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INVESTIGATION OF DIETHYLAMINE, DIPROPYLAMINE, DIBUTYLAMINE COMPLEXES OF ALKYLARYLSULFONIC ACID SYNTHESIZED ON THE BASIS OF GAS OIL FRACTION AS BACTERICIDE

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ABSTRACT

In the research work, diethylamine, dipropylamine, dibutylamine complexes of the mixture of alkylarylsulfonic acids obtained on the basis of the light gas oil fraction obtained from the secondary oil refining process - the catalytic cracking process were synthesized, solutions of the samples were prepared in water, water + ethyl alcohol, water + isopropyl alcohol. Some physico-chemical properties of the samples were studied, bactericidal properties were studied by keeping them in a thermostat at a temperature of 32ºC for 15 days and calculating the amount of H_2S produced at the end. It was determined that the aqueous solution of the diethylamine complex of the mixture of alkylarylsulfonic acids showed a high bactericidal effect (99%) at the concentration of 50 mg/l. Solutions of diethylamine and dipropylamine complexes in water at the concentration of 75 mg/l showed 100% bactericidal effect and reduced the number of bacteria to zero. Solutions of dibutylamine complex in water + ethyl alcohol, water + isopropyl alcohol at the relatively high concentration (150 mg/l) showed 100% bactericidal effect and stopped the life activity of bacteria.

Introduction

Microbiological corrosion is a type of corrosion that occurs as a result of biological damage to metals. The effect of microorganisms on metals occurs in different ways. Among the main factors that cause corrosion are metabolic products with aggressive properties - acids, bases, enzymes, etc. takes the main place. They create a favorable environment for the initiation of the corrosion process according to the laws of electrochemistry [1].

Corrosion damages the economy of developed countries in the amount of 3-3.5% of the national product value. Most of the economic losses in the marine industry are caused by microbiological corrosion. According to statistics, it is about 20% of total economic losses due to corrosion of various equipment. The total global cost of biological damage and marine pollution is estimated at approximately 50 billion dollars annually [2-3].

Sulfate-reducing bacteria play an important role in the occurrence of microbiological corrosion. Sulfate-reducing bacteria are the most studied group of bacteria that cause microbiological corrosion and consist of 220 species and belong to bacteria that use sulfate as an electron acceptor [4,5]. Sulfate-reducing bacteria are anaerobic bacteria, which means they don't require oxygen for growth and activity. This allows sulfate-reducing bacteria not to be destroyed in extreme conditions. These bacteria reduce the sulfate fragment to sulfide. The electrochemical reaction takes place inside the biofilm where the metal interacts with water and sulfate-reducing bacteria. As a result, hydroxyl groups are formed, which facilitate the reaction. Sulfate-reducing bacteria are active in the pH range of 4 to 9.5 and can withstand pressures up to 500 atm [6,8]. The corrosion mechanism caused by sulfate-reducing bacteria can be described using the cathodic depolarization theory. However, other theories describing this process are currently known to science. According to the cathodic depolarization theory, the electrochemical reaction occurs in two sections: anodic and cathodic. In the anodic zone, iron changes into ionic form (Fe^{2+}). Fe^{2+} ions are released from the surface by losing electrons that go to the cathode area. Due to the release of iron ions, pits are formed in the anode. Then the iron ions react with the sulfide (S^{2-}) to form the by-product iron sulfide (FeS). In the cathode zone, electrons move to the surface and react with hydrogen ions (H^+) to form hydrogen gas (H_2). Due to the nature of the biofilm, water molecules ionize into hydroxide (OH^-) and hydrogen ions. Hydrogen ions cause the pH level in the biofilm to become acidic. And hydroxide reacts with iron ions to form iron hydroxide ($Fe(OH)_2$) or rust [9-10].

Anode: $4Fe \rightarrow 4Fe^{2+} + 8e$;

Dissociation/ionization of water: $8H_2O \rightarrow 8H^+ + 8OH^-$;

Cathode: $8H^+ + 8e \rightarrow 8H$;

Cathodic depolarization caused by sulfate-reducing bacteria:

$+ 8H \rightarrow SO_4^{2-} + 8H \rightarrow S^{2-} + 4H_2O$;

Corrosion product: $Fe^{2+} + S^{2-} \rightarrow FeS$; $3Fe^{2+} + 6OH^- \rightarrow 3Fe(OH)_2$;

General reaction: $4Fe + 4H_2O + SO_4^{2-} \rightarrow 3Fe(OH)_2 + FeS + 2OH^-$.

In order to prevent the damage caused by microbiological corrosion to industrial and service areas, bactericides with different compositions are used in industry.

As a result of the studies, it was determined that various alkaline and amine complexes of alkylarylsulfonic and oligoalkylarylsulfonic acids synthesized on the basis of light phlegm of catalytic cracking have a high bactericidal effect compared to industrially applied standart bactericidal-inhibitors (AMDOR-IK-7 and AMDOR-IK-10) [11-14].

Experimental Part

The presented research work is devoted to the synthesis and research of new bactericides against sulfate-reducing bacteria for corrosion protection of metals. At the initial stage, a mixture of alkylarylsulfonic acids was obtained based on the light gas oil fraction obtained from the secondary oil refining process – catalytic cracking process. Some physico-chemical parameters of alkylarylsulfonic acids are mentioned below. Density: 1.32 g/cm^3, freezing temperature: -8 °C, refraction coefficient: 1.48. In the next stage, diethylamine, dipropylamine, dibutylamine complexes of the mixture of alkylarylsulfonic acids were synthesized. Amines used in the experiment were purchased from Sigma Aldrich company. 15% solutions of synthesized complex salts in water, water+ethyl alcohol, water+isopropyl alcohol were prepared and some physico-chemical parameters of the obtained complex salts were investigated. Indicators were determined by the 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 pH-ISE-EC HI 5522 device. The accuracy of the pH measuring device is ± 0.5 % . The results are given in table 1.

Table 1. Physico-chemical properties of diethylamine, dipropylamine, dibutylamine complexes of the mixture of alkylarylsulfonic acids

Symbol of the complexes	Density, g/cm^3 20°C	Freezing temperature, °C	Refraction coefficient, 20°C	pH
K-1	0.9850	-3	1.4874	8.200
K-2	0.9436	-57	1.3807	8.473
K-3	0.9445	-46	1.3871	8.528
K-4	1.010	-5	1.3628	8.357
K-5	0.9615	-42	1.3744	8.437
K-6	0.9375	-40	1.3862	8.586
K-7	0.9253	-43	1.3757	8.672
K-8	0.924	-40	1.3845	8.875

Experiments to study the bactericidal effects of the obtained alkylarylsulfonate samples were carried out in pre-sterilized test tubes according to the known method [15]. 1143 strains of "Desulfovibrio desulfuricans" species of the sulfate-reducing bacteria were taken for the experiment. The bactericidal property of the reagents was studied by keeping them in a thermostat at 32ºC for 15 days and calculating the amount of H_2S formed at the end. At the end of the study, the amount of H_2S in the tested samples was determined by the iodometric method, and based on the results, the reduction rate of sulfate-reducing bacteria was calculated. (OST 39-234-89). The obtained results are given in table 2.

Table 2. Bactericidal effects of diethylamine, dipropylamine, dibutylamine complexes of the mixture of alkylarylsulfonic acids

The content of alkylarylsulfonic acids	Concentration of a substance, C-mg/l	The number of bacteria (number of cells/ml)	Content H_2S, mg/l	Bactericidal effect, Z-%
Solution of diethylamine complex in water (K-1)	50	10^1	4	99
	75	-	-	100
	150	-	-	100
Solution of diethylamine complex in water + ethyl alcohol (K-2)	50	10^2	65	82.6
	75	10^1	39	89.6
	150	10^1	21	94.4
Solution of diethylamine complex in water + isopropyl alcohol (K-3)	50	10^3	116	69
	75	10^3	98.2	73.8
	150	10^2	54.9	85.3
Solution of dipropylamine complex in water (K-4)	50	10^1	5.5	98.5
	75	-	-	100
	150	-	-	100
Solution of dipropylamine complex in water + ethyl alcohol (K-5)	50	10^2	70	81.3
	75	10^1	10.8	97.1
	150	-	-	100

Solution of dipropylamine complex in water + isopropyl alcohol (K-6)	50	10^1	52.3	86
	75	10^1	24.5	93
	150	10^1	16.9	95.4
Solution of dibutylamine complex in water + ethyl alcohol (K-7)	50	10^2	62.5	83.3
	75	10^1	29	92.2
	150	-	-	100
Solution of dibutylamine complex in water + isopropyl alcohol (K-8)	50	10^4	145	61.3
	75	10^3	102	72.8
	150	-	-	100
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				

It is important to firstly ensure complete solubility of amino salts of alkylarylsulfonic acid in various solvents during the study. Additionally, the physico-chemical properties of the solutions obtained in different solvent environments vary depending on the nature of the solvent and the structure of the substance taken. The different solvents widen the application opportunities of the complex salts. When the compositions of the complex salt and solvent change, the size of the resulting micelles varies, as a result, the contact with the surface changes. Even at a low concentrations, synthesized complexes show complete inhibitory effect.

As can be seen from the table, the aqueous solution of the diethylamine complex of the mixture of alkylarylsulfonic acids showed a high bactericidal effect (99%) at the low concentration (50 mg/l) and significantly reduced the number of bacteria, while at the concentration of 75 mg/l it showed a 100% bactericidal effect and completely stopped the life of bacteria. The solution of diethylamine complex in water + ethyl alcohol at the concentration of 150 mg/l showed a result of 94.4% and reduced the number of bacteria from 10^8 to 10^1. Also, the solution of dipropylamine complex in water at the concentration of 75 mg/l showed 100% bactericidal effect, while the solutions in a mixture of water + ethyl alcohol and water + isopropyl alcohol showed 97.1% and 93% bactericidal effect, respectively. Solutions of dibutylamine complex in water + ethyl alcohol, water + isopropyl alcohol mixture completely destroyed bacteria at the concentration of 150 mg/l. The bactericidal effect results of the synthesized complex samples were compared with the bactericidal inhibitors applied as standard in the industry and the results are expressed in the following picture.

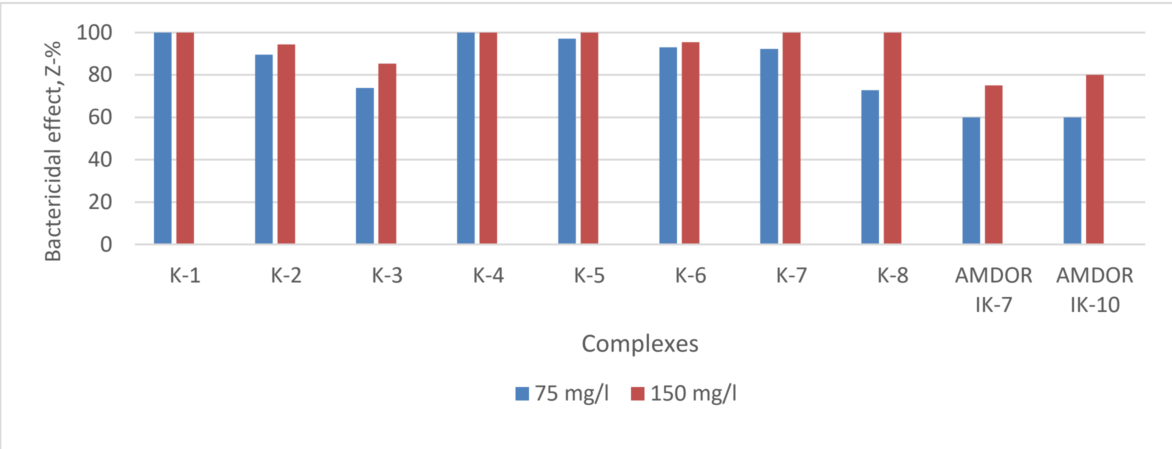

Figure. Comparison of bactericidal effect results of complex samples with standard samples

As can be seen from the figure, each of the samples has a higher corrosion protection property at all concentrations compared to the standard bactericidal inhibitor AMDOR-IK-7 and AMDOR-IK-10. Thus, the highest result shown by standard bactericidal inhibitors was 93% at the concentration of 200 mg/l.

Conclusion

Thus, the aqueous solution of the diethylamine complex of the mixture of alkylarylsulfonic acids showed a bactericidal effect of 99% at the concentration of 50 mg/l, and 100% at the concentration of 75 mg/l, showing successful results in combating microbiological corrosion. Also, it was determined that the solution of dipropylamine complex in water at the concentration of 75 mg/l has 100% bactericidal effect, while the solutions in water + ethyl alcohol and water + isopropyl alcohol have bactericidal effects of 97.1% and 93%, respectively. Based on the obtained results, it was determined that the synthesized complex samples are more promising than AMDOR IK-7 and AMDOR IK-10 bactericidal inhibitors, which are used as standard bactericidal inhibitors in the industry.

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