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MUNDARIJA

MUNDARIJA • СОДЕРЖАНИЕ • CONTENTS

TAILORING ALKYL CHAIN LENGTH IN ISOQUINOLINIUM-BASED INHIBITORS: IMPACT ON ADSORPTION BEHAVIOR AND CORROSION PROTECTION IN OIL REFINING SYSTEMS

Sanalar
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Abstract. In this study, new corrosion inhibitors based on arylcarbonylmethylisoquinolinium chlorides were synthesized and evaluated for application in oil refining systems. The inhibition performance was investigated using electrochemical and gravimetric methods in model oilfield wastewater. The results revealed a strong dependence of corrosion inhibition efficiency on the alkyl chain length. The maximum efficiency (79.8%) was achieved for the compound containing 10 carbon atoms, indicating an optimal balance between hydrophobicity and solubility. Adsorption analysis showed that the inhibition process follows the Langmuir isotherm, suggesting monolayer adsorption of inhibitor molecules on the metal surface. The inhibition mechanism is governed by both electronic effects and molecular structure, leading to the formation of a stable protective film. The synthesized compounds demonstrate high potential as effective corrosion inhibitors for oil refining and transportation systems.

Keywords: *corrosion inhibition, adsorption isotherm, Langmuir model, isoquinolinium compounds, alkyl chain length, electrochemical analysis, oil refining systems*

Аннотация. В данном исследовании были синтезированы и оценены новые ингибиторы коррозии на основе арилкарбонилметилизохинолинийхлоридов для применения в системах нефтепереработки. Эффективность ингибирования исследовали электрохимическими и гравиметрическими

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методами в модельных сточных водах нефтепромыслов. Результаты показали сильную зависимость эффективности ингибирования коррозии от длины алкильной цепи. Максимальная эффективность (79,8%) была достигнута для соединения, содержащего 10 атомов углерода, что указывает на оптимальный баланс между гидрофобностью и растворимостью. Анализ адсорбции показал, что процесс ингибирования соответствует изотерме Лангмюра, что указывает на монослойную адсорбцию молекул ингибитора на поверхности металла. Механизм ингибирования определяется как электронными эффектами, так и молекулярной структурой, что приводит к образованию стабильной защитной пленки. Синтезированные соединения демонстрируют высокий потенциал в качестве эффективных ингибиторов коррозии для нефтеперерабатывающих и транспортных систем.

Ключевые слова: *ингибирование коррозии, изотерма адсорбции, модель Лангмюра, изохинолиниевые соединения, длина алкильной цепи, электрохимический анализ, нефтеперерабатывающие системы.*

Annotatsiya. Ushbu tadqiqotda arilkarbonilmetilizoxinolin xloridlarga asoslangan yangi korroziya ingibitorlari sintez qilindi va neftni qayta ishlash tizimlarida qo‘llanilishi o‘rganildi. Ingibirlash samaradorligi namuna va model neft konlari oqava suvlarida elektrokimyoviy va gravimetrik usullar yordamida o‘rganildi. Natijalar korroziyani ingibirlash samaradorligining alkil zanjiri uzunligiga kuchli bog‘liqligini ko‘rsatdi. Maksimal samaradorlikka (79,8%) 10 ta uglerod atomini o‘z ichiga olgan birikma uchun erishildi, bu gidrofoblik va eruvchanlik o‘rtasidagi optimal muvozanatni ko‘rsatadi. Adsorbsiya tahlili shuni ko‘rsatdiki, ingibirlash jarayoni Lengmyur izotermasiga amal qiladi, bu esa metall yuzasida ingibitor molekulalarining monoqatlamli adsorbsiyasini ko‘rsatadi. Ingibirlash mexanizmi ham elektron effektlar, ham molekulyar tuzilish bilan boshqariladi, bu esa barqaror himoya plyonkasining hosil bo‘lishiga olib keladi. Sintez qilingan birikmalar neftni qayta ishlash va tashish tizimlari uchun samarali korroziya ingibitorlari sifatida yuqori samaradorlikka ega ekanligini ko‘rsatadi.

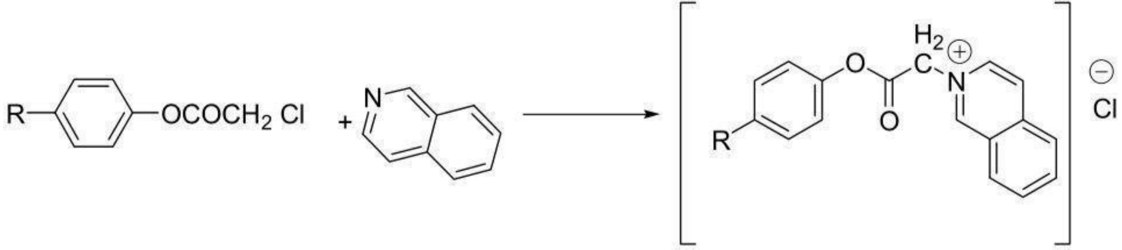
Kalit so‘zlar: *korroziyani ingibirlash, adsorbsiya izotermasi, Lengmyur modeli, izoxinolin birikmalari, alkil zanjir uzunligi, elektrokimyoviy tahlil, neftni qayta ishlash tizimlari.*

Introduction

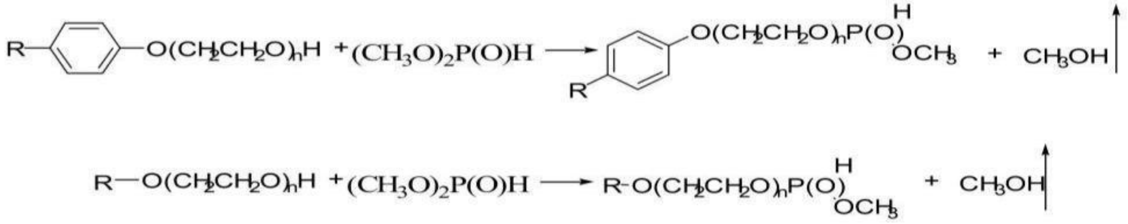
In recent years, many studies have discussed the relationship between the protective effect of inhibitor molecules and various properties: radical size, surface area covered by the radical and its branching, inhibitor solubility, permeability, and dipole moment. The ionization potential of inhibitor molecules, the electron-donating and electron-withdrawing properties of substituents, etc. are key indicators. The vast amount of information on the influence of the structure of inhibitor molecules on their protective properties can be conditionally divided into two groups: 1) the influence of the chemical structure of molecules on their protective properties; 2) the influence of the electronic structure of molecules on their protective properties. The first group of dependencies links the protective properties of organic inhibitors with the structural properties of the molecules, such as the length and distribution of the radical, its size, the surface area of the metal covered by the inhibitor molecule during adsorption, its location, and absorption. The number of multiple bonds in the inhibitor molecule, etc. The second group of dependencies links the protective properties of inhibitors to the electron density at the adsorption center of the molecule, which is significantly affected by the nature and position of various substituents. In terms of energy, three parts can be distinguished in the molecule of a compound with corrosion inhibitor properties. One of the functional groups, as a rule, ensures the interaction of the compound molecule with the surface metal cluster due to chemisorption, the final grouping determines the properties of the metal surface modified due to the adsorption of inhibitor molecules and should provide an ordered dense packed structure of the inhibitor protective layer based on Wander Waals forces. [3, 4]. The above-described structure is described in the synthesis of ammonium compounds of the type N-[isononylphenoxypoly (ethyleneoxy) carbonylmethyl]ammonium chlorides [5,6]. These works demonstrate the high efficiency of the synthesized compounds as corrosion inhibitors and discuss the dependence of the inhibitory properties of N-[isononylphenoxypoly(ethyleneoxy)carbonylmethyl]ammonium chlorides on their structure. Continuing this work, we carried out the synthesis of quaternary ammonium salts based on heterocyclic amines. The aim of this work was to synthesize two types of compounds: arylcarbonylmethylisoquinolinium chlorides and heterolonium salts of phosphoric acids. In addition, the protective properties of the compounds obtained for oil transportation and refining processes were evaluated, and the relationship between the chemical nature of the compound molecule, the concentration used, the duration of contact with the metal, and the protective effect was determined was also analyzed. Arylcarbonylmethylisoquinolinium chlorides have been prepared by the Menshutkin reaction [7]. Functionally substituted alkyl halides are converted to alkylphenols by the reaction of monochloroacetic acid catalytic esterification with aryloxymonochloroacetates was obtained. To expand the range of ideas about the protective effects of the compounds under study, we synthesized a series of alkylphenols with 6 to 18 carbon atoms in the side chain. The synthesis of aryloxymonochloroacetates is characterized by the reaction:

where: R is an alkyl radical C6; C9; C10-12; C16-18;

The resulting alkyl halides are functionalized in isoquinolinium alkylation. used to obtain suppressors and functional exchangers used to obtain arylcarbonylmethylisoquinoline chloride:



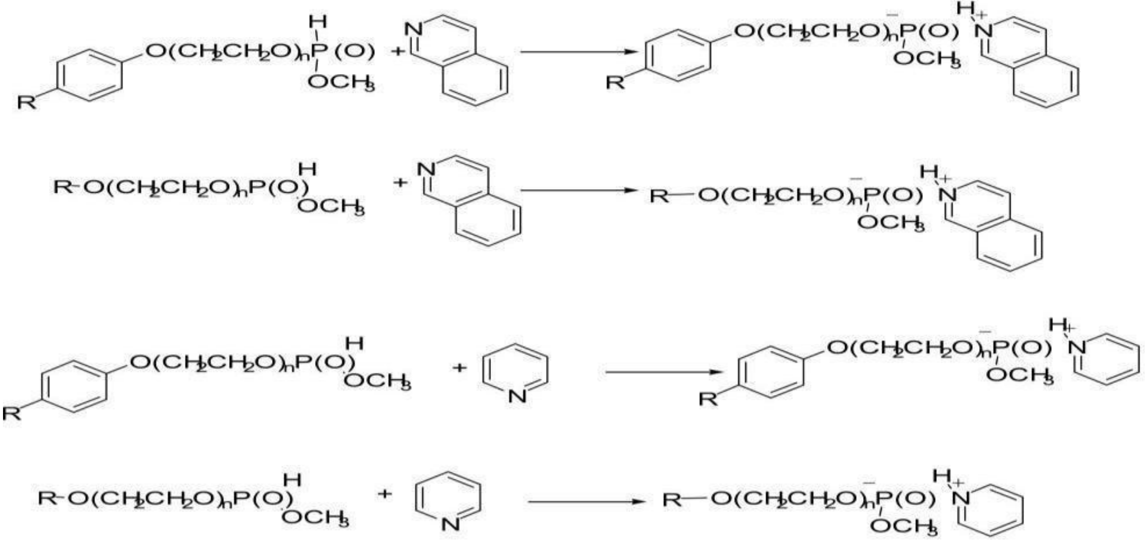
The reaction of isoquinoline with alkylphenoxycarbonylmethyl chlorides was carried out without solvent at 110-120°C for 8-10 hours. The ratio of starting materials was: 1 mol of ester per 1.1 mol of amine (for compounds containing heterocyclic nitrogen). The yield of the materials was theoretically 95.5 - 98.5%. The products obtained are dark brown resins. The IR spectra show absorption bands -(C=O) 1740-1760 cm^{-1}, -(S-O) 1110-1135 cm^{-1}. Elemental analysis and IR spectral data allow us to assign the structure of arylcarbonylmethylisoquinolinium chlorides to these compounds. The synthesis of heteryloninium salts of phosphoric acids was carried out as follows: initially, esters of phosphoric acids containing a phosphoryl functional group were obtained by transesterification of dimethyl phosphite with ethoxylated alkylphenols or ethoxylated alcohols [8]. Conventionally, esterification reactions can be described by the equations:



The synthesis of esters was carried out in a round-bottom three-necked flask equipped with a mechanical stirrer, thermostatic bath, and a dropping funnel at 100-110 °C for 8-10 hours. 1 mole of ethoxylated alkylphenols or ethoxylated alcohols in a ratio of 1.1 moles of dimethylphosphite. The yield of the substances was 90-97% of the theoretical. The obtained compounds were characterized by elemental analysis data, as well as by NMR spectroscopy. The chemical shift signals were 9-13 ppm, spin-spin coupling constants (J) in the region of 700-710 Hz, which allows us to attribute the structure of phosphoric acid esters to these compounds.

Materials and methods

The resulting acidic esters of phosphoric acid have been used to alkylate heterocyclic amines to obtain functionally substituted heteroylionium salts of phosphoric acids. These reactions can be described by the following equations:



The reaction of heterocyclic amines with acidic esters of phosphoric acid was

Table 1. Effect of alkyl chain length on corrosion inhibition parameters

Compound	Carbon atoms	Icorr (μA/cml)	z (%)	Surface coverage (i)
C6	6	12.8	48.5	0.485
C9	9	8.4	66.2	0.662
C10	10	5.1	79.8	0.798
C12	12	6.3	73.1	0.731
C16	16	7.9	67.5	0.675
C18	18	9.6	60.4	0.604

carried out without solvent at a temperature of 110-120 °C for 8-10 hours. The ratio of starting materials: 1 mol of ester per 1.1 mol of amine. The yield of the material was 85-88% of the theoretical value. The mass fractions of the main substance in the preparations were determined by titration. The synthesis scheme we used allows us to design functionally substituted compounds with a set of putatively useful properties (corrosion inhibitors) by dividing the molecule into key functional groups (containing nitrogen or phosphorus) and long-chain hydrocarbon radicals on the donor atoms. The inhibitory effect of the synthesized compounds was studied by electrochemical method. Measurements were carried out on oil refining wastewater models in an electrochemical chamber with a volume of 50-100 ml. The solutions are mixed with a magnetic stirrer. The working electrode is in the form of epoxy resin St3; the surface area is 0.3 cm2. Before measurements, the working surface of the electrode is polished, degreased, washed with bidistillate, and then placed in the solution. A platinum wire was used as the auxiliary electrode. The reference electrode was silver chloride, with respect to which all potential values were given. The studies were conducted using a P-5848 potentiostat. The corrosion rate of steel was studied by the polarization resistance method, which consists in obtaining a potentiostatic polarization curve at low values of polarization.

Results and discussion

The corrosion inhibition performance of the synthesized compounds was evaluated using electrochemical and gravimetric methods. Special attention was paid to the effect of molecular structure, particularly the length of the alkyl chain, on the protective properties of the inhibitors. It is well known that the efficiency of organic corrosion inhibitors is largely determined by their adsorption behavior on the metal surface, which depends on both electronic properties and molecular structure. Therefore, in this study, the relationship between alkyl chain length, adsorption characteristics, and corrosion inhibition efficiency was systematically analyzed.

The data presented in Table 1 clearly demonstrate the influence of alkyl chain length on corrosion inhibition performance. A significant decrease in corrosion current density (Icorr) is observed with increasing carbon number from C6 to C10, indicating improved adsorption and surface protection. The highest inhibition efficiency (79.8%) and surface coverage (и = 0.798) are achieved for the C10 compound, confirming its optimal molecular structure for corrosion protection. This behavior is attributed to the balanced combination of hydrophobicity and solubility, which promotes the formation of a dense and stable protective film on the metal surface. Further increase in alkyl chain length leads to a decrease in inhibition efficiency, which can be explained by steric hindrance effects and reduced solubility of long-chain compounds, limiting their effective adsorption on the metal surface. To further understand the adsorption mechanism of the synthesized inhibitors on the metal surface, the adsorption behavior was analyzed using the Langmuir adsorption isotherm [11,14]. The surface coverage (и) values obtained from inhibition efficiency were used to evaluate the adsorption process according to the following equation:

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C$$

where C is the inhibitor concentration and Kads is the adsorption equilibrium constant.

The linear relationship between C/и and C indicates that the adsorption of inhibitor molecules on the metal surface follows the Langmuir isotherm model [9,10]. This

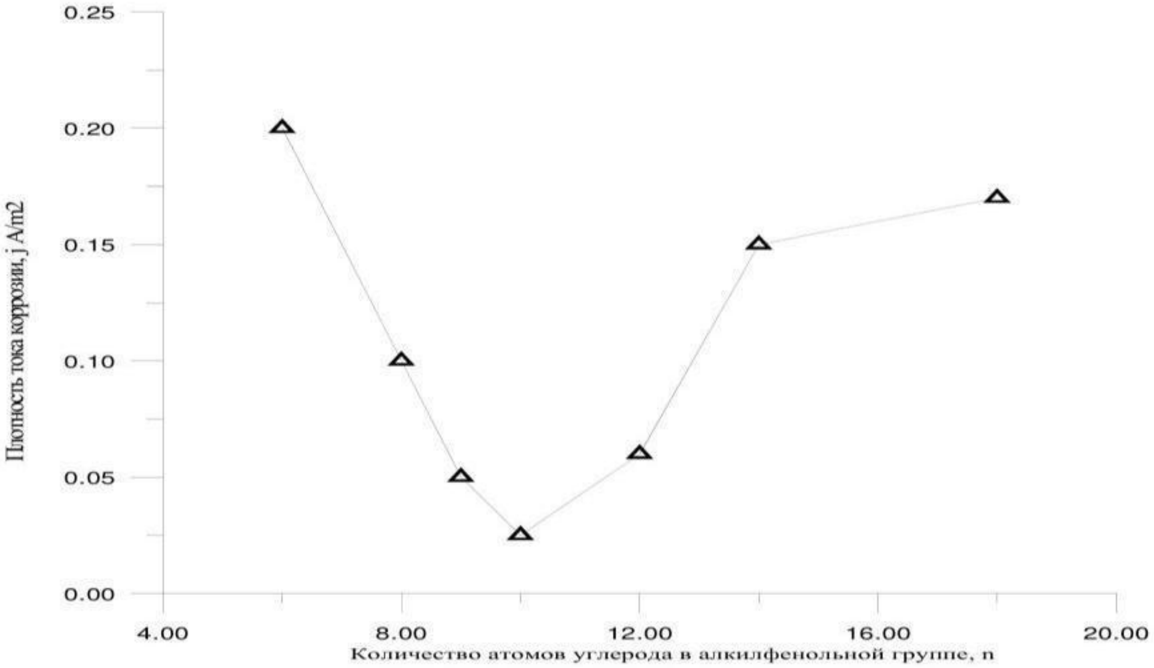


Figure 1 – Corrosion current density and density dependence on the number of carbon atoms in the alkylphenol group. Concentration 25 mg/l, exposure time 24 hours

suggests that the adsorption process involves the formation of a monolayer of inhibitor molecules on the metal surface without significant interaction between adsorbed species. The relatively high values of surface coverage (и), especially for the C10 compound, indicate strong adsorption and high affinity of inhibitor molecules toward the metal surface. This confirms that the inhibition mechanism is predominantly governed by adsorption processes. The adsorption equilibrium constant (Kads) reflects the strength of interaction between inhibitor molecules and the metal surface [12–14]. Higher Kads values correspond to stronger adsorption and improved inhibition efficiency. Thus, the obtained results confirm that the corrosion inhibition process is controlled by adsorption of inhibitor molecules, which form a protective barrier preventing aggressive ions from reaching the metal surface.

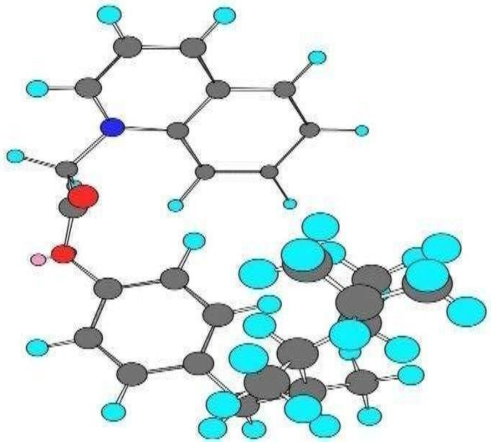


Figure 2. spatial structure model of decaphenoxycarbonylmethylisoquinolinium chloride

$$\Delta G_{ads} = -RT\ln(55.5K_{ads})$$

The negative values of Gibbs free energy (ДGads) indicate that the adsorption process is spontaneous and involves both physical and chemical adsorption mechanisms.

Figure 1 shows the dependence of the corrosion current density on the number of carbon atoms in the alkylphenol group of arylcarbonylmethylisoquinolinium chlorides at a concentration of 25 mg/l and an exposure time of 24 hours. The samples are added to the corrosive medium as 30% alcohol solutions.

The corrosion rate values (Figure 1) indicate that compounds containing different numbers of carbon atoms in the alkylphenol chain differ significantly in their inhibitory effects. A nonlinear dependence of the anti-corrosion effect of the compounds on the number of carbon atoms in the alkylphenol group is observed with the maximum protective effect at 10 carbon atoms in the alkylphenol group. As mentioned above, in many molecules of compounds with corrosion inhibitor properties, three parts can be distinguished in terms of energy.

The final group determines the hydrophobic-hydrophilic properties of the metal surface modified by the adsorption of inhibitor molecules. Figure 2 shows a spatial structure model of decaphenoxycarbonylmethylisoquinolinium chloride synthesized by us.

The Figure 2 clearly shows the isoquinoline cycle due to chemisorption, which ensures the interaction of the compound molecule with the surface metal cluster, the last decyl group, which determines the hydrophobicity of the modified metal surface, and the middle part of the molecule - phenoxy. group, which provides the density of the protective layer inhibitor coating. Additional gravimetric tests conducted to study the protective effect of synthesized samples of the compounds at a concentration of 25 mg/l showed that the nature of corrosion also varies depending on the number of carbon atoms in the alkylphenol group side chain. At the maximum corrosion rate corresponding to the minimum value of carbon atoms in the alkylphenol group, corrosion is localized. Corrosion damage has a wound-like and deep appearance. As the number of carbon atoms in the alkylphenol group increases, corrosion becomes more uniform, indicating the formation of a layer with an apparently regular and uniform structure. With a further increase in the number of carbon atoms in the alkylphenol group, corrosion again becomes localized. The capacity and therefore the inhibitory effect of organic compounds are mainly determined by the electron density at the adsorption center of the molecule and the solubility of the inhibitor. The metal-inhibitor adsorption binding energy depends on the polar properties of the substituents included in the inhibitor molecule, as they change the electronic state of the reaction center of the molecule. Alkylphenoxycarbonylmethylisoquinolinium chlorides exhibit maximum inhibition protection at 10 carbon atoms in the alkylphenol group. Alkylphenols are more hydrophobic than compounds with fewer carbon atoms in the group, and they adsorb better to the metal surface and form stronger metal-inhibitor adsorption bonds.

Conclusion

In this study, new corrosion inhibitors based on arylcarbonylmethylisoquinolinium chlorides and heterocyclic phosphonium compounds were successfully synthesized and evaluated for application in oil refining systems. The obtained results demonstrate that the corrosion inhibition efficiency strongly depends on the molecular structure of the compounds, particularly the length of the alkyl chain. The electrochemical and gravimetric analyses revealed a pronounced nonlinear relationship between alkyl chain length and inhibition performance, with the maximum efficiency achieved for the compound containing 10 carbon atoms. The highest inhibition efficiency (79.8%) and surface coverage (и = 0.798) were observed for the C10 derivative, which confirms the existence of an optimal balance between hydrophobicity and solubility. This balance facilitates the formation of a dense and stable protective film on the metal surface. The adsorption behavior of the synthesized inhibitors follows the Langmuir adsorption isotherm, indicating monolayer adsorption on the metal surface. The negative values of Gibbs free energy (ДGads) suggest that the adsorption process is spontaneous and involves both physical and chemical interactions. The inhibition mechanism is governed by a combination of electronic and structural factors. The presence of heterocyclic nitrogen atoms enhances electron donation and promotes strong adsorption via chemisorption, while the alkyl chain contributes to hydrophobic shielding and surface coverage.

Overall, the synthesized compounds demonstrate high potential as effective corrosion inhibitors for oil refining and transportation systems. The findings provide a scientific basis for the design of new organic inhibitors with optimized molecular structure and improved performance. Future research should focus on evaluating long-term stability and performance under real industrial conditions.

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