

The Results of the Calculation of the Process and Mechanism of Inhibition of the Compound 2,4,6-Triethanolamine-1,3,5-Triazine in 0.5 M H₂SO₄ Medium Using Thermodynamic and Kinetic Parameters

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ABSTRACT

In this article, the mechanism of inhibition and adsorption isotherms of the compound 4,6-triethanolamine-1,3,5-triazine in a 0.5 M sulfuric acid medium are studied. The values of ΔH^* are determined from the slopes of the straight lines and are equal to 17.421 kJ mol⁻¹ for uninhibited 0.5 M H₂SO₄ and 21.627, 26.231, and 28.379 kJ mol⁻¹ for inhibited solutions of 100 mg/l, 200 mg/l, 250 mg/l, respectively. The ΔS^* values were determined from the points of intersection of the straight lines and are equal to -195.371 J mol⁻¹ K⁻¹ for uninhibited 0.5 M H₂SO₄ and are equal to -196.275, -197.456 and -198.954 J mol⁻¹ K⁻¹ for 100 mg /l, 200 mg/l and 250 mg/l corrosion inhibitor TEITA, respectively.

Keywords:

2,4,6-triethanolamine-1,3,5-triazine, H₂SO₄, thermodynamic parameters, adsorption isotherm, inhibition mechanism .

Introduction Carbon steel is one of the most widely used materials in industry due to its high availability, physical and chemical characteristics, and relatively low cost [1].

These processes corrode the AC, and so scientists use corrosion inhibitors to overcome many of the damage that results from AC corrosion and acid consumption. In most previous studies, organic compounds containing N, S, or O atoms were used as corrosion inhibitors for carbon steel. These compounds provide high inhibitory efficiency in reducing the corrosion rate due to their adsorption on the steel surface [2-4]. Unfortunately, most of these organic

substances are imported from abroad. To solve these problems, available substances were used, which have many advantages, including ease of preparation, low cost and availability of substances, as well as local products manufactured by "Navoiazot" JSC. There are many types of corrosion inhibitors that have been used as anticorrosion agents against US corrosion in acidic environments and give high inhibition efficiency due to the ease of adsorption on the steel surface, where there is more than one place, which facilitates the adsorption process [5-7].

The addition of polymeric chemical compounds to a corrosion solution to reduce corrosion

(HCl, H₂SO₄, H₃PO₄ and HNO₃) is referred to as a corrosion inhibitor by forming a protective layer on the surface of the steel, and this form of corrosion protection is called inhibition [8].

2. Experimental Part

2.1. Determination of activation thermodynamic parameters.

The influence of elevated temperature on the rate of corrosion of the US in an uninhibited 0.5 M solution of H₂SO₄ and containing 250 mg/l corrosion inhibitors TEITA was studied by the gravimetric method. Similar curves in Figs. 3 are not displayed, and these corrosion parameters such as R_{corr}, θ and % IE are shown in Table 1. As shown in this figure and Table 1, the R_{corr} parameters increase with increasing temperature. This indicates that increasing the temperature in studies reduces inhibition and improves the inhibition efficiency at low temperatures than at high temperatures, for example, at 298 K, the highest inhibition efficiency is observed [9].

The apparent activation energy (E_a^{*}) of corrosion of carbon steel St20 in uninhibited 0.5 M H₂SO₄ solutions and the presence of 250 mg/l of the tested corrosion inhibitors TEITA in the temperature range of 298–328 K was determined using the Arrhenius equation:

$$\log R_{\text{corr}} = \log A - \frac{E_a^*}{2.303 RT}, \quad (1)$$

where A is the Arrhenius constant, R and T are the gas constant and temperature. On

fig. 1 shows an Arrhenius plot (log R_{corr} vs. 1/T) for uninhibited St20 in 0.5 M H₂SO₄ and in the presence of 250 mg/L of the investigated corrosion inhibitors TEITA.

3. Results And Discussion

The values of E_a are determined from the slope of the straight lines and are equal to 19.214 kJ mol⁻¹ for non-inhibited 0.5 M H₂SO₄, and for 100 mg/l, 200 mg/l and 250 mg/l inhibited samples they are 23.572, 27.846 and 30.765 kJ mol⁻¹ respectively. Obviously, the values increase with increasing concentration of TEIT molecules. This is due to a significant decrease in the process of adsorption of the inhibitor on the surface of carbon steel with increasing temperature. The tested TEITA compounds act as inhibitors, increasing the activation energy of dissolution of St20 carbon steel, creating a mass and charge transfer barrier by adsorption on the surface of St20 steel.

The change in the enthalpy of activation (ΔH^*) and the change in the entropy of activation (ΔS^*) for the corrosion of steel St20 in a 0.5 M solution of H₂SO₄, uninhibited and inhibited solutions of 100, 150, 200 and 250 mg/l corrosion inhibitors TEITA, were obtained using the transition equation states.

$$R_{\text{corr}} = \frac{RT}{N} \exp(\Delta S^*/R) \exp(-\Delta H^*/RT) \quad (2)$$

where N is Avogadro's number and h is Planck's constant.

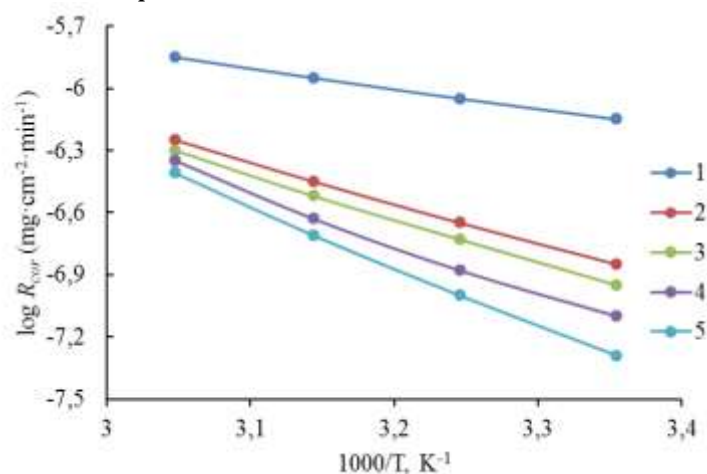


Fig. 1. Arrhenius curves (logR_{corr} from 1/T) for steel Ct20 in the absence of corrosion inhibitor in 0.5 M H₂SO₄ and in the presence of corrosion inhibitors TEITA: (1) 0.5 M H₂SO₄; (2) 100 mg/l; (3) 150 mg/l; (4) 200 mg/l and (5) 250 mg/l

Table 1

Effect of Elevated Temperature on Corrosion Parameters Obtained by the Gravimetric Method

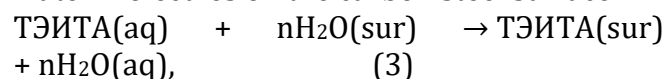
| Inhibitor concentration | Temperature, K | $R_{corr} \times 10^{-7}$, $\text{mg} \cdot \text{cm}^{-2} \cdot \text{min}^{-1}$ | %IE |
|--------------------------------------|----------------|--|-------|
| 0,5 M H ₂ SO ₄ | 298 | 7,12 | – |
| | 308 | 8,23 | – |
| | 318 | 9,36 | – |
| | 328 | 10,77 | – |
| 100 mg/l | 298 | 1,33 | 86,45 |
| | 308 | 2,54 | 85,86 |
| | 318 | 3,48 | 85,01 |
| | 328 | 4,39 | 84,77 |
| 150 mg/l | 298 | 0,87 | 89,32 |
| | 308 | 2,28 | 88,64 |
| | 318 | 3,22 | 87,87 |
| | 328 | 4,16 | 86,31 |
| 200 mg/l | 298 | 0,79 | 91,56 |
| | 308 | 1,97 | 90,89 |
| | 318 | 2,88 | 90,24 |
| | 328 | 4,09 | 89,13 |
| 250 mg/l | 298 | 0,71 | 93,74 |
| | 308 | 1,76 | 93,01 |
| | 318 | 2,63 | 92,37 |
| | 328 | 3,98 | 91,44 |

On fig. 1 shows a plot of $\log(R_{corr}/T)$ versus $1000/T$ for uninhibited St20 carbon steel in 0.5 M H₂SO₄ and in the presence of 100 mg/l to 250 mg/l corrosion inhibitors of TEITA compounds. Graphs are a straight line with slope $(-\Delta H^*/2.303R)$ and intercept $[\log(R/Nh) + \Delta S^*/2.303R]$.

The values of ΔH^* are determined from the slopes of the straight lines and are equal to 17.421 kJ mol⁻¹ for uninhibited 0.5 M H₂SO₄ and 21.627, 26.231, and 28.379 kJ mol⁻¹ for inhibited solutions of 100 mg/l, 200 mg/l, 250 mg/l, respectively. Positive values of ΔH^* reflect that the process of adsorption of TEITA compounds on the surface of St20 steel is an endothermic process. The ΔS^* values were determined from the points of intersection of the straight lines and are equal to -195.371 J mol⁻¹ K⁻¹ for uninhibited 0.5 M H₂SO₄ and are equal to -196.275, -197.456 and -198.954 J mol⁻¹ K⁻¹ for 100 mg/l, 200 mg/l and 250 mg/l corrosion inhibitor TEITA, respectively. The signs of ΔS^* in the control and inhibitor solutions are negative. This means that the

activation of the complex is a defining step, which is a correlation rather than a separation, indicating a decrease in turbulence when moving from the reactants to the activated compound [10].

3.2. Adsorption isotherm. TEITA molecules inhibit corrosion of St20 carbon steel in 0.5 M H₂SO₄ solution by being adsorbed on the surface of carbon steel. The adsorption process can be considered as a single substitution process, in which the inhibitor molecule in the aqueous phase of TEITA(aq) replaces the "z" number of adsorbed water molecules on the carbon steel surface.



where n is the number of adsorbed water molecules replaced by one TEITA molecule. Adsorption depends on several factors, such as the type and chemical structure of the corrosion inhibitor used as an inhibitor, the presence of an active site in the molecule to facilitate the formation of coordination bonds between the inhibitor and the metal used,

temperature, the type of electrolyte used, and other factors.

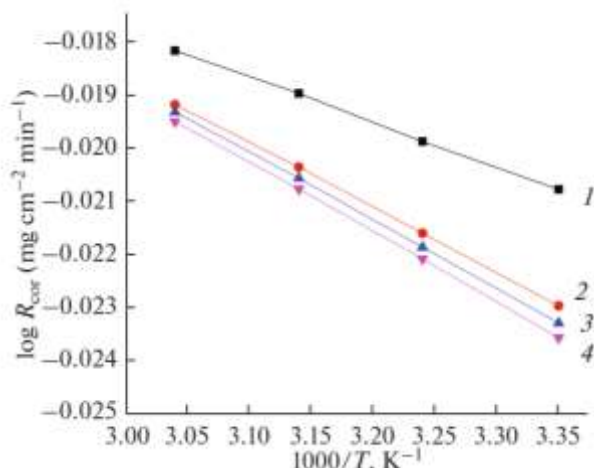


Fig. 2. Transition state curves ($\log R_{\text{corr}}/T$ versus $1/T$) for St20 steel in the absence of 0.5 M H₂SO₄ and in the presence of the corrosion inhibitor TEITA: (1) 0.5 M H₂SO₄; (2) 100 mg/L; (3) 200 mg/l; (4) 250 mg/l.

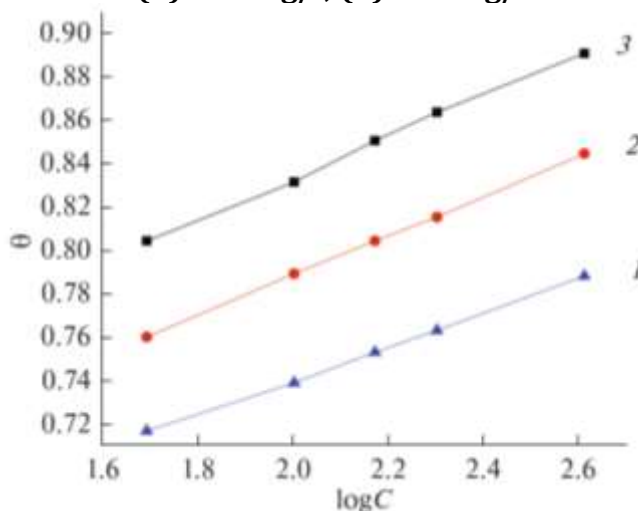


Fig. 3. Dependence of θ on $\log C$ (Temkin isotherm): 1 – 100 mg/l; (2) 200 mg/l; (3) 250 mg/l.

Several mathematical relationships have been proposed for adsorption isotherms that correspond to the experimental data of this work. The Temkin adsorption isotherm is determined by the following equation:

$$\ln K_{\text{ads}}C = a\theta, \tag{4}$$

where K_{ads} is the equilibrium constant of the adsorption reaction, C is the concentration of TEITA in the volume of the solution, and a is the interaction parameter.

Figure 1 shows plots of θ versus $\log C$ (Temkin adsorption plots) for the adsorption of corrosion inhibitor molecules TEITA on the surface of St20 steel in 0.5 M H₂SO₄ solution at 25°C. The data were straight lines indicating that the Temkin isotherm is correct for this system. The Temkin isotherm is applied in the

ideal state of physical and chemical adsorption on a smooth surface without any interaction between the adsorbed particles. The K_{ads} values were calculated from the intersection of the lines and are equal to $35.4, 29.3$ and 26.7×10^{-2} for 100 mg/l, 200 mg/l and 250 mg/l, respectively, which indicates more efficient adsorption and, therefore, better inhibition of TEIT molecules on the surface of carbon steel St20.

The K_{ads} values are related to the standard adsorption free energy (ΔG_{ads}) according to this relationship.

$$K = 1/55.5 \exp(-G_{\text{ads}}^0/RT), \tag{5}$$

where R is the gas constant, the value 55.5 is the concentration of water in the solution in moles. The determined values of

$\Delta G^{\circ}_{\text{ads}}$ are -67.84, -61.57 and -47.64 kJ/mol. The negative values of $\Delta G^{\circ}_{\text{ads}}$ obtained here indicate that the process of adsorption of the corrosion inhibitor TEIT on the surface of carbon steel is spontaneous.

3.3. Mechanism of inhibition

The worthy inhibiting efficiency of the corrosion inhibitor TEITA obtained by three methods in relation to the corrosion of carbon steel St20 in 0.5 M H₂SO₄ solution depends on several factors, such as the presence of electron-donating heteroatoms, ring size, and electron-withdrawing groups in the structure. This inhibitory effect is due to the formation of an insoluble layer as a result of the adsorption of TEITA on the surface of St20 carbon steel. Of all the methods used, %IE increases with increasing concentration of inhibitors due to an increase in the number of adsorbed molecules, resulting in a larger surface area of the metal being covered. Therefore, R_{corr} decreases and %IE increases. The presence of N atoms in the chemical composition of TEITA compounds, such as electron donor heteroatoms, which contain free unshared pairs of electrons on their structures and π -electrons on cyclization, facilitates the adsorption of TEITA on the surface of St20 carbon steel. In addition, the large molecule of TEITA compounds resulted in horizontal adsorption on the surface of carbon steel due to the presence of some active sites. In addition, the presence of electron-donating -OH and electron-withdrawing groups such as C=N or C-N led to an increase in electron movement, resulting in a strong inhibitory effect on the carbon steel surface.

Conclusion.

2,4,6-TRIETHANOLIMINE-1,3,5-TRIAZINE The mechanism of inhibition of steel in 0.5 M H₂SO₄ medium was studied using various thermodynamic and kinetic parameters. From the results obtained, it is known that the value of (E_a) increased with increasing concentration of this inhibitor. It can also be said that the adsorption of TEIT obeys the Temkin isotherm. And the PDP data prove that the TEITA compound is a mixed inhibitor.

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