

**Adsorption isotherm of PFA corrosion inhibitor which obtained based on  
paraphenylenediamine, Formalin, and Alanin**

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The process of adsorption is 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 ( $\gamma$ ) as the inhibitor concentration increases, the surface is covered to a higher degree and the efficiency increases.  $\theta$  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[1-5]. Freundlich adsorption isotherms were obtained, which can be expressed as follows:

$$\theta = K_{ads}C^n \quad (1)$$

or

$$\log\theta = \log K_{ads} + n\log C \quad (2)$$

here  $0 < n < 1$ ;  $\theta$ – 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: 
$$\frac{C_{ing}}{\theta} = \frac{1}{K_{ads}} + C_{ing} \quad (3)$$

Frumkin: 
$$\frac{\theta_{grav}}{1-\theta_{grav}} \exp(-2f\theta_{grav}) = K_{ads}C_{ing} \quad (4)$$

Tyomkin: 
$$\exp(f\theta_{grav}) = K_{ads}C_{ing} \quad (5)$$

here:  $C_{inh}$ - concentration of the inhibitor in the solution(mg/l),  $\theta$ - the full coverage rate,  $K_{ads}$ - adsorption equilibrium constant.

The standard free energy of adsorption ( $\Delta G^{\circ}_{ads}$ ) is calculated by the following equation (6).

$$\Delta G^{\circ}_{ads} = \Delta H^{\circ}_{ads} - T\Delta S^{\circ}_{ads} \quad (7)$$

Here,  $R$  is the universal gas constant,  $T$  is the absolute temperature in Kelvin. The values of  $k_{ads}$  and  $\Delta G^{\circ}_{ads}$  are calculated using the above isotherm equations.

Knowing the thermodynamic energy of the system is very important in determining the mechanisms of action of the corrosion inhibitor. Based on this, we can say that the energy of the thermodynamic system where corrosion is occurring is measured in cases with and without an inhibitor taken at different concentrations. For this, it is found by applying the Arrhenius equation.

$$CR = A \exp\left(\frac{-E_a}{RT}\right) \quad (8)$$

Here:  $E_a$  is the activation energy expressed in kJ/mol moles, R is the universal gas constant value of 8.314 J/mol×K, T is the temperature expressed in K, A is the exponential coefficient[5,6].

The Arrhenius graph is widely used to explain various parameters such as activation energy ( $E_a$ ), enthalpy ( $\Delta H$ ), and entropy ( $\Delta S$ ) and its mathematical form is expressed by the following equations in the broad elucidation of the concepts of corrosion inhibitor's absorption mechanism:

$$CR = A e^{-E_a/RT} \quad (8)$$

$$CR = \frac{RT}{Nh} e^{\frac{\Delta S_a^0}{R}} e^{\frac{-\Delta H_a^0}{RT}} \quad (9)$$

Here, CR is the corrosion rate, mm/year A is the Arrhenius constant for the process, R is the universal gas constant (8.314 J/mol). Temperature on the T-kelvin scale, N-Avagadro number ( $6.12 \cdot 10^{23}$ ), h-Planck's constant ( $6.626 \cdot 10^{-34}$  m<sup>2</sup>kg/s) [7-10].

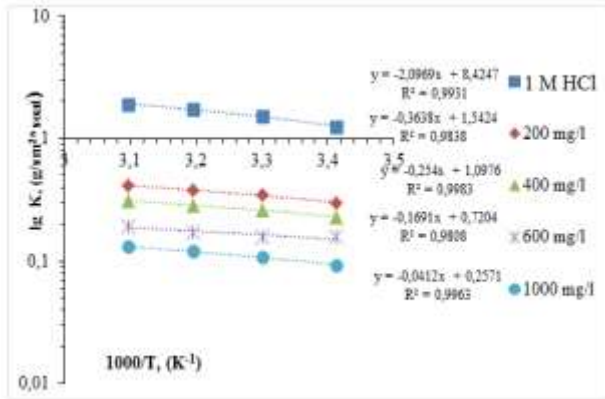
When describing the dependence of  $\ln CR/T$  on  $1/T$  with an Arrhenius graph, I can take the regression coefficient as equal to 1. Thermodynamic parameters of solutions with and without PFA brand corrosion inhibitor was determined. From the results of a series of experiments, we can say that the value of  $E_a$  in solutions with a corrosion inhibitor is somewhat higher than in solutions without an inhibitor, and of course, these values are different at different concentrations.

The values of activation energy and enthalpy were obtained by calculating the transition state values in solutions with and without inhibitors of different concentrations. (formula-3.3) [11-15]. These plots give the slopes (slope =  $\Delta H_a / 2.303R$ ) and intercepts (intercept =  $[\log RNh + (\Delta S_a / 2.303R)]$ ), which give the value of  $\Delta H_a$  in inhibitor and non-inhibitor solutions. It is calculated based on the following formula:

$$CR = \frac{RT}{Nh} \exp\left(\frac{\Delta S_a}{R}\right) \exp\left(\frac{\Delta H_a}{RT}\right) \quad (3.3)$$

In the above equation, h is Planck's constant ( $6.626 \cdot 10^{-34}$  m<sup>2</sup>kg/s) and N is Avogadro's number ( $6.12 \cdot 10^{23}$ ). A higher activation energy indicates physical

adsorption, and a lower one indicates chemical adsorption. Using the Arrhenius equation, kinetic parameters such as activation energies, enthalpy, and entropy of corrosion inhibitors in graded water and 1 M HCl in the steel surface in inhibitor-free and inhibitor-containing environments were studied. In this case, the values of  $E_a$  were found from the dependence of  $\lg W$  on  $1000/T$  in inhibitor-free and inhibitor-containing environments.



**Figure 1. Arrhenius plot of the activation energy of the green corrosion inhibitor in 1 M HCl.**

In Table 1, the activation energy and enthalpy values in the inhibitor-free solution were  $E_a$  40.88 kJ/mol-1 and  $\Delta H_a$  139.77 kJ/mol-1).

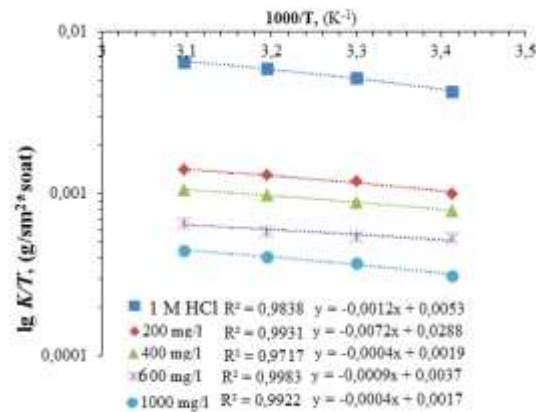
Table-1

**Activation parameters in 1 M hydrochloric acid environment for St20 steel under the influence of corrosion inhibitor**

Inhibitor concentration	$E_a$ (kJ/mol <sup>-1</sup> )	$\Delta H_a$ (kJ/mol <sup>-1</sup> )	$\Delta S_a$ (kJ/mol <sup>-1</sup> K <sup>-1</sup> )
0.0	40,88	139,77	363,43
200	6,66	22,98	-101,84
400	2,20	7,66	-157,37
600	1,65	5,74	-166,94
1000	1,58	4,77	-179,28

When the concentration reached 1000 mg/l,  $E_a$  decreased to 1.58 (kJ/mol-1) and  $\Delta H_a$  decreased to 4.77 (kJ/mol-1).  $\Delta S_a$  decreased from 363.43 (kJ/mol-1K-1) to -179.28

(kJ/mol-1K-1). This confirms that the St20 steel is inhibited during melting and the

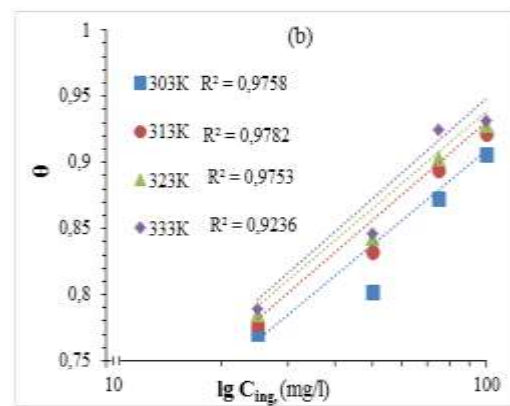
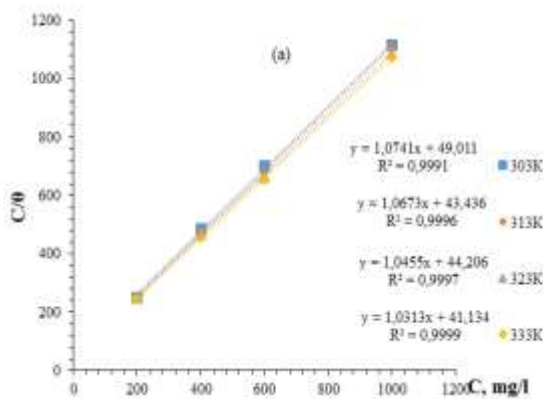


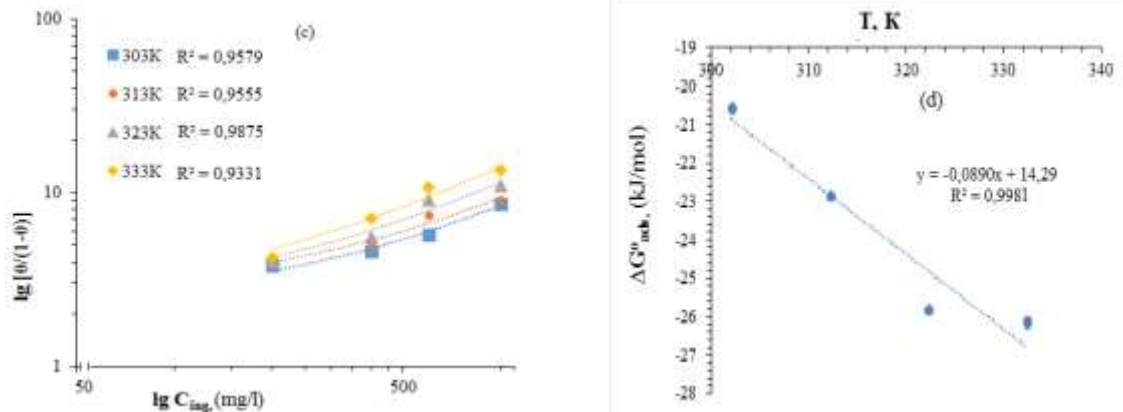
chemisorption process is underway.

**Figure 2. Transition state diagram for the activation process of the inhibitory system in 1M HCl.**

Arrhenius plots (1000/T of lgW) were obtained for St20 steel in 1 M HCl medium with and without green corrosion inhibitor at various concentrations and at various temperatures.

Adsorption isotherm. Langmuir (Figure 3.a), Frumkin (Figure 3.b), and Tymkin (Figure 3.c) isotherms of the green corrosion inhibitor obtained in 1 M hydrochloric acid medium are also plotted.





**Figure 3. (a) Langmuir, (b) Frumkin, and (c) Tyomkin isotherms and (d) temperature dependence of  $\Delta G_{0ads}$ .**

As can be seen from Figure 3.b, a graph of the dependence of  $\lg [\theta/(1-\theta)]$  on  $\lg C_{ing}$  for the Frumkin isotherm was drawn, and the values of the correlation coefficient at each temperature were (0.9758; 0.9782; 0.9753; 0.9236;). Similarly, a graph of the dependence of  $\theta$  on  $\lg C_{ing}$  for the Tyomkin isotherm was drawn (Figure 3.13c). The values of the correlation coefficient for each temperature were (0.9579; 0.9555; 0.9875; 0.9331;). As can be seen from the results obtained, the significant difference in the values of the correlation coefficients based on the Frumkin and Tyomkin isotherms from 1 indicates that the green corrosion inhibitor does not obey both of the above isotherms in a 1 M hydrochloric acid environment. However, the Langmuir isotherm value showed values higher than 0.99, which shows us that the process proceeds completely according to the Langmuir isotherm and that the thermodynamic parameters are consistent with the data obtained from practical experiments.

### Thermodynamics of adsorption.

In this study, green corrosion inhibitor with 1M hydrochloric acid. Table-2. Thermodynamic parameters of corrosion inhibitor

Temperature	$K_{ads}$	$\Delta G_{ads}$ kJ/mol	$\Delta H_{ads}$ , (kJ/mol)	$\Delta S_{ads}$ , (kJ/mol K)
303	348,2	-22,17	-14,29	-119,8
313	412,4	-24,09		
323	510,7	-26,41		
333	601,3	-28,21		

From Table 2, it can be seen that the adsorption process of the inhibitor on steel in 1 M hydrochloric acid solution ( $\Delta H_{0ads}$  value is negative -14.29 kJ/mol) is accompanied

by heat absorption. It can also be concluded from the values of  $\Delta G_{ads}$  that the values of  $\Delta G_{ads}$  were -22.17 kJ/mol at 303 K, -24.09 kJ/mol at 313 K, -26.41 kJ/mol at 323 K and -28.21 kJ/mol at 333 K. Therefore, the adsorption process of the green corrosion inhibitor in 1 M HCl solution is physical and chemisorption, which indicates that it is a mixed type of adsorption. Here, the negative value of  $\Delta S_{ads}$  (-119.8 J/mol) indicates that an inhibitor-metal complex is formed on the surface of the inhibitor and the metal during adsorption[16,17].

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