UDK 632.953.2

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

N.A. Mammadova, S.A. Mamedkhanova

Azerbaijan State Oil and Industry University
20, Azadliq ave., AZ 1010, Baku; e-mail: n.a.mamedova@inbox.ru

The imidazoline complexes obtained by reaction of distilled 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 H₂S- and CO₂-, bio-corrosion have been studied. The tests showed that CO₂- and H₂S- 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° 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, distilled 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 nitrogen-containing derivatives of oil acids are CO₂ - corrosion [5,6].

The article deals with the results of investigations on working out CO₂- H₂O –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” diethylenetriamin (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 cm⁻¹.

NMR¹H spectrums were registered on Bruker Avance (Germany) II+300 (Ultra Shield TM Magnet) 300 MHz, solvent- CD₃COOCD₃, 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,

thermometer, opposite cooler and dropping funnel, then mixed and heated up to 80-90°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°C and maintained for 3.5 hours. It should be noted that at 130°C temperature the amino amid of NOA was obtained as intermediate compound. Mixing continued until the temperature fell to 50-60°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 imidazoline of NOA and allylchloride were used as initial compounds in mol correlation 1:1. The reaction proceeded at 40-50°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°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 distilled 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 ¹H NMR-

spectroscopy method. These are followed by bands of absorption in the IR-spectrum

imidazoline of NOA: deformative ($1552, 1607 \text{ cm}^{-1}$) and valence (3279 cm^{-1}) vibrations of N-H bond in group NH_2 , deformative vibrations ($2923, 1454, 2813, 2853, 1375 \text{ cm}^{-1}$) C-H bond

of CH_2, CH_3 – groups, deformative vibrations ($1010, 1138, 1272 \text{ cm}^{-1}$) C-N bond and deformative vibrations (1655 cm^{-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 $\delta = 0.90$ and 1.35 m.d. correspond to CH_3 and CH_2 resonance signals for alkyl groups, in the range $\delta = 1.5-1.8 \text{ m.d.}$ for the

naphthenic ring. The resonance signals corresponding to amidoamines, in the magnetic field region $\delta = 2.3 - 3.10 \text{ m.d.}$, are characteristic for $-\text{CH}_2 - \text{NH}_2$ groups, and at $\delta = 2.0-2.2 \text{ m.d.}$ is characteristic for NH_2 groups, at $\delta = 3.30-3.60 \text{ m.d.}$ identified by signals related to the ethyl groups (fig.2).

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

Next comes the following band absorption in IR-spectrum Chloride of complex I: valence ($2870, 2925, 2966 \text{ cm}^{-1}$) and deformative vibrations ($1377, 1460 \text{ cm}^{-1}$) of C-H bond of CH_2, CH_3 groups; deformation ($951, 1549 \text{ cm}^{-1}$) vibrations of N-H bond in groups NH_2 ; valence ($1105, 1129, 1160 \text{ cm}^{-1}$) vibrations C-N

bond, valence (1645 cm^{-1}) vibrations C=N bond, deformative (1404 cm^{-1}) vibrations of CH_2 group wide band N^+ , deformative ($922, 977 \text{ cm}^{-1}$) vibrations of C=C bond in α -position and valence (3048 cm^{-1}) vibrations of $=\text{CH}_2$ 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 cm^{-1}) oscillations of C-H bond of CH_2 , deformative ($1457, 1460\text{ cm}^{-1}$) and valence ($2923, 2955\text{ cm}^{-1}$) vibrations of C-H bond of CH_2 group, deformative ($2923, 2955\text{ cm}^{-1}$) vibrations of C-H bond of CH_3 ; valence

(1378 cm^{-1}) for C=O bond of ester and (1647 cm^{-1}) vibrations of C-N bond, deformation (952 cm^{-1}) vibrations of N-H bond in groups NH_2 ; valence ($1129, 1160\text{ cm}^{-1}$) vibrations C-N bond, deformative (1547 cm^{-1}) and valence (3291 cm^{-1}) vibrations of C-N bond 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} kg/m^3	n_D^{20}	Freezing point, $^{\circ}\text{C}$	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, mg/l		
		15	75	150
Amount of forming H ₂ S, 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 CO₂ 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 CO₂ corrosion process is shown in Table 4.

Table 4. Effect of complex solutions on the CO₂ 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 CO₂ in a 1% aqueous solution of NaCl saturated with CO₂ at 100 ppm.

The effect of chlorine-containing imidazoline complexes of NOA on H₂S 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 H₂S 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 H₂S

corrosion which makes it possible to recommend them as an H₂S corrosion inhibitor (Tab.5). Table 4 provides data on inhibiting and bactericidal properties of chlorine-containing complexes I and II.

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

Name of complex	Corrosion protection from H ₂ S		Corrosion protection from CO ₂		Influence on SRB	
	Min. concentration mg/l	Effect protection %	Min. concentration mg/l	Min. concentration mg/l	Effect protection %	Min. concentration mg/l
Chloride of complex N-allyl imidazoline of NOA (Chloride of complex I)	5	92	100	95,35	15	70,9
	10	95,99			75	85,4
	15	100			150	100
Chloride complex N-propyl naphthenate imidazoline of NOA (Chloride of complex II).	5	100	100	93,14	15	100
	10	100			75	100
	15	100			150	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 CO₂ corrosion (100 ppm) the chlorine-containing imidazoline complexes of NOA protect the metal surface at 93.14 and 95.35%, 2) with H₂S 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 naphthenate imidazoline of NOA (5 ppm) protects the metal surface against H₂S corrosion by 100%. The physicochemical characteristics and the effect of the synthesized compounds on the activity of sulfate-reducing bacteria in three concentrations at 30⁰C for 15 days were also studied. It found that the chloride complex N-propyl naphthenate 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.

REFERENCES

1. Tributsch H., Rojas Chapana J.A. Metal sulfide semiconductor electrochemical mechanisms induced by bacterial activity. *Electrochim. Acta*. 2000, vol. 45, pp. 4705-4716.
2. Miranda E., Bethencourt M., Botana F.J., Cano M.J., Sanchez-Amaya J.M., Corzo A., Olivier B. Biocorrosion of carbon steel alloys by an hydrogentrophic sulphate-reducing bacterium *Desulfovibrio capillatus* isolated from a Mexican oil field separator. *Corrosion Science*. 2006, vol. 48, pp. 2417-2431.
3. Abbasov B.M., Jabrailzade Sh.Z., Mursalov N.I. and other. Sulfonous distillates of diesel fuel as corrosion inhibitors and bactericides. *Journal of Natural and Technical Sciences*. 2010, no. 3 (47), pp. 60-64.
4. Abbasov V.M., Haney M. Abd El-Latef, Aliyeva L.I. et al. Evaluation of new complex surfactants based on vegetable oil as corrosion inhibitors for mild steel in CO₂ saturated 1% NaCl solution. *Journal of Materials Physics and Chemistry*. 2013, no. 2, pp. 19-26.
5. Abbasov V.M., Rzayeva N.Sh., Talybov A.G. Synthesis and study of sulfate derivative of N-cyclohexylamides of oleic acid as an inhibitors of CO₂ corrosion. / 13th Ibn Sina

International Conference on Pure and Applied Heterocyclic Chemistry «Heterocyclic Chemistry for Sustainable Future». Hurgada, Egypt, 14-17 february 2015, p. 211.

6.Kuznetsov Y.I. Physio-chemical aspects of the inhibition of corrosion of metals in water governmental solution. *Russian Chemical Reviews*. 2004, vol. 73, no.1, pp.79-93.

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

Н.А. Мамедова, С.А. Мамедханова

*Азербайджанский Государственный Университет Нефти и Промышленности,
Az 1010, г. Баку, пр Азадлыг 20, e-mail: n.a.mamedova@inbox.ru*

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 ¹H ЯМР спектров. Изучены свойства хлорсодержащих имидазолиновых комплексов ПНК в качестве ингибиторов H₂S - , CO₂- и биокоррозий. Испытания показали, что при CO₂- и H₂S- коррозиях комплексы защищают поверхность металла до 95-100%. Эффект воздействия синтезированных комплексов на жизнедеятельность сульфатвосстанавливающих бактерий (СВБ) в трех концентрациях при 30⁰С 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.