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SYNTHESIS OF CORROSION INHIBITOR FOR IN 0.5 M HYDROCHLORIC ACID MEDIUM AND STUDY OF THERMODYNAMIC MECHANISMS OF ITS INHIBITION

Misirov Z.X
Termez State University of Engineering and Technology,
Doctor of Technical Philosophical Sciences, Ph.D.
Gmail: zafarmisirov1986@gmail.com

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 (Ea), activation enthalpy (ΔH) and activation entropy (ΔS) of the steel surface in inhibitory and non-inhibitory environments were determined. Along with this, Langmuir, Frumkin and Temkin adsorption isotherms were studied.

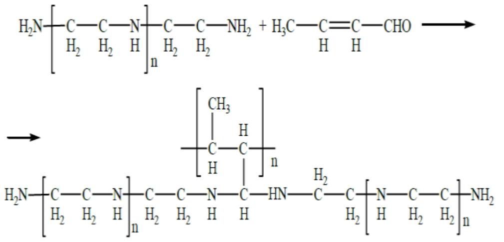
Keywords: polyethylene polyamine, croton aldehyde, Langmuir, Frumkin, Temkin, adsorption isotherms.

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_2 and H_2S 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.

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

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

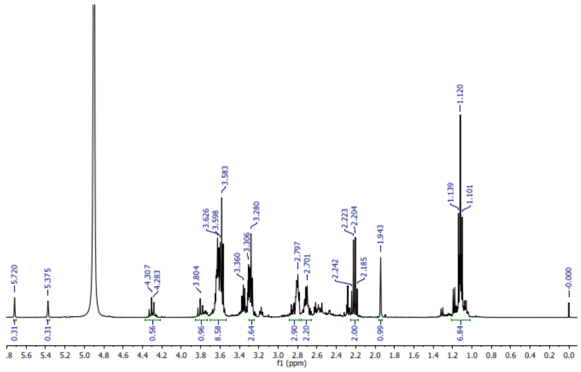


Figure 2.1. YAMR spectrum of corrosion inhibitor PKA-1

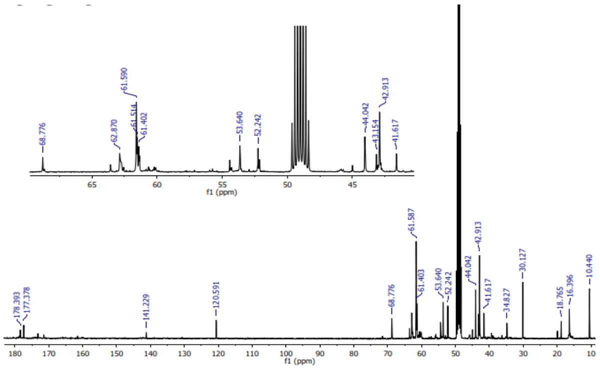


Figure 2.2. PMR spectrum of corrosion inhibitor PKA-1

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 (Ea), activation enthalpy (ΔN) and activation entropy (ΔS) 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_a values were found from the dependence of lg W on 1000/T in the media without and with the inhibitor. The values of E_a 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.

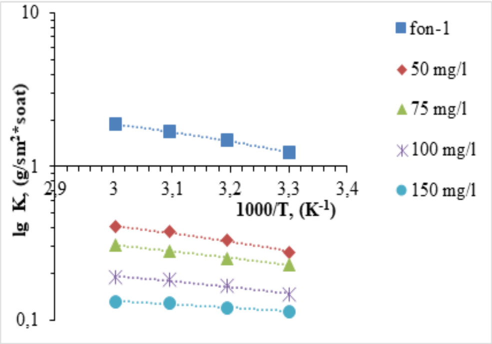


Figure 3.1. Arrhenius plot for the activation energy of PKA-1 inhibitor in 0.5 M hydrochloric acid solution

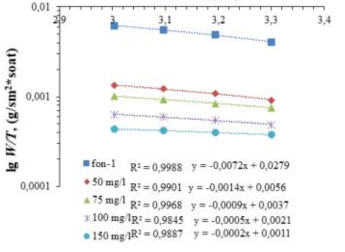
Table 3.1

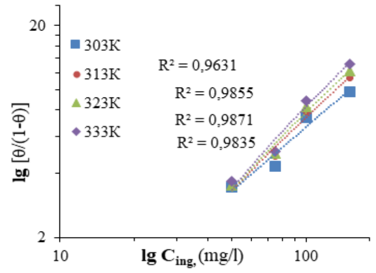
Kinetic and thermodynamic parameters of PKA-1 inhibitor in 0.5 M HCl solution

C_{ing}	-	50	75	100	150
Ea	41,78	56,98	75,58	90,56	103,91
ΔH	38,95	56,81	74,15	88,75	100,83
ΔS	-38,55	-18,35	33,73	57,37	76,52

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 Ea 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.





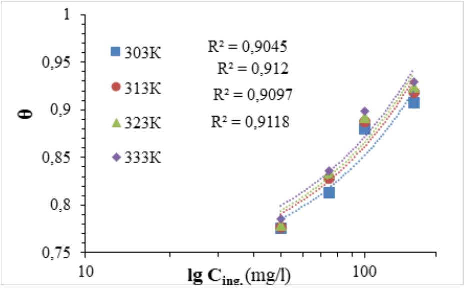


Figure 3.2. Transition state plot of PKA-1 inhibitor in 0.5 M HCl solution

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 (ΔS_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 lgCing on θ (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.

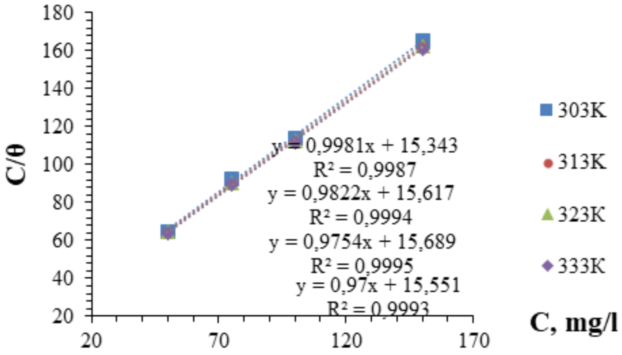


Figure 3.4. Langmuir isotherm of PKA-1 inhibitor in 0.5 M HCl working solution

The Langmuir isotherm was drawn by the dependence of C_{inh}ning C_{inh}/θ (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 Kads, the value of the standard Gibbs energy of adsorption (ΔG_{ads}) 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	Kads	R^2	ΔG^{o}_{ads}	ΔG^{o}_{ads}	ΔH^{o}_{ads} kJ/mol	ΔS^{o}_{ads}, 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}H-YAMR and ^{13}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.

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