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ABSTRACT

of the dissertation for the degree of Doctor of Philosophy

SYNTHESIS OF IMIDAZOLINE AND ITS COMPLEXES BASED ON 5-NORBORNENE-2-CARBOXYLIC ACID AND STUDY OF THE INHIBITOR-BACTERICIDAL PROPERTIES

Speciality: 2314.01 – Petrochemistry

Field of science: Chemical

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The work was performed at the laboratory of «Study of antimicrobial reagents and biodamages» of the Institute of Petrochemical Processes named by acad. Y.H. Mammadaliyev of Ministry of Science and Education of the Republic of Azerbaijan.

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GENERAL DESCRIPTION OF WORK

Relevance and development of the topic. In modern times, the petrochemical industry meets the comprehensive needs of chemical and many other industries. Many fields of both national economy and agriculture are closely connected with the complexes of this field. Petrochemistry creates great opportunities for synthesizing new types of monomers and polymers, which are used in various fields of the national economy, based on petroleum hydrocarbons of different composition and structure. Therefore, the acquisition of valuable products related to petrochemical and organic synthesis based on ecologically clean, local raw materials, with simple technological methods, and the investigation of their properties and characteristics are of great importance both theoretically and practically.

Corrosion and corrosion protection are the basis of scientific, technical and economic problems in modern times. One of the widespread types of corrosion process is microbiological corrosion. Metal equipment in contact with various aggressive environments is exposed to wear and tear due to the influence of external factors, the basis of which is biocorrosion. The main agents of the biocorrosion process are sulfate-reducing bacteria. Their presence causes an increase in the acidity of the environment, which exacerbates the corrosion process. The most effective and economically efficient method of protecting metals from corrosion is the application of bactericide-inhibitors. In industrial fields, inhibitors with high protective ability are required in low concentration, which are synthesized by a simple technological method, do not cause environmental pollution[1]. Therefore, it is important to synthesize new bactericide-inhibitors by environmentally friendly methods. Pollution of water bodies with oil and oil products is the first among environmental problems.

Examples of this type of pollution occur in oil pipelines, oil

[1]Agamaliyeva, D.B. Synthesis of based on synthetic petroleum acids and polyamines imidazoline derivatives and its inorganical complexes and study of theirs properties. / (PhD thesis) / – Baku, 2018. – 206 p.

wells, and ships transporting oil and oil products during oil processingand transportation as a result of the accidents, it is possible to show the spillage of oil-contaminated waste water into water bodies. Thick layers of oil spilled into water bodies as a result of the accident are cleaned by mechanical methods. The thin oil layer is cleaned chemically, that is, with the help of reagents. Oil collecting and oil dispersing reagents play an important role in environmental protection. It is very important to increase the range of oil collectors that turn the oil layer into a spot and dispersants that disperse this layer and lead to its biochemical decomposition.

During the operation of oil and oil products in the petrochemical industry, additives against corrosion and friction are used. The most effective way to protect the equipment and tools used in the processing process from damage is the chemical method, in which biocide and fungicidal additives are added to the lubricating-coolant fluids. Additives not only stop the development of living cells, but also completely destroy them.

In order to solve the listed problems, it is necessary to specially mention the C_5 fraction of liquid pyrolysis products, which is a high-tonnage by-product of the "EP-300" unit of the Sumgayit pyrolysis plant and contains chemically valuable and highly reactive diene hydrocarbons (isoprene, piperylene, dicyclopentadiene). Synthesis of new generation representatives of 5-norbornene-2-carboxylic acid obtained from cyclopentadiene separated from this composition and study of application areas, strengthening of the known useful properties of that class of substances and creating a wide opportunity to obtain new highly effective substances clearly prove the relevance of the presented work.

Object and subject of research. In the dissertation, the research object is 5-norbornene-2-carboxylic acid, which is the basis of the synthesis of imidazoline and amide compounds, and the subject of the research is the synthesis of amide, imidazoline and their inorganic anionic complexes and the determination of their practical applications.

Objectives and tasks of the research. The main goal of the presented dissertation work is to synthesize an antibacterial, antifungal, surface-active reagent with a high protective effect, a wide base of raw materials, highly effective properties, and a multifunctional effect, which does not cause environmental pollution, is obtained with a simple technology without waste, and does not cause environmental pollution. In order to create compounds with the listed properties, synthesis of new amine derivatives based on 5-norbornene-2-carboxylic acid, study of their physico-chemical properties, confirmation of their composition and structure, as well as investigation of application areas were carried out.

To achieve the set goal, the following tasks were performed:

1. Separation of cyclopentadiene from pyrolysis liquid products;
2. Synthesis of 5-norbornene-2-carboxylic acid by Diels-Alder (D-A) reaction based on cyclopentadiene and acrylic acid;
3. Synthesis of imidazolines based on 5-norbornene-2-carboxylic acid and amines (diethylenetriamine and triethylenetetraamine);
4. Synthesis of amides based on 5-norbornene-2-carboxylic acid and amines (diethylenetriamine and triethylenetetraamine);
5. Preparation of inorganic anionic complexes of imidazolines by interaction with alkylhalides, study of basic physico-chemical properties of obtained compounds, confirmation of their composition and structures with modern physical research methods;
6. Obtaining inorganic anionic complexes by the interaction of amides with alkylhalides, studying the basic physical and chemical properties of the obtained compounds, confirming their composition and structure with modern physical research methods;
7. Investigation of the properties of synthesized alkylhalide complexes as bactericidal-inhibitory properties against sulfate-reducing bacteria (SRB);
8. Determination of the surface activity of the obtained complexes;
9. Determination of the specific electrical conductivity of the obtained complexes;
10. Investigation of synthesized inorganic anionic complexes as antimicrobial (antifungal) additives in lubricating-cooling fluids;
11. Study of the oil collection and oil dispersing ability of

complex compounds.

Research methods. The bactericidal-inhibitory properties of the synthesized complexes against sulfate-reducing bacteria were demonstrated. It was tested in accordance with OST 39-151-83 at the Institute of Petrochemical Processes named after academician Y.H. Mammadaliyev.

Synthesized complexes were tested as an antimicrobial additive by the zonal diffusion method in the laboratory of "Additives for lubricating-coolant fluids" of the Institute of Chemical Additives named after acad. A.M. Quliyev.

The synthesized complexes were tested as surfactants in the "Surfactant reagents and preparations" laboratory at the Institute of Petrochemical Processes.

The physico-chemical properties, composition and structures of the synthesized new complex compounds were studied by IR, ^{1}H and ^{13}C NMR spectroscopy methods.

The surface activity of 5-norbornene-2-carboxylic acid-based amide and imidazoline complexes was determined using apparatus KVS Sigma 702 tensiometer.

The main provisions of the defense:

The main provisions of the defense are as follows:

- ✓ Amides were synthesized based on 5-norbornene-2-carboxylic acid and amines;
- ✓ Imidazolines were synthesized based on 5-norbornene-2-carboxylic acid and amines;
- ✓ Inorganic anionic complexes of amides were prepared;
- ✓ Inorganic anionic complexes of imidazolines were prepared;
- ✓ Physico-chemical properties of the synthesized compounds were determined, as well as their composition and structures were confirmed;
- ✓ The possibility of using the obtained compounds as an additive by studying their antifungal properties, as antimicrobial substances by studying their bactericidal properties, and as surfactants by studying their oil collection and dispersing properties was shown.

Scientific novelty of the research. Scientific novelty of the work: imidazoline based on 5-norbornene-2-carboxylic acid and triethylenetetraamine, amide based on 5-norbornene-2-carboxylic acid and triethylenetetraamine, imidazoline based on 5-norbornene-2-carboxylic acid and diethylenetriamine, 5-norbornene-2-carboxylic acid and consists of the synthesis of amide based on diethylenetriamine. In total, 4 main new compounds (amide and imidazoline) and their 82 complexes were synthesized. The synthesized complexes were studied as bactericidal-inhibitors against SRB. The additive antimicrobial properties of the target substances were tested. The oil-collecting and dispersing properties of the studied compounds as surfactants were determined.

Theoretical and practical significance of the research. During the research, a convenient synthesis method of N-alkylation reactions of amide and imidazolines with alkylhalides was developed. It was determined that the synthesized complexes showed high results as antimicrobial reagents in laboratory conditions. Finding an efficient method of synthesis of multifunctional inhibitors will further simplify their production process and thus create conditions for increasing the variety of inhibitors. Complexes synthesized as a result of conducted research can be used as bactericide-inhibitors, antimicrobial additives and surfactants with high quality and multifunctional effect against microbiological corrosion process in the oil industry of our republic.

Approbation and application of the work 40 works have been published on the basis of the dissertation, of which 3 (three) are patents, 13 (thirteen) are articles and 24 (twenty four) are abstracts of reports at international and republican scientific conferences.

The results of the dissertation work were reported and discussed at the following International and Republican scientific conferences: Abstracts of reports of the International Scientific and Technical Conference "Petrochemical synthesis and catalysis in complex condensed systems", devoted to the 100-year anniversary of academician B.K. Zeynalov (Baku 2017, 29-30 june, p. 28), Professor S.A. Sultanov Republican Scientific and Technical Conference dedicated to the 90-th anniversary "Fuels, fuel components, special purpose fluids, oils and additives", abstracts of reports (Baku 2017, 3 october, p. 32), Gandja State University, international scientific conference, Modern Nature and Current Problems of Economic Sciences (Gandja 2019, 2-3 may, p. 233-235), International Conference on "Current Problems of Modern Chemistry" dedicated to the 90-th anniversary of the Institute of Petrochemical Processes named after academician Y.H. Mammadaliyev of ANAS (Baku 2019, 2-4 october, p. 185), XIII Republican Scientific Conference of doctoral students, masters and young researchers "Current Problems of Chemistry" dedicated to the 96-th anniversary of the birth of national leader Heydar Aliyev (Baku 2019, 15-16 may, p. 77), Innovative development prospects of chemical technology and engineering, International Scientific Conference (Sumgayit 2019, 28-29 november, p. 275-276), Republican scientific conference called "Modern view of chemical science" (Nakhchivan 2019, 8 october, p. 90-93), "Problems and development trends of modern chemistry." Republican scientific-practical conference (Baku 2020, 12 december, p. 191-194), II Scientific conference "Dynamic processes in chemistry of element-organic compounds", dedicated to the 75-th anniversary of the IOFH named after acad. A.E. Arbuzov and и Kazan Scientific Center of RAS (Kazan 2020, 11-13 november, p. 131), II International scientific conferences of students and young researchers dedicated to the 98-th anniversary of the birth of the national leader H. Aliyev (Baku 2021, 13-28 april, p. 208-209), Materials of the scientific conference "Science, Technology and Development of Innovative Technologies", dedicated to the 30-th anniversary of the independence of Turkmenistan (Ashgabad 2021, 12-13 june, p. 97-98), Modern Movement of Science: abstracts of the 12-th International Scientific and Practical Internet Conference (Dnepr 2021, Part 1, 1-2 april, p. 143-144), multidisciplinary Republican scientific-practical conference on "The legacy of H. Aliyev in the development strategy of Azerbaijan" (Baku 2021, 1 may, p. 71-74), II International scientific conferences of students and young researchers dedicated to the 98-th anniversary of the birth of the national leader H. Aliyev (Baku 2021, 13-28 april, p. 278-280), the conference of students, postgraduates and young students dedicated to the 65-th anniversary of the UGNTU branch (Salavat 2021, 19-23 april, p. 218-219), Current problems of modern natural and economic sciences (Gandja 2021, 6-7 may, p. 144-145), Karbyshev Readings: Collection of scientific papers of the scientific and practical conference / ed. Groshevoy L.I. in 8 volumes (Tyumen 2021, TVVIKU, Vol. 6, 15-17 december, p. 20-24), Republican scientific conference "Catalysts, olefin-based oils" devoted to the 90th anniversary of academician N.M. Seyidov (Baku 2022, 19-20 may, p. 38), abstracts of reports of the Republican scientific conference dedicated to the 110-th anniversary of academician A.M. Guliyev on "Organic substances and composition materials of various purposes" (Baku 2022, 1-2 june, p. 22-24), Integration of science and education in oil and gas universities-2022. Advanced technologies and modern trends, Proceedings of the International Scientific and Methodological Conference, Ufa UGNTU Publishing House (Salavat 2022, 22 april, p. 46-48), Gandja State University, International scientific conference, Actual problems of modern natural and economic sciences (Gandja 2022, 2-3 may, 1-st part, p. 370), III International Scientific Conferences of Students and Young Researchers dedicated to the 99-th anniversary of the birth of the national leader H. Aliyev (Baku 2022, 18-19 april, p. 411), III International Scientific Conferences of Students and Young Researchers (Baku 2022, 18-19 april, p. 413), International Conference Modern Problems of Theoreticaland Experimental Chemistry devoted to the 90-th anniversary of academician Rafiga Aliyeva (Baku 2022, 29-30 september, p. 248-249).

Name of the organization where the dissertation work is performed. Antimicrobial and surface-active oil collection and oil dispersion properties of compounds were tested at the Institute of Petrochemical Processes named after academician Y.H. Mammadaliyev. The study of complexes as antimicrobial additives in lubricating-coolant fluids was conducted at the Institute of Chemical Additives named after acad. A.M. Quliyev.

Volume and structure of the dissertation. The dissertation is presented in 172 pages of computer text and the introductory part is 8 pages (15285 symbols), four chapters: literature review – 37 pages (68521 symbols), experimental part – 13 pages (19607 symbols), synthesis section – 29 pages (25466 symbols), research and application – 38 pages (39641 symbols); results – 3 pages (3827 symbols); it consists of 28 pages of a list of 226 cited scientific literature. The thesis includes 35 tables and 36 figures, as well as 11 pages of appendices. The total volume of the dissertation consists of 179494 symbols (excluding tables, pictures, bibliography and appendices).

The introduction provides information on the relevance, goals, tasks, scientific innovation, and practical value of the dissertation work.

In **the first chapter**, the synthesis and application areas of amides and imidazolines and the modern state of research conducted in this field were discussed in detail, the opinions of world and Azerbaijani scientists about the synthesis and application areas of amides and imidazolines and their scientific researches were analyzed.

In **the second chapter**, raw materials for the synthesis of amide, imidazoline and their complexes were selected and prepared, their physico-chemical properties, structure-group composition were studied with the help of modern devices, and the methodology of conducting the experiment was discussed.

In **the third chapter**, the synthesis, structure and properties of 5-norbornene-2-carboxylic acid, the synthesis of amide, imidazoline and their complexes based on 5-norbornene-2-carboxylic acid and amines, and the calculation of the material balance of the complexes were discussed.

The fourth chapter is dedicated to the study of the properties of the synthesized amide, imidazoline and their complexes as antimicrobial and surface-active substances. The results obtained from the study of the effects of the synthesized 5-norbornene-2-carboxylic acid and alkylhalide complexes of diethylenetriamine, triethylenetetraamine-based amide and imidazolines on the life activity of SRB were investigated and analyzed. Analysis of the effect of obtained 5-norbornene-2-carboxylic acid and diethylenetriamine, triethylenetetraamine-based amide and imidazoline complexes as antimicrobial additives in lubricating-cooling fluids was carried out. It is dedicated to the study of the surface activity of synthesized 5-norbornene-2-carboxylic acid and diethylenetriamine, triethylenetetraamine-based amide and imidazoline complexes. The specific electrical conductivity of synthesized 5-norbornene-2-carboxylic acid and TETA-based imidazoline and its complexes was determined. The properties of obtained 5-norbornene-2-carboxylic acid and diethylenetriamine, triethylenetetraamine-based amide and imidazoline complexes as oil collecting and dispersing reagents were studied.

Results, list of used literature and appendices are presented at the end of the dissertation.

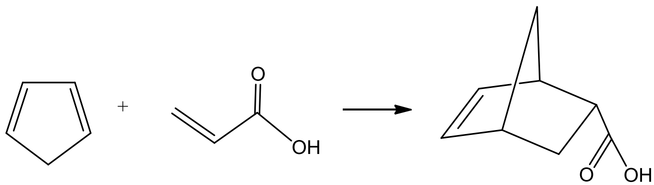
Personal participation of the author. Collecting and summarizing information on the literature review, preparing and conducting experiments, preparing samples to be studied, systematically preparing results, compiling articles and theses, explaining and summarizing data obtained from physical and chemical analyzes took place with the direct participation of the author.

MAIN CONTENT OF THE WORK

The demand of the modern era is to develop new economic and ecologically efficient methods to obtain valuable organic compounds based on local raw materials. In this regard, the C_5 fraction of liquid products of pyrolysis, which is a multi-tonnage by-product in the production of ethylene-propylene at the "EP-300" plant in Sumgait city, should be specially mentioned. Fraction C_5 can be used as a raw material in the production of petrochemical products, which are considered important in the industry, keeping valuable and highly reactive diene hydrocarbons (isoprene, piperylene, dicyclopentadiene). In the presented dissertation, dicyclopentadiene 5-norbornene-2-carboxylic acid-based amide and imidazoline complexes isolated from the C_5 fraction of pyrolysis liquid products were used in the preparation of complexes, and their fields of application were defined.

Synthesis of 5-norbornene-2-carboxylic acid

Preparation of 5-norbornene-2-carboxylic acid (NCA) consists of two stages: monomerization of dicyclopentadiene and interaction of cyclopentadiene with acrylic acid. First, dicyclopentadiene is monomerized. A benzene solution of monomerized cyclopentadiene is poured onto a benzene solution of acrylic acid and mixed. Synthesis reaction of NCA:

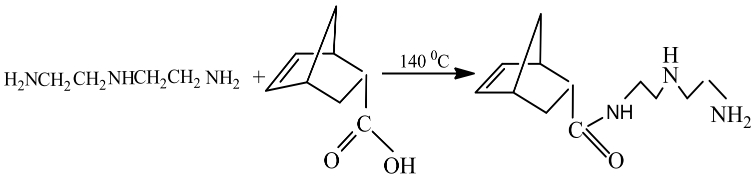


The yield of NCA received during the process was 94% [3, 33, 34].

The physico-chemical properties of the received NCA are shown belowas: iodine number, g J_2/100g–75, refractive index, (n_d^{20})–1.4902, density, g/cm^3–1.1226 at 25°C, boiling point, °C–136–138 (10 mm Hg), relative molecular mass, M_r–138.16.

Synthesis of amide (NDA) based on 5-norbornene-2-carboxylic acid and diethylenetriamine

For the synthesis of NDA obtained NCA and diethylenetriamine (DETA) were taken. The reaction proceeds with the release of 1 mole of water at a temperature of 130-140^oC for 1.5-2 hours. The obtained amide is in amorphous form, soluble in isopropyl alcohol and water. As a result of the reaction, the yield was 92.2% [21]. Synthesis of amide based on NCA and DETA was carried out by scheme:



Absorption bands of the IR spectrum of NDA, ν, δ, cm^{-1} (Fig. 1): 681, 709, 772 is the C-H bond of the HC=CH group in the cyclic ring, 3055 is the valence (ν) vibration of the C-H bond of the HC=CH group in the cyclic ring; 813, 839 is the deformation (δ) oscillation of the N-H bond of the NH_2 group; 1130, 1183, 1220 is the valence (ν) vibration of the C-N bond of the C-NH_2 group; 1251, 1286 "triple amide band", the absorption band corresponding to the valence (ν) vibration of the C-N bond overlaps with the absorption band corresponding to the deformation (δ) vibration of the N-H bond. 1536, 1641 "double and single amide band", 1641 "single amide band", 1536 "double amide band", the absorption band corresponding to the N-H bond overlaps with the absorption band corresponding to the C-N bond. 1334, 1389, 1455 C-H bond of the CH_2 group deformation (δ) oscillation, 2827, 2865, 2936, 2962 valence (ν) oscillation of the C-H bond of the CH_2 group, 3278 is the valence (ν) oscillation of the N-H bond of the NH group.

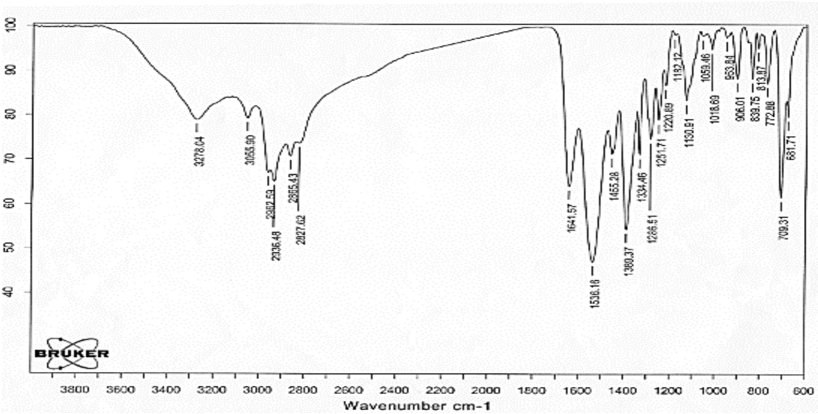


Fig. 1. IR spectrum of NDA

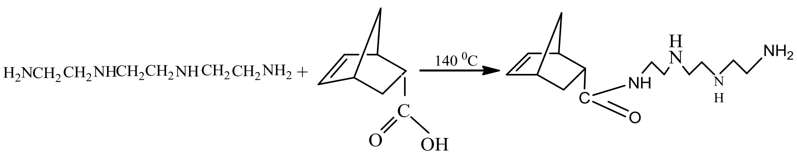
NMR spectrum of amide (NDA) synthesized based on NCA and DETA:

^{1}H NMR spectrum, δ, ppm: 1.21–1.32 m (2H, C^3H), 1.72 d.d.d (2H, C^7H_2, *J*=2.2, 2.1, 1.2 Hs), 1.93 c (2H,CH_2–NH–CH_2), 2.64-2.91 m (3H, $C^{1,2,4}H$), 3.03-3.24 m (8H, 2N$(CH_2)_2$N), 5.1 c (1H,CH_2–NH–CH_2), 5.91-5.98 m (1H, C^5H=), 6.11–6.21 m (1H, C^6H), 8.05 m (1H, CONH).

^{13}C NMR spectrum, δ, ppm: 29.02 (C^3), 38.83 (C^2), 42.01 (C^1), 43.82 (C^4), 45.01 (C^7), 49.02 (N$(CH_2)_2$N), 132 (C^5), 137 (C^6).

Synthesis of amide (NTA) based on 5-norbornene-2-carboxylic acid and triethylenetetraamine

Triethylenetetraamine (TETA) and NCA were used in the synthesis of amide. The reaction was carried out at 130-140^{o}C for 1.5-2 hours. As a result of the reaction with the separation of 1 mole of water, the yield of amide was 91.4%. Synthesis reaction of NTA [5]:



Absorption bands of the IR spectrum of NTA: 707, 774, 838 cm^{-1} N–H and C–H, 905, 940 cm^{-1} C–H, 3056 cm^{-1} C–H, 1334, 1376, 1454, 2815, 2870, 2935 cm^{-1} C–H, 1541 cm^{-1} N–H and C–N, 1642 cm^{-1} C=O and N–H, 3285 cm^{-1} N–H, –C–N and N–H.

NMR spectrum of amide (NTA) synthesized based on NCA and TETA:

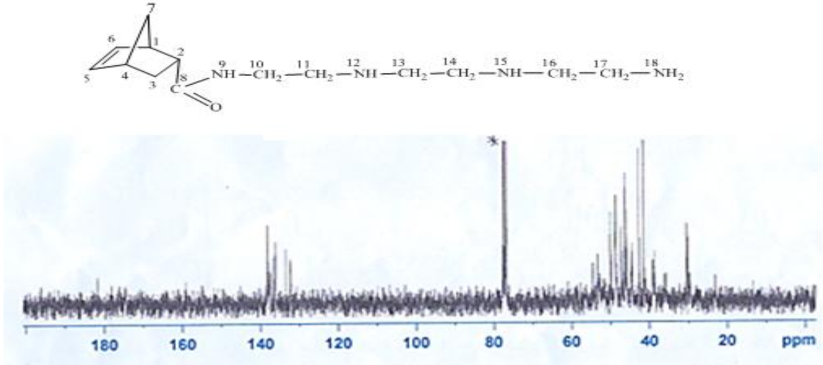


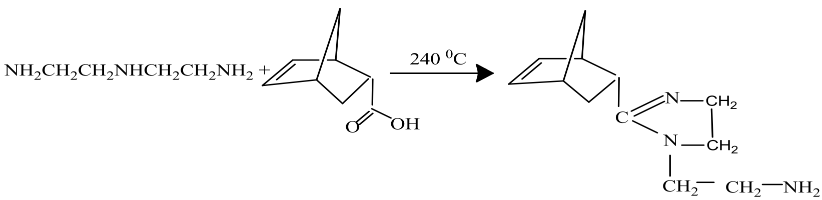
Fig. 2. ^{13}C NMR spectrum of NDA

^{1}H NMR spectrum, δ, ppm: 1.23-1.45 m (2H, C^3H_2), 1.65-1.79 m (2H, C^7H_2), 1.75-2.10 m (5H, $C^{1,2,4}H$, $2CH_2$–NH–CH_2), 3.06-3.28 m (12H, $C^{10,11,13,14,16,17}$), 5.1 c (2H, NH_2), 5.89-6.14 m (2H, $2C^{5,6}H$=), 8.03 m (1H, CONH).

^{13}C NMR spectrum, δ, ppm (Fig. 2): 23 (C^3), 29 (C^2), 30 (C^1), 42 (C^8), 43 (C^4), 45 (C^7), 49(C^8N), 132 (C^5), 137(C^6).

Synthesis of imidazoline (NDI) based on 5-norbornene-2-carboxylic acid and diethylenetriamine

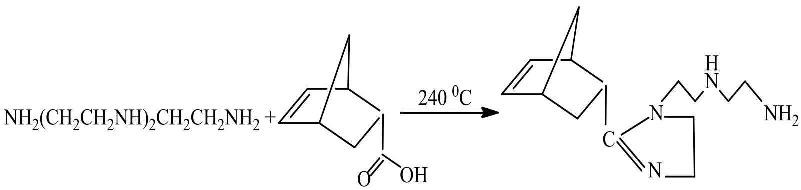
NCA and DETA were taken during the synthesis of NDI. The reaction proceeds with the release of 2 moles of water at a temperature of 240^{o}C for 3-3.5 hours. The yield was 93%. The received imidazoline is in a viscous liquid state, soluble in isopropyl alcohol [11, 13]. Synthesis reaction of NDI:



Absorption bands of the IR spectrum of NDI: 676, 772, 828 cm^{-1} N–H, 933, 969 cm^{-1} C=C, 1087, 1141, 1182, 1260 cm^{-1}C–N, 1315, 1361, 1419, 1486 cm^{-1} C–H, 1606 cm^{-1} N–H, 1661 cm^{-1} C=C and C=N, 2854, 2926 cm^{-1} C–H, 3029 cm^{-1} C–H.

Synthesis of imidazoline (NTI) based on 5-norbornene-2-carboxylic acid and triethylenetetramine

By the synthesized 5-norbornene-2-carboxylic acid with triethylenetetraaminethe N'-(2,2-bicyclo[2.2.1]hept-5-en-2-yl-4,5-dihydro-1-H-imidazolin-1-ylethyl)ethane-1,2-diamine compound was obtained. The synthesis reaction was carried out at 220-240ºC for 3 hours by mixing with 2mol of water separation. The yield was 84.28%. The scheme of the reaction is as follows [3, 26]:



The optimal conditions for the process of obtaining the synthesized NTI have been determined [36, 38]. In order to find the optimal conditions that provide the maximum yield of the target product, the effect of temperature, duration of the experiment and the molar ratio of the reagents on the yield (yield) of the product was studied. The reaction temperature was 170-240ºC, the duration of the experiment was 1-3.5 hours and the molar ratio of reagents was from 1:0.5 to 1:1.5.

Absorption bands of IR spectrum of NTI: 1556, 1642 cm^{-1} C=N, N-H and NH_2, 1036, 1128 cm^{-1} C-N, 1269 cm^{-1} C=N, 3280 cm^{-1} N-H, 1368, 1439, 2819, 2930 cm^{-1} C-H, 3068 cm^{-1} C-H. The absorption band characteristic of the C=C bond of the C=CH group of an unsaturated hydrocarbon coincides with the absorption bands of nitrogen compounds at 1642 cm^{-1}.

NMR spectrum of imidazoline (NTI) synthesized on the basis of NKT and TETA shown at Fig. 3:

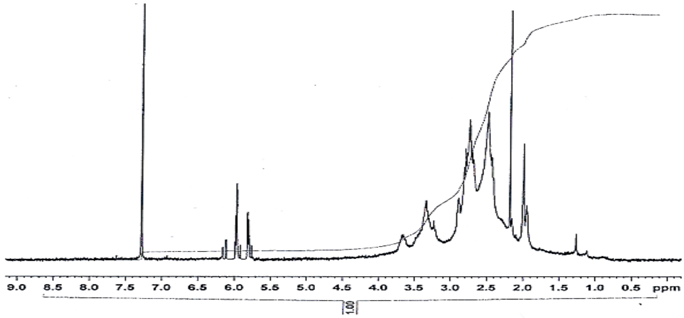


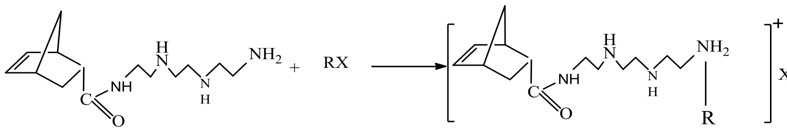
Fig. 3. ^{1}H NMR spectrum of NTI

^{1}H NMR spectrum of NTI, δ, ppm: 1.95-2.52 ppm ($2CH_2$), 2.60-3.00 ppm (3H), 3.6-3.8 ppm (NH and NH_2). Vicinal olefin protons are observed as two doublets at 5.56 and 6.0 ppm. The spin-spin interaction constant of these protons with each other and with the protons in the head of the bridge in the norbornene molecule is equal to 2.5 and 3.4 Hz.

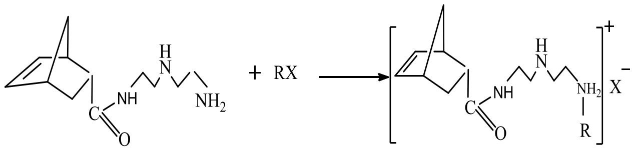
Preparation of complexes of amides (NDA) and (NTA) synthesized based on 5-norbornene-2-carboxylic acid and diethylenetriamine, triethylenetetraamine

Alkylhalides C_4H_9I, C_2H_5I, C_3H_7Br, $C_5H_{11}Br$, $C_6H_{13}Br$, $C_6H_{13}Cl$ and $C_8H_{17}Br$ were used in the synthesis reaction of inorganic anionic complexes of amide based on norborn-5-ene-2-carboxylic acid. During the synthesis, amide and alkylhalides were taken in different molar ratios (1:1; 1:2; 1:3). The reaction is carried out with stirring at 50-60°C for 3 hours [5, 8, 9, 16, 17].

The reaction for obtaining the inorganic complex of the amide (NTA) obtained on the basis of NCA and TETA proceeds according to the following equation:



The reaction for obtaining the inorganic complex of the amide (NDA) obtained on the basis of NCA and DETA proceeds according to the following equation:

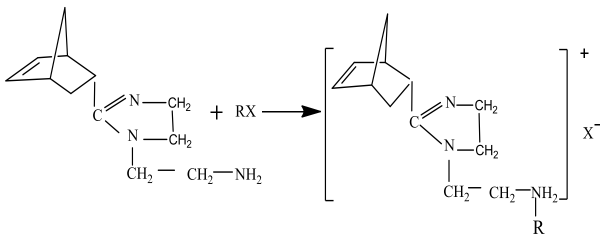


Where, RX = C_4H_9I, C_2H_5I, C_3H_7Br, $C_5H_{11}Br$, $C_6H_{13}Br$, $C_6H_{13}Cl$, $C_8H_{17}Br$.

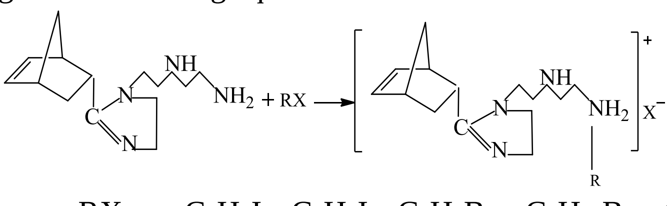
Preparation of complexes of imidazolines (NDI) and (NTi) synthesized based on 5-norbornene-2-carboxylic acid and diethylenetriamine, triethylenetetraamine

In the synthesis reaction of inorganic anionic imidazoline complexes based on norborn-5-ene-2-carboxylic acid and amines alkylhalides C_4H_9I, C_2H_5I, C_3H_7Br, $C_5H_{11}Br$, $C_6H_{13}Br$, $C_6H_{13}Cl$, $C_8H_{17}Br$ (1:1; 1:2; 1:3) were used. The reaction is carried out with stirring at 50-60^oC for 3 hours [1, 2, 4, 11, 18, 19].

The reaction of obtaining the inorganic complexes of the imidazoline (NDI) obtained on the basis of NCA and DETA proceeds according to the following equation:



The reaction of obtaining an inorganic complex of an imidazoline (NTI) obtained based on NCA and TETA proceeds according to the following equation:



Where, RX = C_4H_9I, C_2H_5I, C_3H_7Br, $C_5H_{11}Br$, $C_6H_{13}Br$, $C_6H_{13}Cl$, $C_8H_{17}Br$.

Study of the obtained compoundsas a bactericide-inhibitor against sulfate-reducing bacteria

The obtained norbornene-based complexes were tested as inhibitor-bactericide against SRB. The best results are presented in tables 1, 2, 3, 4 [14, 20, 22, 23, 24, 27].

Table 1.

Bactericidal effect of NDA complexes

Complexes	Concentration of compound, C-mg/l	Number of bacteria (number of cells/ml)	Amount of H_2S, mg/l	Bactericidal effect, Z-%
NDA+C_4H_9I (1:2)	25	10^4	187	61
	50	10^1	25.5	95
	100	–	–	100
NDA+$C_6H_{13}Cl$ (1:2)	25	10^1	21	95.5
	50	10^1	13	97.2
	100	10^1	4.5	99
NDA+$C_6H_{13}Br$ (1:2)	25	10^5	247	48
	50	10^3	136	71
	100	10^1	17	96.4
NDA+$C_5H_{11}Br$ (1:2)	25	10^2	91	81
	50	10^1	42	91
	100	10^1	14	97
Control – I	–	Amount of H_2S in uncultured medium – 30-32 mg/l		
Control – II	10^8	Amount of H_2S in cultured medium – 476 mg/l		

As can be seen from Table 1, some of the complexes slow down the development of bacteria with a biocidal effect at concentrations of 25 and 50 mg/l. The NDA+$C_6H_{13}Cl$ (1:2) complex is 95.5% at a concentration of 25 mg/l, 97.2% at a concentration of 50 mg/l, the NDA+$C_6H_{13}Br$ (1:2) complex is 96.4% at a concentration of 100 mg/l [15] and NDA+C_4H_9I (1:2) the complex has a 95% bactericidal effect at a concentration of 50 mg/l. The NDA+$C_5H_{11}Br$ (1:2) complex shows a bactericidal effect of 91% at a concentration of 50 mg/l and 97% at a concentration of 100 mg/l.

At a concentration of 100 mg/l, the NDA+$C_6H_{13}Cl$ (1:2) complex is 99% and the NDA+C_4H_9I (1:2) complex is 100% bactericidal effect, completely stopping the development of bacteria.

Table 2.

Bactericidal effect of NTA complexes

Complexes	Concentration of compound, C-mg/l	Number of bacteria (number of cells/ml)	Amount of H_2S, mg/l	Bactericidal effect, Z-%
NTA+$C_6H_{13}Cl$ (1:1)	25	10^2	17	92
	50	10^1	10.6	95
	100	10^1	6.3	97
NTA+$C_6H_{13}Cl$ (1:2)	25	10^2	11.9	94.4
	50	10^1	6.9	96.7
	100	10^1	4.1	98
NTA+$C_6H_{13}Br$ (1:1)	25	10^2	12.5	94
	50	1·10	8.4	96
	100	1·10	4.1	98
NTA+$C_6H_{13}Br$ (1:2)	25	10^2	10.5	95
	50	1·10	6.2	97
	100	1·10	2.2	99
NTA+$C_8H_{17}Br$ (1:1)	25	1·10	21	90
	50	1·10	18.6	91.2
	100	1·10	14.3	93.2
NTA+$C_8H_{17}Br$ (1:2)	25	1·10	17	92
	50	1·10	14.2	93.3
	100	1·10	9.8	95.3
Control – I	–	Amount of H_2S in uncultured medium – 34 mg/l		
Control – II	10^6	Amount of H_2S in cultured medium – 213 mg/l		

As can be seen from Table 2, the NTA+$C_8H_{17}Br$ (1:1) complex has a bactericidal effect of 90% at a concentration of 25 mg/l, 91.2% at a concentration of 50 mg/l and 93.2% at a concentration of 100 mg/l [10]. The NTA+$C_8H_{17}Br$ (1:2) complex has a bactericidal effect of 92% at a concentration of 25 mg/l, 93.3% at a concentration of 50 mg/l and 95.3% at a concentration of 100 mg/l. The NTA+$C_6H_{13}Br$ (1:1) complex has a bactericidal effect of 94% at a concentration of 25 mg/l, 96% at a concentration of 50 mg/l and 98% at a concentration of 100 mg/l. The NTA+$C_6H_{13}Br$ (1:2) complex at a concentration of 25 mg/l 95%, at a concentration of 50 mg/l, 97% has a bactericidal effect [6]. The NTA+$C_6H_{13}Cl$ (1:1) complex has a bactericidal effect of 92% at a concentration of 25 mg/l, 95% at a concentration of 50 mg/l, and 97% at a concentration of 100 mg/l. The NTA+$C_6H_{13}Cl$ (1:2) complex has a bactericidal effect of 94.4% at a concentration of 25 mg/l, 96.7% at a concentration of 50 mg/l, and 98% at a concentration of 100 mg/l [12].

The NTA+$C_6H_{13}Br$ (1:2) complex at a concentration of 100 mg/l has a 99% bactericidal effect and completely stops the development of bacteria.

Table 3.
Bactericidal effect of NDI complexes

Complexes	Concentration of compound, C-mg/l	Number of bacteria (number of cells/ml)	Amount of H_2S, mg/l	Bactericidal effect, Z-%
NDI+$C_6H_{13}Br$ (1:2)	25	10^4	178	63
	50	10^2	82	83
	100	10^1	12	97.4
NDI+$C_6H_{13}Br$ (1:3)	25	10^2	84	82
	50	10^1	32	93
	100	10^1	4.6	99
NDI+$C_8H_{17}Br$ (1:2)	25	10^3	148	69
	50	10^1	62	87
	100	10^1	42	91
NDI+$C_8H_{17}Br$ (1:3)	25	10^2	71	85
	50	10^1	29	94
	100	–	6.5	99
NDI+$C_5H_{11}Br$ (1:3)	25	10^2	114	76
	50	10^1	43	91
	100	10^1	5.3	98.8
Control – I	–	Amount of H_2S in uncultured medium – 30-32 mg/l		
Control – II	10^8	Amount of H_2S in cultured medium – 476 mg/l		

As can be seen from Table 3, the NDI+$C_6H_{13}Br$ (1:2) complex and the NDI+$C_8H_{17}Br$ (1:2) complex slow down the development of bacteria by having a biocidal effect at concentrations of 25 and 50 mg/l. NDI+$C_6H_{13}Br$ (1:2) complex 97.4% at 100 mg/l concentration, NDI+$C_6H_{13}Br$ (1:3) complex 93% at 50 mg/l concentration [7], NDI+$C_8H_{17}Br$ (1:2) complex 100 mg/l concentration of 91%, NDI+$C_8H_{17}Br$ (1:3) complex shows 94% bactericidal effect at 50 mg/l concentration, NDI+$C_5H_{11}Br$ (1:3) complex shows 91% bactericidal effect at 50 mg/l concentration and 98.8% at 100 mg/l concentration [13].

NDI+$C_6H_{13}Br$ (1:3) complex and NDI+$C_8H_{17}Br$ (1:3) complex at a concentration of 100 mg/l have 99% bactericidal effect and completely stop the development of bacteria.

Table 4.

Bactericidal effect of NTI complexes

Complexes	Concentration of compound, C-mg/l	Amount of H_2S, mg/l	Bactericidal effect, Z-%
NTI+C_4H_9I (1:2)	50	79	71
	100	28	89.8
	200	25	91
NTI+$C_6H_{13}Cl$ (1:2)	50	80	71
	100	30	89.1
	200	26	90
NTI+$C_5H_{11}Br$ (1:2)	50	28	89.8
	100	27	90.2
	200	25	91
NTI+C_3H_7Br (1:2)	50	34	87.6
	100	29	89.4
	200	25	91
NTI+$C_6H_{13}Br$ (1:2)	50	29	89.4
	100	28	89.8
	200	25	91
NTI+$C_8H_{17}Br$ (1:2)	50	28	89.8
	100	27	90.2
	200	26	91
Medium 1 (uncultured)	28		
Medium 2 (cultured)	276		

As can be seen from Table 4, NTI+C_4H_9I complex shows 71% biocidal effect at 50 mg/l concentration and 89.8% at 100 mg/l concentration and 91% bactericidal effect at 200 mg/l concentration.

$NTI+C_6H_{13}Cl$ complex shows 71% biocidal effect at 50 mg/l concentration, 89.1% at 100 mg/l concentration and 90% bactericidal effect at 200 mg/l concentration. $NTI+C_5H_{11}Br$ complex shows 89.8% biocidal effect at 50 mg/l concentration, 90.2% at 100 mg/l concentration and 91% bactericidal effect at 200 mg/l concentration.

The synthesized complexes were compared with external reagents (АМДОР ИК-7 and АМДОР ИК-10) and the obtained substances showed higher results than them.

Investigation of synthesized norbornene carboxylic acid and amine-based complexes as antimicrobial additives

Synthesized novel norbornene-based complexes were studied as antimicrobial additives in lubricant-coolant fluids [25, 29, 30, 40]. The antimicrobial properties of compounds were determined by the zonal diffusion method based on GOST 9.052-88. The results of the study were compared with the control etalons (lubricant-coolant liquids-YSM) and the results are presented in table 5.

Table 5.
Results of the effect of complexes on YSM

№	Formul of compounds	Concentration of biocide, %	Zone of destruction of microorganisms (cm)
			Fungi (*Aspergillus niger, Cladosporium resiane, Penicillium chrysogenum, Trichoderma viride*)
1	$NTI+C_6H_{13}Br$	0.5	2.4-2.6
		0.25	1.3-1.5
2	$NTA+C_6H_{13}Br$	0.5	2.0-2.2
		0.25	+++
3	$NDI+C_6H_{13}Br$	0.5	1.0-1.0
		0.25	+++
4	$NDA+C_6H_{13}Br$	0.5	1.8-2.0
		0.25	1.0-1.0
5	$NDI+C_6H_{13}Cl$	0.5	1.1-1.1
		0.25	+++
6	$NDA+C_6H_{13}Cl$	0.5	1.6-1.8
		0.25	+++

Continuation of table 5

7	NTI+$C_6H_{13}Cl$	0.5	1.0-1.0
		0.25	+++
8	NTA+$C_6H_{13}Cl$	0.5	1.2-1.4
		0.25	+++
Control-YSM		–	+++

Table 5 shows that DETA-based amide and TETA-based imidazoline hexylbromide complex at both concentrations (0.5, 0.25%) shows high fungicidal properties. TETA-based amide hexylbromide complex and DETA-based amide hexylchloride complex at 0.5% concentration have a slightly higher fungicidal effect compared to other complexes.

As a result of research, the compounds given in (table 5) can be offered as antifungal antimicrobial additives in lubricating-coolant fluids.

Determination of surface activity of synthesized complexes

The surface tension (surface activity) at the water-air boundary was determined by preparing solutions of the synthesized complexes in water. Surface tension measurements were determined with the help of KVS "Sigma-702" Tensiometer and the results are given in tables 6 and 7 [31].

Table 6.

Surface activity of complexes (23^{o}C)

Concentration of reagents, %	Surface activity of reagents, mN/m	
	NTA+$C_6H_{13}Br$	NDA+$C_6H_{13}Br$
0.0025	66.3	59.9
0.0075	55.6	52.7
0.01	53.3	51.1
0.025	46.7	45.9
0.05	41.9	42.8
0.075	40.0	40.8
0.1	38.4	39.4
0.2	35.7	36.0
0.3	34.7	34.1
0.4	34.6	34.2
0.6	34.6	34.2

As can be seen from Table 6, triethylenetetraamine-based amide hexylbromide complex reduced the value of surface tension from 72.1±0.2 mN/m to 38.4 mN/m in the range of 0.025-0.1% concentration. Diethylenetriamine-based amide hexylbromide complex increases the value of surface tension from 72.1±0.2 mN/m at 0.2-0.6% concentration decreased to 34.2 mN/m in the thickness interval. Therefore, the TETA-based amidine complex exhibits surface activity in the concentration of 0.1% and the DETA-based amidine complex in the concentration of 0.6%.

Table 7.

Surface activity of complexes (23°C)

Concentration of reagents, %	Surface activity of reagents, mN/m			
	NTI+$C_6H_{13}Cl$	NDI+$C_6H_{13}Cl$	NTI+$C_6H_{13}Br$	NDI+$C_6H_{13}Br$
0.0025	57.6	51.0	60.5	63.8
0.0075	53.2	49.3	52.7	56.5
0.01	51.7	48.1	50.8	54.4
0.025	48.5	44.6	46.0	49.4
0.05	45.6	42.0	42.8	45.8
0.075	44.1	40.1	40.9	43.8
0.1	42.7	39.1	39.3	42.0
0.2	40.0	37.0	36.1	38.8
0.3	38.4	35.4	33.6	37.3
0.4	37.2	34.2	32.0	35.9
0.6	35.8	34.0	30.4	33.8

Table 7 shows the surface activity of TETA and DETA-based complexes. DETA-based imidazoline hexylchloride complex reduced the value of surface tension from 72.1±0.2 mN/m to 48.1 mN/m in the concentration interval of 0.0025-0.01%. TETA-based imidazoline hexylbromide complex decreased the value of surface tension from 72.1±0.2 mN/m to 30.4 mN/m in the range of 0.2-0.6% concentration. This means that the DETA-based imidazoline complex exhibits more surface activity at 0.1% concentration and the TETA-based imidazoline complex at 0.6% concentration.

Study of synthesized norbornene carboxylic acid and amine-based complexes as a surface-active oil collector and oil dispersantreagent

Pollution of water bodies on Earth with oil and oil products is at the forefront of environmental problems.

The possibility of using the new reagents in the cleaning of water bodies polluted with a thin layer of oil was checked. For this purpose, the oil collection and oil dispersing ability of compounds was determined in laboratory conditions [32, 35].

During the experiment, an oil sample from the Balakhani field was used, an experiment was conducted on a thin layer of oil created on the surface of 3 types of water (distilled, drinking and sea) with different degrees of mineralization, the reagent was applied to the oily water surface in the form of a 5% aqueous solution and undiluted product. The results are reflected in tables 8, 9 and 10 [35].

Table 8.

Results of oil collecting and oil dispersing properties of NDA+$C_6H_{13}Br$ complex

Reagent	Distillated water		Drinking water		Sea water	
	τ, h	К(K_D-%)	τ, h	К(K_D-%)	τ, h	К(K_D-%)
NDA+$C_6H_{13}Br$ (1:2)						
5% water solution (mass)	0-1.0 3.0-27.0 29.0-31.0 48.0	2.13 8.04 30.1 Sp.mark.	0-31.0 48.0	Disp.59.7 Sp.mark.	0 1.0-31.0 48.0	Disp.70.7 Disp.78.6 Sp. mark.
Undiluted product	0-1.0 3.0-27.0 29.0-31.0 48.0	4.25 10.6 45.02 Sp.mark.	0-31.0 48.0	Disp.67.3 Sp.mark.	0 1.0-31.0 48.0	Disp.83.9 Disp.88.7 Sp. mark.

As can be seen from the table, the oil accumulation coefficient of the 5% aqueous solution of hexylbromide complex of NDA in distilled water was equal to K_{max}=30.1, and K_{max}=45.02 in the undiluted case. The reagent showed moderate oil dispersing effect in drinking water and sea water. In the case of undiluted product in drinking water, K_D=67.3% in τ=0-31.0 hours, in sea water 5% aqueous solution in τ=1.0-31.0 hours, K_D=78.6%, in case of undiluted product in τ=1.0-31.0 hours, K_D=88.7% had an oil dispersing effect.

Table 9.

Results of oil collecting and oil dispersing properties of NTA complexes

Reagent	Distillated water		Drinking water		Sea water	
	τ, h	K(K_D,%)	τ, h	K(K_D,%)	τ, h	K(K_D,%)
NTA+$C_5H_{11}Br$ (1:2)						
5% water solution (mass)	0-2.0 3.0 23.0-80.0 152.0	12.39 34.42 77.44 19.36	0-2.0 3.0 23.0-28.0 56.0-62.0 80.0-152.0	Disp.94.6 Disp.94.6 Disp.97.0 Disp.97.0 Disp.95.5	0 1.0 2.0-3.0 23.0-28.0 56.0-62.0 80.0-152.0	Dis.92.9 Dis.94.2 Dis.91.3 Dis.94.1 Dis.94.1 Dis.95.5
Undiluted product	0-2.0 3.0 23.0-80.0 152.0	18.31 37.44 83.56 24.12	0-2.0 3.0 23.0-28.0 56.0-62.0 80.0-152.0	Disp.97.4 Disp.95.5 Disp.97.2 Disp.98.1 Disp.97.6	0 1.0 2.0-3.0 23.0-28.0 56.0-62.0 80.0-152.0	Dis.94.6 Dis.96.3 Dis.93.4 Dis.96.2 Dis.97.3 Dis.96.5
NTA+$C_8H_{17}Br$ (1:1)						
5%water solution (mass)	0-6.0 27.0-31.0 51.0-99.0	24.32 30.40 60.71	0 1.0-6.0 51.0-88.0 99.0	30.40 24.32 Disp.96.7 Disp.95.6	0-6.0 27.0-88.0 99.0	Dis.95.6 Dis.93.4 Dis.95.6
Undiluted product	0-6.0 27.0-31.0 51.0-99.0	28.42 34.25 66.43	0 1.0-6.0 51.0-88.0 99.0	34.46 28.52 Disp.97.3 Disp.96.4	0-6.0 27.0-88.0 99.0	Dis.96.7 Dis.96.4 Dis.97.2

According to Table 9, it can be said that the pentylbromide and octylbromide complex of NTA shows a high degree of oil collection and oil dispersing properties in both forms. Thus, the oil accumulation coefficient of the pentylbromide complex in distilled water of 5% and undiluted was K_{max}=77.44 and 83.56, respectively. A 5% aqueous solution in drinking water and undiluted were K_D=97.0% and 98.1%, respectively [39].

The oil accumulation coefficient of 5% aqueous solution of octylbromide complex of NTA in distilled water was equal to

K_{max}=66.43 at τ=51.0-99.0 hours, and K_{max}=34.46 at drinking water at τ=0 hours. Without rinsing, the reagent had K_D=97.2% oil dispersing effect at τ=99.0 hours [37].

Table 10.

Results of oil collecting and oil dispersing properties of NTI complexes

Reagent	Distillated water		Drinking water		Sea water	
	τ, h	K(K_D, %)	τ, h	K(K_D, %)	τ, h	K(K_D,%)
NTI+$C_5H_{11}Br$ (1:2)						
5%water solution (mass)	0 1.0-6.0 27.0-99.0	1.38 2.5 Sp.mark.	0-6.0 27.0-88.0 99.0	Disp.86.8 Disp.91.1 Disp.60.71	0 1.0-31.0 51.0-88.0 99.0	Disp.78.6 Disp.82.6 Disp.86.8 Disp.91.1
Undilu-ted product	0 1.0-6.0 27.0-99.0	2.63 3.34 Sp.mark.	0-6.0 27.0-88.0 99.0	Disp.89.3 Disp.94.2 Disp.65.8	0 1.0-31.0 51.0-88.0 99.0	Disp.84.5 Disp.86.7 Disp.89.3 Disp.94.7

According to Table 10 5% aqueous solution of pentylbromide complex of NTI has K_D=91.1% in drinking water at τ=27.0-88.0 hours, K_D=91.1% in seawater at τ=99.0 hours. In the case of undiluted product, K_D=94.2% in drinking water at τ=27.0-88.0 hours, and K_D=94.7% at seawater at τ=99.0 hours have a dispersing effect.

Based on the tests carried out in the field of studying the antimicrobial and antifungal properties of the synthesized complexes two acts were obtained.

CONCLUSION

1. Effective methods of thermal synthesis of new derivatives of norbornene (2 amides and 2 imidazolines) based on 5-norbornene-2-carboxylic acid and amines (DETA, TETA) were developed. The yield of the synthesized compounds was as follows: NDI 93%, NTI 84.28%, NDA 92.02%, NTA 91.4%. The physico-chemical properties of the obtained substances were determined, their composition and structure were confirmed by IR, ^{1}H, ^{13}C NMR spectroscopy methods.

2. 82 new alkylhalide complexes were obtained based on N-alkylation reaction of synthesized nitrogenous compounds with C_2H_5I, C_3H_7Br, C_4H_9I, $C_5H_{11}Br$, $C_6H_{13}Br$, $C_6H_{13}Cl$, $C_8H_{17}Br$ alkylhalides. The physico-chemical properties of the obtained complexes were determined, their composition and structure were confirmed by IR spectroscopy.

3. The bactericidal effect of the synthesized imidazoline complexes against microbiological corrosion was determined. During the test, the 1143 strain *"Desulfovibrio desulfuricans"* bacteria species taken from Absheron-Binagadi field based on "OCT 39-151-83" was used as a research object. The obtained complexes were compared with reagents used in industry and it was determined that industrial reagents (АМДОР ИК-7 and АМДОР ИК-10) had 60% biocide effect at 50 mg/l concentration and 75-80% biocidal effect at 100 mg/l concentration. Synthesized NDI+$C_6H_{13}Br$, NDI+$C_8H_{17}Br$, NDI+$C_5H_{11}Br$, NTI+$C_6H_{13}Cl$, NTI+$C_8H_{17}Br$ complexes show 90-99% bactericidal effect at these concentrations.

4. The bactericidal-inhibitory effect of the synthesized amide complexes against sulphate-reducing bacteria was tested. The received complexes NTA+C_4H_9I, NTA+$C_6H_{13}Br$, NTA+$C_8H_{17}Br$, NTA+$C_6H_{13}Cl$, NDA+C_4H_9I, NDA+$C_6H_{13}Cl$, NDA+$C_5H_{11}Br$ complexes were determined to show 90-99% bactericidal effect.

5. Obtained amide and imidazoline complexes were studied as antimicrobial additives in lubricating-coolant fluids. It was determined that NTI+$C_6H_{13}Br$ complex destroys fungi by showing a destruction zone of 1.3-1.5 cm at 0.25% concentration and 2.4-

2.6 cm at 0.5% concentration, NDA+$C_6H_{13}Br$ complex at 0.25% concentration 1.0-1.0 cm and 1.8-2.0 cm at 0.5% concentration. The NDA+$C_6H_{13}Cl$ complex at a concentration of 0.5% destroys fungi by showing a destruction zone of 1.6-1.8 cm, the NTA+$C_6H_{13}Cl$ complex shows a destruction zone of 1.2-1.4 cm.

6. The surface activity of the synthesized complexes was determined. NTA+$C_6H_{13}Br$ complex increased the value of surface tension from 72.1±0.2 mN/m to 38.4 mN/m at 0.1% concentration, NDA+$C_6H_{13}Br$ complex to 34.2 mN/m at 0.6% concentration, NDI+$C_6H_{13}Cl$ complex to 39.1 mN/m at 0.1% concentration. NTI+$C_6H_{13}Br$ complex decreased to 30.4 mN/m at 0.6% concentration, NTI+$C_8H_{17}Br$ complex to 27.0 mN/m at 3% concentration and NDI+$C_8H_{17}Br$ complex to 25.4 mN/m at 3% concentration.

7. Amide complexes synthesized on the basis of 5-norbornene-2-carboxylic acid and amines were studied as surface-active oil collecting and dispersing reagents. A 5% aqueous solution of pentylbromide complex of NDA in seawater had K_D=94.6% oil dispersing effect. The oil accumulation coefficient of 5% aqueous solution of hexylbromide complex of NDA in distilled water was equal to K_{max}=30.1. The oil accumulation coefficient of 5% aqueous solution of pentylbromide complex of NTA in distilled water was equal to K_{max}=77.44, K_D=97.0% in drinking water. The oil accumulation coefficient of the octylbromide complex of NTA in undiluted form was equal to K_{max}=66.43 in distilled water, K_{max}=34.46 in drinking water, and K_D=97.2% oil dispersing effect in sea water.

8. Imidazoline complexes obtained on the basis of 5-norbornene-2-carboxylic acid and amines were tested as surface-active oil collectors and dispersing reagents. The oil accumulation coefficient of the 5% aqueous solution of the hexylbromide complex of NDI was equal to K_{max}=60.79 in drinking water, and K_D=97.0% in sea water, and had an oil-dispersing effect. The oil accumulation coefficient of the 5% aqueous solution of the octylbromide complex of NDI in drinking water was equal to K_{max}=30.4, and in the undiluted case, K_D=94.6% had an oil dispersing effect in sea water.

5% aqueous solution of pentylbromide complex of NTI in drinking water showed K_D=91.1%, K_D=91.1% in sea water. The oil accumulation coefficient of the 5% aqueous solution of NTI octylbromide complex in distilled water was equal to K_{max}=19.36, in drinking water to K_{max}=34.42, and without dilution to K_{max}=82.21.

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