STUDY OF THE INHIBITING MECHANISM OF THE INHIBITOR SYNTHESIZED ON THE BASE OF MALEIC ANHYDRIDE BASED ON THERMODYNAMIC PARAMETERS

Choriev I.K.,

Faculty of Applied Mathematics and Itellectual Ttechnologies, Termez State University, st. Barkamol avlod, 43, Termez, Uzbekistan, 190111

Turaev Kh. Kh.,

Faculty of Chemistry, Termez State University, st. Barkamol avlod, 43, Termez, Uzbekistan, 190111

Normurodov B.A.

Faculty of Chemistry, Termez State University, st. Barkamol avlod, 43, Termez, Uzbekistan, 190111.
Corresponding author: Email: choriyevi@tersu.uz

Abstract. In this article, the thermodynamic and kinetic parameters (Langmuir, Frumkin, and Tyomkin isotherms) of corrosion inhibitor synthesized on the basis of maleic anhydride, monoethanolamine, and phosphoric acid to determine the mechanisms of steel inhibition are studied. According to the results of the research, as the concentration of the inhibitor increases, the level of its coating on the steel surface increases, and its internal energy increases. This shows that the inhibitor protect steel at a high level in various aggressive environments.

Keywords: thermodynamic and kinetic parameters, Langmuir, Frumkin, Tyomkin, inhibitor protect.

Introduction Corrosion is a reversible process, which converts pure metal to different chemical compounds[1]. Nowadays, corrosion is turning into a major issue in many industries, building materials, infrastructure, tools, ships, trains, vehicles, machines, and appliances [2]. Carbon steel experiences extensive corrosion during the cleansing process with acids. The NACE 2016 reported shows that at the world level about 2.5 trillion U.S. dollars economic fall caused by corrosion every year total of 10% of total metal of world is lost due to corrosion which influences the economy of the nation [3]. Corrosion is not only responsible for an economic loss but also associated with safety issues because it decreases the

shelf life of steel[4]. This problem turns into a major issue for the entire world, so researchers are trying to address this issue in various ways[5].

Experimental part

Thermodynamic and kinetic. By finding the activation energy of the obtained composite corrosion inhibitors at different concentrations and temperatures, it is possible to study the mechanism of interaction of the inhibitors with the metal surface. The corrosion rate is determined using the Arrhenius formula to determine the activation energy in solutions with and without inhibitors[6].

$$CR = A\exp(\frac{-Ea}{RT}) \qquad (2.1)$$

Here: Ea is the activation energy expressed in kJ/mol moles, R is the universal gas constant value of 8.314 J/mol×K, and T is the temperature expressed in K A-exponential coefficient.

If we compare the activation energy (E_a) of the solutions with an inhibitor to the solution without the inhibitor, we can see that (E_a) increases as a result of the addition of the inhibitor to the solution, and the activation energy also increases with the increase in the concentration of the inhibitor in the solution. A high activation energy causes physical adsorption, and if it does not change or becomes less, it causes chemical adsorption.

As the inhibitor concentration increased, the activation energy (Ea) values also increased dramatically. Therefore, in preventing corrosion, the primary function of the inhibitor is physical adsorption on the metal surface. From the large negative values of entropies, we can see that the rate-determining step of corrosion, i.e., active complex formation, is more associated than dissociated, which leads to a decrease in disorder.

Results and Discussion

3.1. Adsorption isotherm. The process of adsorption is the desorption of water molecules by adsorbing inhibitor molecules on the metal surface, and this process can also be described as an exchange process. From this we can see that the inhibitor is adsorbed on the metal surface and covers the surface (th) as the inhibitor concentration increases, the surface is covered to a higher degree and the efficiency increases. θ is a quantity indicating the effectiveness of the inhibitor and is taken as 100. Several types of isotherms have been used to describe this process[7,8].. Freundlich adsorption isotherms were obtained, which can be expressed as follows:

$$\theta = K_{ads}C^n \qquad (3.1)$$

or

$$log\theta = logK_{ads} + nlogC \qquad (3.2.)$$

where $0<n<1$; θ– surface coating; C– inhibitor concentration; K_{ads}-equilibrium constant of the adsorption-desorption process.

The following isotherms for adsorption of these corrosion inhibitors were also studied

Lengmyur: $\qquad \dfrac{C_{\text{ing}}}{\theta} = \dfrac{1}{K_{ads}} + C_{\text{ing}}$ $\qquad\qquad$ (3.3.)

Frumkin: $\qquad \dfrac{\theta_{grav}}{1-\theta_{grav}} exp(-2f\theta_{grav}) = K_{ads}C_{ing}$ $\qquad$ (3.4.)

Tyomkin: $\quad exp(f\theta_{grav}) = K_{ads}C_{ing}$ $\qquad\qquad$ (3.5)

where: C_{ing} - concentration of the inhibitor in the solution (mg/l),

θ- the full coverage rate,

K_{ads}- adsorption equilibrium constant.

The Langmuir isotherm provides a more complete understanding of the mechanism of interaction between the metal surface and the inhibitor. Using the Langmuir isotherm with C_{ing} bilan C_{ing}/θ as the adsorption equilibrium constant K_{ads} found by ΔG^0_{ads} value in the temperature range 25 °C - 55 °C is found using Equation 3.7:

$$\Delta G^0_{ads} = -RTln(1000K_{\text{адс}}) \qquad\qquad (3.6)$$

The standard free energy of adsorption (DG°ads) is calculated by the following equation (3.7).

$$\Delta G^o_{ads} = \Delta H^o_{ads} - T\Delta S^o_{ads} \qquad (3.7)$$

Here, R is the universal gas constant, T is the absolute temperature in Kelvin, and g/l. k_{ads} is the density of water in g/l. The values of cads and $\Delta G°_{ads}$ are calculated using the above isotherm equations.

In this case, E_a values were found from the dependence of lgW on 1000/T in mediums without and with inhibitors.
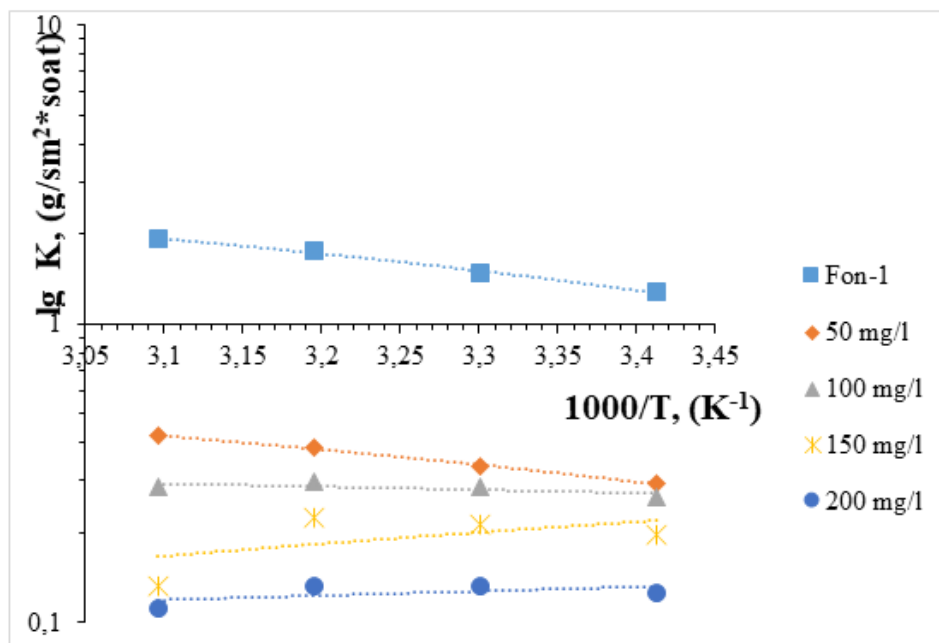
Figure 3.1. Arrhenius plot g for the activation energy of MMF-1 corrosion inhibitor in Fon-1 solution

According to the results presented in Table 3.13, the value of E_a was 41.45 (kJ/mol-1) in solutions without an inhibitor, this value increased with the introduction of MMF-1 brand corrosion inhibitor into the solution, and when the concentration reached 200 mg/l, it was 89.29 (kJ/mol-1). Also, the value of ΔS_a in the solution without inhibitor took a positive value of 101.25 kJ/mol, but with the addition of inhibitor to the solution, this value decreased to negative -75.21 (kJ/mol-1), the smaller this value, the corrosion depends on the concentration of the inhibitor, the association is higher than dissociation in the system, and this indicates that a stable complex is formed between the inhibitor and the metal[9]..

Table-3.1.

Values of activation parameters for steel St20 in graded water without inhibitor and in presence of green inhibitor

Ingibitor konsentratsiyasi	E_a(kJ/mol^{-1})	ΔH_a (kJ/mol^{-1})	ΔS_a(kJ/mol^{-1}K^1)	$E_a - \Delta H_a$
0.0	41.45	38.4	101.25	2.94
50	53.26	51.43	-18.36	2.71
100	64.05	60.93	-23.12	2,64
150	76.30	72.62	-52.36	2.59
200	89.29	85.72	-75.21	2.47

The average energy difference between activation energy and enthalpy for samples without inhibitor and with different concentrations of inhibitor was approximately

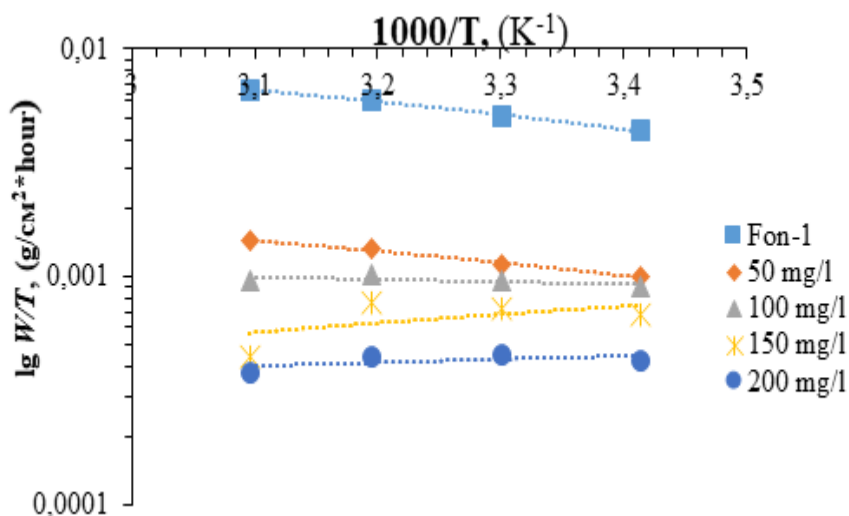2.67 kJ, which confirms the inhibition and adsorption process of St20 steel during melting.

Figure 3.2. Transition state graph for the activation process of MMF-1 brand corrosion inhibitor in Fon-1 solution.

Several researchers have recognized that one of the reasons for the inhibition of the metal surface in the inhibitor solution is the absorption of the corrosion inhibitor on the surface. The presence of free ions in the composition of the corrosion inhibitor leads to the transport of charges, or the presence of functional groups binds to the metal surface through the donor-acceptor mechanism in exchange for negative charges. Langmuir, Frumkin, and Tyomkin isotherms of MMF-1 corrosion inhibitor were also studied.

Figure 3.3 of MMF-1 brand corrosion inhibitor. (a) Tyomkin (Figure 3.3 a), Frumkin (Figure 3.3 b), and Langmuir (Figure 3.3 c) isotherms are also plotted. According to the obtained results, when comparing the values of Frumkin, Tyomkin and Langmuir isotherms, the value of the Langmuir isotherm is higher than 0.99, which shows us that it matches the experimental data for the calculation of thermodynamic parameters. Langmuir, Frumkin, and Tyomkin isotherms for green corrosion inhibitors were also studied[10,11].
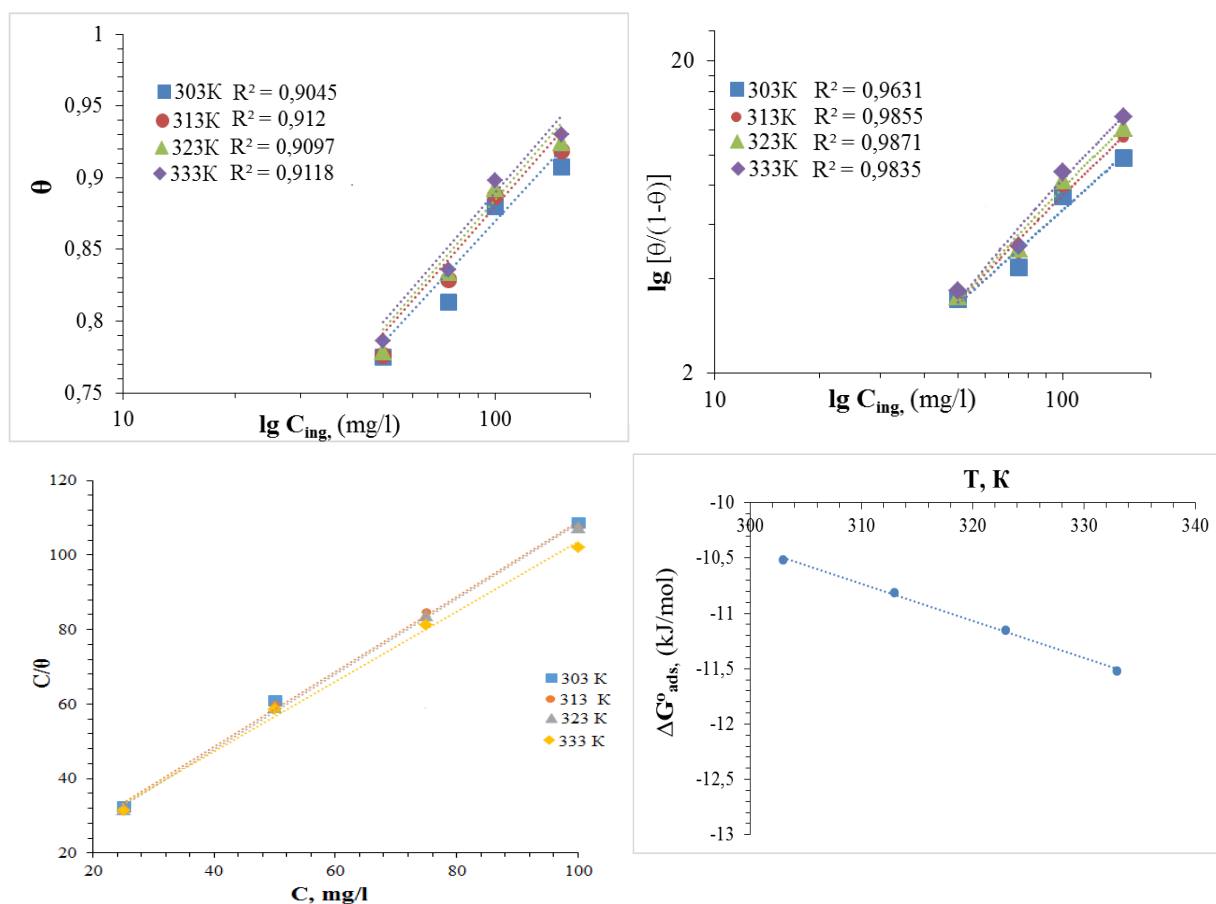
Figure 3.3. (a) Tyomkin, (b) Frumkin and (c) Langmuir isotherms and (d) temperature dependence of ΔG^0_{ads}

Correlation coefficient values were obtained at different temperatures. We can see from Figures 3.3a and 3.3b that the values of the correlation coefficients of the Frumkin and Tyomkin adsorption isotherms are not close to 1, indicating that the adsorption process does not follow these isotherms.

Table-3.2.

Thermodynamic parameters of MMF-1 brand corrosion inhibitor

Temperature	K_{ads}	ΔG_{ads} kJ/mol	ΔH_{ads}, (kJ/mol)	ΔS_{ads}, (kJ/mol K)
303	356,7	-23,12		
313	433,1	-25,23	-15,38	-126,5
323	490,9	-26,25		
333	580,5	-28,29		

Then the values of K_{ads} were calculated based on the intersection of Langmuir isotherms. It follows from the values of $Kads$ that the adsorption of MMF-1 brand corrosion inhibitor on the metal surface is superior to all desorption. Judging from

the data in Table 3.2, the values of ΔG^0_{ads} were obtained in the range of 303−333 K, with results ranging from negative -23.12 kJ/mol to-28.29 kJ/mol provided, thus confirming that the adsorption of MMF-1 brand corrosion inhibitor on the metal surface occurs spontaneously.

3.3 Scanning electron microscope analysis.

A scanning electron microscope (SEM) uses a focused beam of high-energy electrons on the surface of solid samples to produce a variety of signals. SEM allows obtaining information such as the surface structure (external morphology), chemical composition, orientation of components, as well as the crystal structure of the sample from the signals obtained from the electron interaction of the sample. The purpose of SEM analysis is to determine the presence of an inhibitor on the steel surface.

The pre-corrosion, post-corrosion and inhibited states of the steel surface were studied using a SEM-EVO MA 10 (Zeiss, Germany) scanning electron microscope.
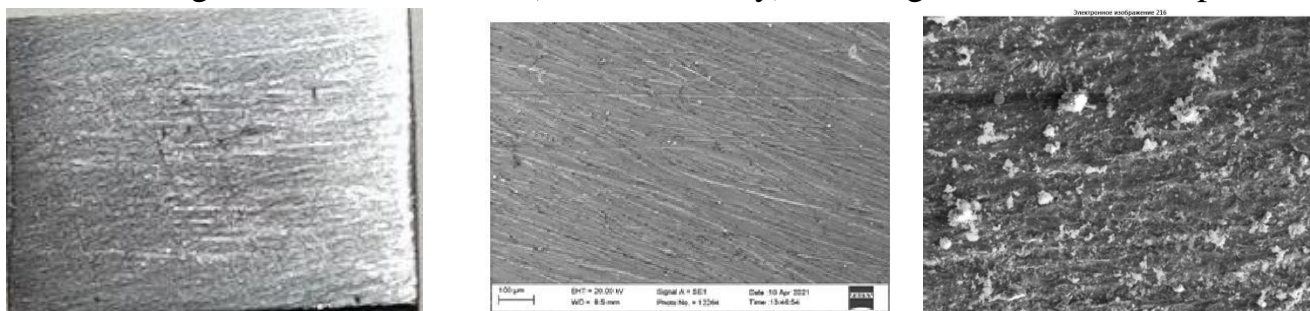
Figure 3.4a. Original photograph of the steel sample

Figure 3.4b. SEM photograph of a steel sample

Figure 3.4c. SEM photograph of annealed steel sample

As you can see from the pictures given above, Figure 3.4a shows the first photo of a steel sample cleaned with different grades of sandpaper and washed in acetone. Also, microphotographs of the initial steel sample were taken using a scanning electron microscope in an environment without an inhibitor (Fig. 3.4b) and with an inhibitor (Fig. 3.4c).
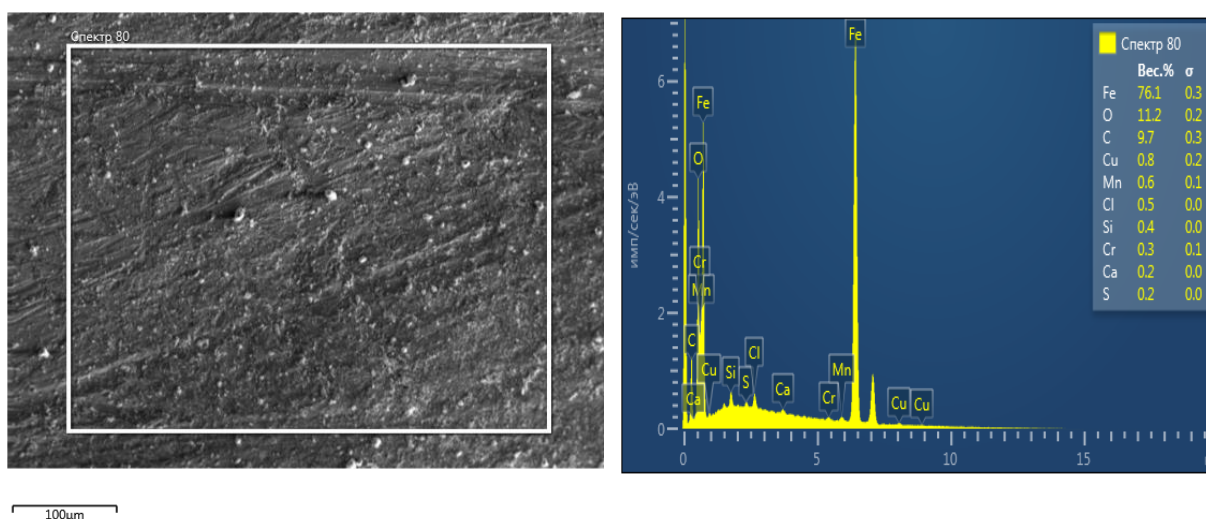
Figure 3.5. SEM and elemental analysis of St20 sample inhibited with MMF-1 inhibitor

It is known from Figure 3.5 that the SEM and elemental analysis of MMF-1 brand corrosion inhibitor in Fon-1 environment using a scanning electron microscope is presented. It is known that the inhibitor is adsorbed on the steel surface and protects against aggressive environments. It can also be seen from the element analysis.

Conclusion.

The inhibition mechanism of this inhibitor was studied based on Langmuir, Frumkin, and Tyomkin isotherms from the adsorption parameters and its effect on the steel surface using a scanning electron microscope.

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