New Sintanyl Phosphonates for Protection of Oil and Gas Pipelines from Steel Corrosion

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Abstract

Many corrosion inhibitors are economically disadvantageous or toxic to the environment. Additionally, there are certain requirements for corrosion inhibitors. Therefore, the development of new corrosion inhibitors is one of the important problems in the oil-producing and oil-refining industry. The purpose of this work is the synthesis of new corrosion inhibitors with high inhibitory activity, the establishment of the structure of the compounds obtained and the determination of the anti-corrosion effect with respect to aggressive media. This paper presents the results of research on the development of new iron corrosion inhibitors. New α-aminophosphonates were synthesized based on the Kabachnik-Fields reaction. Formalin, morpholine, phosphite containing residues of industrial non-ionic surfactants - syntanols as radicals were used as a raw material. The compounds obtained were isolated in high yield. The structure of the compounds obtained is established by modern methods of physico-chemical analysis. The protective effect of the compounds obtained was studied by a gravimetric method for 6, 24, 72 hour exposure and an inhibitor concentration of 10, 25, 50, 100 ppm. As an aggressive medium, a highly mineralized medium containing CO_2 and H_2S was used in simulated formation water. The dynamics of changes in the protective effect of the resulting aminophosphonate from time to time, at dosages of 2.5-100 ppm, were studied using electrochemical analysis methods. The protective effect of syntanyl-O-ethyl- (N-morpholinyl) methylphosphonate obtained at 25 ppm and a shutter speed of 6 hours is 73-82%. The article shows that with increasing concentration, an increase in the protective effect is observed. The greatest protective (89.6) effect showed O-2- [2- [2- [2- [2- [2- [2- [2- [2- (dodecyloxy) ethoxy] ethoxy] ethoxy] ethoxy] ethoxy] ethoxy] ethoxy] ethoxy] ethyl-O-ethyl- (N-morpholinyl) methylphosphone at a dosage of 100 ppm.

Keywords: Green Building Rating Tools; Life Cycle Cost Analysis; Sustainable Development.

1. Introduction

Corrosion is a common problem in the oil and gas industry. Oil and gas pipelines, refineries and petrochemical plants have serious problems with corrosion. Corrosion in the oil and gas industry is often caused by water, carbon dioxide (CO_2) and hydrogen sulfide (H_2S), and can also be enhanced by microbiological activity [1]. The fight against corrosion in the oil and gas industry is of paramount importance, since the economic losses in these industries due to corrosion are extremely high [2]. The use of a corrosion inhibitor is one of the best and most cost-effective methods among various methods of dealing with corrosion in the oil and gas industry [3, 4].

Inhibitors used in oil fields are mainly composed of compounds containing quartenized nitrogen atoms, amides, amines, imidazolines, long-chain carboxylic acids, ethoxylates, multifunctional low molecular weight polymers,

sulfonates, phosphates and their esters, pyridine salts [5]. Phosphates of metals [6], various polymeric ethers of phosphates [7], as well as ethers of phenols, ethoxylated, propoxylated, butoxylated alcohols [8-10], phosphonic acids and their salts [11], thio- and dithiophosphonates [12] are the most common among organophosphate corrosion inhibitors. Often, surfactants are used as inhibitors, the amphiphilic nature of the molecules of which promotes adsorption at metal / metal-oxide-water interfaces and creates a barrier that can inhibit corrosion [13].

Despite the great diversity of existing metal corrosion inhibitors, there is the problem of expanding their range by creating new inhibitors [14].

It is known that α-aminophosphonates are among the active inhibitors of iron corrosion in acidic media containing HCl and sulfuric acid [15-17].

The Kabachnik-Fields reaction is a simple multicomponent organic reaction from aldehydes, amines and dialkyl phosphites, as a result of which the amino phosphonates — compounds with the P (O) –C – N bond [18] are formed. Recently, the synthesis of α-aminophosphonates has attracted much attention due to the structural analogy with α-amino acids and significant biological activity. They are used as HIV protease inhibitors [19]. The α-amino phosphonate based on 4-hydrazino-quinazoline has antimicrobial activity against Escherichia coli, Salmonella sp., Staphylococcus aureus, Saccharomyces cerevisiae [20]. β-lactam derivatives are antitumor agents that are particularly anti-leukemic [21].

Tα-Aminophosphonates have complexing properties that are used as carriers of metals through the membrane [22].

They are used to extract valuable metals from their solutions, in particular gadolinium [23]. Amino-carboxyphosphonate ligand complexes can be used as radiopharmaceuticals [24].

To obtain corrosion inhibitors, we first synthesized α-amino phosphonation of phosphites obtained from industrial grades of Synthanol ALM 2, ALM 7, ALM 10.

2. Materials and Methods

As corrosion inhibitors, we synthesized compositions based on α-amino phosphonation reaction products containing an O -organic substituent based on a long chain of various industrial fractions of synthanols and several active centers of phosphorus, nitrogen, and oxygen.

Synthesis of corrosion inhibitors was carried out according to the Kabachnik-Fields reaction in the three component medium without using a solvent and a catalyst according to the following reaction equation scheme [25] (Equation 1).

$$a \ (n = 2), \ b \ (n = 7), \ c \ (n = 10)$$
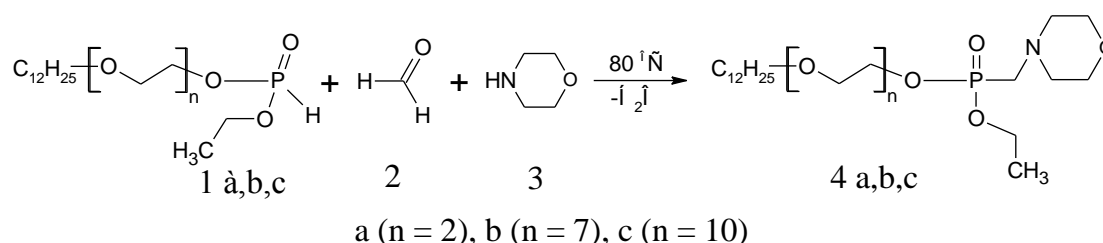
The ^{31}P NMR spectra were recorded on a Bruker Avance-400 instrument (161.94 MHz for ^{31}P and 400.05 MHz for ^{1}H). The ^{13}C NMR spectra are recorded on a Bruker Avance-600 instrument with an operating frequency of 150 MHz. The IR spectra were recorded on a Tenzor 27 spectrometer (Bruker, Germany) on KBr plates in the range of 0–1200 cm^{-1}. Mass spectra were recorded on an AmazonX instrument, electrospray ionization. Elemental analysis performed on the instrument Carlo-Erba brand EA 1108.

Synthesis of *O*- [2- (2-dodecylcyloxy) ethoxy] ethyl-*O*-ethyl- (*N*-morpholinyl) methylphosphonate 4a

5 g (13.6 mmol) of synthanol phosphite **1a**, 1.5 g (15 mmol) of 30% formalin solution and 1.2 g (15 mmol) of morpholine were added to the solution. The reaction mixture was stirred at 800° C for 4 hours under an inert atmosphere of argon. Then the solution was evaporated for 1 h under vacuum (0.02 mmHg) at 60° C. The residue obtained 5.6 g (87%) of the reaction products. Mass spectrum (ESI), m/z (+1): The main signals of molecules with radicals ($C_nH_{2n+1}(OCH_2CH_2)_m$); 422.4 (n=12; m=1); **446.5 (n=12; m=2);** 510.5 (n=12; m=3); 555.4 (n=12; m=4); 606.6 (n=12; m=5); Found, %: C 62.56; H 10.60; N 2.73; P 5.33. Calculated, %: C 59.33; H 10.39; N 3.01; P 5.65. $C_{23}H_{48}NO_6P$.

Synthesis of *O*- [2- [2- [2- [2- [2- [2- (2-dodecyloxy) ethoxy] ethoxy] ethoxy] ethoxy] ethoxy] ethoxy] ethyl-O-ethyl- (N-morpholinyl) methylphosphonate 4b

5 g *(9 mmol)* of phosphite *1 g*, 1.1 g (11 mmol) of 30% formalin solution and 0.9 g (11 mmol) of morpholine were added to the solution. The reaction mixture was stirred at 80° C for 4 hours under an inert atmosphere of argon. Then the solution was evaporated for 1 h under vacuum (0.02 mmHg) at 60° C. 5.1 g (85%) of the reaction products obtained in the residue. Mass spectrum (ESI), m/z (+1): The main signals of molecules with synthanol

radicals($C_nH_{2n+1}(OCH_2CH_2)_m$-); 556,6 (n=9; m=5); 600.6 (n=9; m=6); 642.5 (n=12; m=6); **686.6 (n=12; m=7);** 730.6 (n=12; m=7); 774.6 (n=12; m=8); 818.7 (n=12; m=9); Found, %: C 56.25; H 10.0; N 2.02; P 3.65. Calculated, %: C 57.26; H 9.86; N 1.71; P 3.79. $C_{39}H_{80}NO_{14}P$.

Synthesis of *O*-2- [2- [2- [2- [2- [2- [2- [2- [2- (dodecyloxy) ethoxy] ethoxy] ethoxy] ethoxy] ethoxy] ethoxy] ethoxy] ethoxy] ethyl-*O*-ethyl- (N-morpholinyl) methylphosphonate 4c.

5 g (7 mmol) of phosphite **1c**, *0.9 g (9 mmol)* of 30% formalin solution and *0.7 g, (9 mmol)* of morpholine were poured into the flask. The reaction mixture was stirred at 80° C for 4 hours in an inert atmosphere of argon. Then the solution was evaporated for 1 h under vacuum (0.02 mmHg) at 60° C. In the residue, 5.2 g (88%) of the reaction products were obtained. Massspectrum (ESI), m/z (+1): The mainsignals of molecules with radicals ($C_nH_{2n+1}(OCH_2CH_2)_m$-); 600.6 (n=9; m=6); 644.6 (n=9; m=7); 686.6 (n=12; m=7); 730.6 (n=12; m=8); 774.6 (n=12; m=9); **818.7 (n=12; m=10);** 862.7 (n=12; m=11); 906.7 (n=12; m=12); Found, %: C 56.14; H 10.06; N2.1; P 3.67. Calculated, %: C 57.26; H 9.86; N 1.71; P 3.79. $C_{39}H_{80}NO_{14}P$. The structures of the compounds obtained were proved by ^{1}H, ^{31}P, ^{13}C, IR and mass spectroscopy.

Table 1. Physico-chemical characteristics of compounds 4a-c

No.	NMR $^{31}P\{^{1}H\}$	NMR ^{1}H PC$\underline{H}_2$N		NMR ^{1}H PC$\underline{H}_2$N			IR spectrum	
	δ_P, ppm	δ, ppm	$^2J_{PH}$, Hz	δ, ppm	$^1J_{PC}$, Hz	$^1J_{CH}$, Hz	ν P=O	δ POC
4a	23.84; 24.33; 24.79 (1:1.6:1)	3.46	10.6	48.67	189.27	134.6	1251	807
4b	23.9; 24.46; 24.93 (2 :2.8:1)	2.96	10.6	48.67	143.2	201	1250	806
4c	23.74; 24.24; 24.71 (1.7:2.4:1)	2.49; 2.53; 2.59	10.7	48.51	133.5	185.2	1249	807

Determination of the protective effect of the products was carried out on the IKK-1 research gravimetric complex, 2,49by the gravimetric method, which consists in determining the mass loss of metal samples during their stay in uninhibited and inhibited corrosive environments, on the IKK-1 research gravimetric complex. The standard model of oil field water of the following composition (g/dm^3) was used as the corrosive environment: NaCl – 163.0; CaCl$_2$ 2H$_2$O – 23.0; MgCl$_2$·6H$_2$O – 17.0; CaSO$_4$·2H$_2$O – 0.14 and content of CO$_2$ - 250 g/m^3, H$_2$S-200 g/m^3. Metal samples with dimensions of 25 × 20 × 1 mm were weighed on a laboratory analytical balance AND GR-202 with an accuracy of 0.01 mg. The stirring speed was 700 rpm. The reagent, before entering into a corrosive environment, was dissolved in 1 ml of isopropanol. At the end of the tests, the corrosion products from the samples were removed by holding the plates in an aqueous solution containing sulfuric acid 0.84%, ammonium citrate 1%, thiourea 0.1% for 15 seconds and washed with distilled water. Then the plates were kept in a desiccator with dehydrated calcium chloride for one hour and weighed.

According to the corrosion tests of the compounds obtained, the protective effect *Z* %, was calculated using the Equation 1:

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

Where Δm_1, Δm_2 is the mass loss of the sample after the test in non-inhibited and inhibited media, g.; Δm_3 is weight loss of the sample after as a result of treatment with an etching solution.

Anticorrosion studies by an electrochemical method were carried out on a P-45X potentiostat-galvanostat produced by Elins in a highly mineralized medium (corresponding to the model described above) with a CO$_2$ content of 250 g/m^3, H$_2$S - 20 g/m^3. The electrochemical method for determining the anticorrosion activity consists in obtaining polarization curves that transmit the relationship between the potential of the electrode under study and the current density during polarization from an external source of direct electric current, followed by an assessment of the protective ability of the inhibitor by current density in inhibited and non-inhibited media.

The electrochemical cell (V = 1 l) consisted of working electrodes (metal rods made of steel grade 3.30 mm long and 5 mm in diameter) of an auxiliary platinum electrode, silver chloride reference electrode, magnetic stirrer, a tube for passing carbon dioxide through a medium, a valve for removal of excess gas and temperature sensor.

Carbon dioxide was passed through the solution to obtain the desired concentration, and then the calculated amount of H$_2$S solution was added. The rotation speed of the stirrer was 300 rpm.

The density of the corrosion current, proportional to the corrosion rate of the metal was determined by extrapolating the Tafel section to the value of the corrosion potential on the polarization curves.

The protective effect was determined by the Equation 2:

$$Z = 100 * (1 - I_{coring}/I_{blank}) \tag{2}$$

Where: I_{coring} – Corrosion rate of metal with inhibitor, mA/cm^2; I_{blank} –Corrosion rate of metal with no inhibitor, mA/cm^2.

3. Results and Discussion

Collate As a result of the synthesis by the Kabachnik-Fields reaction, new **synthanol-*O*-ethyl- (*N*-morpholinyl) methylphosphonates 4a-c were synthesized**.

***O*- [2- (2-dodecylcyloxy) ethoxy] ethyl-*O*-ethyl phosphate 1a reacts** with formaldehyde and morpholine at 80°C without solvent for 4 hours to form the corresponding phosphonates **4a**. In the NMR^{31}P- {^{1}H} spectra of the reaction products, the signals of the phosphorus atom shift to weaker fields and appear at 23.84; 24.33; 24.79 ppm in the ratio of 1: 1.6: 1. The manifestation of such a large number of signals of the reaction products occurs due to the formation of a mixture of products. Since we used compounds with a total content of ethoxylated groups n = 2 as the starting phosphite. According to the ESI mass spectrum, it was found that the main aminophoanates contain, as a synthanol radical, $C_{12}H_{25}OCH_2CH_2$-(m/z=422.4); $C_{12}H_{25}(OCH_2CH_2)_2$-(m/z=446.5); $(C_{12}H_{25}(OCH_2CH_2)_3$-(m/z=510.5); $C_{12}H_{25}(OCH_2CH_2)_4$-(m/z =555.4); $(C_{12}H_{25}(OCH_2CH_2)_6$- (m/z + Na$^+$ =606.6) groups. Similarly, in the spectra NMR ^{31}P - {^{1}H}, the reaction products 4b and 4c signals of the phosphorus atom appear as three singlets 23.9; 24.46; 24.93 (2: 2.8: 1) and 23.74; 24.24; 24.71 (1.7: 2.4: 1) respectively. The presence of a doublet from methylene protons of the region δ = 3.46 ppm, with a constant of $^2J_{HP}$ = 10.6 Hz in the spectra NMR ^{1}H of products 4a, confirms the formation of a $PC\underline{H_2}N$ phosphonate bond. Signals of methylene protons from $POC\underline{H_2}$ groups of ethyl and synthanol radicals due to the presence of several compounds in the product appear as multiplets in the region δ = 4.10 - 4.25 ppm.

The signals of methylene protons CH_2OCH_2 of **the morpholinyl radical group** appear as a triplet δ = 2.61 with the characteristic constant $^3J_{HH}$ = 4.4 Hz. In the spectra NMR ^{13}C {^{1}H}, the carbon atom signals of the $PC\underline{H_2}N$ bond appear as a doublet with a characteristic constant $^1J_{PC}$ 189.27 in the region δ = 48.67, which in the spectra NMR ^{13}C are transformed into a doublet of triplets with characteristic constant $^1J_{CH}$ 134.6, $^1J_{PC}$ 189.27 Hz. In the IR spectra of compounds **4a-c** in the region of ν = 1117-1119 cm^{-1}, signals from the P = O groups appear. Elemental analysis of the compounds obtained is slightly different theoretical. In products **4a** carbon is more than 3% calculated, and agrees well with the data of the mass spectra, according to which the main content of the products obtained is shifted towards longer molecules compared to the theoretical one. In products **4b** and **4c**, the difference in elemental composition between the obtained and calculated calculations is insignificant, and is shifted towards obtaining lower molecular weight products than calculated ones. According to the mass spectra of **4b**, phosphonates containing syntanyl radicals are present $C_nH_{2n+1}(OCH_2CH_2)_m$, where n= 9.12; m=5-9 and **4c** $C_nH_{2n+1}(OCH_2CH_2)_m$, where n= 9.12; m=6-12.

All compounds are readily soluble in benzene, alcohols. **4a** is highly soluble in water, **4b** and **4c** are poorly soluble. Therefore, compounds for anticorrosion research were introduced in the form of solutions in isopropanol.

Data of gravimetric studies of compounds **4a-b** are presented in Table 1. **4a** and **4b** exhibits a maximum protective effect after 6 hours of exposure (82.3 and 80.9%). In contrast to **4a,b**, compound **4c** after 6 hours of exposure exhibits the least activity (73.2%). This is due to the slow adsorption of the inhibitor on the metal surface. In our case, the smaller the molecule, the faster the protective film is formed.

Further, with increasing exposure time, the protective effect of compounds **4a, 4b** decreases. The inhibitor activity for **4a** drops by 20%, the decrease for **4b** is insignificant (4%). During this time, a dense adsorption layer is formed on the metal surface. Further, the activity of the inhibitor smoothly decreases. This may be due to a decrease in the concentration of the inhibitor in the solution when the inhibitor molecules interact with iron ions, adsorption of the inhibitor on the walls and details of the cell, or a change in the adsorption-desorption equilibrium. It should be noted that during long-term experiments, black precipitate of iron corrosion products transferred by the flow of corrosive medium from the sample surface to the solution begins to appear in the solution. Loose sediment particles, representing a mixture of varying composition of carbonates and iron sulfides, can adsorb inhibitor molecules and reduce their concentration in solution, which leads to a decrease in the protective effect.

The anticorrosive activity of compound **4c** slowly increases with increasing time from 73.2% (at 6 hours) to 76.2 (72 hours). This is due to the slow adsorption of the inhibitor and the formation of a stable protective layer, due to the presence of an inhibitor in the long radical in the molecule.

With an increase in the concentration of inhibitors at 24 h exposure, an increase in the protective effect is observed in all cases. Already at 10 mg/l, the protective effect of inhibitors is above 50. The greatest protective effect appears at 100 mg/l of compound 4c (89.6%), which is comparable to the indices of industrial inhibitors. For example, INCORGAZ-01ON and INCORGAZ-11ON exhibits a protective effect of 82-88% under similar conditions [26]. Inhibitors representing the product of the interaction of N'N-tetramethyl diaminomethane and alkenyl chlorides exhibit a protective effect of 89–91% [27], mixtures of imidazolines and amidoamines exhibit a protective effect of 85–99% [28], Sulfadoxine – Pyrimethamine show a protective effect of 75–77% [29].

Table 2. The protective effect of the composition 4a-c in a mineralized medium with CO_2 content of CO_2 - 250 g/m³, H2S - 200 g/m³

Time, h	Dosage, mg / l	Protective effect, Z, %		
		4a	4b	4c
6	25	82.3	80.9	73.2
24	10	56.4	71.1	72.9
24	25	64.3	76.8	76.3
24	50	75.8	79.3	81.3
24	100	81.4	86.2	89.6
72	25	65.8	78.4	76.2

The dependence of the inhibitory activity of the composition **4a-c** on the concentration of the inhibitor at 40° C by the electrochemical method was investigated. Figure 2 shows a graph of the polarization resistance for different concentrations of the **4d** inhibitor.
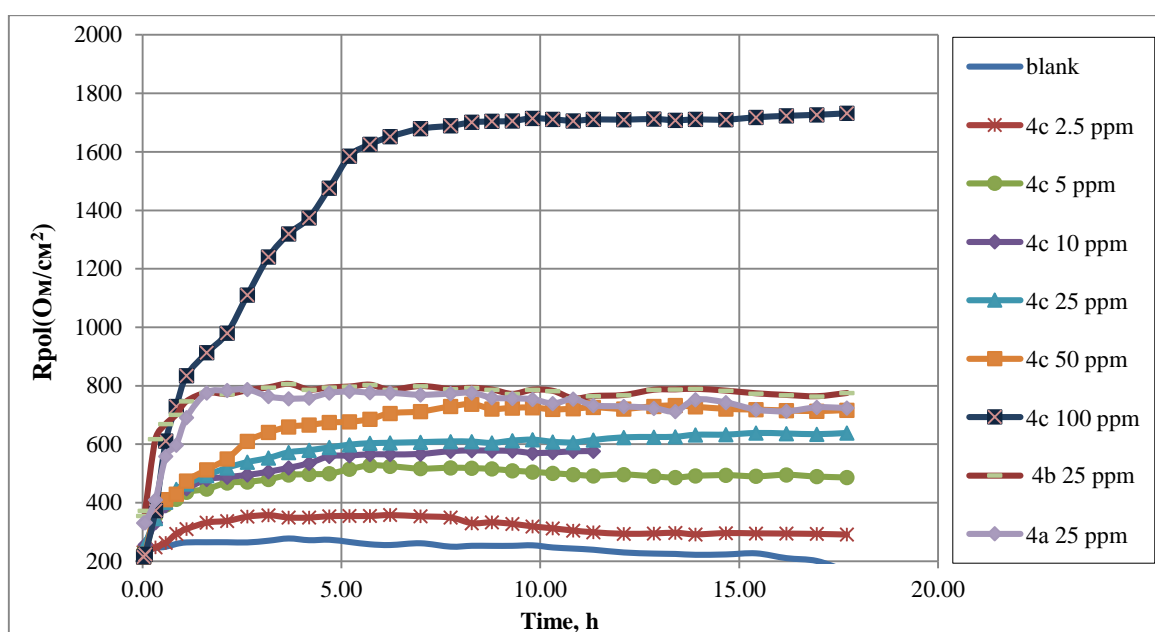

Figure 1. Dynamics of changes in polarization resistance for different concentrations of inhibitor 4c and 25 mg/l 4a, b at 40°C

According to the graph, it can be noted that the curves reach a maximum after 8-9 hours from the start of the inhibitor injection, that is, the full activity of the inhibitor is manifested after 8-9 hours, which then persists.

Table 3. The protective effect of the composition 4a-c at various dosages

Compound	T (ºC)	C (ppm)	E_{cor} (mV)	b_a mV/dec	$-b_c$ mV/dec	LPR Ohmcm²	$I_{cor}^{(LPR)}$ µA/cm⁻²	IE^{LPR} (%)
4a	40	25	-538	54	210	723	25,8	74,5
4b	40	25	-533	56	217	776	24,9	75.4
4c	40	100	-527	71	242	1732	13.8	86.4
4c	40	50	-536	69	219	756	30.2	70.16
4c	40	25	-537	69	182	675	32.7	67.68
4c	40	10	-540	70	167	576	37.1	63.29
4c	40	5	-545	67	162	505	40.8	59.7
4c	40	2.5	- 582	52	206	354	50.8	49.3
4c	40	0	-569	43	142	165	101.2	-

Composition **4c** at a low dosage of 2.5 ppm exhibits inhibitory activity of about 50%. With increasing dosage, the

protective effect slowly increases, reaching 86.4% at 100 mg / l, which is comparable with the results of gravimetric analysis.

At a dosage of 25 ppm, the protective effect of compound **4c** (67.68%) is inferior to **4a** and **4b** (74.5% and 75.4%), but according to Figure 1, an increase in polarization resistance is observed with time and suggests that they will become equal over time.

4. Conclusion

As a result of the conducted research, three new complexes of syntanyl-O-ethyl- (N-morpholinyl) methylphosphonate were synthesized, containing ethoxylated dodecyl alcohol with ethoxylation number for 4a 1-5, for 4b 5-8, for 4c 6-12 as a syntanyl group. The compounds obtained possess high anticorrosion activity in model environments of formation water containing CO_2 and H_2S. As a result of gravimetric tests, it was revealed that the protective effect of the inhibitors depends on the degree of oxidation of the syntanyl radical. Low degree of oxyethylation contribute to a high protective effect with a short holding time. Further, with increasing time, a significant decrease in anti-corrosion activity is observed. With a high degree of oxyethylation, the protective effect increases with time, remains stable for 72 hours. With an increase in the dosage of the inhibitor, the protective effect increases. According to the data of electrochemical tests, inhibitors have been established to reach the peak of activity 8–9 hours after the inhibitor has been injected. The protective effect of 50% is achieved already at a dosage of 2.5 ppm. At 25 ppm of 4a-c inhibitors, the protective effect is 64.38 - 82.3% for different duration of the experiment. Composition 4c was found to exhibit the greatest inhibitory activity of 89.6% at a dosage of 100 mg /l at 24 hours exposure.

5. Funding

6. Acknowledgements

7. Conflicts of Interest

The authors declare no conflict of interest.

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