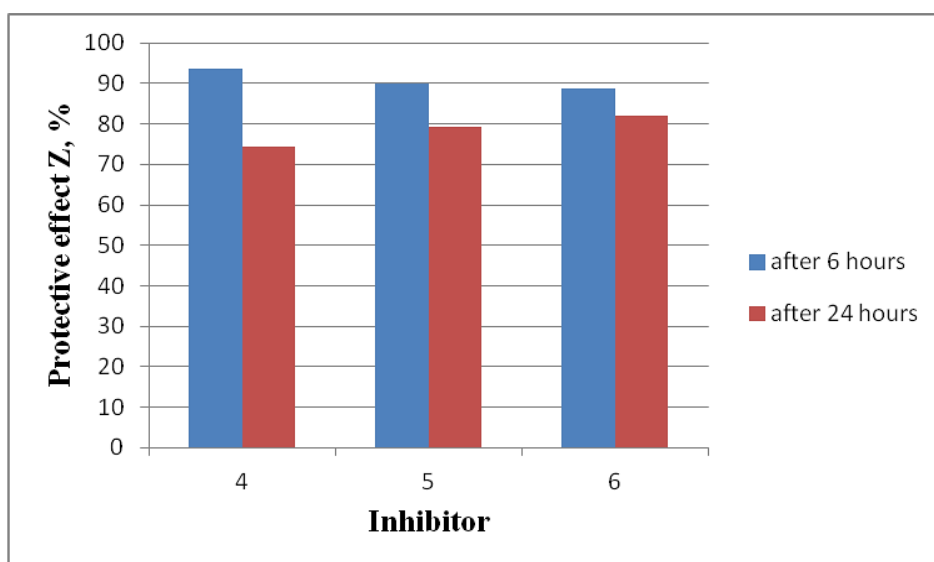


Figure 3. The protective effect of the composition 4-6 on after 6 and 24 hours after treatment in the corrosive media when corrosive media changed (CO₂ - 200 g/m³, without H₂S)

The calculation of the average corrosion rate of steel in the presence of phosphonates 4-6 showed that the corrosion rate of metal at inhibitor concentration of 25 mg/l is 0.043, 0.077 and 0.081 mm/year, respectively, which is less than the average corrosion rate of the metal in a non-inhibited environment (0.343 mm/year).

Comparison of the obtained results with data for inhibitors used in industry showed the advantages of using the phosphonates obtained by us. Thus, the corrosion inhibitors of the INKORGAZ and AMDOR-IK series, which are well known in the oil industry, are compositions based on nitrogen-containing organic compounds and organic solvents. The protective effect of these inhibitors against general corrosion (at an inhibitor concentration of 30 mg/l, in the presence of H₂S and/or CO₂) is inferior to this value for the inhibitors we obtained. Thus, the protective effects for INCORGAZ-21T, AMDOR-IK-5, INCORGAZ-111 are 85, 90 and 90%, respectively, for the 4-6 phosphonates obtained by us - 88, 92 and 96 %, respectively. In addition, it is known that INCORGAZ corrosion inhibitors are moderately hazardous in terms of their impact on the human body and have an irritant local effect and general toxicity. The inhibitors obtained by us will have low toxicity, as well as similar α -amino phosphonates [23].

The protective effect of corrosion inhibitor samples, which are widely used to inhibit pipelines in oil fields in Western Siberia, showed the best results for generally accepted laboratory tests - at least 90 %. However, due to wide industrial application, their lack of effectiveness was discovered due to the presence of through corrosion damage on the oilfield

pipelines protected from corrosion. As known, the relevance of reliable laboratory tests is to simulate specific conditions. For example, for corrosion inhibitors Skimol 2111, Sonkor 9011, Azol 5010A, Kormaster 1035, the protective effect on tests in the U-shaped cell was only 73, 57, 47 and 78%, respectively (at 25 °C, 50 mg/l). This suggests low corrosion protection for turbulent regimes with high flow rates. The values of the protective effect in the case of phosphonates **4-6** obtained by us (at 25 °C, 50 mg/l) under the same conditions of increased aggressiveness of the medium and high flow rates were 91, 84 and 94%, respectively, which far exceeds the values obtained for industrial inhibitors

5. Conclusion

Thus, we obtained new anodic corrosion inhibitors based on phosphonate derivatives with (poly) hydroxyethyl substituents, demonstrating a good inhibitory ability with a high protective effect (94.3%) and a low corrosion rate of steel with the addition of phosphonates to the aggressive medium under study (0.03 mm/year).

6. Funding

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7. Conflicts of Interest

The authors declare no conflict of interest.

8. References

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