

## ARTICLE

# L-Proline as a Green Corrosion Inhibitor in Aqueous Solutions for Carbon Steel

Nisreen Faraj Kareima A. Abdelghani A.A. Idress\* Dalal. M. Ibrahim

Department of Chemistry, Faculty of Science, Omar Al Mukhtar University, Albayda, Libya

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### ABSTRACT

The chemical technique was used to investigate the inhibition and adsorption properties of L-proline for steel corrosion (weight loss method). As the concentration of L-proline increased, the inhibition efficiency increased, but decreased as the temperature increased, according to the findings. The inhibitor's adsorption to the steel surface has been shown to be random, involving both electrostatic and chemisorptions. The Temkin adsorption isotherm governs the adsorption of L-proline to the steel surface. Thermodynamic parameters have been determined in some cases.

## 1. Introduction

Corrosion protection is important in the petroleum industry because carbon steel is commonly used, such as in the construction of oil and gas production pipelines and transmission lines<sup>[1]</sup>.

Corrosion cells form on metal surfaces in contact with an electrolyte due to energy differences between the metal and the electrolyte. In relation to the electrolyte, different potentials can exist between different zones of the metal surface<sup>[2]</sup>. The contents of the cell are as follows:

(1) A loaded anode zone is one of the first things you'll notice. The iron is oxidized in the anode zone.

(2) The cathode is loaded. Electrons are found in the cathode zone. These electrons are capable of reacting with other compounds.

(3) A metal path that allows electrons to pass through.

(4) An electrolyte that coats the iron's surface.

Because of its adsorption at the metal/solution

interface, this compound acts as an inhibitor. Adsorption is influenced by the inhibitor community's physicochemical properties<sup>[3]</sup>. The existence of heteroatoms like N, O, and multiple bonds in its molecular structure, as well as functional and aromatic groups, donor atoms' electron density and p-orbital character, are thought to allow electrons to pass through adsorption centers<sup>[4]</sup>. The toxicity of most corrosion inhibitors, on the other hand, which are toxic to living organisms and should therefore pollute the ecosystem, prompted us to look for environmentally friendly inhibitors<sup>[5,6]</sup>. Heterocyclic compounds with  $\pi$  bonds, such as sulfur, oxygen, and nitrogen, are inhibitors<sup>[7]</sup>. Functional groups, steric influences, electron density at the donor atom, and molecule electronic structure are all responsible for the physical properties of inhibitor molecules<sup>[8,9]</sup>. The inhibitor can adsorb to the metal surface through two types of reactions. Physical adsorption is the electrostatic force between the adsorbed species' ionic or dipolar

\*Corresponding Author:

A.A. Idress,

Department of Chemistry, Faculty of Science, Omar Al Mukhtar University, Albayda, Libya;

Email: [asma.alsalai@omu.edu.ly](mailto:asma.alsalai@omu.edu.ly)

charges and the electrical charge at the metal/solution interface. Chemical adsorption, on the other hand, occurs when charge from inhibitory molecules is shared or transferred to the metal surface, resulting in coordinated forms of bonds<sup>[10]</sup>.

Proline is one of the twenty amino acids found in living organisms that make up their protein building blocks. Since the IUPAC meaning of an imine includes a carbon-nitrogen covalent bond, proline is commonly referred to as an imino acid. Proline is an aminoalkanoic acid that can be synthesized from glutamine. The aim of this study is to evaluate the corrosion inhibition of carbon steel in 1M HCl in the presence of various concentrations of L-proline using the weight loss technique at 298-328K, as well as to measure and discuss the thermodynamic functions for the dissolution and adsorption processes. It was selected as an inhibitor based on molecular structure considerations because it is an organic compound with many adsorption centers.

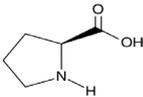
## 2. Experimental

### 2.1 Materials

Carbon steel specimens with the following compositions (percent by weight) were used in the tests: 0.200 C, 0.350 Mn, 0.014 P, and 0.003 S.

### 2.2 Inhibitors

**Table 1.** the molecular structure of L-proline as well as other data.

Structure	Mol. formula	Mol.wt.
	C <sub>5</sub> H <sub>9</sub> NO <sub>2</sub>	115.13 g mol <sup>-1</sup>

### 2.3 Solutions

Analytical grade HCl (37 percent) was diluted with double distilled water to make 1M HCl solutions. The inhibitors were used at various concentrations ranging from 2 X10<sup>-3</sup> to 8 X 10<sup>-3</sup> M.

### 2.4 Weight Loss Measures

In a thermostatically regulated water bath, weight loss measurements were taken in a 100 mL glass beaker. The length of the answer was 50 milliliters. Oblong steel coupons (2 cm long, 2 cm wide, 0.2 cm thick) were used. Before all of the tests, the coupons were polished with metallographic sandpaper with an accelerated fineness of

up to 1200 grains. After that, the electrode was washed twice in water, degreased with acetone, washed twice more in water, and dried at room temperature with a towel. The samples were weighed and suspended for 3 hours at (25-55 °C) in 50 ml of a 1.0 M HCl solution containing L-proline at the necessary concentrations. The coupons were washed in water, degreased with ethanol, washed again in water, dried, and weighed on an analytical balance after the tests were completed (precision: 0.1 mg). The inhibition efficiency (percent IE) was estimated using the equation below overtime periods of exposure:

$$\% IE = \theta \times 100 = \left( 1 - \frac{W_{(inh)}}{W_{(free)}} \right) \times 100 \quad (1)$$

The weight loss in the absence and presence of the inhibitor is represented by surface coverage and W(free), W(inh).

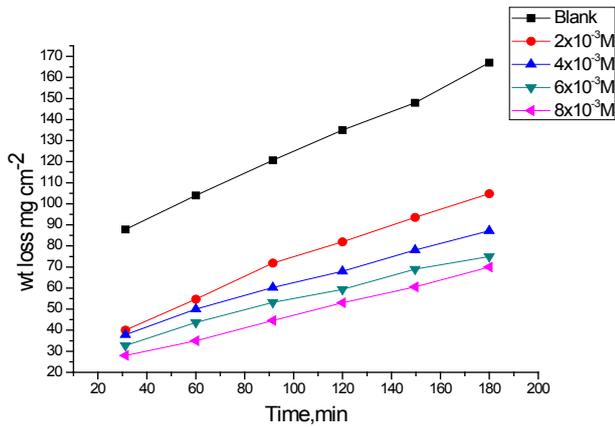
## 3. Results and Discussion

### 3.1 Effect of Concentration

Table 2 shows the difference in weight loss of steel in the presence of varying concentrations (2x10<sup>-3</sup> - 8x10<sup>-3</sup> M) of L-proline in 1 M HCl for 3.0 h at 25 °C. They were plotted out. Figure 1 shows that L-proline inhibits steel corrosion in a 1 M HCl solution at the lowest concentrations used in the analysis, with the highest inhibition efficiency seen at an inhibitor concentration of 8 x 10<sup>-3</sup> M in 1 M HCl at 25 °C. The addition of L-proline reduces the rate of corrosion, as shown in Table 2. The linear change in weight loss over time in uninhibited and inhibited 1 M HCl indicates the absence of insoluble surface films throughout corrosion. This may be because the adsorption of inhibitor molecules on the surface of carbon steel increases with increasing inhibitor concentration, effectively separating the carbon steel surface from the medium<sup>[11,12]</sup>.

**Table 2.** Corrosion rate (C.R.) and inhibition efficiency data for carbon steel in 1 M HCl solutions without and with various concentrations of L-proline at 25 1°C derived from weight loss measurements.

Conc.,M	C.R., mg cm <sup>-2</sup> min <sup>-1</sup>	$\theta$	% IE
1 M HNO <sub>3</sub>	2.68	-	-
2x10 <sup>-3</sup> M	0.80	0.690	69.0
4x10 <sup>-3</sup> M	0.56	0.791	79.1
6x10 <sup>-3</sup> M	0.39	0.832	83.2
8x10 <sup>-3</sup> M	0.35	0.862	86.2



**Figure 1.** Weight loss-time curves of carbon steel in 1 M HCl in the absence and presence of different concentrations of L-proline at 25°C.

### 3.2 Effect of Temperature

Weight loss measurements were used to investigate the impact of temperature on both the corrosion rate and thus the inhibition efficiency of L-proline in each of 1M HCL within the range of 25-55°C with a 10°C increment, Table 3 shows that increasing the temperature causes an increase in steel corrosion rate in both free and inhibited acid solutions, as well as a decrease in L-proline inhibition efficiency, assuming that the test compound prevents steel corrosion by adsorbing an inhibitor molecule, while the test compound desorbs at higher temperatures [13].

The apparent energy of activation ( $E_a^*$ ), activation enthalpy ( $\Delta H^*$ ), and activation entropy ( $\Delta S^*$ ) for steel corrosion in 1 M HCl solution were calculated using the Arrhenius form equation in the absence and presence of various concentrations of L-proline [14].

$$\text{Rate}(k) = A e^{\frac{-E_a^*}{RT}} \quad (2)$$

and transition state equation [15].

$$\text{Rate}(k) = \frac{RT}{Nh} e^{\frac{\Delta S^*}{R}} e^{\frac{-\Delta H^*}{RT}} \quad (3)$$

Where the frequency factor is (A), the Planck constant is (h), the Avogadro number is (N), and the universal gas constant is (R).

The kinetic parameters obtained from log Rate vs. (1 / T) (Figure 2) are mentioned in Table 4 and (1 / T) vs. log (Rate / T) (See Figure 3) showed that the value of  $E_a^*$  in an inhibited solution is higher than in an uninhibited solution, meaning that steel dissolution is slow in the presence of an inhibitor, which can be clarified by physical adsorption [16]. Equation 2 indicates that the higher the  $E_a^*$  value, the less the corrosion risk is. That is frequently way to the advent of a film at the metallic surface, which acts as a strength buffer in opposition to

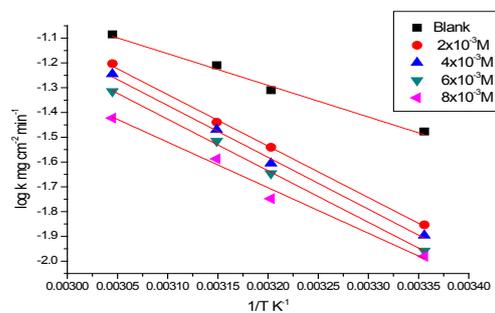
**Table 3.** Weight loss measurements for carbon steel in 1 M HCl solution in the absence and presence of different L-proline concentrations at 25–55°C±1°C.

Conc.	Temp., °C	C.R., mg cm <sup>2</sup> min <sup>-1</sup>	$\theta$	% IE
2x10 <sup>-3</sup> M	25	2.68	0.205	69.0
	35	2.88	0.109	10.9
	45	3.61	0.089	8.9
	55	9.63	0.054	5.4
4x10 <sup>-3</sup> M	25	0.80	0.726	79.1
	35	2.01	0.529	52.9
	45	2.87	0.328	32.8
	55	7.33	0.225	22.5
6x10 <sup>-3</sup> M	25	0.56	0.819	83.9
	35	1.91	0.709	70.2
	45	1.10	0.543	54.3
	55	5.34	0.482	48.2
8x10 <sup>-3</sup> M	25	0.35	0.873	86.2
	35	1.98	0.834	83.4
	45	4.82	0.718	71.8
	55	4.45	0.669	66.9

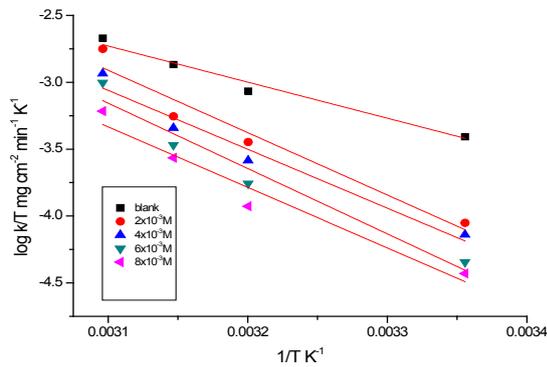
metallic corrosion [17]. Positive  $\Delta H^*$  values indicate that the steel dissolution process is endothermic. The high and negative values of  $\Delta S^*$  indicate that the active compound in the rate-determining phase is an interaction rather than a dissociation, implying that when the reactants and active compound are switched, the perturbation decreases [18].

**Table 4.** Effect of concentration of L-proline on the activation energy of carbon steel dissolution in 1 M HCl.

Conc. M	Activation parameters		
	$E_a^*$ kJ mol <sup>-1</sup>	$\Delta H^*$ kJ mol <sup>-1</sup>	$-\Delta S^*$ J mol <sup>-1</sup> K <sup>-1</sup>
1 M HCl <sub>3</sub>	23.60	21.20	198.9
2x10 <sup>-3</sup> M	40.12	41.52	153.50
4x10 <sup>-3</sup> M	47.20	45.44	141.23
6x10 <sup>-3</sup> M	65.9	57.34	135.12
8x10 <sup>-3</sup> M	89.12	61.96	99.65



**Figure 2.** log corrosion rate vs 1/T curves for carbon steel dissolution in 1M HCl in absence and presence of different concentrations of L-proline.



**Figure 3.** log corrosion rate/T vs 1/T curves for carbon steel dissolution in 1M HCl in absence and presence of different concentrations of L-proline.

### 3.3 Adsorption Isotherm Behavior

The following equation was used to calculate the values of surface coverage for various inhibitor concentrations in 1 M HCl based on weight loss measurements:

$$\theta = \frac{[weight\ loss(pure) - weight\ loss(inh.)]}{weight\ loss(pure)} \quad (4)$$

The values of  $\theta$  increased as the inhibitor concentration increased, as can be seen from the values of  $\theta$ . Using these surface coverage values, different adsorption isotherms can be used to process the experimental results.

It can be seen from the values of  $\theta$  that the values of  $\theta$  increased as the inhibitor concentration increased. Different adsorption isotherms may be used to process the experimental data using these surface coverage values. To investigate the adsorption mechanism, the adsorption mechanism was studied using the Temkin adsorption isotherm. The isotherm is defined by the equation below.

$$\ln K_{ads}C = a\theta \quad (5)$$

$K_{ads}$  is the adsorption constant, and  $C$  is the inhibitor concentration. The plot of  $\theta$  versus  $\log C$  gives linear relation (shown in Figure 4). The adsorption constant  $K_{ads}$  are often calculated from the intercept and  $\Delta G^{\circ}_{ads}$  are often calculated from the subsequent equation:

$$K_{ads} = 1/55.5 \exp(\Delta G^{\circ}_{ads}/RT) \quad (6)$$

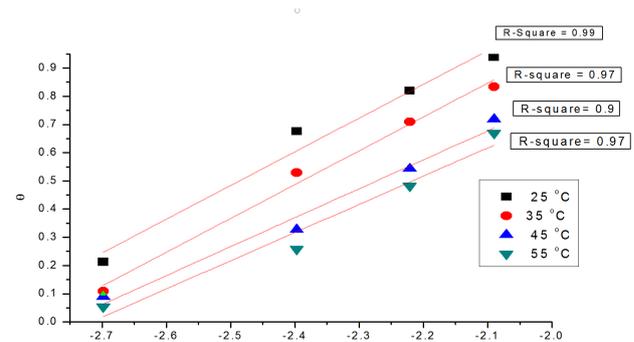
Where 55.5 represents the mole/liter concentration of water in solution<sup>[19]</sup>,  $T$  is the absolute temperature, and  $R$  is the universal gas constant.

The thermodynamic parameters for the adsorption process derived from Figure 4 are shown in Table 5. The increased inhibition efficiency and negative  $G^{\circ}_{ads}$  values indicate that the investigated compound is strongly adsorbed on the metal's surface, and the spontaneity adsorption mechanism aids in the creation of a stable adsorption layer on the metal's surface.

$\Delta G^{\circ}_{ads}$  up to  $-20 \text{ kJ mol}^{-1}$  are based on the electrostatic interaction between charged molecules, and thus the charged metal (physical adsorption).  $\Delta G^{\circ}_{ads}$  less than  $-40 \text{ kJ mol}^{-1}$  involve the exchange or transfer of electrons from inhibitor molecules to the metal surface to form a coordinate bond (chemisorption)<sup>[20]</sup>. The obtained  $\Delta G^{\circ}_{ads}$  values were approximately equivalent to  $-59 \text{ kJ mol}^{-1}$ , indicating that both electrostatic and chemisorption processes are involved in inhibitor molecule adsorption on carbon steel in 1 M HCl solution<sup>[21]</sup>. The thermodynamic parameters relate to the inhibitors' decomposition (primary contributor) and chemical tests (secondary contributor) on the metal surface.  $K_{ads}$  follows a similar pattern, with higher values indicating more effective absorption and, as a result, better inhibition efficiency<sup>[22]</sup>.

**Table 5.** the inhibitor binding constant ( $K_{ads}$ ), free energy of binding ( $\Delta G^{\circ}_{ads}$ ), and later interaction parameter ( $a$ ) for the corrosion of carbon steel in 1 M HCl at 25°C for various inhibitor concentrations.

Conc. M	Temkin		
	a	$K_{ads} \times 10^{-8} \text{ mol L}^{-1}$	$\Delta G^{\circ}_{ads} \text{ kJ mol}^{-1}$
$2 \times 10^{-3} \text{ M}$	11.2	5.15	-58.9
$4 \times 10^{-3} \text{ M}$	10.8	3.38	-57.4
$6 \times 10^{-3} \text{ M}$	10.4	2.33	-55.8
$8 \times 10^{-3} \text{ M}$	10.1	1.65	-53.9



**Figure 4.** Temkin adsorption isotherm for carbon steel corrosion in 1 M HCl solutions at 25°C plotted as vs log C of L-proline.

### 4. Conclusions

The main assumptions are as follows:

- (1) L-proline has a significant inhibitory impact on steel corrosion in 1 M HCl.
- (2) As the inhibitor concentration rises, the value of inhibition efficiency falls, and as the temperature rises, the value of inhibition efficiency falls.
- (3) The Temkin adsorption isotherm governs the adsorption of L-proline on steel.

(4) The fact that the adsorption free energy was negative suggests that the reaction was exothermic and spontaneous.

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