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SYNTHESIS AND RESEARCH INTO ANTICORROSION AND BACTERICIDE PROPERTIES OF CHLORINE-CONTAINING IMIDAZOLINE COMPLEXES OF DISTILLATED NATURAL OIL ACIDS

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The imidazoline complexes obtained by reaction of distillated natural oil acids (NOA) with diethylenetriamin (DETA) have been synthesized. The chlorine-containing complexes of NOA were synthesized on the basis of obtained imidazoline, their physio-chemical characteristics and structure proved true by IR-and NMR spectrums data. The properties of chlorine-containing imidazoline complexes of NOA as inhibitors of H_2S- and CO_2-, bio-corrosion have been studied. The tests showed that CO_2- and H_2S- corrosions of the complexes protect a metal surface up to 95-100%. The effect of the influence of synthesized complexes on life activity of sulphate-reducing bacteriums (SRB) in three concentrations at 30^0 C temperature during 15 days revealed that even at low concentrations these complexes may be recommended as high-effective inhibitors to oppose metal biocorrosion.

Keywords: *corrosion, biodamage, distillated natural oil acids, imidazolines, inhibitors, sulphate-reducing bacteriums*

The use of oilfield equipment is accompanied by various difficulties arising from biostate of charge, carbonic acid and hydrogen sulphide corrosion [1-3], etc. To control this effect, experts apply inhibitors of corrosion based on the basis of organic compounds with atoms of nitrogen, sulphur, oxygen and double bonds to thus favor absorption on metal surface [4]. It revealed that some nitrongen-containing derivatives of oil acids are CO_2 - corrosion [5,6].

The article deals with the results of investigations on working out CO_2- H_2O –and bio-corrosion on the basis of imidazoline chlorine-containing derivatives of natural oil acids (NOA) with diethylenetriamin (DETA).

EXPERIMENTAL PART

To synthesize chloroderivatives of NOA, the natural oil acids of "Karvan-L" diethylentriamin (DETA) (company "Kazanorgsyntensi," Russia), allyl chloride (Moscow company "Component Reactant", Russia) were used while the propyl chloroester of NOA was synthesized by authors of the article. The all reagents were used without any purification.

The structures of the obtained complex compounds were proved out by IR spectral analysis. Also, IR-spectrum of samples were registered on Fourier microscope LUMOS (firm BRUKER Germany) within wave frequency 600-4000 sm^{-1}.

NMR^{1}H spectrums were registered on Bruker Avance (Germany) II+300 (Ultra Shield ™ Magnet) 300 MHz, solvent-CD_3COOCD_3, chemical shifts are cited conformably TMS.

Some physical-chemical indices of complex compounds obtained on the basis of Baku natural oil acids were established. Crystallization temperature was established by standard – 5066-91, index of refraction n_D^{20} on refractometer IRF-22 N700060, relative density (d_4^{20}) by standard 3900-2000.

Synthesis of imidazoline of NOA. The 0.1 mol of NOA was put in a round-bottom-four-neck flask supplied with a mixer,

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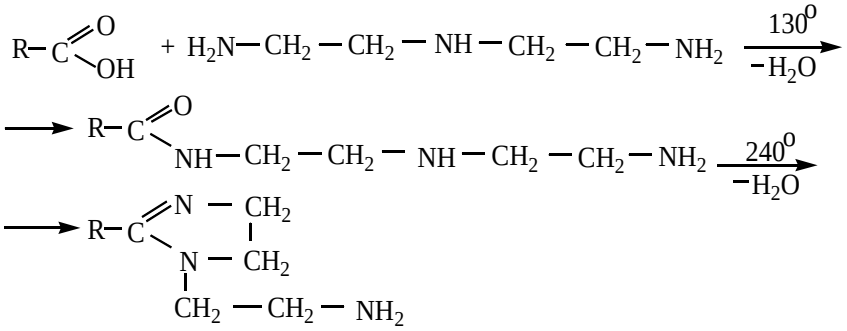
thermometer, opposite cooler and dropping funnel, then mixed and heated up to 80-90^{0}C temperature and DETA was discharged by means of dropping funnel within 1.5 hours. The initial compounds were given by mole correlation equal 1:1. During synthesis process the temperature was raised up to 240^{0}C and maintained for 3.5 hours. It should be noted that at130^{0}C temperature the amino amid of NOA was obtained as intermediate compound. Mixing continued until the temperature fell to 50-60^{0}C. It revealed that through the synthesis of imidazoline derivative of NOA on the basis of DETA a greater quantity of solid substances were formed with yield up to 90% mas synthesis of the chloride complex N-allyl imidazoline NOA (chloride of complex).

Synthesis of the chloride of N-allyl imidazoline complex of NOA (Chloride of complex I). The imidazaline of NOA and allylchloride were used as initial compounds in mol correlation 1:1. The reaction proceeded at 40-50^{0}C by mixing within 3-3.5 hours in the presence of solvent isopropyl alcohol. A yield of chlorine-containing imidazoline derivative of NOA is 95% mass.

Synthesis of chloride complex N-propyl naphtenate imidazoline of NOA (Chloride of complex II). The reaction proceeded on the basis of above-mentioned methods but at a temperature of 80-90^{0}C (a boiling point of isopropyl alcohol) during 3 hours. The imidazoline of NOA and propylchloride ester of NOA were taken as initial compounds. Complex compounds obtained with 97% mass of yield.

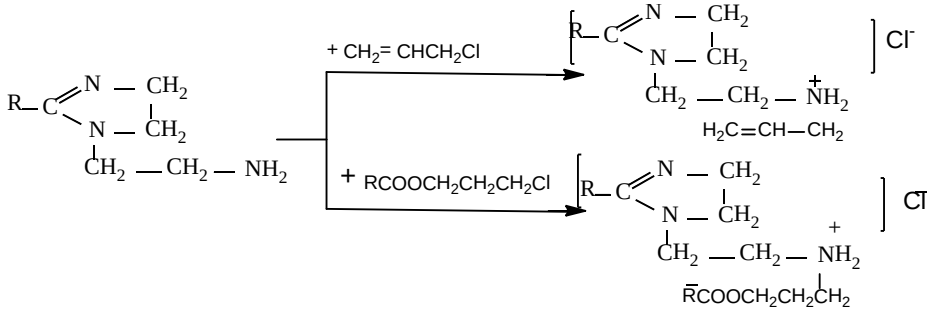
RESULTS AND THEIR DISCUSSION

The synthesis of imidazoline of NOA proceeds by the interaction of NOA with DETA according to the scheme below:



where, R –mixture of alkyl, izoalkyl and naphtenic radicals

The synthesis of chlorine-containing imidazoline complexes of distillated natural oil acids proceeds by the interaction of imidazoline of NOA with chlorine-containing products according to the scheme below:



Note that the synthesized products were identified by IR and ^{1}H NMR-spectroscopy method. These are followed by bands of absorption in the IR-spectrum

imidazoline of NOA: deformative (1552,1607 sm^{-1}) and valence (3279 sm^{-1}) vibrations of N-H bond in group NH_2, deformative vibrations (2923,1454, 2813, 2853,1375 sm^{-1}) C-H bond of CH_2, CH_3 – groups, deformative vibrations (1010, 1138, 1272 sm^{-1}) C-N bond and deformative vibrations (1655 sm^{-1}) C= N bond (Fig1).

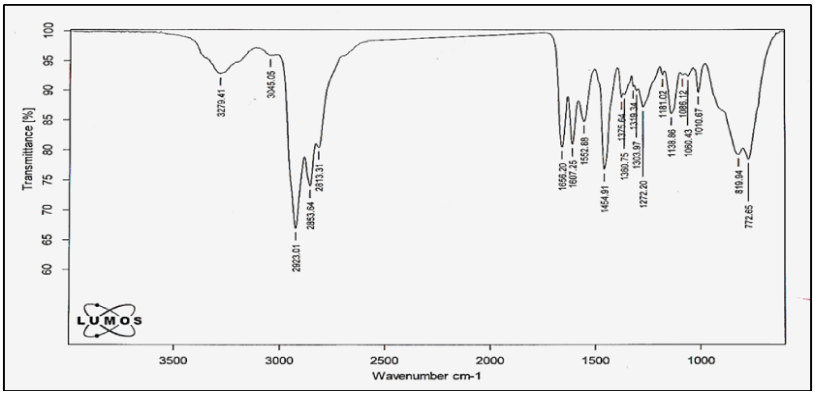


Fig 1. IR Spectrum of imidazoline of NOA

Resonance signals inherent in NOA (CH_3, CH_2, aromatic and naphthenic cycles) are observed in a sample of imidazoline of NOA of the proton spectrum. The chemical shifts at δ = 0.90 and 1.35 m.d. correspond to CH_3 and CH_2 resonance signals for alkyl groups, in the range δ = 1.5-1.8 m.d. for the naphthenic ring. The resonance signals corresponding to amidoamines, in the magnetic field region δ = 2.3 – 3.10 m.d, are characteristic for - CH_2 - NH_2 groups, and at δ = 2.0-2.2 m.d. is characteristic for NH_2 groups, at δ = 3.30-3.60 m.d. identified by signals related to the ethyl groups (fig.2).

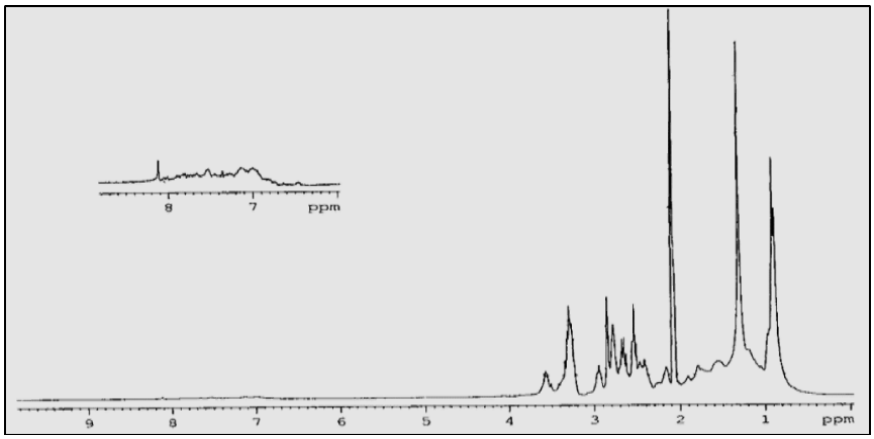


Fig 2. ^{1}H-NMR of imidazoline of NOA

Next comes the following band absorption in IR-spectrum Chloride of complex I: valence (2870, 2925, 2966 sm^{-1}) and deformative vibrations (1377, 1460 sm^{-1}) of C-H bond of CH_2 , CH_3 groups; deformation (951, 1549 sm^{-1}) vibrations of N-H bond in groups NH_2; valence(1105, 1129, 1160 sm^{-1})vibrations C-N bond, valence(1645 sm^{-1}) vibrations C=N bond, deformative (1404 sm^{-1}) vibrations of CH_2 group wide band N^+, deformativ (922, 977 sm^{-1}) vibrations of C=C bond in α-position and valence (3048 sm^{-1}) vibrations of $=CH_2$ groups(fig3).

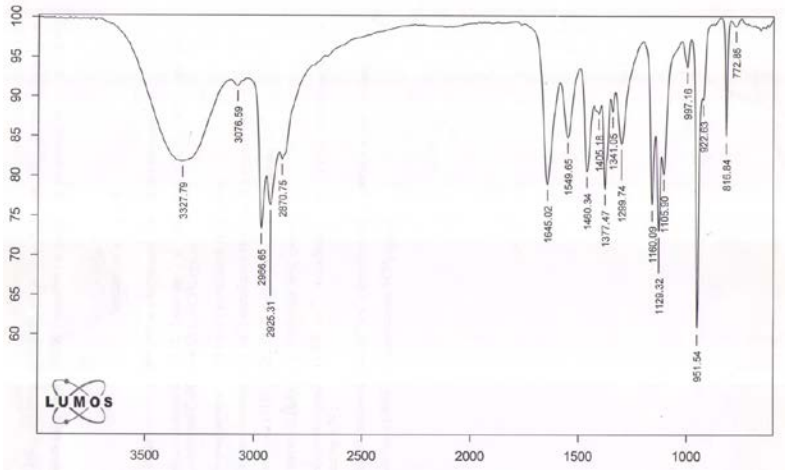


Fig 3. IR Spectrum of chloride of complex I

There is a band absorption in IR-spectrum chloride of complex II as follows: pendular (724 sm^{-1}) oscillations of C-H bond of CH_2, deformative (1457, 1460 sm^{-1}) and valence(2923, 2955 sm^{-1}) vibrations of C-H bond of CH_2 group, deformative(2923,2955 sm^{-1}) vibrations of C-H bond of CH_3; valence (1378 sm^{-1}) for C=O bond of ester and (1647 sm^{-1}) vibrations of C-N bond, deformation (952 sm^{-1}) vibrations of N-H bond in groups NH_2; valence (1129, 1160 sm^{-1}) vibrations C-N bond, deformative (1547 sm^{-1}) and valence (3291 sm^{-1})vibrations of C-N bound NH^+, NH, NH_2 groups (fig 4).

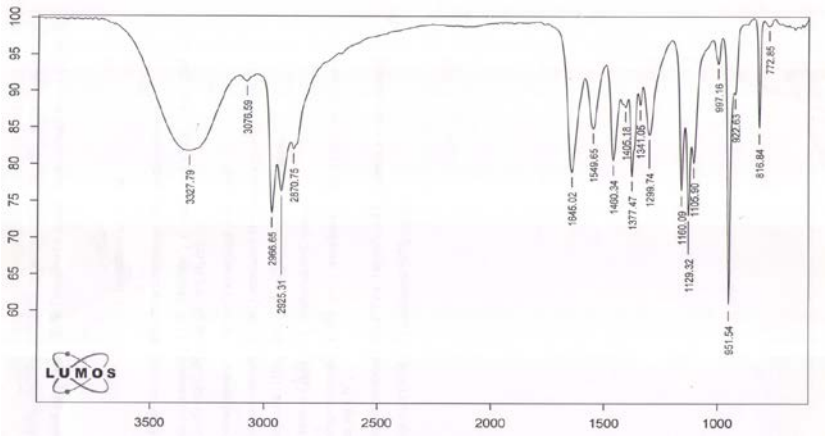


Fig 4. IR Spectrum chloride of complex II

Physio-chemical parameters of synthesized chlorine-containing imidazoline complexes are shown in Table 1.

Table 1. Physio-chemical parameters of synthesized products

Name of complex compounds	Correlation of complexes	d_4^{20} kq/m^3	n_D^{20}	Freezing point, ^{0}C	Yield , %
Imidazoline of NOA	1:1	1086	1.2340	17	89.9
Chloride of complex N-allyl imidazoline of NOA **(**Chloride of complex I)	1:1	1105	1.2160	-	95

Chloride complex N-propyl naphtenate imidazoline of NOA (Chloride of complex II).	1:1	1045	1.1885	-	97

Antibacterial properties of synthesized imidazoline complexes of NOA. The influence of synthesized chlorine-containing imidazolin complexes of NOA on the vital activity of SRB. SRB's 1143 strain was tested. Sterilized test tubes with 20 ml volume were used in the experiment [6]. Bactericidal effect of the reagents mainly manifested itself during 15 days and then examined on the basis of calculation of the generated H_2S content. Note that H_2S was determined iodometrically. The water was chosen as a solvent for the complexes which dissolved well to generate transparent solutions with 1% concentration. SRB are obligate anaerobic bacteriums that dissimilate sulphates into hydrogen sulfide (H_2S). Medium "Postgate - B" is more effective nutrient medium for SRB development. The composition of nutrient medium "Postgate -B" is shown in Table 2. The pH of the medium should be within 7.0-7.5.

Table 2. Composition of feeding medium "Postgate-B"

№	Name of compounds	Gramme	№	Name of compounds	Gramme
1	Potassium salt of dihydrophosphate acid	0.5	4	Magnesium sulphate	2.0
2	Ammonia chloride	1.0	5	Sodium lactate	3.5
3	Calcium sulphate	1.0	6	Sodium chloride	2.0

Special additives were put into the nutrient medium for the development of SRB. These additions have the following composition: 5% solution of $FeSO_4 \cdot 7H_2O$ in 2% solution of hydrochloric acid, 5% aqueous solution of $NaHCO_3$, 1% of crystalline $Na_2S \cdot 9H_2O$ is in the 1% aqueous solution of Na_2CO_3.

The influence of the dependence of chlorine-containing imidazoline complexes of NOA at concentrations of 15, 75, 150 on the growth of the bacterium is shown in Table 3.

Table 3. The effect of protecting chlorine-containing imidazoline complexes of NOA.

Conditional name	Correlation of complexes	Concentration of complexes, mq/l		
		15	75	150
Amount of forming H_2S, mg/l				
Chloride of complex I	1:1	80	40	-
Chloride of complex II	1:1	-	-	-
Medium 1 "Postgate-B"	24-32			
Medium 2 "Postgate-B" and SRB	275			
Corrosion protection of complexes %				
Chloride of complex I	1:1	70,9	85,4	100
Chloride of complex II	1:1	100	100	100

According to Table 3, when SRB affects on chloride of complex II in correlation 1:1 with concentrations of 15, 75, 150 mq/l, no H_2S formation is observed because this complex at all concentration displays a 100% bactericid effect to completely suppress the

growth of SRB. Chloride of complex I exerts biostate action, and at 75 mg/l it demonstrates biocide action and suppresses the activity of SRB. At concentration of 150 mg/l it shows 100% bactericide effect to suppress the growth of SRB.

Anticorrosion properties of synthesized complexes. The ACM GL was used to study the kinetics of the CO_2 corrosion process. The process is carried out at a temperature of 500 °C, with the participation of an electrode of low-carbon steel C1018. During a 20-hour test, the corrosion current and the loss of metal and corrosion rates (mm/year) were calculated automatically every 15 minutes in the research. The obtained chlorine-containing imidazoline complexes of NOA were tested as corrosion inhibitors at 100 ppm. The effect of complex solutions on the CO_2 corrosion process is shown in Table 4.

Table 4. Effect of complex solutions on the CO_2 corrosion process

Solution numbers	Corrosion current, mA/c	Corrosion rate, mm/year	Total metal	Potential (mV)
Chloride of complex I	0.0233	0.2702	0.0006	587.6
Chloride of complex II	0.0158	0.1833	0.0007	619.9
Without inhibitors	0.3406	3.9474	0.0067	-689.6

At the turn of 20 hours, the effect of corrosion protection of these chlorine-containing imidazoline complexes of NOA reached 95.35% and 93.14% mass (Fig.5) respectively.

Fig. 5. The influence of chlorine-containing imidazoline complexes of NOA on the corrosion kinetics of CO_2 in a 1% aqueous solution of NaCl saturated with CO_2 at 100 ppm.

The effect of chlorine-containing imidazoline complexes of NOA on H_2S corrosion was analyzed as well. The two-phase systems of water: kerosene in 9: 1 ratio was used in the investigation. The water was saturated with H_2S to 500 mg / l. The medium was mixed by a magnetic mixer. The experiment lasted for 5 hours. The steel plates for 3 hours. The experiments showed that the best indications proved to be chloride of complex I at a concentration of 5, 10, 15 ppm showing respectively 92, 95.99 and 100 %, chloride of complex II at all concentrations showed 100% protection against H_2S

corrosion which makes it possible to recommend them as an H_2S corrosion inhibitor (Tab.5). Table 4 provides data on inhibiting and bactericidal properties of chlorinecontaining complexes I and II.

Table 4. Comparative analysis of inhibiting and bactericidal properties of complexes

Name of complex	Corrosion protection from H_2S		Corrosion protection from CO_2		Influence on SRB	
	Min. consentration mq/l	Effect protection %	Min. consen-tration mq/l	Min. consentration mq/l	Effect protection %	Min. consen-tration mq/l
Chloride of complex N-allyl imidazoline of NOA (Chloride of complex I)	5 10 15	92 95,99 100	100	95,35	15 75 150	70,9 85,4 100
Chloride complex N-propyl naphtenate imidazoline of NOA(Chloride of complex II).	5 10 15	100 100 100	100	93,14	15 75 150	100 100 100

RESULTS

The imidazolines NOA obtained on the basis of natural oil acids with diethylenetriamine were synthesized. The chlorine-containing imidazoline complexes of NOA were obtained on the basis of synthesized imidazoline NOA having been tested as inhibitors: 1) with CO_2 corrosion (100 ppm) the chlorine-containing imidazoline complexes of NOA protect the metal surface at 93.14 and 95.35%, 2) with H_2S corrosion (5, 10, 15 ppm) the chloride of complex N-allyl imidazoline of NOA protects the metal surface respectively at 92, 95.99 and 100%; Chloride complex N-propyl naphtenate imidazoline of NOA (5 ppm) protects the metal surface against H_2S corrosion by 100%. The physicochemical characteristics and the effect of the synthesized compounds on the activity of sulfate-reducing bacteria in three concentrations at 30^0C for 15 days were also studied. It found that the chloride complex N-propyl naphtenate imidazoline of NOA at low concentrations (15ppm) has higher antibacterial properties and can be recommended as a highly effective inhibitor against bio-corrosion of metals.

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СИНТЕЗ И ИССЛЕДОВАНИЕ АНТИКОРРОЗИОННЫХ И БАКТЕРИЦИДНЫХ СВОЙСТВ ХЛОРСОДЕРЖАЩИХ ИМИДАЗОЛИНОВЫХ КОМПЛЕКСОВ ПРИРОДНЫХ НЕФТЯНЫХ КИСЛОТ

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Синтезированы имидазолиновые комплексы, полученные реакцией дистиллированных природных нефтяных кислот (ПНК) с диэтилентриамином (ДЭТА). На основе полученного имидазолина синтезированы хлорсодержащие комплексы ПНК, определены их физико-химические характеристики; строение подтверждено данными ИК и Н'ЯМР спектров. Изучены свойства хлорсодержащих имидазолиновых комплексов ПНК в качестве ингибиторов H_2S - , CO_2- и биокоррозий. Испытания показали, что при CO_2- и H_2S- коррозиях комплексы защищают поверхность металла до 95-100%. Эффект воздействия синтезированных комплексов на жизнедеятельность сульфатвосстанавливающих бактерий (СВБ) в трех концентрациях при 30^0C в течение 15 суток выявил, что даже при низких концентрациях комплексы могут быть рекомендованы в качестве высокоэффективных ингибиторов против биокоррозии металлов.

***Ключевые слова**: коррозия, биоповреждение, дистиллированные природные нефтяные кислоты, имидазолины,ингибиторы, сульфатвосстанавливающие бактерии.*

TƏBİİ NEFT TURŞULARININ XLORTƏRKİBLİ İMİDAZOLİN KOMPLEKSLƏRİNİN SİNTEZİ, ONLARIN KORROZİYAYA QARŞI VƏ BAKTERİSİD XASSƏLƏRİNİN TƏDQİQİ

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Təbii neft turşularının (TNT) dietilentriaminlə reaksiya nəticəsində imidazolin komplekslər sintez edilmişdir. Alınan imidazolin komplekslər əsasında xlortərkibli komplekslər sintez olunmuş, onların fiziki-kimyəvi xassələri müəyyən olunmuş, quruluşları İQ- və NMR- spektral analizləri ilə təsdiq olunmuşdur. TNT-nın xlortərkibli imidazolin kompleksləri hidrogen sulfid, karbon qazı və biokorroziyaya qarşı inhibitor kimi xassələri tədqiq olunmuşdur. Tədqiqatlar nəticəsində müəyyən edilmişdir ki, karbon qazı və hidrogensulfid mühitində korroziya zamanı bu komplekslər metal səthini 95-100%-ə qədər mühafizə edirlər, sulfatreduksiyaedici bakteriyaların həyat fəaliyyətinə isə ən aşağı qatılıqda, 30^0C temperaturda, 15 sutka ərzində məhvedici təsir göstərmiş və metalların biokorroziyasına qarşı yüksək effektiv inhibitor kimi təklif olunmuşdur.

***Açar sözlər:** korroziya, biozədələnmə, təbii neft turşuları, imidazolin, inhibitor, sulfatreduksiyaedici bakteriyalar*