https://doi.org/10.59849/3006-1318.2025.2.45
UDC 547.781.3

N.R.Abdullayeva, R.Y.Kaziyeva, S.F.Akhmadbayova, E.I.Azizbeyli
Y.G.Mamedaliyev' Institute of Petrochemical Processes
Ministry of Science and Education of the Republic of Azerbaijan
Baku, 30 Khojaly Ave.
E-mail: rtahirova@mail.ru

RESERCH ON STRUCTURAL FEATURES AND PHYSICO-CHEMICAL PARAMETERS OF PLANT-BASED BISIMIDAZOLINES

The intensive development of industry, the expansion of production processes, and the improvement of key process parameters require the reliable operation of process equipment and building structures. Reliable corrosion protection plays a key role in ensuring the continuous operation of equipment. This article presents the results of a study of certain structural features and physicochemical characteristics of bisimidazolines synthesized based on a oxidized in the presence of manganese naphthate mixture of corn, palm, and cottonseed oil fatty acids with triethylenetetramine. The aim of this study is to further investigate their potential as corrosion inhibitors in preservative formulations. The cyclic structure of the bisimidazolines is confirmed, and the intensity and optical density of the main functional groups, as well as their solubility in various hydrocarbon environments are determined.

Keywords: bisimidazolines, structure, optical density, intensity, solubility

Introduction

Corrosion affects various sectors, from energy and transport to petrochemicals and construction. Globally, according to various estimates, the annual economic losses from corrosion range from 3 to 4% of the world's gross domestic product (GDP), which is equivalent to hundreds of billions of dollars. Corrosion also poses a significant threat to ecosystems, as the destruction of structures like pipelines, storage tanks, and offshore platforms can lead to leaks of chemicals, oil, and other toxic substances into the environment. These leaks often result in ecological disasters, contaminating water, soil, and air, and damaging flora and fauna.

Effective diagnosis of corrosion processes and the selection of appropriate protection methods help reduce this percentage, increasing the economic efficiency of enterprises and preventing emergency situations [1].

Among various protection methods, chemical-technological methods based on the use of inhibitors occupy a special place [2, 3]. Organic compounds are a universal and effective basis for their creation. Their efficiency can be significantly enhanced through structural modifications, the use of composite systems, and the application of environmentally friendly natural components. In the future, the development of organic inhibitors is focused on creating complex, multifunctional protective compositions adapted to specific operating conditions.

Thus, an analysis of inhibition methods reflected in modern scientific literature reveals the following. There is active use of heterocyclic inhibitors and their salts [4]. Six-membered aromatic heterocycles—pyridinium salts of alkylphenols—have been studied as biocides and inhibitors of hydrogen sulfide corrosion in oil production [5]. Corrosion inhibitors for steel in water-salt environments, which are fully conjugated organic compounds of quinone derivatives, have also been investigated [6]. The six-membered polycyclic amine, urotropine, is used for inhibiting acid corrosion [7]. It has been established that protective layers formed on the surface of 12Cr18Ni10Ti stainless steel in H_2SO_4 solutions containing inhibitor compositions based on a five-membered triazole derivative – ИФХАН-92, exhibit a protective effect [8]. The corrosion rate of ferrous metals in hydrogen sulfide-containing environments has been studied. The inhibitor contains an organic ammonia derivative and aminotriazole or its derivative [9].

Imidazoline salts prove to be particularly effective, demonstrating resistance to temperature fluctuations and chemical aggression [10]. The anti-corrosion protection of metals in highly mineralized hydrogen sulfide-containing environments has been studied. The corrosion inhibitor contains imidazoline derivatives in its active base [11]. The corrosion of an API 5L X-70B pipeline was tested in the presence of an imidazoline derivative under constant flow conditions in a brine solution containing kerosene [12]. The inhibition of mild steel corrosion in a CO_2-containing 0.5 M NaCl solution was investigated using imidazolines having mono-, di-, and triphenyl substituents on C and N in $CH_2CH_2NH_2$ and $(CH_2CH_2NH)_2$ $CH_2CH_2NH_2$ suspensions [13]. The case of retarding the corrosion process of steel rebar in a steam solution containing 3.5% NaCl in the presence of a specialized cationic imidazoline quaternary ammonium salt inhibitor was considered [14]. The inhibiting properties of imidazoline derivatives based on diethylenetriamine and natural petroleum acids have been studied in a 1% aqueous sodium chloride solution saturated with carbon dioxide and in a hydrogen sulfide environment [15]. The kinetic effect on the corrosion of Ст3 steel of inorganic complexes of imidazoline derivatives, obtained from synthetic petroleum acids and polyethylene polyamines with nitric acid, in a hydrogen sulfide environment was studied in work [16].

In recent years, considerable attention has been paid to the development of environmentally friendly corrosion inhibitors, based on plant compounds that contain nitrogen-bearing functional groups. These substances are renewable, biodegradable, and less toxic compared to traditional synthetic analogs. The advantages include: availability of raw materials, absence of toxic components and heavy metals, biodegradability, and compatibility with water treatment systems. Moreover, the growing popularity of biodegradable inhibitors stimulates further research into the synthesis and modification of imidazolines based on plant-derived raw materials to enhance their effectiveness and stability under various conditions [17][18].

In this work, we present the results of studies on the structure and physicochemical characteristics of bis-imidazolines synthesized based on a mixture of fatty acids (oxidized in the presence of manganese naphthenate) of certain vegetable oils with triethylenetetramine (TETA). The goal is the subsequent investigation of their potential as corrosion inhibitors in the composition of lubricants and preservation fluids.

Experimental part

Corn, cotton and palm oils were used as the starting raw materials. The process of isolating fatty acids from vegetable oils was carried out by hydrolysis. The oxidation of the isolated acids was performed with atmospheric oxygen in the presence of a manganese naphthenate catalyst according to the method presented in [19]. The synthesis of bis-imidazolines was conducted following the procedure in [20]. Given the number of amine fragments in the polyamine used, the ratio of acids to triethylenetetramine was taken as 2:1 for the preparation of bis-imidazolines.

The synthesized bis-imidazolines were identified by IR spectroscopy using an ALPHA spectrometer (BRUKER, Germany) in the wavenumber range of 600−4000 cm^{-1}. The IR spectra of the bis-imidazolines are presented in figures 1-3.

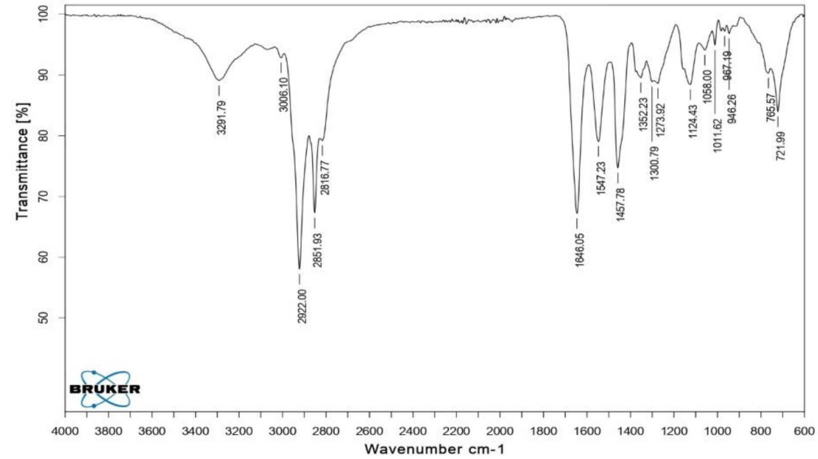

Fig. 1. IR Spectrum of Bis-imidazoline synthesized based on a mixture of corn oil acids (oxidized in the presence of Mn aphthenate) with triethylenetetramine.

The following absorption bands are observed in the IR spectrum of the sample presented in figure 1:

• Deformation (721,1457 cm^{-1}) and stretching (2816,2852,2922 cm^{-1}) vibrations of the C–H bond in CH_3 and CH_2 groups;

• Stretching (3006 cm^{-1}) vibrations of the C=C bond;

• Deformation (1547 cm$^{-1)}$ and stretching (3291 cm^{-1}) vibrations of the N–H group;

• Stretching (1273 cm^{-1}) vibrations of the C–N bond;

• Stretching (1646 cm^{-1}) vibrations of the C=N bond.

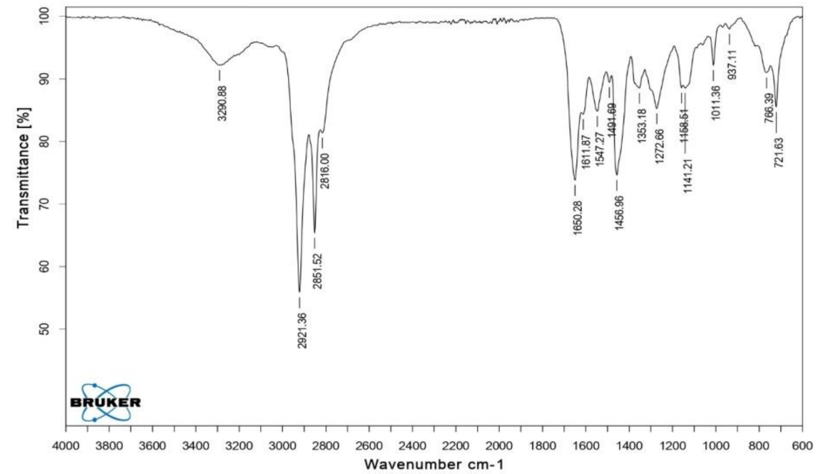

Fig. 2. IR spectrum of bis-imidazoline synthesized based on a mixture of palm oil acids (oxidized in the presence of Mn naphthenate) with triethylenetetramine.

The following absorption bands are observed in the IR spectrum of the sample presented in figure 2:

• Deformation (721,1353,1456 cm^{-1}) and stretching (2816,2851,2921 cm^{-1}) vibrations of the C–H bond in CH_3 and CH_2 groups;

• Deformation (1491,1547,1611 cm^{-1}) and stretching (3290 cm^{-1}) vibrations of the N–H group;

• Stretching (1272 cm^{-1}) vibrations of the C–N bond;

• Stretching (1650 cm^{-1}) vibrations of the C=N bond.

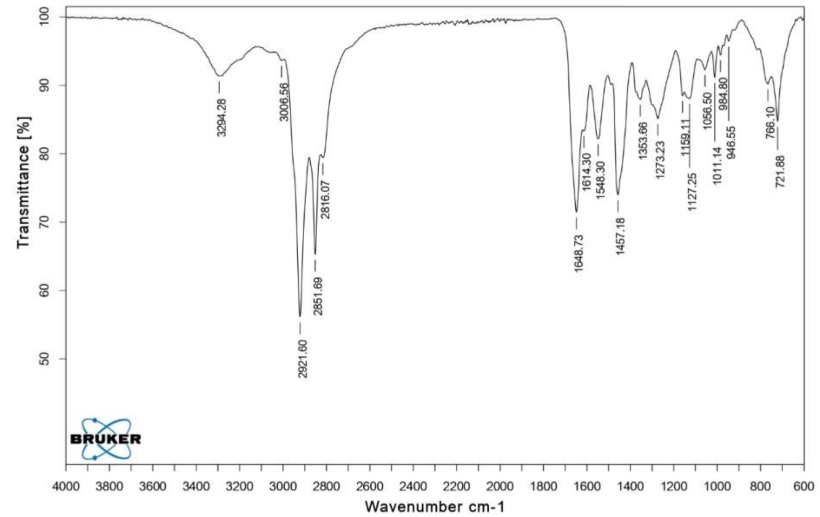

Fig. 3. IR Spectrum of bis-imidazoline synthesized from a mixture of cottonseed oil acids (oxidized in the presence of Mn naphthenate) with triethylenetetramine.

The following absorption bands are observed in the IR spectrum of the sample presented in figure 3:

• Deformation (721,1353,1457 cm^{-1}) and stretching (2816,2851,2921 cm^{-1}) vibrations of the C–H bond in CH_3 and CH_2 groups;

• Stretching (3006 cm^{-1}) vibrations of the C=C bond;

• Deformation (1548,1614 cm^{-1}) and stretching (3294 cm^{-1}) vibrations of the N–H group;

• Stretching (1273 cm^{-1}) vibrations of the C–N bond;

• Stretching (1648 cm^{-1}) vibrations of the C=N bond.

Results and discussion

The intensities of the absorption bands and the optical densities of the C–N and C=N bonds of the bis-imidazolines were studied. The results of the research are presented in table 1.

Table 1

Intensities of Absorption Bands and Optical Densities of Certain Bis-imidazoline Bonds

Sample Name	Intensity of absorption bands, I		Optical Density of Bonds, D	
	C=N 1648 см$^{-1}$	C-N 1273 cm^{-1}	C=N 1648 cm^{-1}	C-N 1273 cm^{-1}
Bis-imidazoline based on a mixture of oxidized fatty acids of corn oil (MOACO) with TETA	67.18	79.03	0.173	0.102
Bis-imidazoline based on a mixture of oxidized fatty acids of palm oil (MOAPO) with TETA	73.70	84.84	0.132	0.071
Bis-imidazoline based on a mixture of oxidized fatty acids of cottonseed oil (MOACsO) with TETA	71.46	82.12	0.146	0.085

The analysis of the absorption band intensities (I) for the C=N bonds at 1648 cm^{-1} in the bis-imidazolines showed an increase in the sequence: MOACO ($I_{C=N}$1648 cm^{-1}) = 67.18 → MOACsO ($I_{C=N}$1648 cm^{-1}) = 71.46 → MOAPO ($I_{C=N}$1648 cm^{-1}) = 73.70.

The absorption band intensity for the C–N bond at 1273 cm^{-1} changes in the same order: MOACO ($I_{C–N}$1273 cm^{-1}) = 79.03 → MOACsO ($I_{C–N}$1273 cm^{-1}) = 82.12 → MOAPO ($I_{C–N}$1273 cm^{-1}) = 84.84.

A comparison of the optical density (D) of the C=N bonds at 1648 cm^{-1} in the studied bis-imidazolines is reflected in the following absolutely inverse intensity sequence: MOAPO ($D_{C=N}$1648 cm^{-1}) = 0.132 → MOACsO ($D_{C=N}$1648 cm^{-1}) = 0.146 → MOACO ($D_{C=N}$ 1648 cm^{-1}) = 0.173.

The accumulation of the optical densities (D) of the C–N bonds at the 1273 cm^{-1} peak of the bis-imidazolines occurs in the following similar increasing sequence: MOAPO ($D_{C–N}$ 1273 cm^{-1}) = 0.071 → MOACsO ($D_{C–N}$1273 cm^{-1}) = 0.085 → MOACO (D $_{C–N}$1273 cm^{-1}) = 0.102.

Some physicochemical characteristics of the synthesized bis-imidazolines were studied. The research results are presented in table 2.

Table 2

Physicochemical characteristics of bis-imidazolines

Sample Name	Appearance	Elative density, d_4^{20}, g/cm³	Dropping point temperature, °C	Solubility indicators				
				Benzene	Gasoline	Ethanol	White Spirit	DMFA
Bis-imidazoline based on a mixture of oxidized fatty acids of corn oil with TETA	Viscous mass light brown color	0.940	34	+	+	+	+	+
Bis-imidazoline based on a mixture of oxidized fatty acids of palm oil with TETA	Viscous mass yellow color	0,942	49	+	±	±	±	±
Bis-imidazoline based on a mixture of oxidized fatty acids of cottonseed oil with TETA	Viscous mass dark yellow color	0,935	48	+	±	±	±	±

Note:

• + - *completely soluble*

• ± - *soluble with cloudiness*

Conclusions

Based on the conducted IR spectroscopy studies, the cyclic structure of the bis-imidazolines was proven, and the intensity and optical density of their main functional groups were determined. An inverse relationship between these specified values (I and D) was established. The investigation of the physicochemical characteristics of the bis-imidazolines determined their solubility in various hydrocarbon media, dropping points, and density, which varied within the range of 0.935 to 0.942 g/cm^3.

REFERENCES

1. Zhang, X., Yang, B. Corrosion and protection of materials in extreme environments. Springer, 2021.
2. Жуков А.И. Коррозия и защита металлов. М.: Металлургия, 2019.
3. Козлов А.П. и др. Ингибиторы в защите оборудования. Химическая технология. 2021, 4, с. 22–30.
4. Lin C. et al. Corrosion Inhibitors in Petroleum Industry. Applied Sciences. 2020, v. 10,10, p. 767-772.
5. Труфанова А.И. Повышение экологической надежности ингибитора ГПИ-4. Материалы Международного конгресса «Зашита-92». Москва, 1992, с. 47.
6. Грибанкова А.А., Агиевич М.А. Исследование производных бензохинона, как ингибиторов сероводородной корозии. Сборник докладов 2-ой международной научно-технической конференции, повященной 115-и летию со дня рождения професоора Г.В. Акимова «Коррозия, старение и биостойкость материалов в морском климате», Москва, Курчатовский НИИ, 2016, с. 8.
7. Шипигузов И.А., Колесова О.В., Вахрущев В.В., Казанцев А.Л., Пожлов В.З., Лановетский С.В., Черезова Л.А. Современные ингибиторы коррозии. Вестник Пермского Национального Исследовательского Политехнического Университета. Химическая Технология и Биотенология. 2016, 1, с.114-129.
8. Авдеев Я.Г., Макаричев Ю.Б., Кузнецов Д.С. Защитное последействие ингибитора ИФХАН-92 при коррозии хромоникелевой стали в серной кислоте. Коррозия: материалы, защита. 2020, 12, с. 23-31.
9. Кузнеуов Ю.И., Фролова Л.В., Авдеев Я.Г., Андреев Н.Н., Зель.О.О. Ингибитор сероводородной коррозии и наводороживания металлического оборудования. Патент РФ №. 2539132, 2015.
10. Wang L., Zhang D., Tang Y. Imidazolium-based ionic liquids as effective corrosion inhibitors for mild steel in HCl. Corrosion Science. 2021, v. 185, p. 109402.
11. Мазитова А.К., Могучев А.И., Даминов Р.Р., Буилова Э.А., Аглиулин А.Х. Ингибитор коррозии. Патент РФ. № 2706927, 2019.
12. 40. Diaz-Cruz M., Dominguez-Aguilar M. A., Cervantes-Tobon A. Corrosion inhibition of pipeline steel X-70 in sour brine by an imidazoline derivative under flow assisted conditions. International Journal of Electrochemical Science. 2017. v. 12 (8). p. 7481-7501.
13. Mazumder M.A.J., Nazal M.K., Faiz M., Ali Sh.A. Imidazolines Containing single, twin- and triple-tailed hydrophobes and hydrophilic pendants (CH2CH2NH)nH as inhibitors of mild steel corrosion in CO2-0.5 M NaCl. RSC Advances, 2016, v. 6, 15, p. 12348-12362.
14. Fei F.L., Hu J., Wey J.X., Yu Q.J., Chen Zh. Sh. Corrosion performance of steel reinforcement in simulated concrete pore solutions in the presence of imidazoline quaternary ammonium salt corrosion inhibitor. Construction and Building Materials, 2014, v. 70, p. 43-53.

15. Аббасов В.М., Мурсалов Н.И., Джабраилзаде Ш.З. Исследование производных имидазолинов в качестве ингибиторов коррозии стали. Практика противокоррозионной защиты. 2015, 2 (76), с. 38-43.
16. Аббасов В.М., Мамедбейли Э.Г., Агамалиева Д.Б. Синтез неорганических комплексов производных имидазолина на основе синтетических нефтяных кислот и их кинетическое действие на сероводородную коррозию. Транспорт и хранение нефтепродуктов и углеводородного сырья. 2018, 2, с. 39-43.
17. Abbasov V.M., Ismayilova O.D. Synthesis and evaluation of novel bismidazolines as green corrosion inhibitors. Journal of Molecular Liquids, 2019. v. 274. p. 837–845.
18. Abbasov V.M., Aliyev R.A. Bio-based corrosion inhibitors: prospects and challenges. Environmental Chemistry Letters, 2022. v. 20. p. 235–246.
19. Казиева Р.Ю. Каталитическое окисление кислот, выделенных из растительных масел. Сборник научных трудов XX международной конференции студентов, аспирантов и молодых ученых «Перспективы Развития Фундаментальных Наук» Томск, 2023г. с. 99-101.
20. Абдуллаева Н.Р. Азотсодержащие моноалкил(С8-С12)фенол формальдегидные олигомеры в качестве компонента консервационных жидкостей. Коррозия: материалы, защита. 2019, 4, с.26-32.

UOT 547.781.3

N.R.Abdullayeva, R.Y.Kazıyeva, S.F.Əhmədbəyova, E.İ.Əzizbəyli
AR Elm və Təhsil Nazirliyi
Akad. Y.H.Məmmədəliyev adına Neft-Kimya Prosesləri İnstitutu, Bakı ş.

BİTKİ ƏSASLI BİSİMİDAZOLİNLƏRİN STRUKTUR XÜSUSİYYƏTLƏRİNİN VƏ FİZİKİ-KİMYƏVİ XASSƏLƏRİNİN TƏDQİQİ

XÜLASƏ

Açar sözlər: bisimidazolinlər, struktur, optiki sıxlıq, intensivlik, həllolma

Sənayenin intensiv inkişafı, istehsal proseslərinin genişləndirilməsi, əsas proses parametrlərinin təkmilləşdirilməsi texnoloji avadanlıqların və tikinti konstruksiyalarının etibarlı istismarını tələb edir. Korroziyadan etibarlı qorunma avadanlığın fasiləsiz işləməsini təmin edən tədbirlər kompleksinin əsas komponentidir. Məqalədə manqan naftenatın iştirakında oksidləşməyə məruz qalmış qarğıdalı, palma, pambıq yağ turşuları qarışığı və trietilentetramin əsasında sintez olunmuş bisimidazolinlərin bəzi struktur xüsusiyyətlərinin və fiziki-kimyəvi xassələrinin tədqiqi nəticələri təqdim olunub. Məqsəd onların sonradan qoruyucu tərkiblərdə korroziya inhibitorları kimi potensialını müəyyən etməkdir. Bisimidazolinlərin siklik quruluşu təsdiqlənib, əsas funksional qrupların intensivliyi, optiki sıxlıqları və həmçinin müxtəlif karbohidrogen mühitlərdə həllolma qabiliyyətləri müəyyən olunub.

УДК 547.781.3

Н.Р.Абдуллаева, Р.Ю.Казиева, С.Ф.Ахмедбекова, Э.И.Азизбейли
Институт Нефтехимических Процессов им. акад. Ю.Г.Мамедалиева, г. Баку
Министерства Науки и Образования АР

ИССЛЕДОВАНИЕ СТРУКТУРНЫХ ОСОБЕННОСТЕЙ И ФИЗИКО-ХИМИЧЕСКИХ ПОКАЗАТЕЛЕЙ БИСИМИДАЗОЛИНОВ РАСТИТЕЛЬНОГО ПРОИСХОЖДЕНИЯ

РЕЗЮМЕ

Ключевые слова: бисимидазолины, структура, оптическая плотность, интесивность, растворимость

Интенсивное развитие промышленности, увеличение производственных процессов, повышение основных технологических параметров требуют надежную эксплуатацию технологического оборудования и строительных конструкций. Особое место в комплексе мероприятий по обеспечению беспрерывной эксплуатации оборудования отводится надежной защите его от коррозии. В статье представлены результаты исследований некоторых структурных особенностей и физико-химических характеристик бисимидазолинов, синтезированных на основе смеси окисленных в присуствии нафтната марганца жирных кислот кукурузного, пальмового и хлопкового масел с триэтилентетрамином с целью дальнейшего исследования их в качестве ингибиторов коррозии в консервационных составах. Подтверждена цикличекская структура бисимидазолинов, определены интенсивность, оптическая плотность основных функциональных групп, а также растворимость в различных углеводородных средах.

Daxil oldu: 14.09.2025-ci il