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Nitrogen-containing inhibitors and their link to their protective mechanism with molecular structure

Abstract: A potentiometric method was employed to determine the protective effects of the investigated heterofunctional organic compounds, which are potential inhibitors of corrosion of steel, by hydrogen sulfide. According to the results of potentiometric measurements, the most effective of the studied substances can be classified as film-forming inhibitors of mixed effect with anodic predominance. The analysis of the change of the inhibitory properties of aminodiesters was carried out to explain the connection of the protective effect of the inhibitors with their molecular structure. It was based on the principle of linearity of free energy. It was found that the most effective aminodiesters are characterized by the high hydrophobicity and electron-deficient property of the substituents. The article presents an explanation of the difference of the protective effects of the studied compounds based on their molecular structure and the nature of the corrosive environment. The obtained results can be used when synthesizing organic compounds with high inhibitory efficiency.

Key words: Steel, Corrosion, Protective effect, Adsorption, Hydrogen sulfide inhibitor, Molecular structure, Hydrophobicity

Introduction

The material, economical and particularly losses from corrosion during extraction, storage, transportation and refining of oil. The equipment of oil wells and systems of oil and gas collection of numerous fields are intensely corroding as a result of rising from the layers of great amounts of corrosive and highly mineralized waters, which include in composition sodium, calcium, magnesium chlorides. Corrosive activity of layer waters is high due to the presence in them of carbonic acid, hydrogen sulfide, oxygen.

For the Republic of Kazakhstan, which is in possession of gigantic hydrocarbon resources the problem of anticorrosive defence of oil field industry is very topical. Great problems, posed before the workers of oil and gas industry for the further increase of volumes of production of oil and gas make it necessary the further increase of reliability and longevity of production equipment. Related to the development of oil fields of Western Kazakhstan containing in their products the high concentration of hydrogen sulfide, the corrosion of oilprocessing and mining equipment increases. Application of inhibitors during mining and transportation of oil and gas in the Republic of Kazakhstan is constrained by the deficit of domestic inhibitors of corrosion. Thus, the development of new highly effective inhibitors of hydrogen sulfide corrosion of steel is important problem of oil industry.

Dominant part of inhibitors of hydrogen sulfide corrosion, used for the protection of metallic equipment of oilgas complex represents the organic nitrogen containing compounds, in particular, amines and their derivatives. Their protective action is explained by the fact, that in the environment of hydrogen sulfide the adsorption of HS^{-1} ions is observed on the surface of the metal. These ions (HS^{-}) form the dipoles, negatively charged ends of which are directed towards the side of corrosive environment, which contributes to the adsorption of inhibitors of cationic type [1]. The strength of bond of inhibitor with the surface in the first approximation is determined by its adsorption properties (affinity of functional group twoards the surface, which being protected, and its surface activity). The necessary condition of the efficiency of inhibitors of hydrogen sulfide corrosion is their ability for donor-acceptor chemosorption, hydrophobicity and high surface activity.

The problem of relationships between the structure of inhibiting additives and their protective action have been discussed in literature for relatively long time. V.P. Grigoriev and V.V. Ekilik wrote remarkable monograph [2], where the link is considered between the chemical structure of organic surfactants

(SAS) with their inhibiting action on corrosion, hydrogenation of metals and other electrochemical processes. From the review of studies it is apparent, that there is no unique form of relationship. At present time in the question of link between the structure of SAS and their inhibiting action the dominating is the activation-blocking mechanism of action of inhibitors. Under this the main factors during selection of inhibitors are electronic density on adsorption center of molecule and its dipole moment. Structural factors causing the change of electron density on adsorption-active regions of molecule of organic compounds affect the protective properties. Introduction of electron-donor substituents (R) increases protective effect of aromatic and heterocyclic compounds. The presence of branched hydrocarbon chains near the functional group, center of adsorption decreases the efficiency of inhibitor. This is caused by the decrease of adhesion and difficulties in orientation of molecules during adsorption. Introduction into the molecule of inhibitor of aromatic cycles, as a rule, increases inhibiting effect, while benzene radicals, contributing to the formation of more dense protective layer, act more efficiently than phenolic. The substitution of simple bond by unsaturated, and also the increase of the number of last improves the adsorption of organic compounds on metals.

Triple bond from the viewpoint of adsorption is more effective than double bond, while the maximal effect is exhibited by the compounds with the end triple bond. High mobility of electronic cloud of multiple bonds makes them extremely reactive.

And, when in the result of occurrence of various chemical reactions with indicated compounds in the conditions of corrosion the products are formed contributing the main input into the inhibition of the process, the secondary inhibition takes place.

Great value is attributed to the interaction of inhibitors of corrosion due to P-electrons with the surface of metals. Among the compounds with double bonds the most effective molecules are with conjugated and aromatic systems. Such compounds are being held on the surface both due to the adsorption bond «nitrogen-metal», and P-electron interaction. Corrosion process is a very complex phenomenon, because the complication of molecules of inhibitor and the change of external condition may lead to observation of deviation from the regularities indicated above. Besides, during investigation of the effect of structure of the inhibitor on its protective properties the account of the charge of the metal is needed and its nature. Thus, for example, very often the strengthening of the adsorption bond «metal-inhibitor» with the formation of surface complexes contributes to the growth of the protection from the corrosion. But, if the strength of the bond «metal-inhibitor» approaches corresponding bond of individual compound, then the decomposition of the metal lattice occurs. As a result, inhibiting effect gets transformed to the stimulating effect.

It must be noted, that the account of simultaneous effect of various structural factors and electronic effects of the molecule on the dissolution of the metal is a very complex problem. Hence the degree of protection from corrosion is determined mainly by blocking and hydrophobisation of the metal surface by adsorbed molecules of inhibitor.

Some regularities of protective effect of inhibitors of corrosion may be explained by the presence of specific interaction «metal-inhibitor». During consideration of questions of inhibiting protection of metals it is usefull to apply the electronic conceptions of heterogeneour catalysis about chemosorptive ability of metals. According to these conceptions it is possible to expect the high protective effect, which is due to chemosorption for primarily transition metals. It is shown, that metals with completed d-levels hold on their surface the molecules of inhibitor primarily due to the forces of purely physical adsorption. Metals with incompleted d-level are characterized by the presence of notable specific adsorption. Formation of surface complexes has proven in the row of cases by spectral, crystallochemical and radiochemical measurements.

The main qualitative relationships between chemical structure and inhibiting effect of surface-active substances are presented above. The methods exist for quantitative account of the effect of chemical structure on inhibiting action of SAS. The attempts are presented in literature of utilization for these purposes of the ability of additives to change the value of certain factors influencing the occurrence of corrosive process.

Such factors were electric resistance on the boundary corroding metal — solution, the value of the potential of the corroding metal, the change of effective energy of activation of corrosive process. But the analysis of numerous experimental data shows, that there is no unique linked between these characteristics of corrosive process and inhibiting effect. Of significant interest is the comparison of data on adsorption of SAS and their effect on corrosion of metals. For the qualitative and quantitative assessment of adsorption of SAS on solid electrodes in comparison with their inhibiting action the great abundance was achieved by the method of measurement of differential capacity.

It must be noted that in contrast from the earlier works, when at the foundation of choice of inhibitors of corrosion was almost strictly empirical method, the number of research studies increases, where for the quantitative assessment of the effect of the structure of compounds on their inhibiting action the correlation analysis was used base on the principle of linearity of free energies (LFE principle) [3].

LFE principle of the reaction and activation found wide applications during interpretation of the effect of the nature of surface-active substances on the efficiency of their defensive action in acidic and neutral environments [4-6].

At present is may be considered proven the applicability of the principle of LFE for numerous electrochemical processes with participation of organic substances [7, 8].

During investigation of the mechanism of action of inhibitors of corrosion the link is important between electronic structure, physical-chemical properties and protective efficiency of compounds. This leads to possible interpretation and prognosis of anticorrosive properties based on molecular-mechanical and quantum-chemical investigations of the structure of molecules of inhibitors. For the solution of the problem “structure of inhibitor- anticorrosive efficiency”, along with the widely used principle of linearity of free energies, the principle of “rigid” and “soft” acids and based (RSKB) may be used [9-11]. In works [12, 13] for the description of the process of inhibition of corrosion of metals the scheme of quantitative assessment of parameters “rigidity” based on the energies of highest occupied molecular orbitals (HOMO) and lowest unoccupied (LUMO).

In work [14] the possibility of inhibition of hydrogen sulfide corrosion of steel by quaternary ammonium salts (QAS), synthesized from amines and aminoalcohols with various substituents R_i according to their reaction with benzene chloride. The main problem of this work was the investigation of the effect of chemical structure of QAS on their protective properties. It is noted, that efficiency of the protection of steels from corrosion with the help of QAS depends on their chemical structure, while hydrophobicity of inhibitor is the dominating factor. But the adequacy of description of protective properties increases under additional account of polar properties of substituents.

At present time there is no unique opinion related to the nature of the link of polar groups of organic inhibitors with protective metal. Definitely, the active participant in the process of adsorption is the polar end of molecule. It must be noted, that the formed surface compounds during chemosorption do not get released in the form of a new phase. The majority of organic inhibitors in acidic environments form with surface ions of the metal insoluble complex compounds. That is why the primary process during the action of numerous efficient inhibitors is the formation on the surface of the metal of protective film, representing the product of interaction between the metal, inhibitor and ions of corrosive active environment. The most important factor, determining the strong bond of inhibitor and the protected metal is the electronic density of the main metal of inhibitor, i.e. The number of free electrons, which it can spend on coordination bond. This condition is completely met of the nitrogen atom, which easily forms the coordination bond with metal.

Materials and methods

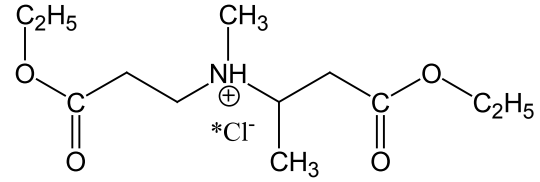
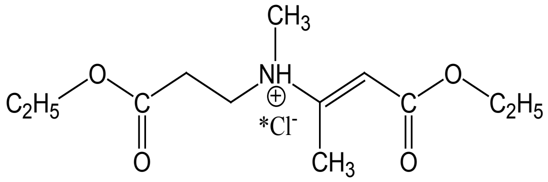
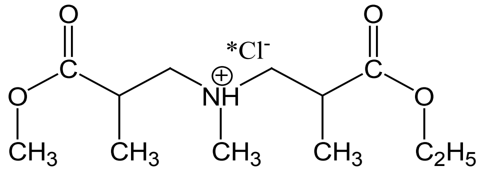
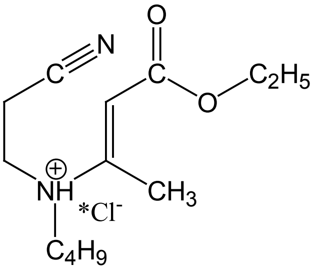
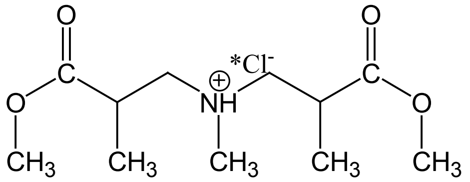
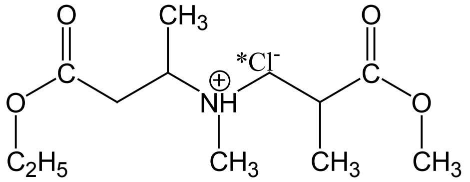
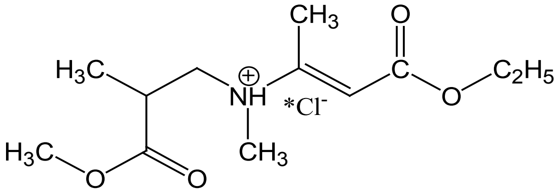
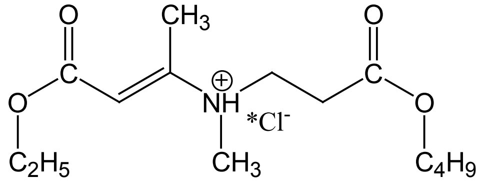
Objects of investigation in present work — nitrogen and oxygen containing organic compounds, synthesized on the basis of available raw materials and simple technology, which are the intermediate products of synthesis of new biologically active substances (table 1).

For the experimental determination of the rate of corrosion of steel electrode, the three-electrode cell was used with steel working electrode, platinum auxiliary electrode and silver-chloride comparative electrode. Polarization curves were images using potentiostat-galvanostat «PGSTAT30» (AUTOLAB, Netherlands, 2001).

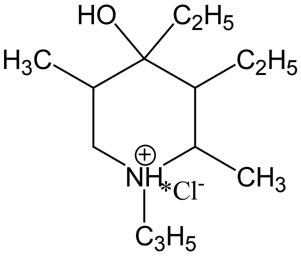
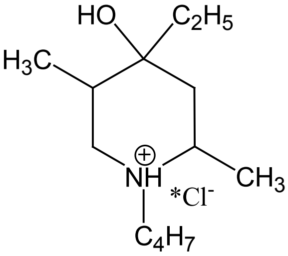
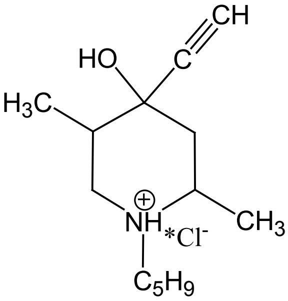
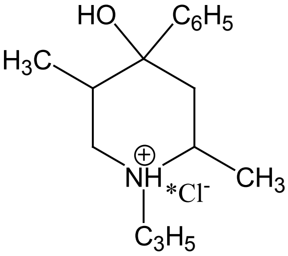
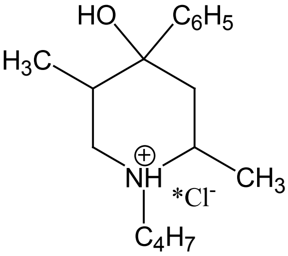
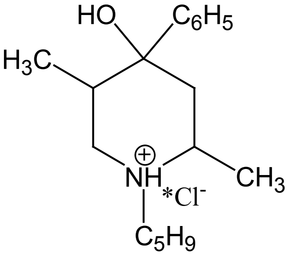
The working electrode was the rotating disk steel electrode. The background solution was the corrosive model environment (NACE), representing a 3% solution of sodium chloride, saturated H_2S (0,8g/l). For the saturation of the solutions of sodium sulfide was used. The concentration of hydrogen sulfide was controlled by iodometric method of back titration. The variation of concentrations of potential inhibitors of corrosion was carried out by the method of additives.

The preparation of the surface of working electrode before the imaging of polarization curves was carried out by mechanical technique. The surface of electrode was cleaned by micron abrasive material until the stage of smooth surface, was degreased by alcohol and washed by distilled water. The processing of surface of working electrode was carried out before every measurement.

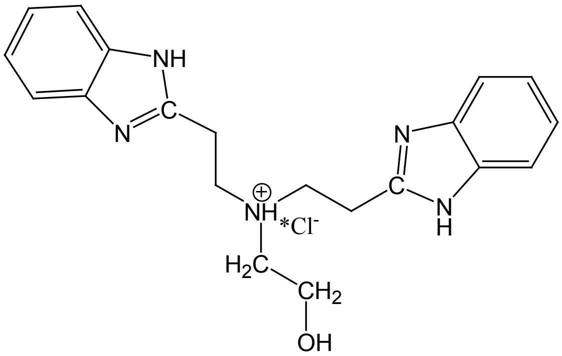
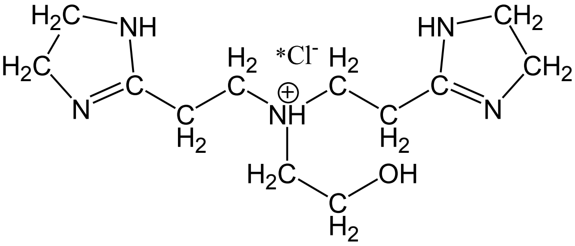
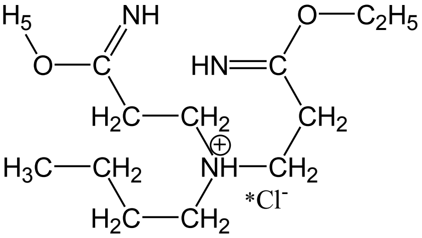
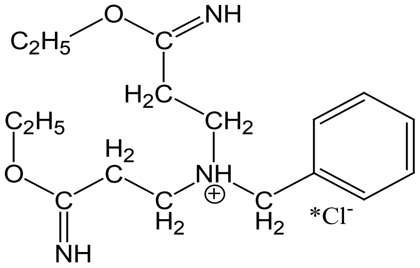
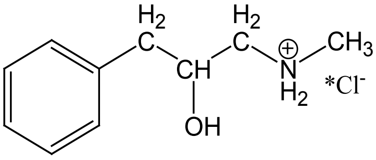
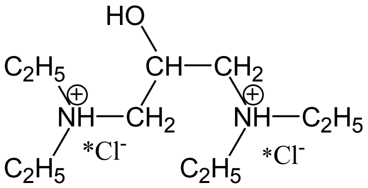
Table 1 – Structural formulae and names of investigated compounds

N	Structural formula	Title
1		N-(1-methyl-2-carboethoxyethyl)- N-(2-carboethoxyethyl)- methylamine hydrochloride
2		N-(1-methyl-2-carboethoxythene)- N-(2-carboethoxyethyl) methylamine hydrochloride
3		N-(2-methyl-2-carbomethylethoxyethyl)-(2-methyl-2-carboethoxyethyl)methylamine hydrochloride
4		N-(1-methyl-2-carboethoxyethene)- N-(2-cyanethyl)buthylamine hydrochloride
5		N,N -bis(2-methyl- 2-methoxyethyl)-methylamine hydrochloride
6		N -(2-methyl-2-carbomethoxyethyl)- N-(1-methyl-2-carboethoxy)-methylamine hydrochloride
7		N -methyl-(2-carbmethoxyethyl)-(1-methyl-2-carboethoxyethene) methylamine hydrochloride
8		N-(1-methyl-2-carboethoxyethene)- N-(2-carbobutoxyethyl)methylamine hydrochloride

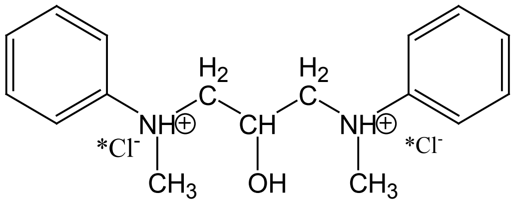
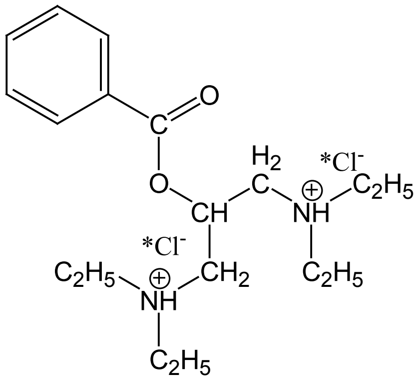
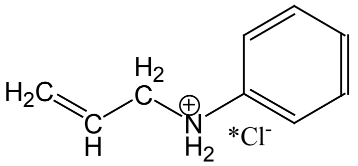
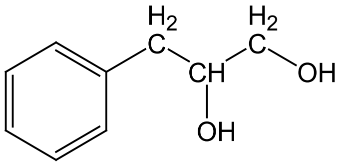
Continued table 1

N	Structural formula	Title
9		N- propenyl-2,5-dimethyl-4-ethylpiperidine-4-ol hydrochloride
10		N-(butene-2-yl)-2,5-dimethyl-4-ethylpiperiine-4-ol hydrochloride
11		N-(3-methylbutene-2-yl)-2,5-dimethyl-4-ethynylpiperidine-4-ol hydrochloride
12		N-allyl-2,5-dimethyl-4-phenylpiperidine-4-ol
13		N-butenyl-2,5-dimethyl-4-phenylpiperidine-4-ol hydrochloride
14		N-(3-methylbutene-2-yl)-2,5-dimethyl-4-phenyl-piperidine-4-ol hydrochloride

Continued table 1

N	Structural formula	Title
15		N, N-bis-[β, β`-ethyl-2-benzylimidazolyl]-2-hydroxyethylamine hydrochloride
16		N, N-bis-[β, β`-imidazolylethyl]-2-hydroxyethylamin hydrochloride
17		N, N-bis-(3-imino-3-ethoxypropyl)-N-butylamine hydrochloride
18		N, N-bis-(3-imino-3-ethoxypropyl)-N-benzylamine hydrochloride
19		1-phenyl-3-methylaminoisopropanole hydrochloride
20		1,3-bis-(diethylamino)isopropanol hydrochloride

Continued table 1

N	Structural formula	Title
21		1,3-bis-(N-methyl- N-phenyl)-isopropanol dihydrochloride
22		bensoate 1,3-bis-(diethylamino)-isopropanol dihydrochloride
23		N-allylaniline hydrochloride
24		3-phenyl-1,2-propandiole

Electrodes were placed into electrochemical cell with investigated medium and connected to the instrument. Polarization measurements were started after stabilization of stationary potential of corrosion. Obtained potentiodynamic curves were processed using Microcalc Origin program, which allowed determining the values of the rates of corrosion of steel electrode in various inhibited and non-inhibited environments [15].

Results and their discussion

Usually, the polarization curves that characterize the partial corrosion processes are presented in the form of semi-logarithmic dependence.

Polarization curves were obtained for all the above inhibitors at different concentrations in a corrosive environment. Figures 1-4 show the potentiodynamic curves for compounds 4, 8, 19, 21. Because of the large number of studied inhibitors, polarization curves are shown only for some of the substances. The selection of these inhibitors by the need to reflect the relationship of protective properties of the compounds with the values of corrosion currents observed at different concentrations of additives in a corrosive environment.

Based on potentiodynamic measurements the protective effects were computed of the investigated substances under corrosion of steel in the sodium chloride and chloride environment, saturated by hydrogen sulfide (tables 2 and 3). An important feature of the electrochemical reactions is the equivalence of their speed and the current density. This equivalence follows from Faraday's law. Protection efficiency is expressed by the degree of protection Z, which indicates how full to suppress the corrosion due to the use of a method:

$$Z = \left[(i_0 - i) / i_0 \right] * 100\%$$

where i_0 – corrosion current density of metal in the solution without inhibitor; i – current density of corrosion in solution in the presence of the inhibitor.

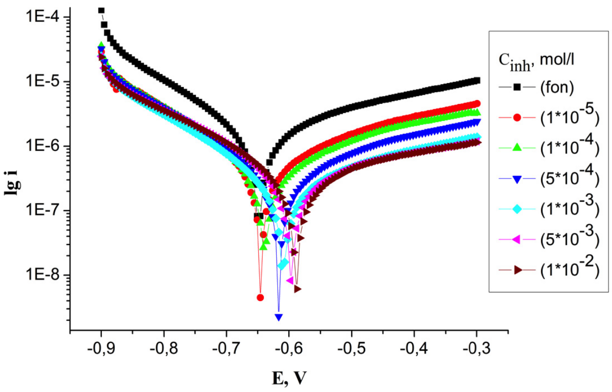


Figure 1 – Potentiodynamic curves of St3 in the solution of 3% NaCl + 0.8 g/l H_2S (pH = 5) with addition of inhibitor 8

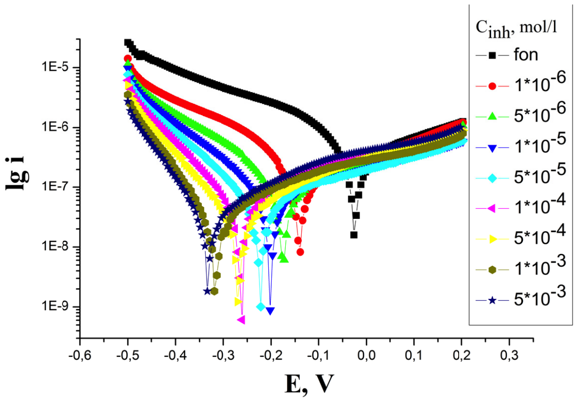


Figure 2 – Potentiodynamic curves of St3 in the solution of 3% NaCl with addition of inhibitor 4

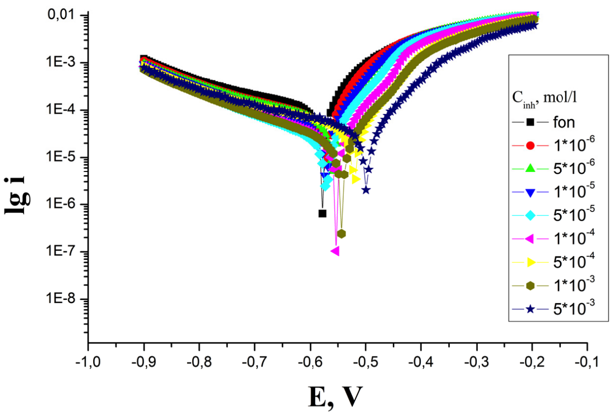


Figure 3 – Potentiodynamic curves of St3 in the solution of 3% NaCl + 0.8 g/l H_2S (pH = 5) with addition of inhibitor 19

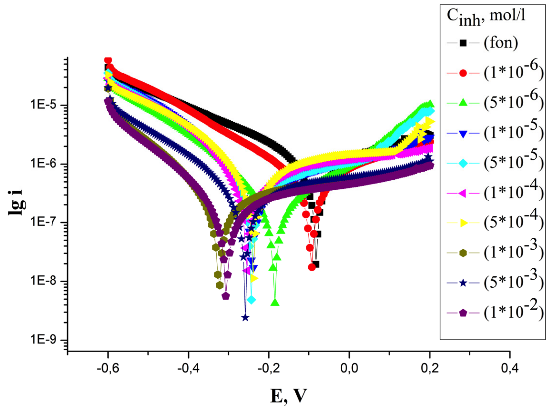


Figure 4 – Potentiodynamic curves of St3 in the solution of 3% NaCl with addition of inhibitor 21

Table 2 – Protective action of organic compounds (C=1*10^{-2} mol/l) in 3% solution NaCl

Inhibitor	Z_k ,%	Z_a, %	Inhibitor	Z_k ,%	Z_a, %	Inhibitor	Z_k ,%	Z_a, %
1	64.2	68.2	9	81.3	86.7	17	42.3	62.7
2	87.7	71.3	10	91.2	94.8	18	0	0
3	76.1	67.8	11	59.5	56.6	19	15.9	10.9
4	90.3	88.2	12	72.1	71.1	20	36.4	36.1
5	71.2	65.5	13	57.8	52.2	21	50.1	58.7
6	67.5	61.2	14	0	0	22	52.8	42.6
7	79.1	75.4	15	50.8	55.6	23	21.6	54.2
8	91.2	87.4	16	0	0	24	52.4	62.6

The presence of hydrogen sulfide in a corrosive environment increases the adsorption and, consequently, the protective ability of cationic inhibitors. Strengthening the protection of steel by organic cations is largely due to the fact that the specific adsorption of HS^- is recharge the surface facilitating the interaction with surface and cations, which creates an energy barrier (due to changes ψ_1-potential) and blocks the surface. In the sodium chloride medium, the additions of inhibitors cause displacement of the stationary potential of steel electrode in the cathode area and preferential inhibition of the cathodic process of discharge of hydrogen ion on the metal.

Accordingly, in a solution of sodium chloride cathodic protective effect of inhibitors are slightly higher. Apparently, at the cathodic areas of surface of the steel electrode take place the adsorption of cation-active inhibitors, which slow down the cathodic reaction. This is explained by a better adsorption of the tested inhibitors in comparison with the specific adsorption of chloride ions.

Table 3 – Protective action of organic substances (C=1*10^{-2} mol/l) in 3% solution NaCl + 0.8g/l H_2S

Inhibitor	Z_k ,%	Z_a, %	Inhibitor	Z_k ,%	Z_a, %	Inhibitor	Z_k ,%	Z_a, %
1	63.1	81.7	9	61.2	63.4	17	82.9	85.6
2	45.3	97.1	10	30.6	51.2	18	44.1	62.2
3	67.3	88.6	11	12.9	85.1	19	79.5	85.9
4	95.8	98.3	12	54.7	28.3	20	75.9	74.9
5	74.1	74.4	13	49.6	83.2	21	82.5	88.1
6	67.3	88.6	14	77.2	78.9	22	62.1	72.1
7	83.5	92.4	15	77.4	96.9	23	72.6	58.5
8	97.8	94.9	16	78.1	79.3	24	61.2	66.3

Most of the investigated compounds showing weaker protective properties in a sodium chloride medium. This is probably explained by lower adsorption of chloride ions in comparison with the hydrosulfide ions, i.e. “The effect of overcharges” in the hydrogen sulfide-containing medium is significantly higher than in the chloride medium.

According to the results of potentiodynamic measurements, the compounds investigated by us can be attributed to film-forming inhibitors. In contrast to the passive films, the defensive films are formed in the result of such interaction of inhibitor with metal or products of corrosion of metal, during which the material of the film contains either the molecules of inhibitor itself, or functional groups, cations or anions of inhibitor. Film-forming inhibitors exhibit the mixed character of protective action, i.e. form the films both on cathode and anode sections. Such inhibitors include the compounds investigated in our work. They may be attributed to the inhibitors with mixed anode-cathode control, but with domination of anodic. This is evidenced by the results of our potentiodynamic studies. In favor of the formation of protective films, say also a very small concentration of these compounds, leading to considerable lowering of the rate of corrosion.

There exist various approaches during consideration of the problem «structure – inhibiting action». The majority of experimental data on the link between the structure and inhibiting properties of SAS is possible based on assessment of electronic density on adsorption-active heteroatom. During this, the main criteria must be the electronic density and its dipole moment. However, in case of complex compounds, which are presented in this work, the account of simultaneous effect of various structural factors and electronic effects of molecule is very difficult.

Electronic density on adsorption center of molecule determines the donor function of molecule of inhibitor and, consequently, its surface activity. Introduction of substituents into the SAS molecule affects the electron density of adsorption center. To account the donor-acceptor properties of substituents σ^* – Taft constants are used, which reflect the inductive influence of substituent on reactive center of organic compound [16]. For R–CH_3 $\sigma^*=0$, i.e. methyl group — standard substituent. More electro-donor substituents, than metal are characterized by $\sigma^*<0$, and electro acceptor $\sigma^*>0$.

Molecules of inhibitor may be adsorbed on the surface of corroding metal, both by polar part, and lipophilic part, and also hydrophobic end. During description of physical-chemical interactions of inhibitor with metal hydrophobicity must be taken into account along with main parameters of molecules, polar and steric. Analysis of correlation «structure-property» for primary, secondary and tertiary amines evidences about the presence of quite clear dependence of protective effect on hydrophobicity coefficient. Hydrophobicity of organic compounds in various chemical and biochemical processes have been estimated for a long time by coefficient of their distribution (D) in the system composed of two immiscible liquids, for instance, octanol-water, or sum of constants of Rikker, computed using these coefficients of distribution. Constants of Rikker are known for the majority of fragments of molecules and reflect their relative hydrophobicity in comparison with hydrogen atom. Constant f is positive for hydrophobic and negative for hydrophilic substituent.

In our work the analysis is carried out of correlation of protective properties of the row of aminodiethers with their chemical structure based on the above described principle of linearity of free energies using f – constants of hydrophobicity and σ – Taft constants, taking into account the polar properties of substituents [17].

During analysis of presented in table 4 results with protective action of aminodiesters it can be seen, that the most effective are characterized by the highest hydrophobicity and more electron-acceptor properties of substituents, which is in accordance with peculiarities of hydrogen sulfide corrosion of steel.

Table 4 – Total hydrophobicity (∑f) and inductive effect (∑σ) of substituents in molecules of aminodiesters

Compound	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
∑σ	1.3	1.8	1.4	2.3	1.4	1.4	1.8	1.7
∑f	3.1	2.7	3.0	3.4	2.4	2.8	2.6	3.8

The investigated compounds may be separated into three groups. The first group (compounds 1-8) – these are the aminodiesters, the protective action of which is due to the presence of several reactive centers. Compounds 1, 3, 5, 6 have practically similar structure, composition and equal «concentration» of carbonyl and ether oxygen, which determines their similar efficiency. Compounds 2 and 7 are in possession of higher activity, which is due to the presence in their structure of C=C double bond, which leads to the increase of adsorption. Increase of adsorption during this leads to the increase of efficiency of inhibitor. Aminodiesters 4 and 8 are distinct from others relative by structure and composition compounds by the presence of cyanide group (inhibitor 4) and long hydrocarbon radical C_4H_9, which ensures high protective properties of these molecules.

Nitryl group possesses the high electron density of triple bond, which is characterized by a more strong electronegative inductive effect (Taft constant $\sigma = 3.38$). Besides, the long chain hydrophobic radical C_4H_9, oriented perpendicularly to the surface, creates the shielding protective layer and contributes to the strengthening of inhibiting activity of compounds 4 and 8. Increase of surface activity is related to the growth of hydrophobicity of molecules, more hydrophobic molecules are easily squeezed out from the volume of aqueous solution.

The second group – compounds 9-14 has similarities in chemical structure, namely, all of them contain heterocycle, which includes nitrogen heteroatom, existing in the state of sp^3 hybridization, due to which the nitrogen atom has unshared pair of ē able to enter the donor-acceptor interaction with hydrogen cations and metal surface. But the presence of hydrocarbon radical at nitrogen atom producing funnel-like rotational motion around the singular axes N-C, effectively shields the pair of electrons of nitrogen, which leads to the considerable decrease of adsorption properties of inhibitor molecule. In case of acidic environment, positively charged hydrogen — nitrogen center is also shielded by these radicals. Thus, the presence in molecules of heterocycles 9-14 of voluminous organic radical at nitrogen atom practically eliminates their ability to act in the quality of effective inhibitor of corrosion. It must be noted, that inhibitor 11, contains acetylenic bond, which is composed of hydrogen atom of end carbon atom, possessing acidic properties, i.e. having positive charge and allowing a nonsmall anodic protective effect of this compound. Inhibitors 12, 13, 14, are having in their composition phenyl group, possessing the high electronic density, exhibit particular activity. Electronic interaction due to the pi-electronic system of aromatic radical with incomplete d-levels of iron strengthen both adsorptive ability and input of shielding effect into the total protective effect.

The third group is the derivatives of aminodiesters and aminoalcohols. Compounds 17 and 18 contain in their composition -O-C=NH group. Nitrogen and oxygen of this group do not exhibit donor properties. Donor ability of unshared electronic pair of nitrogen atoms in these molecules is lowered. The reason is in the double bond C=N and oxygen atom, pulling the electronic density from nitrogen atom, which explains not considerably high protective properties. Active in all of these large molecules are only nitrogen atoms N*, possessing donor properties.

Relatively high protective properties are exhibited by compounds 21 and 22, which is due to the presence in the molecule of sp3-hybrid two atoms of nitrogen containing the unshared pairs of electrons and phenyl radicals. The presence of hydroxyl groups in compounds 19, 20 increases their hydrophilicity and lowers their inhibiting activity. Weak protective properties of substance 23 are due to the fact, that the pair of electrons of nitrogen to higher degree compared to other compounds exists in conjugation with benzene ring.

Inhibiting properties of compounds 15, 16 are not considerably high due to the weak donor activity of nitrogen atoms, entering the 5-member cycle, and also the presence of hydroxyl groups. In both inhibitors the actual active nitrogen atom is N*, entering the interaction with metal surface.

Inhibitor 24 does not possess protective properties, because it doesn't contain nitrogen atom, besides, the presence in its molecules of two hydroxyl groups having alcoholic character, makes them very hydrophilic. This compound exhibits non-high activity in the solution of sodium chloride. This, apparently, is related to the fact, that chloride ions possess the smallest adsorption ability, rather than hydrosulfide ions, which allows the presence of competing adsorption of organic molecules.

The major part of compounds of third group contains from 2 to more atoms of nitrogen. Usually the increase in the molecule of the number of nitrogen atoms, leads to the increase of efficiency of inhibition, because they bind the molecule with high number of surface atoms of iron. Besides, the molecules containing no less than 2 atoms of nitrogen, during interaction with charged surface of metal must exhibit the tendency towards the planar location. But this is true for flat configurations. In our compounds, having the complex structure the account of effect of various substituents on reactive centers of molecules is necessary, i.e. on electronic density of adsorption center, which determines the donor function of molecule of inhibitor and, consequently, its surface activity.

In inhibition of corrosion a substantial role is played by protonated and unprotonated molecules. The higher the negative charge on nitrogen atom of reactive center and higher the positive charge on hydrogens in protonated form, the better they will inhibit the corrosion due to the formation of strong coordination and hydrogen bonds with metallic surface.

In hydrogen sulfide containing environment the surface of the steel is charged negatively due to the specific adsorption of sulfide and hydrosulfide ions. Adsorption of HS- is proven by the method of radioactive measurements. Thus, electron acceptor properties of substituent groups increase the effective positive charge on reactive center – organic cation and increase it electrostatic interaction with the surface of steel, which is charged negatively due to the specific adsorption of sulfide- and hydrosulfide- ions.

Great part of studied substances exhibit more weaker protective properties in the sodium chloride medium. This, apparently, is explained by lower adsorption of chloride ions in comparison with hydrosulfide ions, i.e. «effect of recharge» in hydrogen sulfide environment, is considerably higher, then in chloride.

The link is established between protective effects of investigated compounds with their molecular structure. Higher inhibiting properties are possessed by compounds, having unsaturated bonds (compounds 2, 4, 7, 8, 11), phenyl radical (14, 21), ester group (1-8), hydrophilic radical C_4H_9 (4, 8). Compound 4, in molecule of which the triple end bond and double bond are present, may be attributed to the highly effective inhibitors of hydrogen sulfide corrosion. The increase in the molecule of inhibitor of the number of nitrogen atoms does not lead to the ordinary increase of protective action, which is related, apparently, with the complexity of the structure of investigated compounds and necessity of account of effect of various substituents on reactive centers of molecules, i.e. on electronic density of adsorption center. This says about the effect of spatial structure of molecules of inhibitor on its protective properties. Presence of nitrogen atom in compounds (9-14) leads to the decrease of their efficiency. The presence of hydroxylic groups in molecules of compounds (16, 19) increases hydrophilicity and lowers their inhibiting activity. Absence of nitrogen atom in molecule of compound 24 leads to a complete disappearance of protective ability in hydrogen sulfide environment.

Thus, the investigation of protective action of newly synthesized nitrogen-containing organic substances allowed to identify from them the most effective. Analysis of link of protective properties of investigated compounds with their chemical structure may form the foundation of aim-driven synthesis of organic substances with potentially high inhibiting efficiency.

Conclusions

1. Using the method of imaging of polarization curves the protective effects of a row of organic nitrogen-containing compounds were determined.

2. The link is established between inhibiting properties of investigated compounds and their molecular structure using the principle of linearity of free energies.

3. It is determined, that the effective inhibitors are characterized by the maximal hydrophobicity and higher electron acceptor properties of substituent groups. This is in accordance with the main peculiarities of corrosion of steel in hydrogen sulfide environments.

SAS– surface active substances

LFE principle – principle of linearity of free energies

RSKB – principle of "rigid" and "soft" acids and based

HOMO – highest occupied molecular orbitals

LUMO – lowest unoccupied molecular orbitals

QAS – quaternary ammonium salts

NACE – corrosive model environment

Z – degree of protection

i_0 – corrosion current density of metal in the solution without inhibitor;

i – current density of corrosion in solution in the presence of the inhibitor

σ* – Taft constants

f – constants of hydrophobicity

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