The Study of Thioimidazoline and Its Complex as CO_2 Corrosion Inhibitor

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Abstract – **Thioimidazolidine was synthesized by the reaction of polyethylene polyamine and thiocarbamide in 1:1 molar ratio at 180°C during 5 hours, while the synthesis of thio-imidazolidinamide was carried out by the reaction of thioimidazolidine with oleic acid in 1:1 molar ratio at 130°C during 2 hours. Some physicochemical properties of thioimidazolidine and thioimidazolidine derivatives were determined, and their structures were confirmed by IR and NMR spectroscopy methods. The corrosion protection properties of these compounds for C1018 steel were studied using ACM GILL AC potentiometer. Corrosion measurements were conducted in 1% NaCl solution saturated continuously with CO_2 at 50°C during 20 hours. It was found that thioimidazolidine and tioimidazolidinamide compounds exhibited corrosion protection efficiency above 98% starting from the proves their ability of forming a stable protective layer on the surface through chemical adsorption.**

Keywords: – corrosion inhibitor, polyethylene polyamine, thiocarbamide, CO_2 corrosion, thioimidazolidine, adsorption energy.

I. INTRODUCTION

Equipment and devices are subjected to corrosion during the extraction, transportation, and processing of oil resulting in contamination of environment by oil and oil products that leads to ecological consequences. Therefore, corrosion inhibitors are widely used to protect the equipment from corrosion used in oil transportation and processing [1-3]. The constant changes in the processing conditions of oil lead to a decrease in the protective effects of the applied inhibitors, creating a need for more effective inhibitors in the oil industry. Extensive research is being conducted on the development of new inhibitors for CO_2 and H_2S-containing acidic media [4-6]. Nitrogen and sulfur-containing organic compounds such as amines, amides, imidazolines, imidazoles, and thioimidazoles are used as corrosion inhibitors [7,8]. The corrosion inhibitive properties of these compounds as inhibitors have been explained by their molecular structure dependencies. The adsorption of these molecules on the metal surface is determined by the presence of a double bond and a lone electron pair on the heteroatom. Numerous studies have been conducted on the corrosion inhibition properties of sulfur-containing compounds on metal surfaces in acidic media and their synthesis [9-12]. The presented work is dedicated to the synthesis of heteroatom-containing organic compounds with nitrogen and sulfur possessing corrosion protection capabilities in acidic media, the study of their protection properties against CO_2 corrosion, and the creation of corrosion inhibitors on the basis of these compounds.

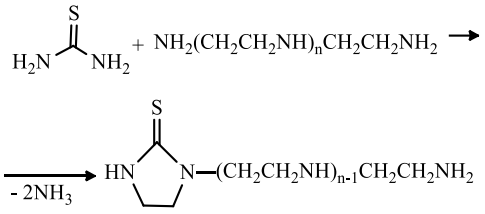
II. EXPERIMENTAL PART

Polyethylene polyamine (PEPA), thiocarbamide, and oleic acid were used for the experiments. Cylindrical electrodes made of C1018 steel with an area of 7.9 cm² were used in the corrosion studies. The composition of C1018 steel consists of 98.81-99.26% Fe, 0.14-0.20% C, 0.60-0.90% Mn, 0.04% P, and 0.05% S. Electrochemical corrosion studies were conducted in 1% NaCl solution continuously bubbled with CO_2 at 0.9 bar pressure for 20 hours at 50°C. The solution was continuously stirred using a magnetic stirrer until the end of the experiment.

The synthesis of thioimidazolidinamide was carried out in two stages: the first stage resulted in obtaining thioimidazolidine, and the second stage - thioimidazolidinamide.

In the initial stage, 24 g (0.1 mol) of polyethylene polyamine was heated to 80°C, then 50 ml of o-xylol was added as a solvent, and 7.6 g (0.1 mol) of thiocarbamide was added to the mixture. An inert atmosphere was created by continuously supplying nitrogen to the reaction medium. Thioimidazolidine from polyethylene polyamine and thiocarbamide was synthesized at 180°C during 5 hours with continuous stirring. At the end of the reaction, the synthesized compound was purified by crystallization in alcohol. As a result of the reaction, 23.2 g of thioimidazolidine was obtained with 82% yield.

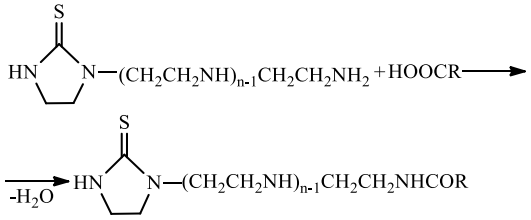
The scheme of the thioimidazolidine synthesis reaction is as follows (Scheme 1):



Scheme 1. Thioimidazolidine obtained from thiocarbamide and PEPA, here n=3-6

In the second stage, thioimidazolidinamide was obtained by the reaction of thioimidazolidine with oleic acid.

24 g (0.1 mol) of thioimidazolidine and 24 g (0.1 mol) of oleic acid were taken and mixed in a three-necked flask equipped with a Dean-Stark apparatus and a reflux condenser. The reaction was carried out at 130°C during 3 hours with stirring. The reaction medium was purged with nitrogen to create an oxygen-free atmosphere. The reaction for obtaining thioimidazolidinamide on the basis of thiocarbamide and PEPA is represented by the following equation:



Scheme 2. The reaction for obtaining the amide of thioimidazolidine,
where R = $C_{17}H_{33}$-.

IR (KBr) of Thioimidazolidine. δ (CH_2) – 1450, ν (CH_2) – 2870, 2923, 2964 $см^{-1}$; ν (C=S) – 1273 $см^{-1}$; δ (NH) – 1595, 1659, ν (NH) – 3271 $см^{-1}$.

^{1}H NMR (BRUKER-Fourier 300 MHz, $CDCl_3$, δ, m.h.): 2.78-2.96 (m., 6H, $\underline{CH_2}$-N), 3.19-3.25 (m., 2H, $\underline{CH_2}$-N), 3.56-3.69 (m., 4H, $\underline{CH_2}$-N), 5.16 (s., 2H, NH_2), 6.04 (s., NH), 7.32 (s., 1H, NH).

^{13}C NMR (BRUKER-Fourier 75 MHz, $CDCl_3$, δ, m.h.): 42.03, 44.22, 46.63, 49.72, 50.30, 52.09 ($\underline{CH_2}$-N), 183.39 (COO)

IR (KBr) of Thioimidazolidinamide. δ (CH_3, CH_2) – 1378, 1452 $см^{-1}$; ν (CH_3, CH_2) – 2859, 2925, 2969 $см^{-1}$; ν (C=S) – 1276 $см^{-1}$; δ (NH) – 1501, 1556 $см^{-1}$; ν (C=O) – 1655 $см^{-1}$.

1H NMR (BRUKER-Fourier 300 MHz, CDCl3, δ, m.h.): 0.91 (3H, CH3), 1.15-1.39 (20H, m., CH2), 1.51 (2H, CH2), 2.12 (2H, CH2-COO), 2.18-2.21 (4H, CH2-CH=CH), 2.64-2.97 (m., 6H, CH2-N), 3.22-3.29 (m., 2H, CH2-N), 3.58-3.72 (m., 4H, CH2-N), 5.06 (s., 2H, NH2), 5.31, 5.36 (2H, CH=CH), 5.81 (s., NH), 7.23 (s., 1H, NH).

13C NMR (BRUKER-Fourier 75 MHz, CDCl3, δ, m.h.): 13.56 (CH3), 23.44, 24.17, 25.41, 26.18, 25.86, 27.03, 27.83, 28.16, 28.32, 28.70, 29.51 (CH2), 32.40, 32.87 (CH2CH=), 35.02 (CH2COO), 41.15, 43.44, 46.84, 48.93, 50.35, 51.90 (CH2-N), 182.82 (COO).

Corrosion protection properties of thioimidazolidine and thioimidazolidinamide in co_2 medium. were studied at concentrations of 5, 25, and 100 mg/l. Inhibitor efficiency was calculated by determining the corrosion rate, current density, and metal loss of C1018 mild steel in the presence and absence of inhibitors using a potentiometer. The effectiveness of the inhibitor, adsorption constant, and Gibbs free energy were calculated according to the following equations [13]:

$$\eta = \frac{(k_{free-k_{inh}})}{k_{free}} \times 100$$

η – inhibition efficiency (in percentage), k_{free} – corrosion rate without inhibitor (mm/year), k_{inh} – corrosion rate with inhibitor (mm/year).

The adsorption equilibrium constant (K_{ads}) was calculated from the next equation [13]:

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

Here, K_{ads} – adsorption constant, C – inhibitor concentration (mol/l).

The value of Gibbs free energy is calculated using the equation[13]:

$$\Delta G^0_{ads} = -RT\, ln(55.5K_{ads})$$

The effect of these compounds on the corrosion of C1018 steel in a carbon dioxide medium was tested over a period of 20 hours. The results for thioimidazolidine corrosion tests at the 20th hour are presented in Table 1.

TABLE 1. VALUES OF LINEAR POLARIZATION RESISTANCE, CURRENT DENSITY, CORROSION RATE, METAL LOSS, AND PROTECTION EFFICIENCY IN THE PRESENCE OF THIOIMIDAZOLIDINE

C, mg|l	Time, h	i_{cor}, mA/cm^2	K, mm|year	Weight loss, mm	η, %
blank	10	0,190	2,209	0,0023	-
	20	0,296	3,434	0,0054	-
5	10	0,009	0,113	0,0003	94,8
	20	0,007	0,081	0,0004	97,7
25	10	0,006	0,070	0,0006	96,8
	20	0,005	0,056	0,0007	98,3
100	10	0,006	0,066	0,0003	97,0
	20	0,004	0,048	0,0004	98,6

Figure 1 shows the time dependence of the corrosion rate in the presence of CO_2 for various concentrations of thioimidazolidine in an inhibitor-free medium. The corrosion rate is 3.43 mm/year in the inhibitor-free medium.

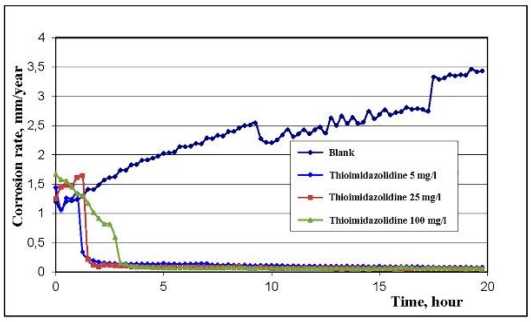


Figure 1. Time dependence of the corrosion rate in the presence of thioimidazolidine in CO_2 medium

Thioimidazolidine exhibits a very high protection efficiency starting from a concentration of 5 mg/l. At this concentration, the protection efficiency reaches 97.7% at the 20th hour of the test. The protection efficiency at a concentration of 5 mg/l is considered a high result for corrosion inhibitors. When the concentration of thioimidazolidine is increased to 100 mg/l, the protection efficiency slightly increases, reaching 98.6%.

The results of the effect of the obtained thioimidazolidinamide on the corrosion of C1018 steel are presented in Table 2. Corrosion rate is 4.5 mm/year in the inhibitor-free medium.

TABLE 2. RESULTS OF THE EFFECT OF THIOIMIDAZOLIDINAMIDE ON CO_2 CORROSION DEPENDING ON TEST DURATION

Imidazo	C, mg/l	K, mm|year	η, %	γ	K, $M^{-1}\cdot10^4$	ΔG^0_{ads} kJ/mol
Thioimidazolidina	5	0,0612	98,6	70,5	34,0	-36,6
	10	0,0598	98,7	74,0	37,6	-37,0
	25	0,0544	98,8	80,3	45,0	-40,0
	50	0,0409	99,0	108,5	47,0	-40,0

Although there is no significant change in the corrosion rate within the concentration range of 5-50 mg/l for thioimidazolidinamide, when the concentration is increased from 5 mg/l to 50 mg/l, the corrosion rate decreases from 0.061236 mm/year to 0.040893 mm/year, respectively. The graph of the time dependence of the corrosion rate reveal that the inhibitory properties of the compound slow down the metal corrosion from the moment of introducing into the medium, and the time-dependent corrosion rate curves overlap at these concentrations (Figure 2).

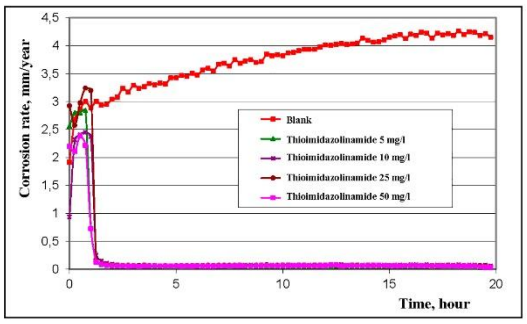


Figure 2. Time dependence of the effect of thioimidazolidinamide on the corrosion rate of steel in CO_2 medium

The thioimidazolidinamide compound, starting from a concentration of 5 mg/l, meets the requirements for corrosion inhibitors, showing a protection efficiency of 98.6%. Increasing the concentration to 50 mg/l has little effect on the already high protection efficiency.

IV. CONCLUSIONS

1. The studies allowed determine that thioimidazolidine and its amide formed with oleic acid at the concentrations of 5-100 mg/l provide the protection of the metal surface from corrosion by 94-95.9%.
2. The Gibbs free energies of thioimidazolidine and thioimidazolidinamide compounds below -35 kJ prove their ability of forming a stable protective layer on the surface through chemical adsorption.

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