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KINETICS AND CATALYSIS

KINETIC PROPERTIES OF BICYCLIC SULFUR ORGANIC INHIBITORS

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КИНЕТИЧЕСКИЕ СВОЙСТВА БИЦИКЛИЧЕСКИХ ИНГИБИТОРОВ СЕРЫ-ОРГАНИЧЕСКИХ СРЕДСТВ

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ABSTRACT

In this paper, the inhibitory effect of synthesized bicyclic sulfur α-aminoketones on the corrosion of metals in aggressive environments 15% HCl and 20% H_2SO_4, as well as 1M HCl, 1M H_2SO_4. The inhibitors studied were found to slow down the cathode process and inhibit metal corrosion due to electrostatic adsorption in strongly acidic environments and undistributed free electron pairs of nitrogen, sulfur, and oxygen in the molecule in weakly acidic and neutral environments.

АННОТАЦИЯ

В данной работе показано ингибирующее действие синтезированных бициклических серных α-аминокетонов на коррозию металлов в агрессивных средах 15% HCl и 20% H_2SO_4, а также 1M HCl, 1M H_2SO_4. Было обнаружено, что исследованные ингибиторы замедляют катодный процесс и ингибируют коррозию металлов из-за электростатической адсорбции в H_2SO_4 среде и нераспределенных свободных электронных пар азота, серы и кислорода в молекуле в слабокислой и нейтральной средах.

Keywords: inhibitor, corrosion, corrosion rate, a-piperidino-5-acetyl-2-methyl-1-thiaine, a-morpholinio-5-acetyl-2-methyl-1-thiaine, a-piperidino-6-acetyl- 1-thiochroman, α-morpholino-6-acetyl-1-thiochroman, α-diethylamino-5-acetyl-2-methyl-1-thiaine, α-diethylamino-6-acetyl-1-thiochroman, polar resistance, polarity resistance.

Ключевые слова: ингибитор, коррозия, скорость коррозии, α-пиперидино-5-ацетил-2-метил-1-тиаин, α-морфолинио-5-ацетил-2-метил-1-тиаин, а-пиперидино-6-ацетил-1-тиохроман, α-морфолино-6-ацетил-1-тиохроман, α-диэтиламино-5-ацетил-2-метил-1-тиаин, α-диэтиламино-6-ацетил-1-тиохроман, полярная устойчивость, сопротивление полярности.

Introduction. Today, all sectors of the economy, including the chemical industry, oil and gas industry, can not be imagined without metal devices. When metal-construction materials are used in these industries, they are constantly exposed to the external environment, and as a result of these interactions, the primary properties of metal devices lose their original properties. As a result, oxides and hydroxides of metals are formed, leading to their decomposition and polluting the environment.

General and local corrosion is one of the most common types of corrosion in the oil industry. Another major problem encountered in the operation of pipes is internal corrosion [1; 2104-2113 p.], It is mainly manifested in the appearance of corrosion cracks under various stresses. Martines and both authors [2; Pp. 255-258] points out that the addition of corrosion and erosion is a major problem of pipe erosion. In recent years, there has been an increase in the incidence of galvanic corrosion due to the combined use of different materials. Wilhelm [3; 691-703 p.] Shows that a common condition of accumulation of various materials in drilling wells is the connection of pump-compressor pipes made of corrosion-resistant steel with columns made of low-quality steel. In addition, the metal materials prepared for the connection will cause cracking corrosion in the closed area between the pipe and the column. In recent years, the volume of sulfur gases and oil production is increasing, the amount of hydrogen sulfide in gas and oil products reaches 500 g / ml, so the metal equipment of oil production and refining enterprises are seriously damaged due to hydrogen sulfide corrosion. Dissolved

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carbon dioxide and hydrogen sulfide in gas and oil have unique aggressive properties, causing chemical and electrochemical corrosion.

In this paper, a number of inhibitors synthesized by us are α-piperidino-5-acetyl-2-methyl-1-thiaine (AIT-1), α-morpholinio-5-acetyl-2-methyl-1-thiaine (AIT-2). , a-piperidino-6acetyl-1-thiochroman (AIT-3), α-morpholino-6-acetyl-1-thiochroman (AIT-4) and α-diethylamino-5acetyl-2-methyl-1-tiaindan (AIT-5)) and α-diethylamino-6-acetyl-1-thiochromanes (AIT-6) in 15% HCl and 20% H_2SO4 and 1M HCl, 1M H_2SO4, which served as aggressive environments in steel St.3, were studied to inhibit metal corrosion.

The cathode and anode phases of the polarization measurements were performed on a spatially separated three-cell P-5827m potentiostat. The study of the kinetic laws of melting of iron and steel under cathodic polarization is of great interest for the practice of cathodic and tread protection of metal structures and for the development of fundamental concepts about corrosion processes in low electrode potential environments. From a practical point of view, the study of such processes is very important, according to which under these conditions the cathodic separation reaction of hydrogen in the metal takes place and leads to the decomposition of the material.

At present, the kinetics of the melting process of iron at cathode potentials differs from the laws of anodic melting of metal in an environment in which the separation of hydrogen does not occur. For example, the melting rate of iron from a corrosion potential negative to 100 mV is practically independent of the potential value. Such a phenomenon is called anomalous melting of a metal, i.e. it does not obey the laws of electrochemical kinetics. One of the most common theories in explaining the laws of this phenomenon is the theory of the chemical melting of iron in the presence of hydrogen ions, water molecules and particles of other solvents. However, the causes and kinetic laws of iron melting in the environment of cathode potentials have not yet been fully elucidated. In various industrial processes, including smelting, thermal or chemical treatment of the metal, and electrochemical processes (cathode purification or electrolytic treatment), hydrogen enters the metal. Sources of hydrogen formation are the main stages of these chemical processing and galvanic processes, in which mineral acids are used to remove rust formed on the metal surface. Some of the atomic hydrogen released during the chemical treatment acts on the metal surface and the other part is released in the form of molecular hydrogen. The proportion of hydrogen atoms falling on the metal surface in the working solution has a detrimental effect on the mechanical properties of iron or steel, i.e. its plasticity, abrasion and mechanical strength. Inhibitors based on organic compounds typically slow down the interaction of the metal with the external environment and are added to chemical treatment baths to limit the release of hydrogen in the working medium. In this study, the volume of gaseous hydrogen released was determined in an sulfuric acid environment without inhibitors and in the presence of an inhibitor, which was done to determine the effectiveness of the inhibitors studied in reducing the amount of gaseous hydrogen released on the corroded surface of steel.

The amount of hydrogen released during the corrosion process of steel at 30–60 ° C in a 1 M H_2SO_4 solution containing an inhibitor-free solution and inhibitors AIT-1, AIT-3, AIT-4, and AIT-5 inhibitors was measured as a function of time. Figure 1 shows that the volume of hydrogen released in a corrosive environment increases over time due to the constant effect of the active hydrogen ion on the metal surface during the corrosion process. The introduction of inhibitors prepared on the basis of bicyclic sulfur organic compounds into the corrosive medium leads to a gradual decrease in the amount of hydrogen released, and in practice these inhibitors effectively inhibit the corrosion process of steel St.3 sample in an acidic environment. The volume of gaseous hydrogen released increases with increasing temperature in an inhibitor-free environment and in an environment with inhibitors. However, the volume of hydrogen released showed that it was directly proportional to the inhibitor concentration.

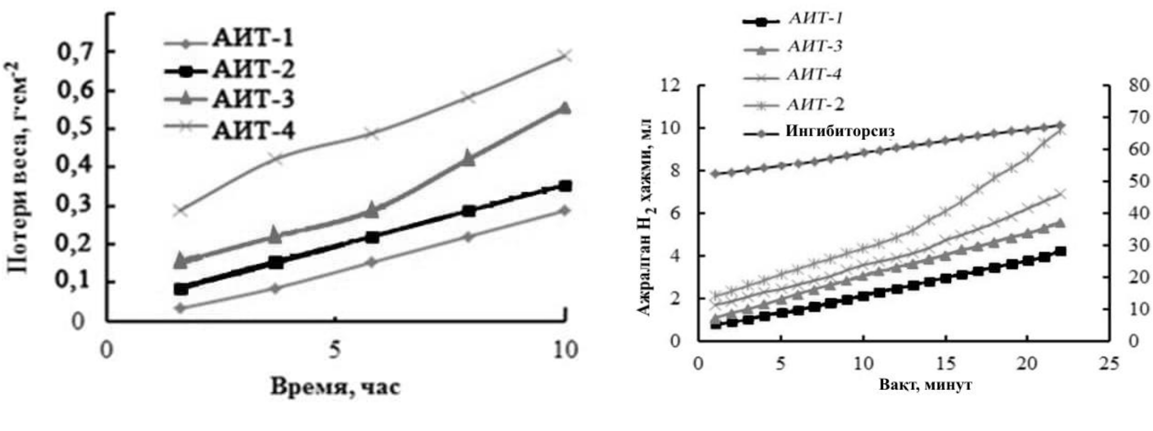

Figure 1. Time-dependent graph of the volume of hydrogen released in steel
St.3 sample in 1M H_2SO_4 solution without inhibitors and inhibitor storage. (A) at 30 ° C, (B) at 60 ° C. The uninhibited sample is described as an additional bullet. The inhibitor concentration is 0.5 mg / l.

Table 1.

Sample hydron of H_2SO_4 steel St.3 in inhibiting and storing a hydrogen divorce rate and validity values of divorce (at 30-60 °C)

Concentration	Hydrogen divorce Fasting, ml · min^{-1}		Ingredient level, Z %	
	30 °C	60 °C	30 °C	60 °C
No inhibiter	0,59	2,67	-	-
AIT-1	0,13	0,98	77,9	63,3
AIT -2	0,08	0,76	86,4	71,5
AIT -3	0,09	0,94	84,7	64,8
AIT -4	0,05	0,72	91,5	73

It can be seen from the table that the difference between the values of the inhibitor-free sample obtained on the release of hydrogen in 1 M H_2SO_4 medium and the release values of the hydrogen obtained in the presence of inhibitors in this solution is quite significant. This indicates that in the processes carried out in the presence of inhibitors leads to a sharp decrease in the corrosion process and reduces the rate of decomposition of the hydrogen atom. The rate of decomposition of a hydrogen atom from a corrosive medium increases slightly with increasing temperature, and its rate of decomposition slows with increasing inhibitor concentration in solution. This indicates a decrease in the rate of erosion of the metal surface as the inhibitor concentration increases. Cathode and anode typical polarity resistance curves and inhibitor properties were studied during the experiments. The values of total resistance and R_p were calculated using the polarity resistance method. The polarization curves of the above inhibitors in one molar sulfuric acid and one molar hydrochloric acid as well as in an inhibitor-free medium are shown in Figure 2 at 333 K. It was found that the polarization resistance also increases with increasing concentration of the inhibitor in the working solution.In cathode reactions, the effect of inhibitors on the corrosion process is aimed at slowing down the cathode process, and the discharge of hydrogen in the atomic form as a result of the passage of hydroxyone ions through the double electric field.

Table 2.

Inhibitors in 1M HCl and 1M H_2SO_4 medium cathode and anode current polarization values

Inhibitor	Environment	Concentration, C/mol	$\varphi_{ст.}$ mB	(φ=0,6 B), $\gamma_к$	(φ=0,38 B), γ_a	Caloning resistance, R_p, om.sm^2
AIT -2	HC1	1x10^{-3}	436	46,8	3,2	1250
AIT -3	HC1	1x10^{-3}	450	23,5	4,0	900
AIT -5	HC1	1x10^{-3}	448	14,8	3,7	700
AIT -2	H_2SO_4	1x10^{-3}	426	2,5	0,4	147
AIT -3	H_2SO_4	1x10^{-3}	402	5,0	5,0	233
AIT -5	H_2SO_4	1x10^{-3}	402	2,8	4,0	110

Table 3 shows the results of polarity resistance at 333 K in 1M HCl solution of inhibitor AIT-4 at different concentrations. The study found that this inhibitor had a high metal sample protection rate of 97.8%, reduced the corrosion rate to 0.350 (mm^{-1}), reduced the Rp value to 20.33 (kohms), and reduced the corrosion potential to 241.6 Ecorr (mV).Thus, the presence of a sulfur atom in the inhibitor molecule studied suggests that the binding of this sulfur atom to the phenyl group on the one hand and the methylene group of the poluaromatic ring on the other exhibits high protective properties as a result of strong physical and chemical sorption of the amino ketones studied.

Table 3.

1M HCl of inhibitor AIT-4 at different concentrations results in polar resistance at 333 K in solution

Concentration (ppm)	E_{corr} (mV)	R_p (kohms)	Corrosion rate (mmy^{-1})	Inhibitor efficiency, η%
Metal sample	-290.5	1.115	28.45	-
100	-1198. 5	14.07	1.84	91.78
150	-227.1	15.45	1.12	93.18
200	-23.4	17.12	0.71	93.98
250	-241.6	20.33	0.35	97.80

The effect of inhibitors on the cathode and anode half currents is shown in Figure 2 (333 K). In a non-inhibitory environment, it was found that the polarization curves shifted towards a positive value of the potential and the corrosion rate was very high. Experiments have shown that when an inhibitor is added to the working solution, these polarization curves shift in the negative direction, blocking the melting rate of the metal in the cathode and anode processes as an inhibitorю.

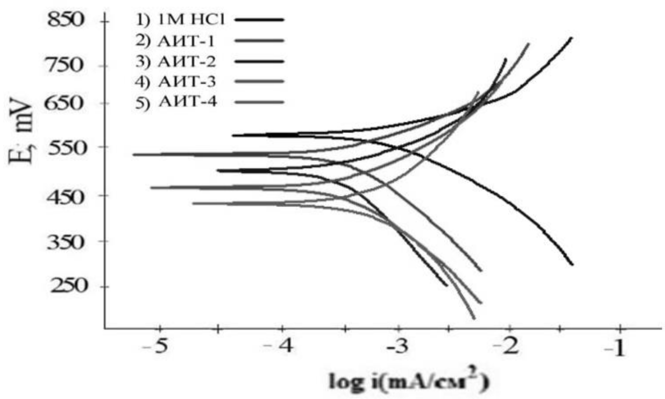

Figure 2. Inhibitor and non-inhibitor in different concentrations.
Pole curves for a steel sample in 1M HCl solution. (333 K)

As can be seen from the figure, the effectiveness of inhibitors in 1M HCl solution is much higher. It can be seen that while the general rule inhibits the cathode process to a greater extent, the melting rate of the anode process also decreases significantly under the same conditions.

Based on the results of the study, it can be said that bicyclic poluaromatic compounds containing α-aminocetone-type sulfur belong to the type of inhibitors that slow down the cathode process, resulting in inhibition due to electrostatic adsorption from a positively charged amino group in a strongly acidic environment. The inhibitory properties of metals in bicyclic poluaromatic systems containing α-aminocetone-type sulfur in weakly acidic and neutral environments can be determined by the adsorption of chemisorption-type adsorption by transferring atoms of nitrogen, sulfur, and oxygen to the d-orbital of iron. In any case, it forms a protective shell on the metal surface, making it difficult for protons to attack the metal surface and for the ion-atom to pass from the metal to the solution.

α-Aminoceton-type sulfur-containing bicyclic poluromatic compounds are among the most effective inhibitors and can be used in the cleaning of metal surfaces from rust, mineral deposits, as well as in acid refining of wells in oil and gas extraction and various other sectors of the economy.

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