

## **SYNTHESIS OF CORROSION INHIBITOR IN A 0.5 M HCl MEDIUM AND ITS THERMODYNAMIC MECHANISMS OF ITS INHIBITION**

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**Abstract.** In this article, the PKA-1 corrosion inhibitor was synthesized based on polyethylenepolyamine and croton aldehyde, its structure was analyzed in YAMR and PMR devices, and its formula was proposed. Also, the inhibition mechanism of this corrosion inhibitor was studied through various thermodynamic parameters. Using the Arrhenius equation, the activation energy ( $E_a$ ), activation enthalpy ( $\Delta H$ ) and activation entropy ( $\Delta S$ ) of the steel surface in inhibitory and non-inhibitory environments were determined. Along with this, Langmuir, Frumkin and Temkin adsorption isotherms were studied.

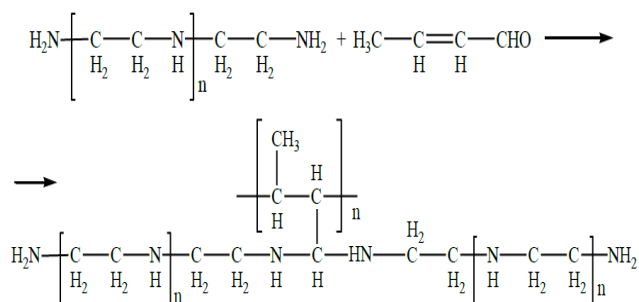
**Keywords:** polyethylene polyamine, croton aldehyde, Langmuir, Frumkin, Temkin, adsorption isotherms.

### **INTRODUCTION**

Corrosion is the destruction of materials, especially metal and metal-based structures, as a result of chemical reactions or electrochemical processes [1]. In general, there are several types of corrosion, which are characterized by the source of origin and properties [2]. In preventing corrosion, the use of corrosion inhibitors can allow us to use structures for a relatively longer period [3]. Hydrochloric acid is widely used in oil and gas extraction. Therefore, in the oil and gas industry, not only corrosion inhibitors for CO<sub>2</sub> and H<sub>2</sub>S environments, but also synthesis of corrosion inhibitors with high inhibition efficiency for HCl environments play an important role [4,5].

#### **Experimental part**

A chemical compound with the following formula was synthesized in the presence of polyethylene polyamine and croton aldehyde in the presence of dimethylformamide solvent.



It was obtained by mixing the starting materials in a ratio of 1:1 at a temperature of 50 °C for 2 hours. The process was then cooled to room temperature and left for 24 hours.

#### **Table 2.1**

**Effect of temperature on the formation of corrosion inhibitor PKA-1 based on PEPA and croton aldehyde.**

Mole ratio of PEPA and croton aldehyde	Temperature °C	Yield %	Temperature °C	Yield %
1:1	50	92.12	30	89.24
1:2		96.51		82.05
2:1		87.61		72.62

The resulting product is a hard polymeric solid, soluble in alcohol and acetone, insoluble in water at normal temperature, but soluble at a slight temperature rise.

*NMR and PMR spectroscopic analysis of corrosion inhibitor PKA-1.*

<sup>1</sup>H-YAMR and <sup>13</sup>C-YAMR spectra of the compound of polyethylene polyamine taken as a sample with croton aldehyde were obtained (Fig. 2.1-2.2).

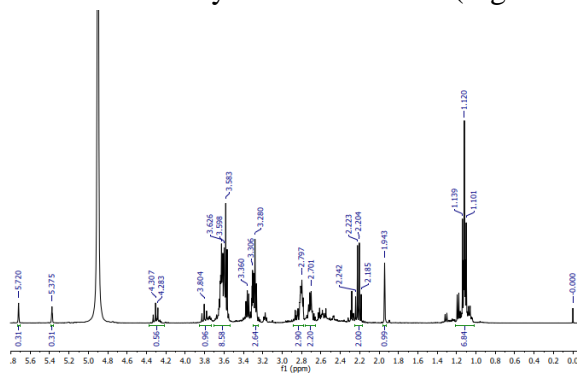


Figure 2.1. YAMR spectrum of corrosion inhibitor PKA-1

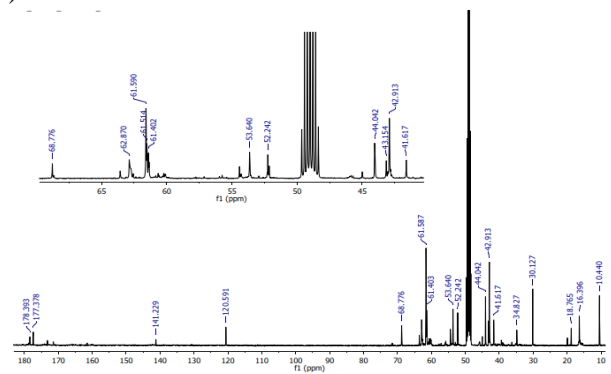


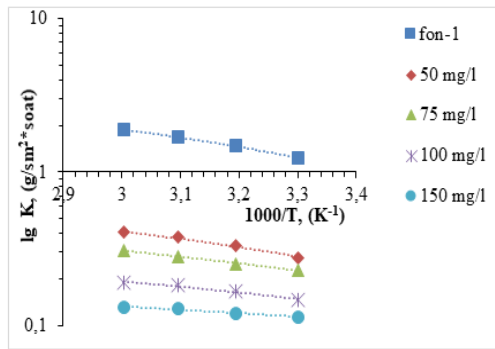
Figure 2.2. PMR spectrum of corrosion inhibitor PKA-1

When analyzing the NMR and -spectrum of the synthesized PKA-1 corrosion inhibitor (Fig. 2.1), proton (N -8) 4.74-4.76 m.d., (N-2 and N -6) 5.10-5.12 m.d. and (N -5 and N -3) 7.38-7.45 m.d. showed that Also, carbon (C-2 and C-3) bound with nitrogen is 53,640., (C-3 and C-4) -42,913-41,617 m.d. showed carbon atoms with double bond. The obtained spectra confirm the formation of corrosion inhibitor PKA-1.

**Results and Discussion**

**Kinetic study results of synthesized corrosion inhibitors**

The activation energy (*E<sub>a</sub>*), activation enthalpy ( $\Delta N$ ) and activation entropy ( $\Delta S$ ) of the steel surface in inhibitor and non-inhibitor environments were determined using the Arrhenius equation of the oligomeric type PKA-1 corrosion inhibitor at different concentrations. Also, *E<sub>a</sub>* values were found from the dependence of lg W on 1000/T in the media without and with the inhibitor. The values of *E<sub>a</sub>* were determined at concentrations of 50, 75, 100 and 150 mg/l. According to the data obtained as a result of the research, the activation energy of the system without an inhibitor is high, and with the introduction of an inhibitor, we can see that the activation energy of the system decreases depending on the concentration of the inhibitor.



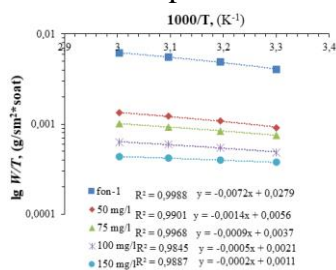
**Table 3.1**  
**Kinetic and thermodynamic parameters of PKA-1 inhibitor in 0.5 M HCl solution**

$C_{ing}$	-	50	75	100	150
$E_a$	41,78	56,98	75,58	90,56	103,91
$\Delta H$	38,95	56,81	74,15	88,75	100,83
$\Delta S$	-38,55	-18,35	33,73	57,37	76,52

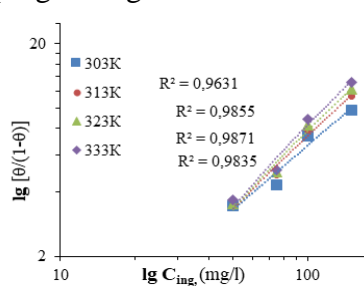
**Figure 3.1. Arrhenius plot for the activation energy of PKA-1 inhibitor in 0.5 M hydrochloric acid solution**

Based on the data presented in Table 3.1, it can be said that at concentrations higher than 150 mg/l, the inhibition efficiency was almost unchanged, so it was taken as the optimal concentration. It was determined that the value of  $E_a$  is equal to 42.17 kJ/mol through the tangent of the slope angle of the corrosion rate in a 0.5 M solution of hydrochloric acid without an inhibitor. In the solution containing the inhibitor, this value decreased proportionally to the concentration.

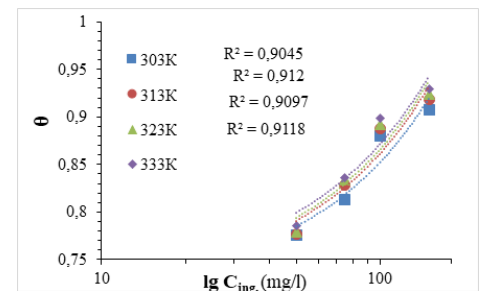
Activation enthalpy and entropy were determined using transition state curves of  $\lg W/T$  versus  $1000/T$  (Fig. 3.5). The activation enthalpy was found to be 38.95 kJ/mol, and the value of the activation entropy was equal to -38.55 J/mol in the solution without inhibitor. It was found that the activation energy received positive values, its value was small in the environment without corrosion inhibitor, and the activation energy increased when the corrosion inhibitor was introduced. The activation of an inhibitor-free medium requires less energy than a process with a corrosion inhibitor, indicating that it is easier to incorporate a corrosion inhibitor into the process. A negative entropy value in an environment where a corrosion inhibitor is not used indicates that the corrosion process is self-progressing.



**Figure 3.2. Transition state plot of PKA-1 inhibitor in 0.5 M HCl solution**



**Figure 3.3. Frumkin isotherm of PKA-1 oligomeric inhibitor in 0.5 M HCl working solution**

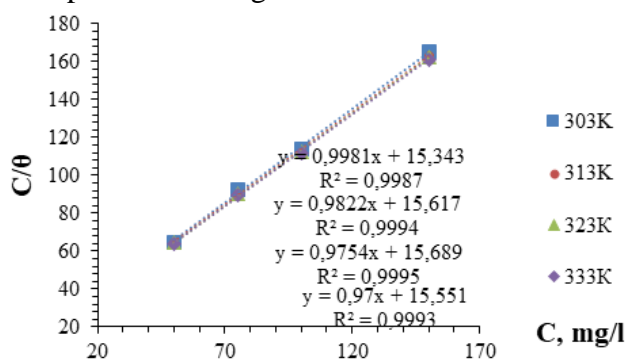


**Figure 3.3. Temkin isotherm of PKA-1 inhibitor in 0.5 M HCl working solution**

In solutions without an inhibitor, the value of  $(\Delta S_a)$ , is negative, which indicates that the process proceeds by itself. However, with the introduction of an inhibitor into the solution, the value of entropy increased depending on the concentration of the inhibitor (50 mg/l -18.35; 75 mg/l 33.73; 100 mg/l 57.37; 150 mg/l 76.52). takes positive values.

*Adsorption isotherms.* One of the most important mechanisms of inhibition is adsorption. The (a) Langmuir, (b) Frumkin, and (c) Temkin isotherms of corrosion inhibitor PKA-1 in 0.5 M hydrochloric acid medium are also plotted. By the dependence of  $\lg [\theta/(1-\theta)]$  on  $\lg C_{inh}$ , the Frumkin isotherm of PKA-1 inhibitor in 0.5 M hydrochloric acid working solution was obtained (Fig. 3.2). Taking into account that the correlation coefficient of the corrosion inhibitor PKA-1 is significantly different from 1 (0.9631; 0.9855; 0.9871; 0.9835;), it was found that the inhibitor adsorption does not correspond to the Frumkin isotherm.

In this case, the Temkin isotherm was obtained from the dependence of  $\lg C_{ing}$  on  $\theta$  (Fig. 3.3). Taking into account that the value of the correlation coefficient of PKA-1 corrosion inhibitor is significantly different from 1 (303K 0.9045; 313K 0.912; 323K 0.9097 and 333K 0.9118;), showed adsorption according to the Temkin isotherm of the inhibitor.



**Figure 3.4. Langmuir isotherm of PKA-1 inhibitor in 0.5 M HCl working solution**

The Langmuir isotherm was drawn by the dependence of  $C_{inh}/\theta$  on  $C_{inh}$  (Figure 3.4). When the value of the correlation coefficient of PKA-1 corrosion inhibitor is considered to be almost equal to 1, it means that the adsorption of the inhibitor on the metal surface follows the theory of monomolecular adsorption, and it can be seen that this is an indicator of Langmuir's isotherm.

Using the value of  $K_{ads}$ , the value of the standard Gibbs energy of adsorption ( $\Delta G_{ads}^0$ ) was determined in the temperature range of 303-333 K.

**Table 3.2.**

**Thermodynamic parameters of adsorption of PKA-1 inhibitor in 0.5 M HCl solution obtained by Langmuir isotherm**

T, K	$K_{ads}$	$R^2$	$\Delta G_{ads}^0$	$\Delta G_{ads}^0$	$\Delta H_{ads}^0$ kJ/mol	$\Delta S_{ads}^0$ J/mol
303	0,0652	0,9978	-10518	-10,52	-0,37	33,4
313	0,0640		-10818	-10,82		
323	0,0637		-11152	-11,15		
333	0,064		-11522	-11,52		

Here, one of the reasons why the enthalpy takes positive values is that during adsorption, it is endothermic due to the breakdown of the solvate complex of the inhibitor and the breaking of the interaction bonds of water molecules with the steel surface. Also, heat release is observed during inhibitor adsorption. However, since the endothermic process occurring on the surface is higher than the exothermic process, the enthalpy takes positive values.

### CONCLUSION.

The structure of this synthesized corrosion inhibitor was proposed to be based on  $^1\text{H}$ -YAMR and  $^{13}\text{C}$ -YAMR. The inhibition mechanisms of this corrosion inhibitor in 0.5 M HCl medium were studied. The degree of absorption of this branded inhibitor is high, and it has been proven that this absorption proceeds on the basis of Langmuir isotherms.

### REFERENCES

1. Rani B.E.A., Basu B.B.J. Green inhibitors for corrosion protection of metals and alloys: An overview // *Int. J. Corros.* 2012. Vol. 2012.
2. Z. Ahmad. Principles of Corrosion Engineering and Corrosion Control // Oxford, UK Butterworth-Heinemann. 2006.
3. Magerramov A.M. et al. Synthesis of hydrogen sulfide corrosion inhibitors for oil production // *Pet. Chem.* 2013 536. Springer, 2013. Vol. 53, № 6. P. 423–425.
4. Latyuk V.I. et al. Sulfides of the sym—Triazine Series as Oil—soluble Corrosion Inhibitors // *Chem. Technol. Fuels Oils* 2002 385. Springer, 2002. Vol. 38, № 5. P. 312–315.
5. Mokhichekhra Shaymardanova, Kholtura Mirzakulov, Gavkhar Melikulova, Sakhomiddin. Khodjamkulov, Abror Nomozov, Oybek Toshmamatov. Studying of The Process of Obtaining Monocalcium Phosphate based on Extraction Phosphoric Acid from Phosphorites of Central Kyzylkum. Baghdad Sci.J. 2024.;22(1).  
<https://bsj.uobaghdad.edu.iq/index.php/BSJ/article/view/9836>
6. Nazirov Sh S, Turaev Kh Kh, Kasimov Sh A, Normurodov B A, Jumaeva Z E, Nomozov A K. *et al.* Spectrophotometric determination of copper(II) ion with 7-bromo-2-nitroso-1-oxinaphthalene-3,6-disulphocid. **Indian J of Chem.** 2024; 63(5): 500-505. <https://doi.org/10.56042/ijc.v63i5.9289>.
7. K. K. Turaev, K.N. Eshankulov, I.A. Umbarov, S.A. Kasimov, A.K. Nomozov, and D.A. Nabiev Studying of Properties of Bitumen Modified based on Secondary Polymer Wastes Containing Zinc. *Inter J. of Engin. Trends and Tech.* 2023, 71 no. 9, 248-255, Crossref, <https://doi.org/10.14445/22315381/IJETT-V71I9P222>
8. A. K. Nomozov, Kh. S. Beknazarov, S. Z. Khodjamkulov, Z. K. Misirov, **Salsola Oppositifolia acid extract as a green corrosion inhibitor for carbon steel.** *Indian J Chem Tech.* 2023, 30, no.6, 872-877. <https://doi.org/10.56042/ijct.v30i6.6553>.
9. M. A. Shaymardanova, Kh. Ch. Mirzakulov, G. Melikulova, S. Z. Khodjamkulov, A. K. Nomozov, and Kh.S. Shaymardanova, Study of process of obtaining monopotassium phosphate based on monosodium phosphate and potassium chloride. *Chemical Problems.* 2023, 3, no. 21, 279-293. <https://doi.org/10.32737/2221-8688-2023-3-279-293>.