

The inhibitive action of eco-friendly compound on the corrosion of mild steel in brine water

S.Karthikeyan ^{1*}, P.A.Jeeva ¹, R.Dinakaran², S.Narayanan¹

¹ Centre for Innovative Manufacturing Research, VIT University, Vellore– 632 014, India.

² School of Mechanical Engineering, VIT University, Vellore– 632 014, India.

^{1*} corresponding author (skarthikeyanphd@yahoo.co.in)

Abstract

The inhibitive action of Dicloxacillin (DCX) on corrosion of mild steel in brine water (5% NaCl) has been studied using weight loss, gasometric measurements, potentiodynamic polarization and impedance studies. The studies clearly indicated that DCX acted as cathodic inhibitor. The adsorption of the compound on mild steel surface obeyed Temkin's adsorption isotherm. Diffused reflectance spectra and SEM images confirmed the formation of adsorbed film of inhibitor on metal.

Keywords : Corrosion inhibitor, Antibiotic compounds, Impedance measurements, Adsorption

Introduction

Mild steel is an important category of materials due to their wide range of industrial applications. It is used in many industries due to its excellent mechanical properties. These are used in industries as pipelines for petroleum industries, storage tanks, reaction vessels and chemical batteries (1). Acids are widely used for Pickling, Descaling, Acid Cleaning, Oil Well acidizing and other applications. Due to their high corrosive nature acids may cause damage to the system components. Various methods are used to decrease the corrosion rate of metals in acids, among the different methods use of inhibitors is most commonly used (2–7). The use of corrosion inhibitors is most economical and practical method to reduce electrochemical corrosion. Heterocyclic compounds containing hetero atoms such as S, N & O act as effective corrosion inhibitors for mild steel in acid media and have been the subject of many publications(8–11).

Organic compounds have been widely used as corrosion inhibitors for metals in acidic media (12–18). The effective and efficient corrosion inhibitors were those compounds which have π bonds and contains hetero atoms such as sulphur, nitrogen, oxygen and phosphorous which allows the adsorption of compounds on the metal surface(19–21). The organic inhibitors decrease the corrosion rate by adsorbing on the metal surface and blocking the active sites by displacing water molecules and form a compact barrier film on the metal surface. The most of the organic inhibitors are toxic , highly expensive and environment unfriendly. Research activities in recent times are geared towards developing the cheap, non-toxic and environment friendly corrosion inhibitors.

The present paper describes a study of corrosion protection action of DiCloxacillin on mild steel in brine water using weight loss, electrochemical techniques and hydrogen permeation studies. Dicloxacillin is a narrow-spectrum β -lactam antibiotic of the penicillin class.[21] It is used to treat infections caused by susceptible (non-resistant) Gram-positive bacteria.[21] It is active against beta-lactamase-producing organisms such as *Staphylococcus aureus*, which would otherwise be resistant to most penicillins. This compound shows π -electrons, heteroatom's S, N & O in its structure. The molecule is big enough (Molecular Mass; 457.86) and sufficiently planar to block more surface area (due to adsorption) on mild steel. These factors favour the interaction of DCX with steel . As far as we know no concrete report has been published so for Dicloxacillin in brine water with use of electrochemical techniques, hydrogen permeation and diffuse reflectance spectra. Hence the present study. The structure of the cloxacillin is shown in the **fig.1**. Different concentrations of inhibitor were prepared and there inhibition efficiency in acidic media was investigated.

The structure of the DCX is shown in the figure.1. Different concentrations of inhibitor were prepared and their inhibition efficiencies in 5% salt water were investigated.

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 gasometric studies. The weight loss study was carried out at room temperature for three hours in 5% NaCl. The inhibition efficiency (IE %) was determined by the following equation, $IE (\%) = (W_0 - W_i / W_0) \times 100$

Where W_0 & W_i are the weight loss values in the absence and presence of the inhibitor. 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 potentiodynamic polarisation and AC impedance measurements.

The inhibitor was preliminarily screened by a weight loss method described earlier⁹. Both cathodic and anodic polarisation curves were recorded in brine water (5% NaCl) potentiodynamically (1 mA s⁻¹) using corrosion measurement system BAS Model: 100A computerised electrochemical analyzer (made in West Lafayette, Indiana) and PL-10 digital plotter (DMP-40 series, Houston Instruments Division). A platinum foil and Hg/Hg₂Cl₂/5%NaCl were used as auxiliary and reference electrodes respectively. Double layer capacitance (C_{dl}) and charge transfer resistance values (R_{ct}) were measured using AC impedance measurements¹⁰⁻¹⁸. 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).

Results and Discussion

Weight loss and Gasometric measurements

Table 1 gives the values of inhibition efficiency for different concentrations of Dicloxacillin(DCX) for the corrosion of mild steel in brine water obtained from weight loss and gasometric measurements. It is found that the compound inhibits the corrosion of mild steel effectively in salt water. The presence of tolyl and two -CH₃ groups in the molecule which shows inductive (+I) effect may increase the electron density on the sulfur atom that leads to better performance than the unsubstituted thiourea.

A good conformity between the values of inhibition efficiency obtained by weight loss and gasometric methods is found.

Potentiodynamic polarization studies

The corrosion kinetic parameters such as Tafel slopes (b_a and b_c), corrosion current (I_{corr}) and corrosion potential (E_{corr}) and inhibition efficiency obtained from potentiodynamic polarization curves for mild steel in brine water containing different concentrations of inhibitor are given in table 2.

The values of b_a , b_c and I_{corr} are very much similar to those reported earlier¹¹⁻¹³. Further it is ascertained that increasing concentrations of DCX 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 salt water 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 results of potentiodynamic polarization for the corrosion of mild steel in brine water are given in figure 2.

Impedance measurements

Corrosion inhibition of mild steel in brine water solution with and without inhibitor was investigated by electrochemical impedance spectroscopy measurements and it is shown in figure .3 and the results are presented in table 3. At all concentrations range of DCX, large capacitive circle at higher frequency range followed by small capacitive loops at lower frequency range. The diameter of the circles increased with increase in inhibitor concentration. The higher frequency capacitive loop is due to the adsorption of inhibitor molecule¹⁴⁻¹⁸. Also the values of R_{ct} are found to increase with increase in concentrations of compound in brine water solution whereas values of C_{dl} are reduced considerably. This can be ascribed to the strong adsorption of the compound on the metal surface. Similar observation was reported by Harikumar²¹ and others²²⁻²⁵ for the corrosion inhibition of mild steel in acidic media by Ampicilin drug and thio compounds.

Diffused Reflectance Studies

The formation of thin film on the surface of mild steel is ascertained by UV reflectance studies carried out using spectrophotometer in different concentrations of inhibitor with different mild steel specimens. The reflectance curves for polished specimen, specimen dipped in salt water and different concentrations of inhibitor are shown in the figure 4. The percentage of reflectance is maximum for polished mild steel and it gradually decreases for the specimen dipped in brine water solution. This observation reveals that the change in surface characteristic is due to the corrosion of mild steel in salt water. When compared with uninhibited solution, the reflectance percentage increased as the concentration of the inhibitor increased. This can be ascribed to the increase in film thickness formed on mild steel surface^{19,21}. A plot of surface coverage (θ) versus $\log C$ gives a straight line displaying that the adsorption of DCX on the mild steel surface from brine water obeys Temkin's adsorption isotherm (Figure 5).

Conclusions

1. Dicloxaciilin retards the corrosion of mild steel effectively in brine water.
2. The inhibition of corrosion of mild steel in salt water, by the compound followed cathodic control.
3. R_{ct} and C_{dl} values obtained from impedance measurements confirm the better enactment of the inhibitor.
4. The adsorption of the compound on mild steel surface observes Temkin's adsorption isotherm.
5. UV –reflectance studies disclose the mere adsorption of the inhibitor on the mild steel surface responsible for the corrosion inhibition of steel in brine water.

References:

1. Zhang, J.; Liu, J.; Yu, W.; Yan, Y.; You, L.; Liu, L. *Corros. Sci.* 52 (2010) 2059–2065.
2. Singh, A. K.; Shukla, S. K.; Singh, M.; Quraishi, M. A. *Mater. Chem. Phys.* 129 (2011) 68–76.
3. Shukla, S. K.; Quraishi, M. A. *Mater. Chem. Phys.* 120(2010) 142–147.
4. Shukla, S.K.; Singh, A. K.; Ahamad, I.; Quraishi, M. A. *Mater. Lett.* 63(2009) 819–822.
5. Shukla, S. K.; Quraishi, M. A. *Corros. Sci.* 51(2009)1007–1011.
6. Shukla, S. K.; Quraishi, M. A.; Prakash, R. *Corros. Sci.* 50(2008) 2867–2872.
7. Ranney, M. W. *Inhibitors—Manufacture and Technology*; Noyes Data Corp: NJ, 1976.
8. Bentiss, F.; Traisnel, M.; Vezin, H.; Hildebrand, H. F.; Lagren, M. *Corros. Sci.* 46 (2004) 2781–2792.
9. Prabhu, R. A.; Venkatesha, T. V.; Shanbhag, A. V.; Praveen, B. M.; Kulkarni, G. M.; Kalkhambkar, R. G. *Mater. Chem. Phys.* 108(2008) 283.
10. Lowmunkhong, P.; Ungthararak, D.; Sutthivaiyakit, P. *Corros. Sci.* 52(2010) 30–36.
11. Bentiss, F.; Jama, C.; Mernari, B.; Attari, H. E.; Kadi, L. E.; Lebrini, M.; Traisnel, M.; Lagren, M. *Corros. Sci.* 51(2009) 1628–1635.
12. R. Hasanov, M. Sadikoglu, S. Bilgic, *Appl. Surf. Sci.* 253 (2007) 3913–3921.
13. A. Chetouani, B. Hammouti, T. Benhadda, M. Daoudi, *Appl. Surf. Sci.* 249 (2005) 375–385.
14. M. Bouklah, B. Hammouti, M. Lagren, F. Bentiss, *Corros. Sci.* 48 (2006) 2831–2842.
15. M. Benabdellah, R. Touzani, A. Aouniti, A. Dafali, S. El-Kadiri, B. Hammouti, M. Benkaddour, *Mater. Chem. Phys.* 105 (2007) 373–379.
16. A. Yildirim, M. Cetin, *Corros. Sci.* 50 (2008) 155–165.
17. I.B. Obot, N.O. Obi-Egbedi, *Colloids surf. A Physicochem. Eng. Aspects* 330(2008) 207–212.
18. K.F. Khaled, M.M. Al-Qahtani, *Mater. Chem. Phys.* 113 (2009) 150–158.
19. H. Ma, T. Song, H. sun, X. Li, *Thin solid films* 516 (2008) 1020–1024.
20. E.H. El Ashry, A. El Nemr, S.A. Essawy, S. Ragab, *Prog. Org. Coat.* 61 (2008) 11–
21. Hari Kumar, S. and Karthikeyan, S., *Journal of Materials and Environmental science*, 3 (5) (2012) 925–934.

22. Lane, T.J., Yamaguchi, A., Quachano, J.V., Ryan, R.A., Muzhushi, A., Infrared Studies of Methylthiourea and its Metal Complexes (1959) J. Am. Chem. Soc., 81, 3824–3831.
23. Gu Hough, Zhou Zhongbai, Tao Yingachu and Yao Luaw, Study on the effect of thiourea and its derivatives on hydrogen permeation rate in steel in hydrochloric acid solution, Chemical abstracts, 98, 38540n.
24. . H. Ju, Z.P. Kai, Y. Li, Corros. Sci. 50 (2008) 865–871.
25. S. El Issami, B. Hammouti, S. Kertit, E. Ait Addi, R. Salghi, Pigment Resin Technol. 36 (2007) 161–168.

Table 1. Values of inhibition efficiency for the corrosion of mild steel in brine water in the presence of different concentrations of Dicloxacin obtained from weight loss and gasometric measurements.

Concentration of Inhibitor (ppm)	Inhibition efficiency (%)	
	Weight loss Studies	Gasometric measurements
Blank	---	---
50	85.2	85.7
100	89.2	88.2
150	97.4	96.9

Table 2: Corrosion kinetic parameters of mild steel in brine water in the presence of different concentrations of Dicloxacin obtained from potentiodynamic polarization studies.

Con.	E_{corr}	I_{corr}	b_a	b_c	IE	θ
DCX	(mV vs SCE)	($\mu A\ cm^{-2}$)	(mV dec ⁻¹)	(mV dec ⁻¹)		(%)

Blank	-379.70	559	81.0	131.2	-	-
50 PPM	-336.12	84.9	69.1	120.7	84.8	0.85
100 PPM	-370.63	60.93	67.3	109.1	89.1	0.89
150 PPM	-395.39	15.09	60.9	99.8	97.3	0.97

Table 3. Impedance values for the corrosion of mild steel in brine water in the presence of different concentrations of DCX molecules .

Concentration of Inhibitor (ppm)	brine watersolution		
	Charge resistance (R_{ct})	Transfer Ohm.cm ²	Double layer capacitance (C_{dl}) $\mu\text{F.cm}^{-2}$
Blank	37.7		169
50	81.2		25.01
100	108.3		18.42
150	114.2		4.56

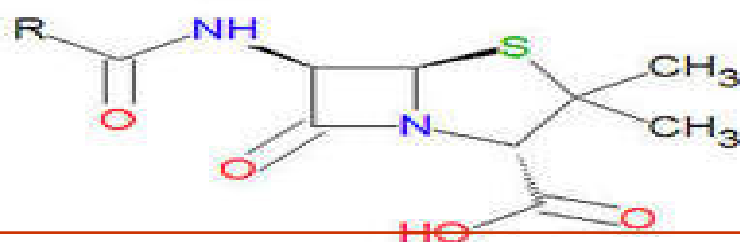


Figure 1. Structure of Dicloxacillin

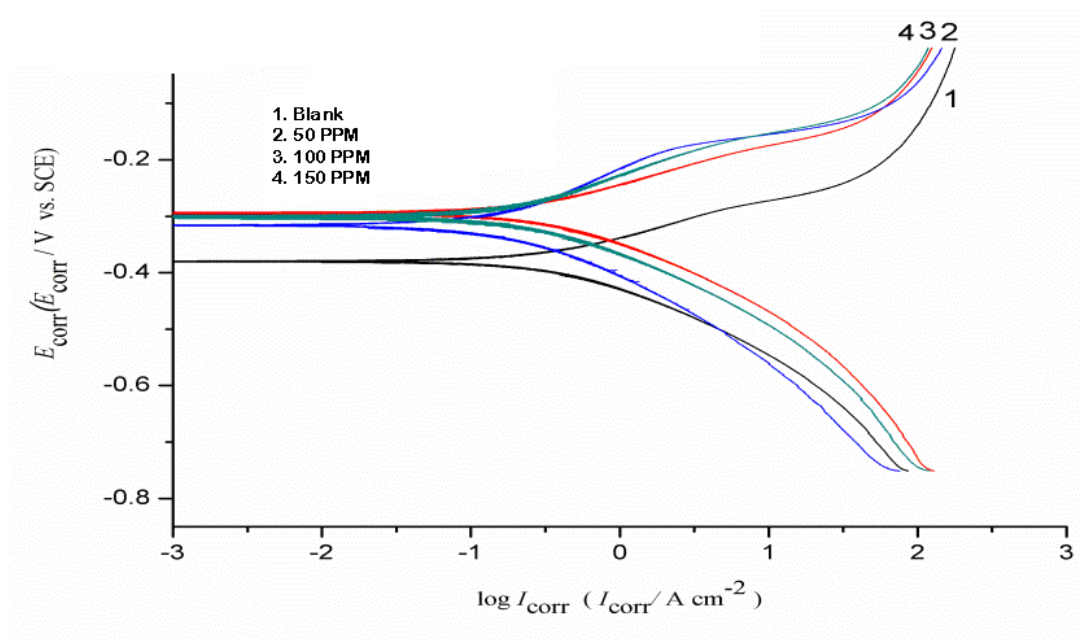


Figure 2. Potentiodynamic polarization plot for mild steel in brine water with different concentrations of DCX compound

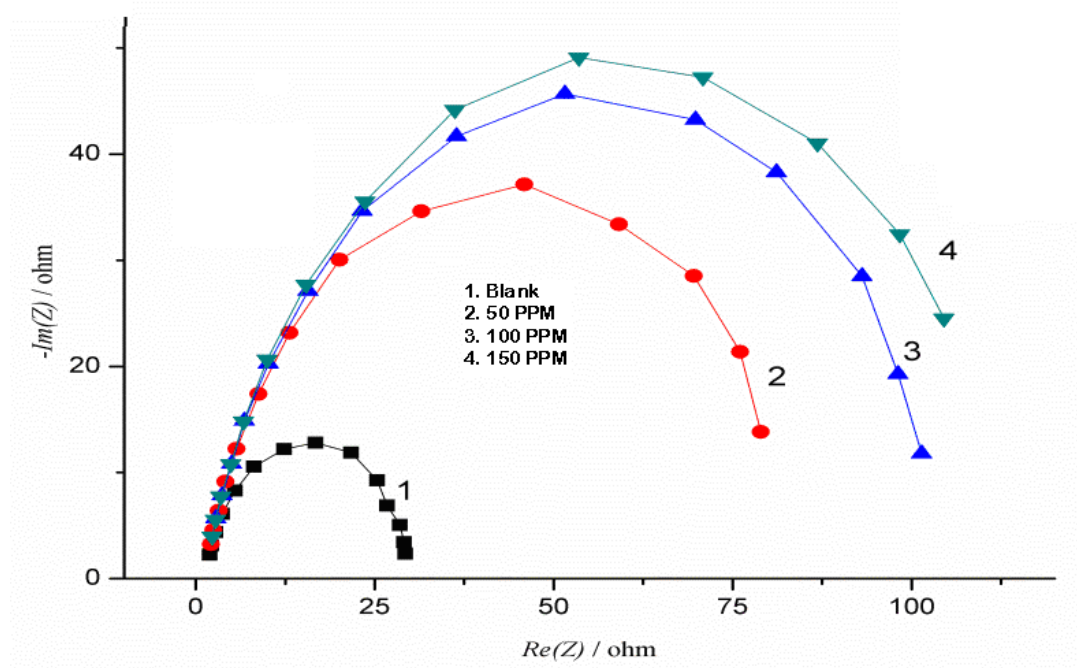


Figure 3. Impedance curves for the corrosion of mild steel in brine water in the presence

and absence of Dicloxacin.

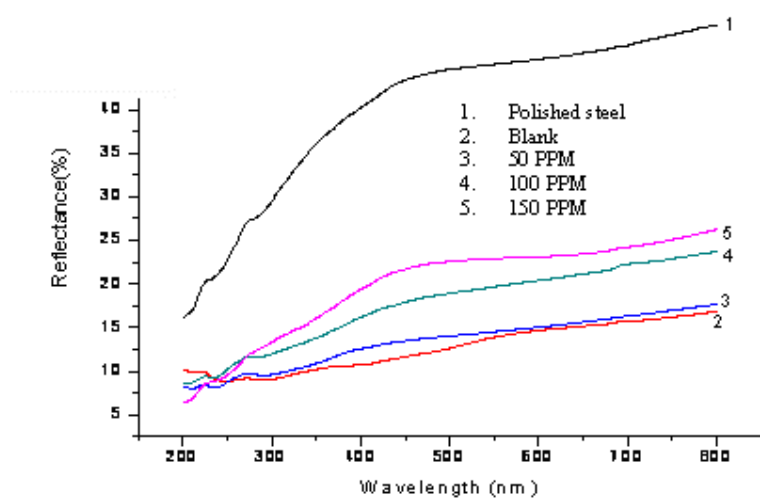


Figure 4. UV Reflectance curves for Mild Steel in salt water with different concentrations of DCX compound.

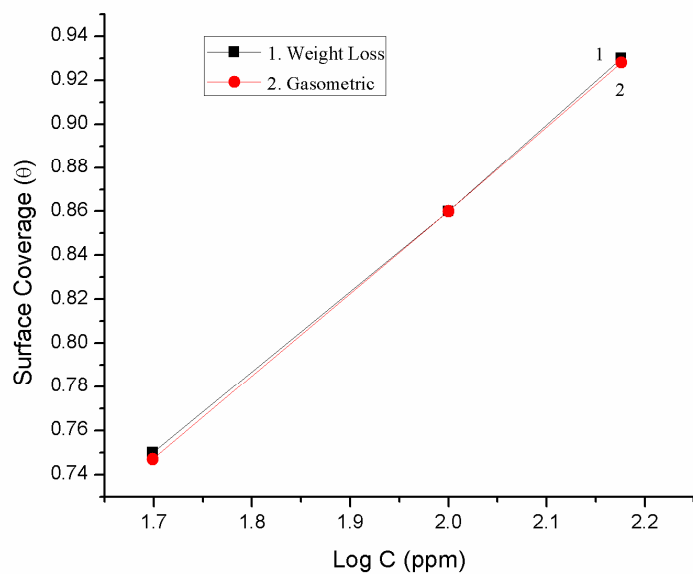


Figure 5. Temkin's adsorption isotherm for Dicloxacillin in brine water.