

A New Highly Effective Inhibitor Based On 2,7-Dimethyl-2,7-Dicyano-3,6-Diazaoctan

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Abstract

The effectiveness of corrosion inhibition based on the organic compound 2,7-dimethyl-2,7-dicyanide-3,6-diazaoctan (MAD-20) was studied on low-carbon steel in 15% H₂SO₄ solution. The samples were exposed in a 15% H₂SO₄ solution without an inhibitor and with different concentrations of MAD-20 inhibitors. Weight loss measurements, scanning electron microscope (SEM) were used to study the inhibitory effects of MAD-20. It has been shown that the MAD-20 inhibitor is an effective inhibitor of acid corrosion.

Keywords: corrosion inhibition, weight loss measurement, 2,7-dimethyl-2,7-dicyanide-3,6-diazaoctan, condensation reaction, acetone cyanhydrin, low carbon steel.

1. INTRODUCTION

Due to the need to increase production efficiency, there is a need to develop new technologies that ensure the integrated use of raw materials and the disposal of industrial waste, which in turn will lead to the preservation of raw materials and improve the environmental situation. The use of inhibitors in the oil and gas industry is an effective means of reducing corrosion damage. The problem of developing corrosion inhibitors became especially acute with the discovery of deposits in Central Asia, and subsequently in the Kashkadarya region, whose gas contains hydrogen sulfide.

The exploitation of hydrogen sulfide-containing deposits has raised a number of questions concerning the effectiveness of the use of corrosion inhibitors. The practice of exploitation of gas deposits containing aggressive components such as hydrogen sulfide, carbon dioxide, low molecular weight organic acids has shown that the use of corrosion inhibitors is indeed one of the most technically justified and cost-effective means of corrosion protection of gas field equipment. Corrosion in environments typical of the gas industry is a complex and not yet fully understood process. Corrosion manifestations in the presence of hydrogen sulfide, carbon dioxide and other aggressive agents are not limited to simply dissolving the metal, causing thinning of the walls of the equipment. Besides the fact that corrosion has a more dangerous uneven, local character in the form of pitting and ulcers, it causes a buildup and leads to hydrogen sulfide and carbonate cracking of steel [1-10].

In countries with developed chemical and petrochemical industries, as a result of metal corrosion, great economic damage is caused, therefore, the creation and use in practice of highly effective corrosion inhibitors is even more important.

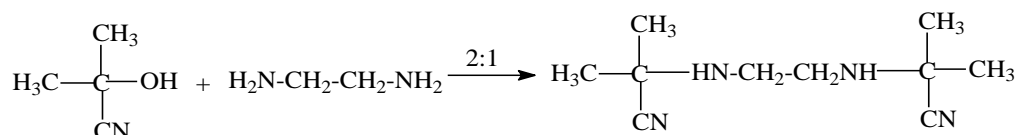
The aim of the study is to obtain and use new nitrogen-containing corrosion inhibitors based on the 2,7-dimethyl-2,7-dicyanide-3,6-diazaoctan molecule and to develop a technology for producing corrosion inhibitors based on them [11-14].

1. MATERIALS AND METHODS

1.1. Materials and sample preparation

1.1.1. Synthesis of 2,7-dimethyl-2,7-dicyanide-3,6-diazaoctan

To perform this work, we synthesized 2,7-dimethyl-2,7-dicyanide-3,6-diazaoctan (MAD-20) in the laboratory. To do this, we conducted a condensation reaction of acetone cyanhydrin with ethylenediamine in the ratio of 2:1 mole. A schematic representation of the reaction is given below:



Compounds 2,7-dimethyl-2,7-dicyanide-3,6-diazaoctan (MAD-20) is a crystalline substance of light yellow light, melting point 53-54 °C. The yield of the main product is 89%. The purity and course of the reaction was controlled by thin-layer chromatography on a Silufol plate, in the benzene: acetone (2:1) system. 0.058 mol of ethylenediamine and 30 ml of hexane were placed in a flat-bottomed flask equipped with a magnetic stirrer. The contents of the flask were stirred with a magnetic stirrer for 20 minutes. Then, using a dividing funnel at room temperature for 2 hours, add 5.5 ml (0.058 mol) of acetone cyanhydrin drop by drop. The contents of the flask are still mixed for 1 hour.

After that, the solvent is distilled in vacuum, after which we use vacuum distillation to drive away the reaction product. The yield of the main product is 89% (6.6 g). Melting point: T_{pl} = 53-55 °C. After the solvent is distilled, chromatography is performed on the "Silufol" plate. To determine the R_f constant, benzene and acetone were used in ratios of 2:1. R_f = 0.5000.

Table 1. Physico-chemical constants of the MAD-20 inhibitor

Name of the inhibitor	Gross formula	Melting point, °C	Exit %	Elemental analysis					
				Found, %			Calculated, %		
				C	H	N	C	H	N
MAD-20	C ₁₀ H ₁₈ N ₄ M _r = 194 g	53-54	89	61,98	9,21	28,73	61,85	9,27	28,86

2. Test methods

2.1. Weight Loss Measurements

Distilled water was used to prepare the test solutions for all measurements. 15% H₂SO₄ solutions containing various concentrations of MAD-20 were prepared. The inhibitory effect of MAD-20 on corrosion was studied in a 15% H₂SO₄ solution on steel samples with a size of 100 mm high, 15 mm wide and 20 mm thick. The steel panels were mechanically sanded with 400, 600, 800 and 1200 sandpaper, degreased with acetone and washed with distilled water. Then they were washed with 15% (weight/volume) NaOH solution and rinsed with distilled water. Finally, the samples were immersed in 5% (vol./vol.) H₂SO₄, washed twice with distilled water and dried.

Samples with a prepared surface were weighed and then immersed in 15% H₂SO₄ without and with different concentrations of MAD-20 for 24-96 hours. The contents of the glass were stirred using a magnetic stirrer. After the time of the experiment, the samples for removing corrosion products were washed in a stream of cold water, treated with a special detergent solution, degreased with acetones, kept in a desiccator and after that the samples were weighed. The corrosion rate was calculated from the change in the mass of the samples before and after the tests according to the equation:

$$r = \frac{(m_1 - m_2)}{S} \times t$$

Where: m_1 is the mass of the sample before the test, g; m_2 is the mass of the sample after the test, g; S is the surface area of the sample, m^2 ; t is the duration of the experiment, per hour.

The protective effect of the corrosion inhibitor ($Z\%$) was determined by the formula:

$$Z = \frac{K_0 - K}{K_0} \cdot 100\%$$

Where: K_0 is the corrosion rate of samples in the presence of an inhibitor, g/m^2 . K is the corrosion rate of the samples.

3. Results and discussion

3.1. Study of the structure of the test sample

Currently, the need of the Republic of Uzbekistan for anticorrosive materials is provided by imports. The creation of technological bases for the production of import-substituting and highly effective corrosion inhibitors based on nitrogen-containing compounds is relevant.

This paper proposes the creation of physico-chemical and technological bases for the production of corrosion inhibitors based on the 2,7-dimethyl-2,7-dicyanide-3,6-diazaoctan (MAD-20) molecule. For this purpose, the structure and composition of the 2,7-dimethyl-2,7-dicyanide-3,6-diazaoctan molecule was studied and established.

To obtain X-ray diffraction data, Xcalibur Ruby (CCD) and Crystal diffractometers were used. To remove and establish the structure, crystals with a size of $0.60 \times 0.50 \times 0.05$ mm were obtained. Data calculated 300 K. The X-ray structural formula of 2,7-dimethyl-2,7-dicyanide-3,6-diazaoctan is as follows [15-19].

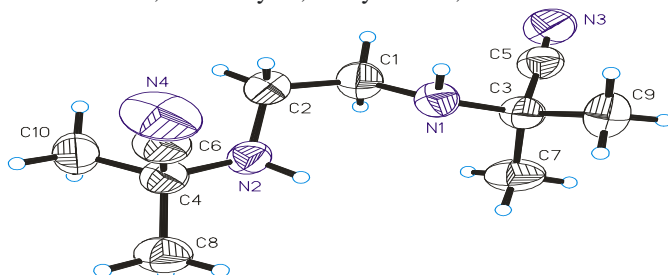


Figure 1. X-ray structural formula of 2,7-dimethyl-2,7-dicyanide-3,6-diazaoctane

In addition, IR spectra of 2,7-dimethyl-2,7-dicyanide-3,6-diazaoctan were obtained. The structure of 2,7-dimethyl-2,7-dicyanide-3,6-diazaoctan was established by IR and NMR spectroscopy data and the results of the data obtained are as follows: $\nu_s(\text{CN})$ 2220 cm^{-1} , $\nu_s(\text{NH})$ 2988 cm^{-1} , $\nu_{as}(\text{CH}_3)$ 2942 cm^{-1} , $\nu_{as}(\text{CH}_2)$ 2853 cm^{-1} , $\rho(\text{C-C})$ 1464 - 1627 cm^{-1} , $\gamma(\text{NH})$ $763, 783 \text{ cm}^{-1}$, $\delta(\text{CH}_3)$ 1441 cm^{-1} , $\delta(\text{CH}_2)$ 1385 cm^{-1} ; $^1\text{H NMR}$ spectrum (8 MHz.) 1.40 (s, 6H, $-(\text{CH}_3)_2$), 2.74 (m, 4H, N- CH_2 CH_2 -N).

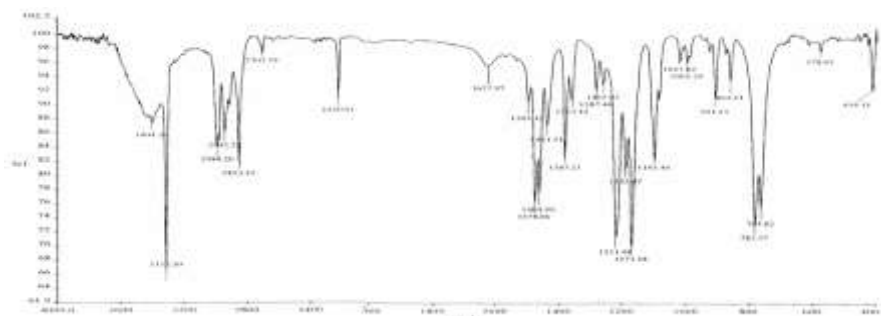


Figure 2. IR spectra of 2,7-dimethyl-2,7-dicyanide-3,6-diazaoctane

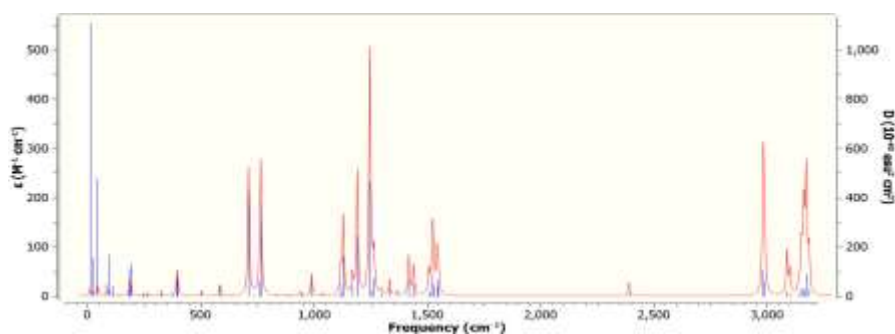


Figure 3. DFT IR spectra of 2,7-dimethyl-2,7-dicyanide-3,6-diazaoctane

Table 2. Comparison of IR spectra of 2,7-dimethyl-2,7-dicyanide-3,6-diazaoctane

No	Functional groups	The value of experiments	The value of the DFT program
1	$\nu_s(\text{CN})$	2220	2351
2	$\nu_s(\text{NH})$	2988	2933
3	$\nu_{as}(\text{CH}_3)$	2942	2939
4	$\nu_{as}(\text{CH}_2)$	2853	2933
5	$\rho(\text{C-C})$	1464-1627	1485-1526
6	$\gamma(\text{NH})$	763,783	751,756
7	$\delta(\text{CH}_3)$	1441	1418
8	$\delta(\text{CH}_2)$	1385	1397

For a detailed study and obtaining of the data, we studied the distribution of electron densities in the molecule by atoms of 2,7-dimethyl-2,7-dicyanide-3,6-diazaoctane. This work was carried out by the method of molecular electrostatic potential in the range from -1.004 eV to +1.004 eV

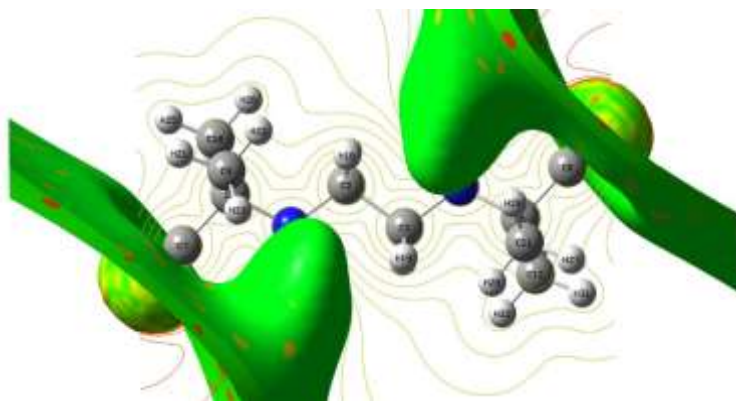


Figure 4. MEP surface of 2,7-dimethyl-2,7-dicyanide-3,6-diazaoctane

From these figures it can be seen that the highest electron densities are observed in the green and red areas in the 2,7-dimethyl-2,7-dicyanide-3,6-diazaoctane molecule. These sites belong to the vacant electrons of the functional groups $\text{N}\equiv\text{C}$ and NH in the molecule and by their chemical property they create a reaction center for an electrophilic charged particle. These sites in nucleophilic substitution reactions repel a negatively charged particle. In addition, in strongly acidic environments, the molecule is positively charged and due to the positively charged NC and NH groups, electrostatic adsorption occurs on the iron surface. In addition, there are black spots in Figure 5 and these places are the electron-deficient place of the molecule.

3.2. Determination of the effectiveness of inhibition

The stage of laboratory testing of corrosion inhibitors includes the determination of the physico-chemical and technological characteristics of the inhibitors and the determination of the protective properties of the corrosion inhibitor. Inhibitory protection significantly reduces the rate of corrosion processes [20-23].

The purpose of laboratory research is a comprehensive study of the properties of the corrosion inhibitor 2,7-dimethyl-2,7-dicyanide-3,6-diazaoctan (MAD-20). To study the anticorrosive properties of the obtained compounds, we used gravimetric methods of analysis. The inhibitory properties of 2,7-dimethyl-2,7-dicyanide-3,6-diazaoctan were studied by gravimetric methods at room temperature on samples of plate steel St.235 with a size of 100 mm high, 15 mm wide and 20 mm thick in different concentrations. The aggressive medium was 15% H₂SO₄. The results of the study are summarized in the form of tables.

From the results of the above tables, it can be said that the studied inhibitor MAD-20 with the addition of 100 mg /l in 15% sulfuric acid for 96 hours exhibits high inhibitory properties (93.56-96.8%). The protective effect of the MAD-20 inhibitor at a concentration of 250 mg/l for 96 hours is 96.95% and at a concentration of 500 mg / l is equal to 98.60%. This is indicated by the fact that the effectiveness of the inhibitor at a temperature of 20 ° C increases in parallel with an increase in concentration. Table 3 provides information on the rate of corrosion process and the degree of protection of the MAD-20 inhibitor.

Table 3 The effectiveness of the MAD-20 inhibitor in solution 15% H₂SO₄ at 20°C

The inhibitor cipher	Amount of inhibitor mg/l	Time, hour	15% H ₂ SO ₄	
			$K_{\Gamma / M^2 \cdot c}$	Z%
MAD-20	100	24	1,81	93,56
		48	0,87	95,73
		96	0,95	96,80
	250	24	0,85	95,22
		48	0,91	96,24
		96	0,92	96,95
	500	24	0,45	98,34
		48	0,36	98,58
		96	0,39	98,60

4. Surface Characteristics

4.1. SAM analysis

SEM analysis of the morphology of the surface of the samples was studied using SEM analysis. The experiments were conducted without an inhibitor and with inhibitors of various concentrations (100, 250 and 500 mg/l MAD-20). The resulting SEM micrographs are shown in Figure 5. Figure 5 shows that the surface of low-carbon steel is severely damaged in H₂SO₄ solution without MAD-20. The results show a strong dissolution of steel exposed to H₂SO₄ solution without an inhibitor. This led to an increase in surface porosity along with the formation of large and deep holes on the metal surface. According to Figure 5, the addition of MAD-20 caused a significant decrease in the dissolution rate of low-carbon steel and the formation of fewer corrosion products on the metal surface in the presence of MAD-20. It can be seen that an increase in the concentration of MAD-20 to 500 mg/l caused a decrease in the degradation of the steel surface.

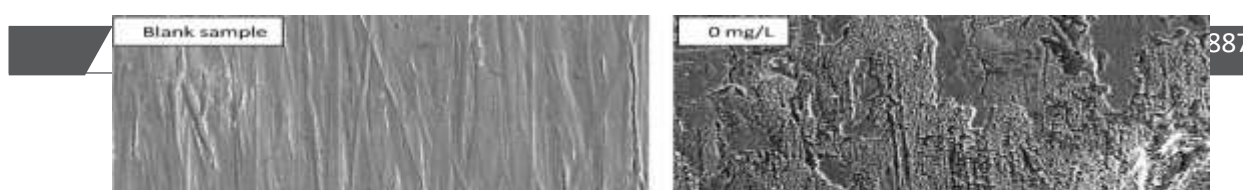


Figure 5. SEM-micrographs of the surface of St.235

Figure 5 shows SEM micrographs of the surface of low-carbon steel exposed to 15% sulfuric acid solution with MAD-20 in different concentrations. These observations show that the adsorption of MAD-20 molecules on the surface of low-carbon steel reduces its dissolution and protects against corrosion.**5**.

CONCLUSIONS

The effect of the addition of a MAD-20 inhibitor in a 15% H₂SO₄ solution on the corrosion of a low-carbon steel sample was investigated. The results obtained have been summarized in the following:

1. MAD-20 showed relatively good corrosion inhibition properties of low-carbon steel in 15% H₂SO₄ solution. The effectiveness of inhibition increased with an increase in the concentration of MAD-20
2. A sample immersed in a H₂SO₄ solution containing 500 mg/l MAD-20 showed less surface damage than other samples. A higher edge angle and lower free surface energy were obtained when the steel sample was immersed in an H₂SO₄ solution containing MAD-20 than a sample without MAD-20.
3. The protective effect of the MAD-20 inhibitor in solutions of 15% sulfuric acid ranges from 93.5% to 98.6%. The inhibitory properties of the compound in strongly acidic media are dehumidified by protonated positively charged nitrogen atoms. In slightly acidic and neutral media, the inhibitory properties are carried out due to chemical adsorption, which interact with unsheltered nitrogen electron pairs and vacant iron d-orbitals.

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