THE ROLE OF DIETHYL- AND PROPYLAMINE COMPLEXES OF THE MIXTURE OF OLIGOALKYLARYLSULFONIC ACIDS IN MICROBIAL CORROSION

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Received 01.08.2024
Accepted 21.10.2024

Abstract: *Diethyl- and propylamine complexes of a mixture of oligoalkylarylsulfonic acids, synthesized on the basis of the light gas oil fraction obtained from the catalytic cracking process, are proposed as bactericides in combating sulfate-reducing bacteria that cause microbial corrosion. Some physico-chemical properties of the solutions prepared in water, water+ethyl alcohol, water+isopropyl alcohol mixture of these complex samples were determined, bactericidal properties were studied. Solutions of diethylamine complex of oligoalkylarylsulfonic acids mixture prepared in water+ethyl alcohol, water+isopropyl alcohol mixture showed 91% and 93.7% bactericidal effect at a concentration of 150 mg/l, respectively. The aqueous solution of the propylamine complex at a concentration of 150 mg/l showed the highest (95%) bactericidal effect among the samples, reducing the number of bacteria from 10^8 to 10^1. Also, solutions of the propylamine complex in the same concentration of water + ethyl alcohol, water + isopropyl alcohol showed an effect of 92.2% and 91%, respectively, and significantly minimized the number of bacteria.*
Key words: *microbial corrosion, sulfate-reducing bacteria, bactericide, oligoalkylarylsulfonic acid, oligoalkylarylsulfonate*
DOI: 10.32737/2221-8688-2025-3-407-413

Introduction

Although the topic of microbial corrosion has been studied for decades, this process poses major challenges in many industries and its understanding, prevention and monitoring are still in focus. Collaborative efforts of various scientific and technical disciplines, including mainly microbiology, materials science and electrochemistry, biochemistry and corrosion engineering, contribute to the understanding of the microbial corrosion process [1-2].

Microorganisms are found almost everywhere in soil, fresh water, sea water and air. Therefore, the presence of microorganisms in the environment does not necessarily reflect that a corrosion problem will occur. Among the main characteristics of these microorganisms are that they are small, ubiquitous, potentially grow very rapidly, and are subject to certain general limitations such as temperature, pH, and nutrient availability. Corrosion problems only arise when conditions are favorable for a specific microbial population to "explode", when the environment causes millions of cells to form per gram of material [3-6].

The process of microbial corrosion begins with the formation of a biofilm on metallic or non-metallic surfaces. First, the cells adhere to the surface, then grow and multiply on it. All these processes result in the formation of a complex biofilm. Biofilm formation occurs in three different stages. In the first stage, macromolecules, including proteins, lipids, polysaccharides, and humic acids, are adsorbed on surfaces and act as conditioners. With the help of these macromolecules, the physical and chemical properties of the interface, including hydrophobicity and electric charge, change. At this stage, the rate of bacterial transfer, the degree of adhesion, and the size of the biofilm formed are determined by the characteristics of the microorganisms, the surface, and the aqueous environment. The adhesion of microbial cells, which is an important step in biofilm formation, occurs in the second step. In fact, microorganisms move from the bulk phase to the surface. These sessile cells are located on the metal surface and produce metabolic products based on numerous cathodic reactions, which in turn lead to corrosion [7-11]. Lactobacillus, Acetobacter, Azospirillum and Azotobacter are considered microbes that are metabolized to secrete organic and inorganic acids (lactic, acetic and formic acids) and affect the microbial corrosion process. Sessile cells in biofilms are 1000 times more resistant to biocides and 100 times more corrosive than their so-called planktonic counterparts [12-14].

Sulfate-reducing bacteria play an important role in the formation of microbial corrosion. Due to the fact that sulfate-reducing bacteria are the main cause of the microbial corrosion process, attention has been focused on the research of these bacteria in our modern times. Sulfate-reducing bacteria are commonly found in many ecosystems, including marine sediments, oil fields, hydrothermal vents, as well as oil and gas production facilities such as wells, distribution pipelines, treatment plants and refineries, and transportation and delivery infrastructure. It has an irreversible negative effect on the internal properties of materials. It presents significant problems in many industrial sectors, including nuclear power plants, fuel processing facilities, power plants, sewage drainage channels, storage and pumping, valves and vessels, oil reservoirs, sprinkler systems and many other industries. The size of sulfate-reducing bacteria is 3-10 μm. They are anaerobic microorganisms and can thrive in soil, fresh water, and almost any environment with traces of water and nutrients. All or most of the cellular carbon of sulfate-reducing bacteria is derived from organic matter, so they are heterotrophic bacteria. In order to effectively combat the problems caused by this group of bacteria, it is important to understand the molecular mechanism of biofilm formation and corrosion caused by them. Microbial corrosion accounts for about 40% of oil pipeline corrosion. The oil industry uses chemical biocides such as chloride, glutaraldehyde, and various ammonium salts to inhibit the biofilm of sulfate-reducing bacteria. However, chemical biocides are considered toxic to humans and aquatic resources because they persist in the environment. In our modern era, the synthesis of new types of bactericidal inhibitors with different compositions is one of the urgent problems in the fight against sulfate-reducing bacteria [15-22].

Our country has a sufficient amount of oil reserves and therefore the identification of areas of application of products obtained from oil refining, mainly in the process of recycling, is very promising from an economic and environmental point of view [23-26]. Based on this, the development of waste-free and "green" technologies for the production of new bactericide inhibitors based on by-products of oil refining is of practical and scientific importance.

It was determined that various amino and alkaline complexes of alkylarylsulfonic acids and oligoalkylarylsulfonic acids obtained on the basis of the light gas oil fraction obtained from the catalytic cracking process against sulfate-reducing bacteria have high bactericidal properties [27, 28].

Experimental part

The light gas oil fraction obtained from the catalytic cracking process was taken as the main raw material in the research work. A mixture of alkylarylsulfonic acids based on aromatic hydrocarbons contained in light gas oil fraction, and in the next step, a mixture of oligoalkylarylsulfonic acids was obtained based on this mixture of alkylarylsulfonic acids by a known method [27]. Diethylamine and propylamine complexes of the obtained mixture of oligoalkylarylsulfonic acids were synthesized and 15% solutions were prepared in different solvents (water, water + ethyl alcohol, water + isopropyl alcohol).

Physico-chemical properties of samples were determined by accepted standard methods- density by ASTM D5002 method in DMA 4500 M device, freezing temperature by GOST 20287-91, refraction coefficient in Abbemat 500 device, and pH indicator in HANNA device. The results are given in table 1.

Table 1. Physico-chemical properties of diethylamine and propylamine salts of a mixture of oligoalkylarylsulfonic acids.

The mixture of oligoalkylarylsulfonic acids	Density, g/cm^3 20°C	Freezing temperature, °C	Refraction coefficient, 20°C
Solution of diethylamine complex in water (N-1)	0.9850	-4	1.3519
Solution of diethylamine complex in water + ethyl alcohol (N-2)	0.9176	-55	1.3748
Solution of diethylamine complex in water + isopropyl alcohol (N-3)	0.9153	-40	1.3821
Solution of propylamine complex in water (N-4)	0.9851	-4	1.3518
Solution of propylamine complex in water + ethyl alcohol (N-5)	0.9186	-45	1.3743
Solution of propylamine complex in water + isopropyl alcohol (N-6)	0.9042	-37	1.3812

The bactericidal properties of diethylamine and propylamine complex samples of oligoalkylarylsulfonic acids mixture were studied using 1143 strains of "Desulfovibrio desulfuricans" type of sulfate-reducing bacteria according to the known method [29] . The bactericidal effect of the reagents was determined by keeping them in a thermostat for 15 days at a temperature of 32ºC and finally calculating the amount of H_2S produced. The amount of H_2S was determined by iodometric titration and the reduction rate of sulfate-reducing bacteria was calculated [30]. Fixanol solutions of iodine and sodium hyposulfite were used for titration. The H_2S content is calculated by the following equation:

$$X = \frac{[\mathrm{N(iodine)} \cdot \mathrm{V(iodine)} - \mathrm{N(sodium\ hyposulfite)} \cdot \mathrm{V(sodium\ hyposulfite)}]}{\mathrm{V\ (water)}}\ x\ 17000$$

N (iodine) – 0.1 N;
V (iodine) – 10 ml;
N (sodium hyposulfite) - 0.1 N;
V (sodium hyposulfite) - 7 ml;
V (water) - 20 ml;
17000 - indicates the solubility of 0.1 N hyposulfite in 1000 ml.

The bactericidal effect of the studied samples was determined by the following equation based on the calculated value of H_2S:

$$Z = [(C_0 - C)/C_0]\cdot 100\%,$$

C_0 - amount of hydrogen sulfide in the control environment, mg/l;
C - amount of hydrogen sulfide formed in the reagent environment, mg/l.

Results and discussion

The results obtained from the study of diethyl- and propylamine salts of the synthesized oligoalkylarylsulfonic acid mixture as bactericides in different solvent are given in Table 2.

Table 2. Bactericidal results of diethylamine and propylamine salts of a mixture of oligoalkylarylsulfonic acids

Conventional symbol of the complex	**Concentration of a substance, C-mg/l**	**The number of bacteria (number of cells/ml)**	**Content H_2S, mg/l**	**Bactericidal effect, Z-%**
N-1	50	10^4	139.8	62.7
	75	10^3	96.4	74.2
	150	10^1	51.8	86.1
N-2	50	10^3	102	73
	75	10^2	69	81.6
	150	10^1	35	91
N-3	50	10^3	105	72
	75	10^2	67.2	82
	150	10^1	23.5	93.7
N-4	50	10^2	72	80.8
	75	10^1	39.7	89.4
	150	10^1	19	95
N-5	50	10^3	106	71.7
	75	10^2	63	83.2
	150	10^1	29	92.2
N-6	50	10^3	114	69.6
	75	10^2	71.3	80.9
	150	10^1	35	91
AMDOR-IK-7 (standart)	75	10^4	84.8	60
	150	10^3	53.2	75
	200	10^1	43	90
AMDOR-IK-10 (standart)	75	10^4	84.8	60
	150	10^3	44.8	80
	200	10^1	3	93
Control-1. Amount of H_2S in without SRB conditions -24 mg/l				
Control-2. Amount of H_2S in with SRB conditions -375 mg/l				
Control-3. Number of bacteria in the nutrient medium -10^8 number of cells /ml				

As it can be seen, the aqueous solution of the diethylamine complex of the oligoalkylarylsulfonic acid mixture shows a relatively low bactericidal effect compared to the aqueous solution of the propylamine complex. Thus, the solution of propylamine salt in water at a concentration of 150 mg/l showed a 95% bactericidal effect and significantly reduced the number of bacteria. The bactericidal effect of the solutions of the prepared samples in a mixture of water + ethyl alcohol at a concentration of 150 mg/l was 91% for the diethylamine complex and 92.2% for the propylamine complex. Solutions of diethylamine and propylamine complexes in water + isopropyl alcohol showed 93.7% and

91% bactericidal effect, respectively, and reduced the number of bacteria from 10^8 to 10^1.

Conclusion

The solutions of diethyl- and propylamine complexes of the oligoalkylarylsulfonic acids obtained on the basis of the light gas oil fraction of the catalytic cracking process were prepared in water, water + ethyl alcohol, water + isopropyl alcohol mixtures at concentrations of 50, 75, 150 mg/l, and their bactericidal effects were studied. It was determined that solutions of diethylamine and propylamine complexes of oligoalkylarylsulfonic acids in a mixture of water + ethyl alcohol, water + isopropyl alcohol have a bactericidal effect in the range of 91% - 93.7% at a concentration of 150 mg/l. The solution of propylamine salt in water at a concentration of 150 mg/l showed the highest bactericidal effect (95%) among complex samples. At a concentration of 150 mg/l, the bactericidal effect of AMDOR-IK-7 and AMDOR-IK-10 bactericidal-inhibitors used as a standard in the industry is 75% and 80%, respectively. Also, while the concentration at which each of the complex samples reduces the number of bacteria from 10^8 to 10^1 is 150 mg/l, this concentration is 200 mg/l for standard bactericide-inhibitors. Thus, based on the given results, we can note that the synthesized samples have a higher bactericidal effect than the samples used as a standard in the industry.

Acknowledgment

The work was supported by the SOCAR Science Foundation within the framework of the project «Synthesis and research of bactericide-inhibitors based on the light gasoyl fraction obtained in the secondary oil refining process».

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