THERMODYNAMIC AND KINETIC STUDY OF THE INHIBITION PROCESS OF COMPOSITE CORROSION INHIBITORS

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Abstract. In this article, the thermodynamic and kinetic parameters of the synthesis mechanism of the corrosion inhibitor obtained based on monoethanolamine, methyl methacrylate, and phosphoric acid are studied. The special inhibition mechanism of this corrosion inhibitor was widely studied at temperatures of 298, 303, 313, and 323 K, and confirmed that it follows the Langmuir adsorption isotherm. Adsorption isotherm parameters of carbon steel electrode surface in 1.0 M HCl containing different concentrations of inhibitor at different temperatures.

Keywords: thermodynamic and kinetic parameters, Langmuir adsorption, Adsorption isotherms.

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 that across the world about 2.5 trillion U.S. dollars economic fall due to corrosion and Every year 10% of metal is lost due to corrosion which severely affects the country's economy[3]. Corrosion is not only responsible for economic loss but also related with safety issues because it decreases the shelf life of steel[4]. It has already been recognized as a major issue for the entire world, so researchers are trying to protect the corrosion process in various ways[5]. Mostly inhibitor is typically used to protect metal from corrosion and environmental friendly inhibitors have wide application in corrosion fields and it is generally added in the metal as a low concentration[6]. We believe this study is a small initiative to find a suitable corrosion inhibitor which can able to protect materials form corrosion process. According to this study, a corrosion inhibitors were prepared based on poly(methyl methacrylate-maleic anhydride)P(MMA-MAH)s accompanied with different percentage of methyl methacrylate and maleic anhydride and the inhibitory potentiality of this inhibitor has checked on simple carbon steel in a 0.5 M HCl [7-10].

Experimental part

Thermodynamic and kinetic study of the inhibition process of composite corrosion inhibitors

The graph has plotted of C/θ vs. C against the four temperatures (298, 303, 313, and 323 K) in the Figure 1 and curve intersections provided the calculation of C_{ads} values, these results are presented in Table 1. The obtained results showed that the adsorption of the selected compounds at the

boundary of St20 steel/acid solution obeyed the Langmuir adsorption isotherm according to equations (1 and 2).

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \qquad (1)$$

$$K_{ads} = \frac{1}{55.5} = \exp\left(\frac{\Delta G^0_{ads}}{RT}\right) \qquad (2)$$
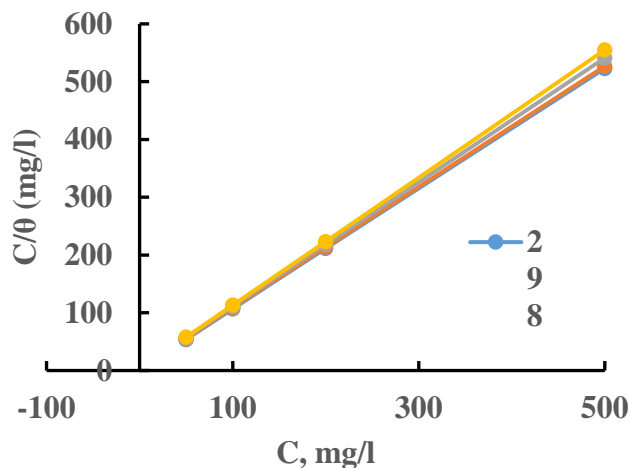

Figure 1. Langmuir adsorption isotherms for St20 in 1.0 M HCl solutions at different concentrations of inhibitor at different temperatures.

Table 1. Adsorption isotherm parameters of carbon steel electrode surface in 1.0 M HCl containing different concentrations of inhibitor at different temperatures.

Inhibitor name	Temp. K	K_{ads} M^{-1}	ΔG^o_{ads} kJ·mol^{-1}
MMF-1	298	0,206	-29,462
	303	0,118	-30,735
	313	0,068	-30,121
	323	0,072	-29,482

It is is clear from Table 1 data that the addition of inhibitors leads to negative values of ΔG^o_{ads}, which indicates the self-adsorption process of the studied MMF-1 corrosion inhibitors. When the value of ΔG^o_{ads} was up to -20 kJ/mol then inhibition mostly depended on the electrostatic interaction between charged molecules and charged metal that's why physical adsorption was mainly observed. However, we know the chemical sorption in which the formation of covalent bonds between the inhibitor molecules and the metal surface occurs at values of approximately -40 kJ/mol or less. According to Table 5, in our experiments the ΔG^o_{ads} values exhibit a range from -29.456 to -30.735 kJ/mol, indicating that the adsorption of these MMF-1 compounds was two different types of interactions where chemical sorption and physical sorption were produced at the same time.

Since the temperature factors that can change the actions of inhibitors and substrates in certain aggressive environments and Organic compounds dissolve more easily with increasing temperature. Thus, an increase in temperature can lead to a weakening of the corrosion resistance of metals. We studied the influence of this parameter on the performance MMF-1 and we performed mass loss measurements at temperatures of 298, 303, 313, and 323 K. The results were summarized in Table-5 and the results obtained after the samples were stored in water for 1 day. In Table 5, it can be seen that the corrosion rate (C.R) in 1 M HCl solution was increased with increasing temperature. Conclusively, all inhibitors concentrations and the corrosion rate (C.R) increased with increasing temperature, however lower values were observed at higher inhibitor concentrations. It means that IE% was increased as the temperature decreases. However, this evolution was more noticeable for the highest inhibitor concentrations

Table 2. Values of activation parameters for carbon steel in 1.0 M HCl in the absence and presence of different concentrations of the studied inhibitor at different temperatures

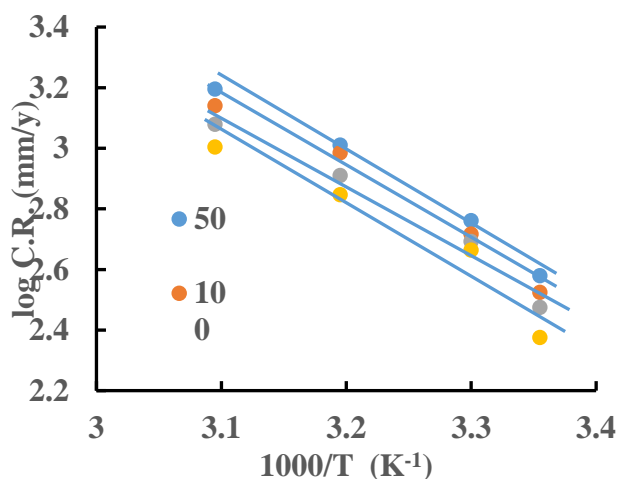| Inhibitor	C, mg/l	Rs, (Ω cm^2)	Rct (Ω cm^2)	Y0 (Ω^{-1} s^{n}cm^{-2})	n	Cdl (μF cm^2)	θ	IE, EIS %
Without an inhibitor	0.0	0,4721	23,54	733,27	0,965	478,31	–	–
MMF-1	50	1,867	239,7	501	0,735	269,44	0,91	91,47
	100	1,094	284,7	278	0,765	186,86	0,93	93.27
	200	1,374	351,6	184	0,773	71,7	0,95	95,29
	500	1,142	396,1	101	0,802	21,64	0,96	96,18

Figure 2. Arrhenius plot for St20 steel in 1.0 M HCl solution of different concentrations of inhibitors.

Using the Arrhenius equation, the activation energy of the corrosion process (E_a) was found based on equation (3) as follows.

$$log C.R. = \frac{-E_a}{2.303RT} + log A \qquad (3)$$

R is gas constant (8.31 J/mol/K), A is pre-exponential Arrhenius factor, T is temperature.

At different concentrations MMF-1, the probable activation energy (–E_a/2.303R) and the pre-exponential factor (A) were determined by linear regression between log(C.R) and 1/T. Table 3 and also Figure 3 have shown clearly activation energy values without inhibitors and with certain concentrations of inhibitors at different temperatures. In the presence of an inhibitor, the E_a values were remained higher than the sample without the inhibitor. This behavior was fully characteristic for the case of physical adsorption of the inhibitor on the metal surface. But the recovery rate was very low at higher temperatures indicating that at these temperatures the rate of inhibition of the physical sorption was faster than the rate of its formation. This phenomenon could also be explained by the fact that the corrosion process of steel in the presence of an inhibitor depended not only on the reaction occurring on the pure metal surface, but also on the diffusion of iron ions through the adsorbed layer of the inhibitor. It was thus confirmed that higher concentration of inhibitors participated in stronger physical absorption due to the formation of a stronger surface film and were therefore more effective. The values of kinetic parameters such as enthalpy (ΔH) and entropy (ΔS) of the corrosion process (4) can be estimated from the effect of temperature on the steel surface.

$$C.R. = \frac{RT}{N_A h} exp\left(\frac{\Delta S}{R}\right) exp\left(-\frac{\Delta H}{RT}\right) \qquad (4)$$

where, h - Planck's constant, N_A - Avogadro's number.
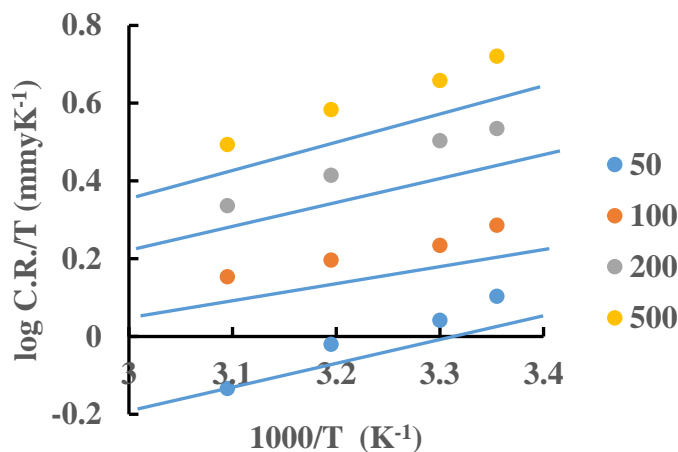

Figure 3. Graphs of transition states for dissolution of St20 steel without inhibitors and in the presence of inhibitors.

The enthalpy and entropy values of the inhibitor compounds MMF-1 on the surface of carbon steel was calculated using the transition state equation. Figure 3. shows the logarithm of (C.R./T) versus 1000/T, with a slope of -ΔH/2.303R and an intercept of [log(R/NAh) + (ΔS/2.303R)] gives straight lines. For carbon steel the compounds were studied in the absence and presence of the inhibitor at concentrations of 50, 100, 200 and 500 mg/l in 1M HCl solution.

Table 3 shows that ΔH^* values are positive. Positive values indicated the endothermic nature of the low-carbon steel melting process. The endothermic process also showed that the melting of steel has decreased at low temperatures and also increased with increasing temperature. Negative ΔS^* values indicated the formation of the activated complex in the rate-determining step, which

was revealed the association rather than the dissociation step, i.e., a decrease in disorder has occurred during the transition from the reactants to the activated complex.

Conclusion: The inhibition mechanism of the composite corrosion inhibitor was studied and it was evident that its inhibition efficiency increased with the increase of concentration and its effect on the metal surface was also examined thoroughly by inhibited steel surface. Finally, MMF-1 corrosion inhibitor can easily use it commercially as a corrosion inhibitor based on its efficiency.

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