



Dicloxacillin: An effective retarder for steel dissolution in acid medium

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Abstract: The dissolution mild steel in 1M H₂SO₄ has been retarded by Dicloxacillin (DCN) as corrosion inhibitor was investigated using weight loss, Potentiodynamic polarization, Electrochemical impedance spectroscopy, Hydrogen permeation and diffuse reflectance spectroscopic studies. All these techniques reveal that inhibition efficiency increases with increase in the concentration of DCN. Polarization studies indicated that Dicloxacillin behaved as cathodic inhibitor. Diffuse reflectance spectroscopy confirmed the adsorption of inhibitor on the mild steel surface obeying Langmuir adsorption isotherm. The quantum chemical analysis substantiates the inhibition efficiencies of the compound determined by electrochemical methods.

Keywords: Adsorption isotherm; Dicloxacillin; Corrosion inhibition; Mild steel.

Introduction

Thiourea and its derivatives have been discussed and used for many years for their better inhibition to the corrosion of steels. Sulphur, nitrogen and oxygen atoms present in the organic compounds are capable of impeding metallic corrosion. As the thiourea molecule contains one sulphur and two nitrogen atoms, thiourea and its derivatives are potential corrosion inhibitors[1-5].

The detailed investigations have been carried out on inhibitor properties of thiourea, due attention has not yet been paid to a systematic study of inhibitor action of thiourea derivatives. However, several substituted thiourea have been investigated as corrosion inhibitors [6-8]. Most of the effective organic inhibitors have heteroatoms such as O, N, S containing multiple bonds in their molecules through which they can adsorb on the metal surface [9-12]. The corrosion inhibiting property of these compounds is attributed to their molecular structure. The lone pair determines the adsorption of these molecules on the metal surface. All the above studies reveal the one common observation that thiourea derivatives can be regarded as excellent corrosion inhibitors. But studies on the influence of DCN on hydrogen permeation through steel substrate during pickling are very scarce. A good inhibitor should have the following two important requisites: (1) it should have very good inhibition efficiency and (2) it should bring down the hydrogen permeation current to a considerable extent. Some organic compounds give very high values of inhibition efficiency, but they have a negligible effect in reducing the hydrogen permeation current and vice versa. Compounds which come under this class produce hydrogen embrittlement in a later stage by the combination of permeated atomic hydrogen[13-15]. This delayed failure creates cracking, pitting, breakage, etc., on the metal surface.

Experimental

Mild steel specimens of compositions, C = 0.08%, P = 0.07%, Si = 0%, S = 0%, Mn = 0.41% and Fe remainder, and of size 4 x 1 x 0.020 cm were used for weight loss and hydrogen permeation studies. A mild

steel cylindrical rod of the same composition as above and embedded in araldite resin with an exposed area of 0.283 cm² was used for galvanostatic polarisation and AC impedance measurements.

The inhibitor was preliminarily screened by a weight loss method described earlier. Both cathodic and anodic polarisation curves were recorded potentiodynamically (1 mA s⁻¹) using corrosion measurement system BAS Model: 100 A computerised electrochemical analyser (made in West Lafayette, Indiana) and PL-10 digital plotter (DMP-40 series, Houston Instruments Division). A platinum foil, Hg/Hg₂Cl₂/1 N HCl and Hg/HgSO₄/1 N H₂SO₄ were used as auxiliary and reference electrodes, respectively. The hydrogen permeation study was carried out using an adaptation of the modified Devanathan and Stachurski's two compartment cell, as described earlier. Double layer capacitance (C_{dl}) and charge transfer resistance values (R_t) were obtained using AC impedance measurements as described in an earlier publication." The surfaces of corroded and corrosion inhibited mild steel specimens were examined by diffuse reflectance studies in the region 200- 700 nm using U-3400 spectrometer (UV-VIS-NIR Spectrometer, Hitachi, Japan).

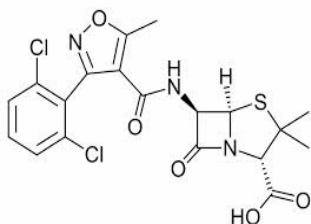


Figure 1. Structure of Dicloxacillin

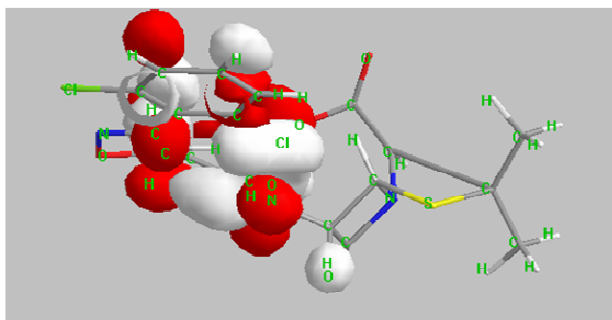


Figure 2. HOMO of Dicloxacillin

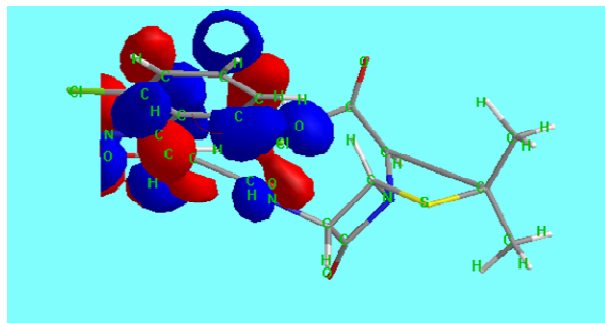


Figure 3. LUMO of Dicloxacillin

Results and discussion

The inhibition of corrosion of brought about by the compound can be due to the following interactions:

1. The interaction between the lone pairs of electrons of the sulfur atom of the organic molecule and the positively charged metal surface.
2. The interactions between lone pairs of electrons of the nitrogen atoms and the positively charged metal surface.
3. The presence of 7-oxo-4-thia-azabicyclo heptane group in the molecule which shows inductive (+I) effect may increase the electro density on the sulfur atom that leads to better performance than the sulphur containing organic compounds¹².

The increasing concentrations of inhibitor enhances the values of both b_a and b_c , but the values of b_c are enhanced to greater extent. So the inhibition of corrosion of mild steel in both acids is under cathodic control. Values of E_{corr} is shifted to less negative values in the presence of different concentrations of compound. This can be ascribed to the formation of closely adherent adsorbed film on the metal surface. The presence of increasing concentrations of dicloxacillin retards I_{corr} values in both the acids. It can also be seen that most of the values of inhibition efficiency obtained by weight loss measurements and Potentiodynamic polarization studies agree very well.

The presence of dicloxacillin and sulphuric acid enhances the permeation current. The enhancement in permeation current can be attributed to the decomposition of the compound on the mild steel surface. In all the mechanisms suggested so far, invariable the product of decomposition of inhibitor is H₂S, which is evolved on the metal surface. Its formation can be detected by radiometric measurements, if labeled thiourea 35 s or its derivatives are used. The whole process takes place in two stages. In the first stage, cyclohexyl thiourea molecules are adsorbed on the metal surface by virtue of the interaction of lone pairs of electrons of nitrogen sulfur. In the second stage, the adsorbed molecules of the compound slowly undergoes chemical changes. The molecule usually decomposes with the formation of H₂S by the action of hydrogen evolved on the metal.

Hough et al investigated that the enhanced permeation of hydrogen ions through the metal surface in acidic solutions in the presence of thiourea and derivatives may be due to the presence of increased concentration of surface hydrogen atoms. This can be attributed to the inhibition of the recombination of hydrogen atoms to form hydrogen molecules. Trabaneli and Zucchi reported that sulfur of hydrogen sulfide can act as negative catalyst for the recombination of hydrogen atoms into molecular hydrogen. It can be seen from the table that the enhancement of permeation current is more, if the concentration of inhibitor is more. A similar observation has been made by Lahiri et.al that hydrogen permeation current increases with increase in the concentration of di-ortho tolyl thiourea.

Values of charge transfer resistance (R_t) and double layer capacitance (C_{dl}) derived from Nyquist plots are shown in table 4. It can be seen in table that the values of R_t is found to increase with increase in concentration of compound in 1M H₂SO₄. It is found that values of C_{dl} are brought down by increasing concentrations of inhibitor in acid medium. This can be attributed to increasing adsorption of the compound on the metal surface with increase in its concentration.

A plot of $\log(C/\theta)$ versus $\log C$ gives a straight line showing that the adsorption of dicloxacillin on the mild steel surface in 1M H₂SO₄ obeys Langmuir's adsorption isotherm. These points to corrosion inhibition by this compound, being a result of its adsorption on the metal surface.

Table 1. Quantum mechanical studies of corrosion of mild steel in 1M H₂SO₄

Compound	E _{HOMO} (eV)	E _{LUMO} (eV)	ΔE (eV)	μ (Debye)
Dicloxacillin	-7.31	-2.92	4.29	5.4

Table 2. Values of inhibition efficiency for the corrosion of mild steel in 1 M H₂SO₄ in the presence of different concentrations of dicloxacillin obtained from weight loss and gasometric measurements.

Concentration of Inhibitor (mM)	Inhibition efficiency (%)	
	Weight loss method	Gasometric method
1	91.2	91.8
5	94.3	95.2
10	95.7	96.4
50	97.2	97.9
100	99.2	99.6

Table 3. Corrosion kinetic parameters of mild steel in 1M H₂SO₄ in the presence of different concentrations of dicloxacillin obtained from galvanostatic polarization studies.

Concentration of Inhibitor (mM)	E _{corr} (mV)	Tafel slopes in mV in dec ⁻¹		I _{corr} mA cm ⁻²	Inhibition efficiency (%)
		b _a	b _c		
Blank	-909	70	130	2.25	---
1	-889	70	137	0.20	91.0
10	-880	76	137	0.14	93.6
50	-874	79	139	0.07	96.7
100	-868	80	149	0.03	98.5

Table 4. Values of permeation current for the corrosion of mild steel 1M H₂SO₄ in the presence of different concentrations of inhibitor.

Concentration of Inhibitor (mM)	H ₂ SO ₄	
	Charge Transfer resistance (R _t) Ohm.cm ²	Double layer capacitance (C _{dl}) μF.cm ⁻²
Blank	6.8	187
1	31	172
10	44	133
50	78.4	109.2
100	90.5	98.2

Table 5. Impedance parameters for the corrosion of mild steel in 1 M H₂SO₄ in the presence of different concentrations of dicloxacillin.

Concentration of Inhibitor (mM)	Steady state permeation current (μA) 1M H ₂ SO ₄
Blank	12.7
1	12.8
10	13.7
50	14.4
100	15.9

Conclusions

1. Dicloxacillin inhibits the corrosion of mild steel in 1M H₂SO₄ very effectively.
2. The inhibition of corrosion of mild steel in both the acids, by the compound is under cathodic control.
3. The presence of inhibitor in both the acids is found to enhance the extent of ingress of hydrogen through mild steel.
4. R_t and C_{dl} values obtained from impedance measurements confirm the better performance of the compound.

5. The adsorption of the compound on mild steel surface obeys langmuir's adsorption isotherm.
6. Quantum mechanical indices substantiate the performance of the antibiotics as the efficient inhibitor for steel corrosion.

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