

Corrosion Inhibition Properties of Norepinephrine Molecules on Mild Steel in Acidic Media

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Abstract

Inhibition performance of norepinephrine was investigated as corrosion inhibitors by Gravimetric technique and carried out with mild steel samples in 1 M hydrochloric acid solution at room temperature. Norepinephrine exhibited maximum efficiency of 79% at 500 mg/L. The results of Gravimetric studies revealed that the investigated compound acted as good corrosion inhibitor and the inhibition efficiencies increased with increase in the concentrations of the inhibitor IC. The experimental data complied with the Langmuir adsorption isotherm. Thermodynamic parameters, such as ΔG° , ΔH° , and ΔS° , were calculated using adsorption equilibrium constant obtained from the Langmuir isotherm. Results suggested that the norepinephrine adsorption on mild steel surface was a spontaneous and exothermic process. Scanning electron microscopy was used to investigate the mild steel surface at the highest corrosion inhibition studied concentration.

Keywords

Corrosion Inhibition, Adsorption, Efficiency, Langmuir Isotherm, Thermodynamic Parameters, Scanning Electron Microscopy (SEM)

1. Introduction

The action of corrosion inhibitors is closely related to factors such as: the types of functional groups, the number and type of adsorption sites, the charge distribution in the molecules and the type of interaction between the inhibitors and the metal surface [1]. A large number of organic compounds have been investigated as corrosion inhibitors for different types of metals [2]-[4]. Corrosion problems arise as a result of the interaction between the

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aqueous acid solutions and mild steel, especially during the pickling process in which the alloy is brought in contact with highly concentrated acids. This process if not combated can lead to economic losses due to the corrosion of the alloy [5]. The use of inhibitors is one of the best options of protecting metals against corrosion. Several inhibitors in use are either synthesized from cheap raw material or chosen from compounds having heteroatoms in their aromatic or long-chain carbon system. The use of organic molecules as corrosion inhibitor is one of the most practical methods for protecting metals against the corrosion and it is becoming increasingly popular. The existing data show that organic inhibitors act by the adsorption and protect the metal by film formation.

Most of the effective inhibitors contain heteroatoms such as O, N, and S and multiple bonds in their molecules through which they are adsorbed on the metal surface [6]-[15]. It has been observed that adsorption depends mainly on certain physicochemical properties of the inhibitor group, such as functional groups, electron density at the donor atom, p-orbital character, and the electronic structure of the molecule [16]-[20]. The efficiency of an organic compound as an inhibitor is mainly dependent on its ability to get adsorbed on the metal surface which consists of a replacement of water molecules at a corroding interface.

However, most of these inhibitors are toxic to the environment. This has prompted the search for green corrosion inhibitors [21]. Acids and bases were utilized widely in industry for acid cleaning [22]. Mild steel is generally utilized as a part of different industries. Inhibitors are utilized as a part of industry to reduce the corrosion rate of diverse metals and amalgams which are in contact with forceful situations [23]. Previously the utilization of pickling inhibitors in descaling ways in the industry after hot moving utilizing inorganic acids has turned out to be compelling. Various organic compounds are utilized as consumption inhibitors for steel in acidic environments [24] [25]. Such compounds ordinarily contain heteroatoms and conjugated pi-systems [26] [27]. Numerous organic inhibitors adsorbed on the surface of the mild steel [28]. A coordinate covalent bond involving transfer of electrons from inhibitor to the metal surface may be formed. The strength of the chemisorptions bond depends upon the electron density on the donor atom of the functional group and also the polarizability of the group. When an H atom attached to the C in the ring is replaced by a substituent group (-NH, -NO, -CHO, or -COOH), it improves inhibition [29]. The aim of this work is to study, using norepinephrine (Figure 1) and weight-loss measurements, on the corrosion inhibition of carbon steel in 1.0 M HCl solution.

Weight loss and scanning electron microscopy (SEM) techniques prove that the investigated inhibitor could be an effective corrosion inhibitor and its molecules adsorbed on the surface of mild steel. The output of this study is intended to be a cheap and an eco-friendly that can be used as a corrosion inhibitor for metals and alloys. No studies have been reported on the norepinephrine, as corrosion inhibitor, in terms of studying the gravimetric effect on the corrosion inhibition of carbon steel in 1.0 M HCl solution.

2. Experimental

2.1. Chemicals

All chemicals were used as received and were purchase from Sigma-Aldrich. Norepinephrine were purchase from local company in Baghdad-Iraq. Mild steel specimens were squeeze cut to form various specimens, with dimensions 1 cm × 2 cm × 0.05 cm.

2.2. Gravimetric Method

The specimens were washing double with distilled water then acetone and dry. Solutions of 1 M of hydrochloric

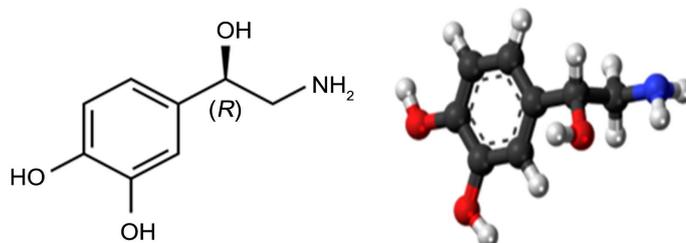


Figure 1. The chemical structure of the studied norepinephrine compound.

acid were used as a blank solution. The inhibitor norepinephrine with concentrations 0.0 , 1×10^{-3} , 2×10^{-3} , 3×10^{-3} , 4×10^{-3} and 5×10^{-3} mg/ml, were added to the acid solution. Mild steel specimens were immersed in 250 ml of the various amounts of inhibitors for 6 hours of immersion each specimen in range of temperatures 30°C , 40°C , 50°C and 60°C . The mass of the specimens before and after immersion was determined using an analytical balance of 0.001 mg accuracy. Averages of the duplicate values were used. After that the specimens were taken out, washed in a solution of NaOH and zinc dust, allowed to air dry and weighted accurately. Inhibition efficiencies (IE%) and corrosion rates (CR) were calculated by using of the Equations (1) and (2):

$$\text{IE}\% = \left(\frac{W_2 - W_1}{W_2} \right) \times 100 \quad (1)$$

$$\text{CR} = \frac{w}{At} \quad (2)$$

where W_1 and W_2 are the weight loss value in the presence and absence of inhibitor in HCl solution, respectively, w is the corrosion weight loss, A is the area of the mild steel specimen, t is the immersion time. The surface coverage θ and IE% is the inhibition efficiency was calculated according to Equations (3) and (4).

$$\theta = \left(\frac{\text{CR}_2 - \text{CR}_1}{\text{CR}_2} \right) \times 100 \quad (3)$$

$$\text{IE}\% = \theta \times 100 \quad (4)$$

2.3. Morphology

The surface morphology of the mild steel specimen was evaluated by scanning electron microscope (SEM) analysis. The specimen was immersed in 1 M hydrochloric acid solution with and without 5×10^{-3} mg/ml, of the inhibitor. The specimen that shows high inhibition was examined with specimens without inhibitors and fresh steel.

3. Results and Discussion

Organic inhibitors represent cathodic and or anodic and play through a process of adsorption and formation of coating-film. Offer of molecules, display a strong affinity for metal surfaces and that will lead to formation a coordination compound with privilege of useful inhibition activity and reducing risky [30]. Inhibitors provide a barrier of protective hydrophobic film that adsorbs inhibitor molecules on the mild steel surface.

3.1. Weight Loss Technique

Corrosion inhibitor norepinephrine at various concentrations and temperatures were represented by **Figure 2**, in 1 N of hydrochloric acid with and without of norepinephrine. The corrosion rate (CR) in hydrochloric acid without of the norepinephrine was starting from 10 at 30°C and raised to 70 at 60°C as increasing sharply (see in **Figure 2**). Increasing of norepinephrine concentration lead to reducing the corrosion rate sharply at deferent temperatures.

IE% increase with increasing of norepinephrine concentration. The effect of temperature on IE% as shown from **Figure 3** that the IE% decrease with increasing of temperature and the maximum IE% was at the maximum concentration 5×10^{-3} mg/mL and the lowest temperature value at 30°C . The increasing of IE% with raise of norepinephrine is due to an increase in adsorption of the inhibitor at the higher concentration or increasing of the complexity between the metal surface and the corrosion inhibitor molecules via coordination bonds. At highest experimental temperature 50°C the IE% was the lowest and this may be due to the denaturation of norepinephrine molecules with rising of temperatures.

3.2. Mechanism of Inhibition

The results obtained from weight loss measurements showed that norepinephrine inhibits the corrosion of mild steel in acidic media. This is due to the adsorption at the mild steel solution interface through film formation. It is a general assumption that the adsorption of norepinephrine at the metal surface interface is the first step in the

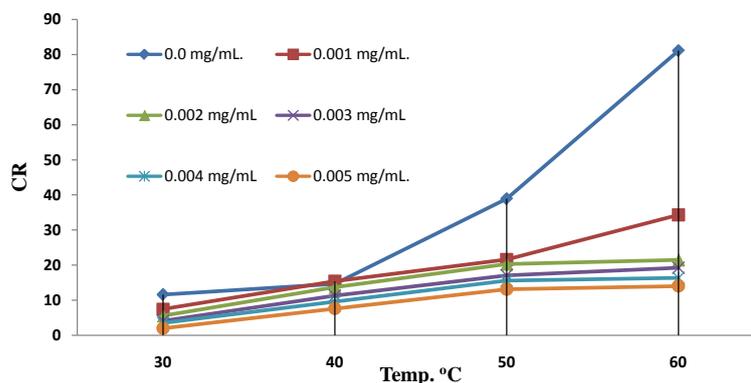


Figure 2. The corrosion rate for the mild steel corrosion at different temperature 1 N HCl for various concentrations of inhibitor.

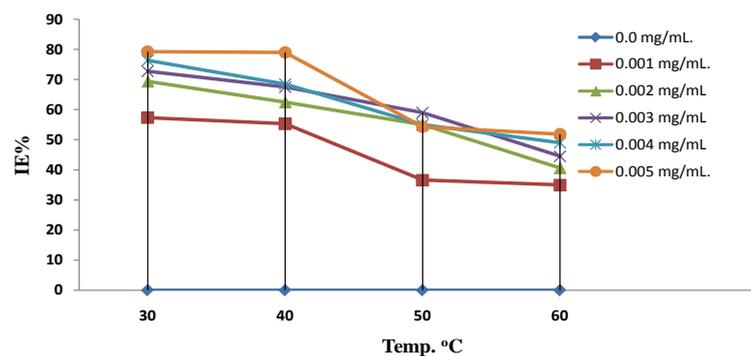


Figure 3. The inhibition efficiency for the mild steel corrosion at different temperature 1 N HCl for various concentrations of inhibitor.

mechanism of the inhibitor action. The inhibitor may adsorb on the metal/acid solution interface by one or more of types, namely:

- Electrostatic interaction between the charged molecules and the charged metal.
- Donor-acceptor interactions between the p-electrons of aromatic ring and vacant d orbital of surface iron atoms.
- Interaction of unshared electron pairs in the molecule with vacant d orbital of iron surface atoms.
- A combination of types a)-c).

It is often not possible to assign a single general mechanism of action to an inhibitor, because the mechanism may change with experimental conditions. Thus, the predominant mechanism of action of an inhibitor in acidic solutions may vary with factors such as concentration of the extracts, the nature of the anion of the acid, the presence of other species in the solution, the extent of reaction to form secondary inhibitors and the nature of the metal [31]. In this investigation two modes of adsorption could be considered, the neutral norepinephrine may adsorb onto the metal surface via the chemisorption mechanism, involving the displacement of water molecules from the metal surface and sharing electrons between the O and N atoms and Fe. The norepinephrine molecules can also adsorb on the metal surface on the basis of donor-acceptor interactions between π -electrons of aromatic ring and vacant d-orbitals of Fe. It is well known that iron has coordinate affinity toward nitrogen, and oxygen-bearing ligand; hence, adsorption on iron can be attributed to coordination through the -NH group. These complexes might be adsorbed onto steel surface by vander Waals force to form a protective film to prevent mild steel from corrosion.

3.3. Adsorption Isotherm

Adsorption of the organic compound depends upon the charge and the nature of the metal surface, electronic characteristics of the metal surface on adsorption of solvent and other ionic species, temperature of the corrosion

reaction and the electrochemical potential at the metal solution interface [32]. Adsorption of the norepinephrine involves two types of the possible interaction with the metal surface. The first one is weak undirected interaction due to electrostatic attraction between inhibiting organic ions or dipoles and the electrically charged surface of the metal. This interaction is termed physical adsorption or physisorption. The second type of interaction occurs when there is interaction between the adsorbate and adsorbent. This type of interaction involves charge sharing or charge transfer from adsorbate to the atoms of the metal surface in order to form a coordinate type bond and the interaction is termed chemical adsorption or chemisorptions [33]. It describes the adsorptive behavior of organic inhibitors to know the adsorption mechanism [34]. It depends mainly on the nature and charge of the metal surface, adsorption of solvent and other ionic species, electronic characteristics of the metal surface, temperature of the corrosion reaction at solution interface. The Langmuir isotherm was showed according to the adsorption isotherm of the corrosion rate (CR) data. Adsorption isotherm equilibrium constant is a very good indicator for the mechanism of inhibition, so if the value of adsorption isotherm equilibrium constant is high that mean strongly adsorbed on the metal surface.

$$\theta = \frac{KC}{KC + 1} \quad (5)$$

where K is the adsorption isotherm equilibrium constant and C is concentration of the inhibitor.

$$\theta(KC + 1) = KC \quad (6)$$

$$K + \frac{1}{C} = \frac{K}{\theta} \quad (7)$$

$$C + \frac{1}{K} = \frac{C}{\theta} \quad (8)$$

To indicate that the adsorption mechanism was according to the Langmuir adsorption isotherm for different temperatures in hydrochloric acid we plot **Figure 4**, that represent the C/θ vs. C . Straight line indicating that norepinephrine was adsorbed according to the Langmuir adsorption isotherm.

The Langmuir isotherm, which is presented in Equation (8) is most often used to calculate the equilibrium constant [35] [36]. According to the Langmuir isotherm, K_{ads} values can be calculated from the intercepts of the straight line of plotting C/θ versus C (see **Figure 4**). The parameters of Langmuir isotherm are presented in **Table 1**. The R^2 values of 0.9562, 0.9682, 0.9576 and 0.9666 indicate strong adherence to Langmuir adsorption isotherm [37].

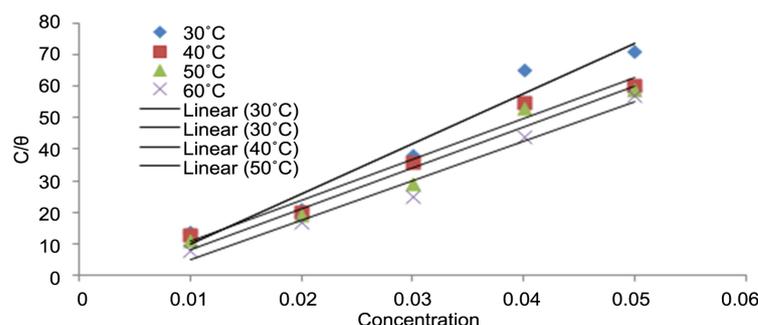


Figure 4. Langmuir plots for the corrosion inhibitor.

Table 1. Langmuir adsorption parameters for the inhibition of the corrosion of mild steel by norepinephrine.

T (K)	$1/K$	K (L/mol)	R^2
303	444×10^{-8}	225419	0.9562
313	624×10^{-8}	160270	0.9682
323	797×10^{-8}	125520	0.9576
333	1167×10^{-8}	85709	0.9666

3.4. Thermodynamic Characterisation

There are ways that can enable us to get more information regarding the interaction of the studied inhibitor and metal surface at different temperatures. A good method is to use the thermodynamic model which can clarify the adsorption phenomenon of the inhibitor molecule. ΔH_{ads} may be determined from the Van't Hoff equation [38] [39]:

$$\ln k_{ads} = -\frac{\Delta H_{ads}}{RT} + \text{Constant} \quad (9)$$

where ΔH_{ads} and K_{ads} are the adsorption heat and adsorptive equilibrium constant, respectively. The adsorptive equilibrium constant (K_{ads}) is related to the standard free energy of adsorption (ΔG_{ads}) with the following Equation (10) [40]-[42]:

$$\Delta G_{ads} = -RT \ln K_{ads} \quad (10)$$

where R is the gas constant and T is the absolute temperature. **Figure 5** is the straight line, a plot of $\ln K_{ads}$ versus $1/T$. The adsorption heat (ΔH_{ads}) can be approximately regarded as the standard adsorption heat under the experimental conditions [39] [43]. Then the standard adsorption entropy ΔS_{ads} can be obtained by the thermodynamic basic Equation (11):

$$\Delta G_{ads} = \Delta H_{ads} - T\Delta S_{ads} \quad (11)$$

Figure 5 shows that $\Delta H_{ads} = (-26.00 \text{ kJ/mol})$. Adsorption equilibrium constant K_{ads} and other thermodynamic parameters for the adsorption process are listed in **Table 2**.

A general analysis of the thermodynamic parameters shows that the complexation process is favored in terms of enthalpy ($\Delta H^\circ < 0$) but not in terms of entropy ($\Delta S^\circ < 0$) in all the above systems. Therefore, the complexation process is enthalpically controlled. The negative sign of ΔH_{ads} shows that the adsorption of norepinephrine molecules is an exothermic process. In an exothermic process, physisorption is distinguished from chemisorption by considering the absolute value of ΔH_{ads} . For physisorption process, the enthalpy of adsorption is lower than $40 \text{ kJ}\cdot\text{mol}^{-1}$ while that for chemisorptions approaches $100 \text{ kJ}\cdot\text{mol}^{-1}$ [44]. In this investigation, the standard adsorption heat ($-26.00 \text{ kJ}\cdot\text{mol}^{-1}$) shows that a comprehensive adsorption (physical adsorption) might occur [38]. The adsorption of inhibitor molecules is accompanied by positive values of ΔS_{ads} .

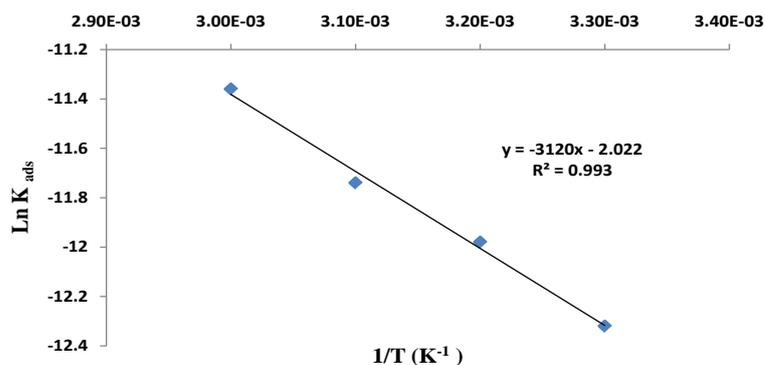


Figure 5. The relation between $\ln K_{ads}$ and $1/T$.

Table 2. Thermodynamic parameters for studied norepinephrine from experimental adsorption isotherm.

T (K)	$\ln K_{ads}$	ΔG_{ads} (kJ/mol)	ΔH_{ads} (kJ/mol)	ΔS_{ads} ($\text{J}\cdot\text{mol}^{-1}\cdot\text{k}^{-1}$)
303	12.32	-31.05	-26.00	16.00
313	-11.98	-31.19	-26.00	16.50
323	-11.74	-31.53	-26.00	17.00
333	-11.36	-31.45	-26.00	16.36

The negative value of ΔG_{ads} means that the adsorption of norepinephrine molecules on steel surface is a spontaneous process, and furthermore the negative values of ΔG_{ads} also show the strong interaction of the inhibitor molecule onto the mild steel [45].

Generally, values of ΔG_{ads} around ($-20 \text{ kJ}\cdot\text{mol}^{-1}$) or lower are consistent with the electrostatic interaction between the charged molecules and the charged metal (physisorption). If the results are more negative than $-40 \text{ kJ}\cdot\text{mol}^{-1}$ it will involve charge sharing or transfer from the inhibitor molecules to the metal surface to form a coordinate type of bond (chemisorption) [16] [46]. In this investigation, the calculated values of ΔG_{ads} are greater than $-40 \text{ kJ}\cdot\text{mol}^{-1}$, indicating that the adsorption of mechanism of norepinephrine molecules on steel in 1.0 M HCl solution at the studied temperatures may be a chemisorptions [47].

3.5. Surface Morphology

Figure 6 shows the corrosion surface of mild steel immersed in 1 M HCl with (Figure 6(b)) and without (Figure 6(a)) the inhibitor norepinephrine. Creating a rougher surface for the mild steel was done by aggressively acid. The difference was shown by Figure 6 in HCl with smoother surface due to the presences of norepinephrine. Mild steel in Figure 6 is due to the ability of prepared norepinephrine and an adsorbed film on the surface of mild steel that not found in Figure 6. The light damage a mechanism that leads to Figure 6 can explain under one of the following reasons; thin protective layer between the metal surface and anti-corrosion material through two ions. The chemical reaction between the inhibitor and the metal surface as the fact that the metal has d-orbitals and therefore bonds will be formed through the formation of coordination bonds between the metal and the inhibitor on the basis that the inhibitor is a ligand that containing nitrogen and oxygen-rich of electronic pairs as well as possession of double bonds and these electrons combine with the metal by transfer electrons from the ligand to the unoccupied d-orbitals of the metal and the formation of coordination bonds.

4. Conclusion

Norepinephrine acted as a good inhibitor for the corrosion of mild steel in 1 M HCl solution. Inhibition efficiency values increased with increase in inhibitor concentration but decreased with increase in temperature and had the highest inhibition efficiency of 79%. The absorption of norepinephrine on mild steel in 1 M HCl solution obeys Langmuir isotherm. The value of ΔH_{ads} was negative, indicating that the sorption reaction was exothermic. The positive value of ΔS_{ads} shows the increasing randomness at the solid/liquid interface during the sorption of mild steel ions onto norepinephrine molecules. The negative value of ΔG_{ads} confirmed the feasibility of the process and the spontaneous nature of sorption and chemically adsorbed (chemisorption) onto the steel surface with a high preference for mild steel to norepinephrine. Scanning Electron Microscopy (SEM) studies revealed that the corrosion of mild steel in 1 M HCl was reduced by the addition of the inhibitor. Smoother surfaces were observed to the treated mild steel with the inhibitor.

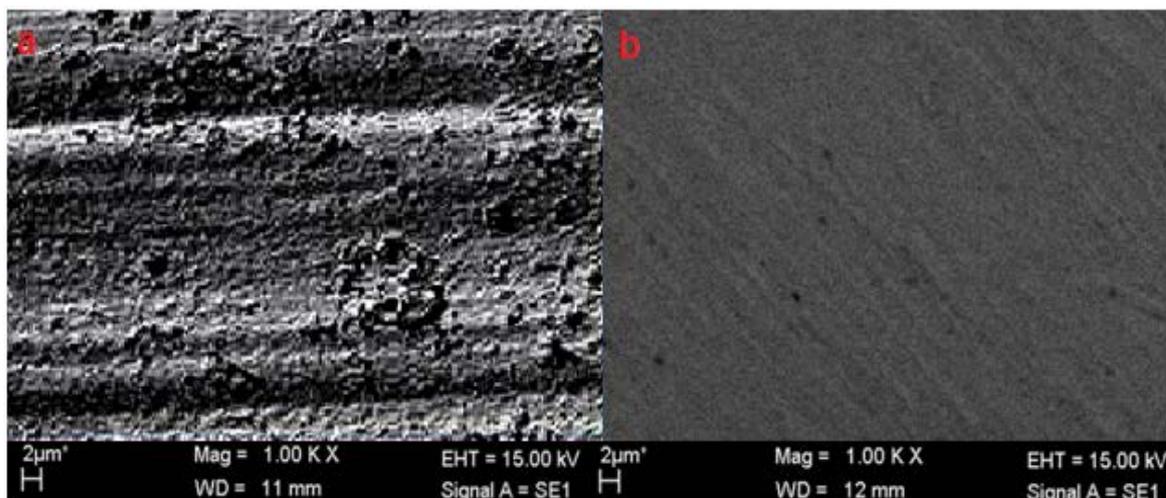


Figure 6. The scanning electron microscope micrographs 5000 \times . (a) Without inhibition; (b) With inhibition.

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