STUDY OF BACTERICIDE-INHIBITOR PROPERTIES AGAINST MICROBIOLOGICAL CORROSION PROCESS OF BROMIDE COMPLEX OF IMIDAZOLINE BASED ON NORBORNENE CARBOXYLIC ACID AND DIETHYLENETRIAMINE

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Abstract: *The article investigates the bactericidal-inhibitory properties against microbiological corrosion of imidazoline bromide complex synthesized based on norbornene carboxylic acid and diethylenetriamine. For this purpose, in the first stage, imidazoline was synthesized from the interaction of norbornene carboxylic acid with diethylenetriamine. In the second step, an inorganic anionic complex was obtained from the reaction of imidazoline with allyl bromide. The structure of the obtained compound was confirmed by the IR spectroscopic method. The synthesized complex was tested as a bactericide-inhibitor. Solutions of the complex in two concentrations (25 and 50 mg/l) were prepared, and the effect on the life activity of sulfate-reducing bacteria was checked at a temperature range of 30-32˚C for 7-14 days. Based on the test results, it was determined that the obtained complex has a bactericidal effect of 97.3% at a concentration of 25 mg/l and 100% at a concentration of 50 mg/l. It was determined that the obtained complex completely stopped the life activity of SRB. The synthesized complex was compared with industrial inhibitors and it was determined that the inhibitor of Dodigen-414 (Germany) biocidal effect is 45% at a concentration of 25 mg/l, 60% at a concentration of 50 mg/l, and 85% at a concentration of 100 mg/l. The inhibitor of Sever-1 (Russia) biocide effect is 20% at a concentration of 25 mg/l, 35% at a concentration of 50 mg/l, and 60% at a concentration of 100 mg/l.*

It was determined that the synthesized imidazoline bromide complex completely stopped the life activity of SRB with a high bactericidal effect at all three concentrations.

Keywords: *norbornene carboxylic acid, diethylenetriamine, imidazoline, microbiological corrosion, inhibitor, bactericidal property*
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Introduction

One of the global issues that is prevalent in the present era is corrosion, which is being studied by multidisciplinary scientists in an effort to find a solution [1].

Metals with many valuable properties, such as strength, friction resistance, thermal and electrical conductivity, are considered very favorable construction materials. However, metals are subject to corrosion since they are thermodynamically unstable.

There are many methods and means of protecting metal tools from the corrosion process. The cost-effectiveness of these methods varies depending on the circumstances. The production of equipment used in various industries from corrosion-resistant materials cannot ensure their long-term use and reliability. For this, it is required to use other methods and means of corrosion protection. Among them, the most convenient and widespread method of protection is the method of using inhibitors of various types and compositions, which are simple, effective and economically efficient [2, 3]. The advantage of this method over other methods is that when inhibitors are applied in the industry, the devices and equipment used are not often replaced with new ones. Currently, the number of inhibitors with different compositions is constantly increasing. However, apart from the positive aspects of these

inhibitors, there are also some disadvantages. So, the used inhibitors are intended for small application areas. Sometimes, the raw materials required for the production of the inhibitor are ordered from abroad, so it is not economically beneficial.

The basis of inhibitors used in corrosion protection are nitrogen-containing compounds - amino alcohol, nitro compound, imidazoline, amidoamine, amide, etc. compounds. Amine compounds are cationic compounds that can be used as bactericides and corrosion inhibitors. The bactericidal indicator of these compounds is that they cause their destruction by dissolving the cell walls of bacteria. Corrosion protection inhibitors prevent oxidizing agents from approaching the metal surface by forming a protective layer inside metal systems.

In today's oil-industrial countries, oil is obtained by applying water of various origins to oil wells, and these wells are infected with various microorganisms. As a result, there are optimal conditions for microbiological corrosion. One of the actual problems in various areas of the farm is the damage caused by the settlement of microbes on the substrate. Thus, in oil extraction facilities, during oil processing and transportation, this type of bacteria adheres to the surface of devices and tools and damages them, and as a result, the microbiological corrosion process occurs [4].

The most optimal method of protection against biocorrosion is the application of bactericide inhibitors. However, due to the rapid adaptation of microbiological corrosion-causing bacteria (sulfate-reducing bacteria - SRBs) to inhibitors, it is necessary to constantly replace them with new ones. Also, since the corrosion process is caused by various reasons, the inhibitors applied against it must be multifunctional [5]. Aerobic and anaerobic bacteria are involved in the biocorrosion process. Anaerobic bacteria develop in sulfur environments when pH=5-9 in an oxygen-free environment. The main species of SRB that cause biocorrosion are *Desulfovibrio desulfuricans, Desulfovibrio gigas, Desulfovibrio salexigens, Desulfovibrio vulgari* and *Desulfovibrio africans*. *Desulfovibrio desulfuricans* is the most active bacteria in the corrosion process.

SRBs obtain energy by oxidizing organic compounds or hydrogen by reducing sulfates to hydrogen sulfide. At this time, they carry out the respiration process in an anaerobic form, that is, without oxygen, with sulfates. Some of them can also reduce forms of sulfur such as sulfites, thiosulfites, and elemental sulfur [6].

It is known that microbial corrosion occurs faster in the oil industry than other types of corrosion, and sulfate-reducing bacteria (SRB) are the main cause of H_2S formation in the environment [7].

In the world, including in our country, extensive research is being conducted in the field of protection against biocorrosion and other forms of corrosion, increase of inhibitor types and their application. Both chemical and biocorrosion are complicated processes [8, 9].

Experimental part

The IR spectra of the obtained compounds were recorded on diamond crystals at a wavelength of 400-4000 cm^{-1} in "BRUKER" brand spectrometers from German company "ALPHA IR FOURYE".

In order to determine the bactericidal properties of the inhibitor, "Desulfovibrio desulfuricans" SRB strain 1143 from the Absheron-Binagadi field based on "OST 39-151-83" was used as a research object. Nutrient medium was prepared and sterilized to obtain SRB culture. Postgate B medium is the nutrient medium necessary for bacteria's development and intensive reproduction. The pH of the environment should be equal to 7.0-7.5. Content of Posgate B nutrient medium: (KH_2PO_4) – 0.5 g (GOST 4198–75); ($MgSO4{\cdot}7H_2O$) – 2 g (GOST 4523–77); (NH_4Cl) – 1.0 g (GOST 3773–72); (NaCl) – 2 g (GOST 4233–77). Additives included in it to optimize the nutrient medium: $FeSO_4{\cdot}7H_2O$ (5% solution in 2% hydrochloric acid)-0.5-2ml (GOST 4148–78); $NaHCO_3$ (5% solution in water)-1ml (GOST 4201–79); Crystalline sodium sulfide solution prepared in a 1% solution of Na_2CO_3.

Sterilizing the medium, containers, and other items is necessary while dealing with microorganisms in order to stop the growth of

more bacteria in the media under study. The prepared nutrient medium is filled to half the container and closed with a plug. Sterilization is carried out in 1 atmosphere at 120°C for 30 minutes. After all solutions are sterilized, 30% sterilized reservoir water is added to the reagent solution. The mixture is boiled and rapidly cooled under water, removing dissolved oxygen from the nutrient medium. Additions are then added – liquid extract, ferrous sulfate, ascorbic acid and $NaHCO_3$ solution are added dropwise to pH 7–7.5. If necessary, a 1% solution of HCl is also added. The pH is checked with indicator paper and bromothymol-platinum indicator. This process is performed under gas-side, sterile conditions. The flasks, stoppers, and tips of the pipettes are sterilized by putting them on fire. To determine the number of bacteria in an inhibitor-free environment, the bacteria are first diluted and planted, and the incubation period is 7-14 days in a thermostat (TU 64-1-1382-83) with a temperature range of 30-32 ^{0}C. It was determined that the number of bacteria in the medium without inhibitors taken for control is $n=10^8$. Then, 1% solutions of the complexes in isopropyl alcohol and 1 ml of bacteria were added to the Postgate B medium at concentrations of 25 and 50 mg/l and kept in a thermostat at a temperature of 30-32°C for 14 days. The bactericidal effect of the inhibitor is studied based on the amount of H_2S formed in the medium. The amount of treated H_2S is determined by the iodometric titration method (OST 39-234-89).

The development of SRB can be determined by the following signs: the formation of a dark-colored sediment at the bottom of the container; the formation of hydrogen sulfide; presence of live forms of SRB.

The total content of hydrogen sulfide and its associates (mg/L), recalculated to undissociated hydrogen sulfide, is calculated using the following formula:

$$C_s = \frac{17040 \cdot (V_1 \cdot K_1 - V_2 \cdot K_2) \cdot N \cdot K_r}{V_\rho}$$

Where:

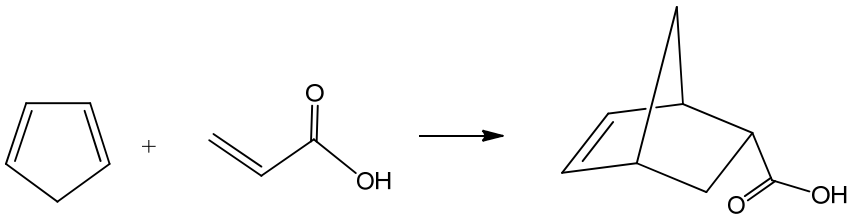
- V_1 — amount of added iodine solution, ml;
- K_1 — correction factor for bringing the concentration of iodine solution to the exact value;
- V_2 — the amount of sodium thiosulfate solution used for back titration, ml;
- K_2 — the correction factor for bringing the concentration of sodium thiosulfate solution to exact value;
- N — normality of the titrated thiosulfate or iodine solution;
- V_ρ— the amount of test water taken with a pipette for analysis, ml;
- K_r — the correction factor for the addition of a preservative reagent (sodium hydroxide solution), equal to 1.01. In the absence of sample preservation, K=1.

The bactericidal effect of the studied samples was determined by the following equation based on the calculated value H_2S:

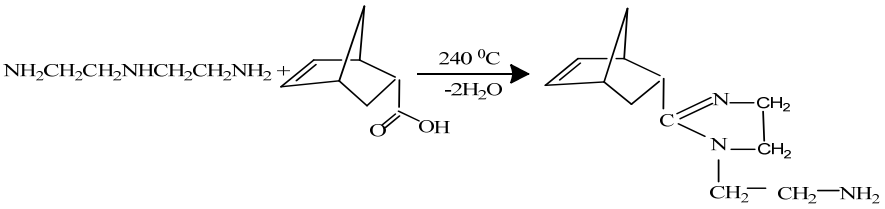
$$Z = [(C_0 – C)/C_0] \cdot 100\%,$$

C_0 - amount of hydrogen sulfide in the control environment, mg/l;
C - amount of hydrogen sulfide formed in the reagent environment, mg/l

During the experiment, norbornene carboxylic acid (NCA) was first synthesized. The acquisition of acid was carried out in two stages. In the first step, cyclopentadiene was obtained by monomerizing dicyclopentadiene [10]. Norbornene carboxylic acid was synthesized from the reaction of cyclopentadiene obtained in the second step with acrylic acid. The yield of the NCA is 94%. The reaction scheme is as follows:



Later, imidazoline (NDI) was obtained from NCA and diethylenetriamine (DETA). 0.5 mol of norbornene carboxylic acid is added to the flask and heated to 80-100ºC. Then 0.5 mol of amine (DETA) is slowly added to the acid dropwise. To obtain NDI, the temperature is raised to 240 °C, and the reaction at this temperature is carried out for 3-3.5 hours. The yield of obtained imidazoline was 93%. During the synthesis, imidazoline was obtained by separating two moles of water [10]. The synthesis of NDI based on NCA and DETA proceeds according to the following scheme:



The IR spectrum of NDI obtained based on NCA and DETA is shown in Fig. 1 and has the following absorption bands:

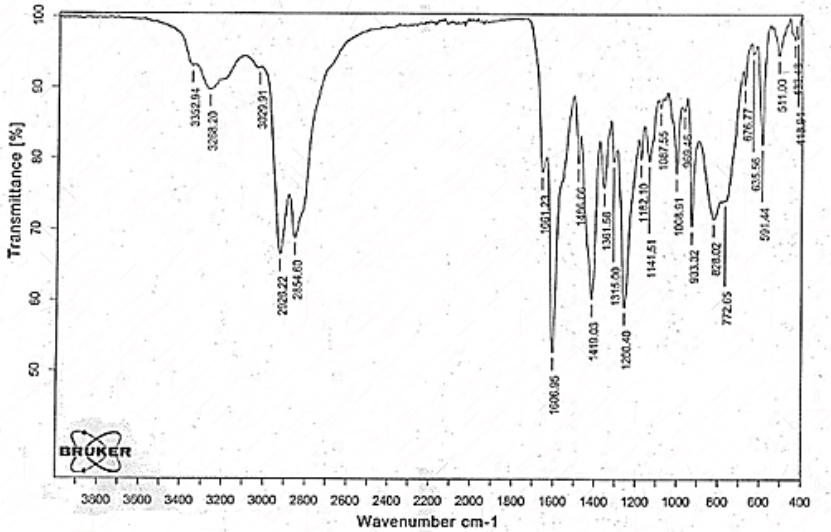
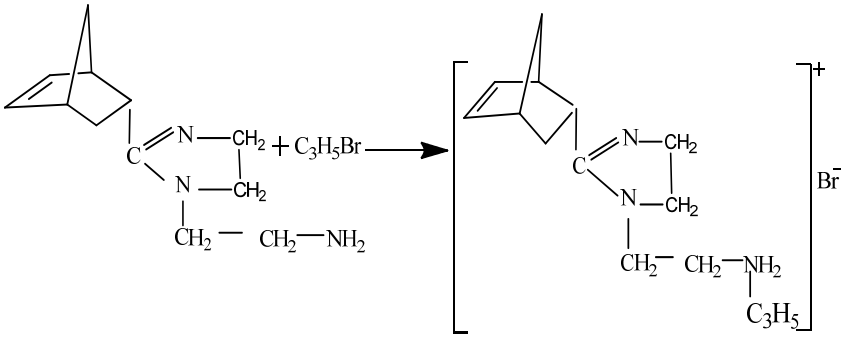


Fig. 1. IR-spectra of the NDI

Absorption bands of the IR spectra of NDI: 676, 772, 828 cm^{-1} – deformation vibration of N–H bond of C–NH_2 group, 933, 969 cm^{-1} – C=C bond, 1087, 1141, 1182, 1260 cm^{-1} – C–N bond, 1315, 1361, 1419, 1486 cm^{-1} – deformation vibration of C–H bond of CH_3, CH_2 and CH groups, 1606 cm^{-1} – C=C of aromatic ring and N–H bond of C–NH_2 group, 1661 cm^{-1} – C of unsaturated hydrocarbon The absorption bands characteristic of C=C bond and C=N bond overlap. 2854, 2926 cm^{-1} – valence vibration of C–H bond of CH_3, CH_2 and CH groups, 3029 cm^{-1} – valence vibration of C–H bond of HC=C– group.

To synthesize the imidazoline complex, imidazoline and alkene halide were taken in different molar ratios (1:1, 1:2, 1:3). The synthesis reaction was carried out in a three-necked flask at 80-90 ºC for 3 hours. The reaction of obtaining the inorganic complex of NDI is as follows [11, 12]:



The following absorption bands were observed in the IR spectrum of the synthesized complex (Fig. 2).

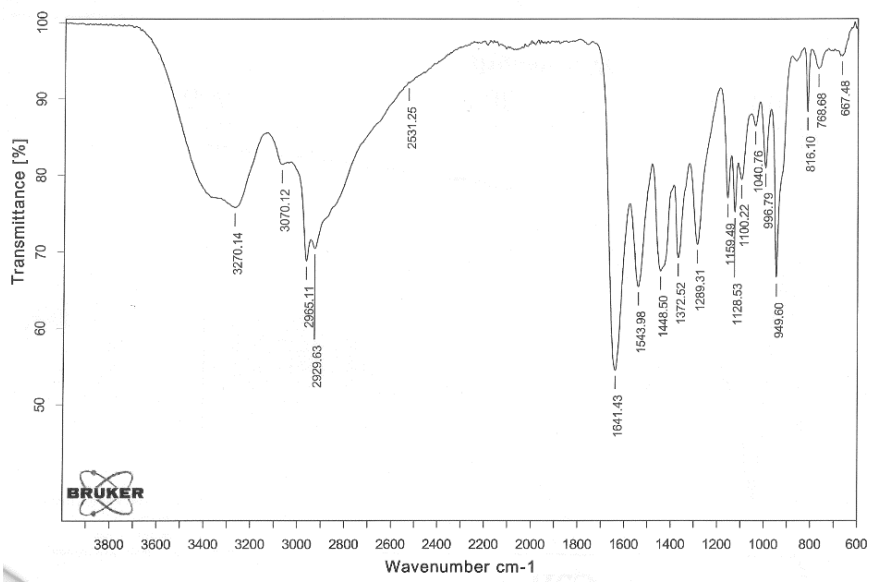


Fig. 2. IR-spectra of the NDI+C_3H_5Br complex

1372, 1448 cm^{-1} deformation and 2929, 2965 cm^{-1} valence vibration – CH_2 and CH_3 groups of C-H bond, 1641 cm^{-1} valence vibration of C=N bond, 1543 cm^{-1} deformation and 3270 cm^{-1} valence vibration of N-H bond, 1289 cm^{-1} is the valence vibration of the C-N bond, and 2418, 2539 cm^{-1} is the ammonium band.

Results and Discussion

The bactericidal-inhibitory properties of the obtained imidazoline allylbromide complex were determined. The bactericidal results of the studied complex are shown in the table.

Table. Results of bactericidal effect of the complex

Complexes conventional name and composition	Concentration of compound, C- mg/l	Amount of bacteria (number of cell/ml)	Amount of H_2S, mg/l	Bactericidal effect, Z-%
NDI+C_3H_5Br	25	10^1	9.1	97.3
	50	-	-	100
Control-I Amount of H_2S in SRB-free medium		24 mg/l		
Control-II Amount of H_2S in an environment with SRB		342 mg/l		

Control-III- Number of bacteria in the nutrient medium	10^8 cell/ml

Based on the test results, it was determined that the obtained complex completely stops the development of bacteria, showing a bactericidal effect of 97.3% at a concentration of 25 mg/l, and 100% at a concentration of 50 mg/l. The synthesized complex was compared with industrial inhibitors and it was determined that this inhibitor has a higher bactericidal effect than other reagents at the same concentration. Thus, the Dodigen-414 (Germany) reagent taken for comparison has a biocidal effect of 45% at a concentration of 25 mg/l, 60% at a concentration of 50 mg/l and 85% at a concentration of 100 mg/l, while the Sever-1 (Russia) reagent has a biostat effect of 20% at a concentration of 25 mg/l, a biocidal effect 35% at a concentration of 50 mg/l and 60% at a concentration of 100 mg/l. The synthesized complex of imidazoline with bromide showed a bactericidal effect of 97.3% at a concentration of 25 mg/l, and 100% at a concentration of 50 mg/l, completely destroying bacteria by stopping their development.

Thus, in order to synthesize a corrosion inhibitor with a new composition and structure, norbornenecarboxylic acid, diethylenetriamine and allyl bromide were taken. For this purpose, in the initial stage, norbornene carbonic acid was synthesized based on local raw materials, cyclopentadiene and acrylic acid, which are by-products of the EP-300 unit. In the second stage, imidazoline was obtained from norbornene carbonic acid and diethyltriamine. In the final stage, in order to further enhance the bactericidal properties of imidazoline, its inorganic anionic complex was synthesized. For this, allyl bromide, which is more environmentally friendly, was used.

The presence of a heptene fragment and bromine ions in the structural composition of the synthesized inhibitor further increases the effect of its corrosion protection ability and allows it to have a high effect.

This complex, based on norbornenecarboxylic acid, can be proposed as a bactericidal inhibitor against the corrosion process.

Conclusion

1. Synthesis of imidazoline allylbromide complex has been carried out based on norbornene carboxylic acid and diethylenetriamine. The structure of the obtained compound was confirmed by IR spectroscopic method. The bactericidal-inhibitory properties of the synthesized imidazoline bromide complex were tested.

2. It was determined that the obtained complex has a bactericidal effect of 97.3% at a concentration of 25 mg/l, 100% at a concentration of 50 mg/l, completely stopping the life activity of SRB. The synthesized complex was compared with industrial inhibitors and it was determined that this inhibitor has a higher bactericidal effect than other reagents at the same concentration.

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