

Studies on the reduction of mild steel corrosion and hydrogen permeation in acidic media***S.Karthikeyan* , P.A.Jeeva, K.Raja, M.Paramasivam#***

* Manufacturing Division, School of Mech.and Building Sciences, VIT University,
Vellore, India-632014

CP-BED research lab , Batteries Division,CSIR-CECRI,Karaikudi-630006,India

Abstract

The reduction of corrosion and hydrogen permeation through mild steel in 0.5M H₂SO₄ and 1M HCl has been studied using weight loss measurements and various electrochemical techniques in the presence and absence of a green inhibitor viz., Carbenicillin(CBN) . The inhibitor is found to be more inhibitive in H₂SO₄ than in HCl. Potentiodynamic polarization studies clearly justify the fact that this compound acted as a mixed inhibitor; but predominantly as a cathodic inhibitor. Hydrogen permeation studies and AC impedance measurements also confirm the improved performance of the compound in H₂SO₄. The adsorption of this compound on the mild steel surface follows Temkin's adsorption isotherm.

Keywords : Corrosion inhibitor, Carbenicillin(CBN) , hydrogen permeation

* corresponding author (skarthikeyanphd@yahoo.co.in)

1.Introduction

Mild steel is an important category of metals due to its excellent mechanical properties. It is extensively used under different conditions in chemical and allied industries in handling acidic, alkaline and salt solutions. Mild is used in industries as pipelines for petroleum industries, storage tanks, reaction vessel and chemical batteries [1]. Acid solutions are widely used in many industrial processes. Acids are used for acid cleaning, pickling and descaling due to their chemical properties [2–5]. Acids cause damage to the substrate, because of their corrosive nature. Several methods were used to decrease the corrosion of metals in acidic medium, but the use of inhibitors is most commonly used [6–10].

Organic compounds are widely used as corrosion inhibitors for mild steel in acidic media [11–16]. The rate of corrosion decreases by adsorption of organic inhibitors on the metal surface. The inhibitors block 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 non environment friendly. Research activities in recent times are geared towards developing the cheap, non-toxic drugs as environment friendly corrosion inhibitors [17–21].

The aim of this work is to investigate the corrosion protection efficiency of Carbenicillin(CBN) for mild steel corrosion in 1M H₂SO₄. We came to know that exceedingly few reports are available by using this compound as corrosion inhibitor in 0.1M H₂SO₄ [22–24]. No concrete report is available for the use these compounds as corrosion inhibitors in 1M H₂SO₄. From the literature the higher concentration of H₂SO₄ acts as pickling solution for mild steel for electroplating, battery electrodes using sulphur containing organic compounds. Use of this inhibitor in 1M H₂SO₄ will reduce the metal loss in acid medium. The compound is large enough and sufficiently planar to block more surface area on the mild steel.

The inhibition efficiency was calculated using weight loss measurement, potentiodynamic polarization studies, impedance techniques, hydrogen permeation studies and diffuse reflectance methods. A definite correlation exists between different types of descriptors and measured corrosion inhibition efficiency for Carbenicillin(CBN) using chemical and electrochemical techniques.

2.Experimental

Mild steel specimens of compositions, C = 0.07%, P = 0.08%, Si = 0%, S = 0%, Mn = 0.34% and Fe remainder, and of size 5 x 2 x 0.025 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.

All the inhibitors were preliminarily screened by a weight loss method described earlier. [9] Both cathodic and anodic polarisation curves were recorded galvanostatically (1 mA s⁻¹) using corrosion measurement system BAS Model: 100A 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 M HCl and Hg/HgSO₄/0.5 M 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.⁴ Double layer capacitance (C_{dl}) and charge transfer resistance values (R_c) were obtained using AC impedance measurements as described in an earlier publication."

3. RESULTS AND DISCUSSION

3.1 Weight loss and Gasometric measurements

Table 1 gives the values of inhibition efficiency for different concentrations of Carbenicillin(CBN) for the corrosion of mild steel in 1M HCl and 0.5 M H₂SO₄ obtained from weight loss and gasometric measurements. It is found that the compound inhibits the corrosion of mild steel in both acids, but more effectively in H₂SO₄. This can be attributed to the lesser adsorption of sulphate ions on the metal surface, thereby leaving more space for the organic molecules to get adsorbed.

But in the of HCl the stronger adsorption of the chloride ions on the metal surface leaves less space for organic molecules to get adsorbed. So in H_2SO_4 , the coverage of the metal surface by the organic molecules is significantly more, giving rise to higher values of inhibition efficiency for all concentrations of the compound used [9–12].

It is found that there is very good conformity between the values of inhibition efficiency obtained by weight loss and gasometric methods.

3.2 Galvanostatic polarization studies

Table 2(a) and 2(b) give values of 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 galvanostatic polarization curves for mild steel in 1M HCl and 0.5 M H_2SO_4 containing different concentrations of Carbenicillin(CBN) . It can be seen from this table that values of Tafel slopes and I_{corr} are very much similar to those reported earlier [12,13].

It can also be seen from these tables that increasing concentrations of Carbenicillin(CBN) 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 Carbenicillin(CBN) brings down 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 galvanostatic polarization studies agree very well.

3.3 Hydrogen permeation measurements

Hydrogen permeation measurements results for the corrosion of mild steel in the presence and absence of the inhibitor are presented in Table 3. Hydrogen permeation current for mild steel in 1M HCl is more, because of the aggressive nature of chloride ions. It can be seen from the table that the presence of Carbenicillin(CBN) in both acids enhances the permeation current.

The enhancement in permeation current can be attributed to the decomposition of the compound on the mild steel surface [14]. In all the mechanisms suggested so far, invariably the product of decomposition of Carbenicillin(CBN) is H_2S , which is evolved on the metal surface. Its formation can be detected by radiometric measurements, if labeled thiourea or its derivatives are used [15]. The whole process takes place in two stages. In the first stage, Carbenicillin(CBN) molecules are adsorbed on the metal surface by virtue of the interaction of lone pairs of electrons of nitrogen and sulfur. In the second stage, the adsorbed molecules of the compound slowly undergo chemical changes. The molecule usually decomposes with the formation of H_2S by the action of hydrogen evolved on the metal.

Hough et al [16] 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. TrabANELLI and Zucchi [17] 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 Carbenicillin (CBN) is more. A similar observation has been made by Lahiri et al [18] that hydrogen permeation current increases with increase in the concentration of di-ortho tolyl thiourea.

3.4 Impedance studies

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 Carbenicillin (CBN) in both the acids. Values of double layer capacitance are found to be more for 1M HCl than for 0.5M H_2SO_4 . It is found that values of C_{dl} are brought down by increasing concentrations of Carbenicillin (CBN) in both the acids.

This can be attributed to increasing adsorption of the compound on the metal surface with increase in its concentration.

A plot of surface coverage (θ) versus $\log C$ gives a straight line showing that the adsorption of CBN on the mild steel surface from both acids obeys Temkin's adsorption isotherm. This points to corrosion inhibition by this compound, being a result of its adsorption on the metal surface.

3.5. Quantum chemical calculations

Quantum chemical calculations were carried out to investigate the adsorption and inhibition mechanism of the inhibitors. Figure 1 shows the optimized structure of Carbenicillin. The values of calculated quantum chemical parameters i.e. E_{HOMO} (highest occupied molecular orbital), E_{LUMO} (lowest unoccupied molecular orbital), ΔE (energy gap), μ (dipole moment), σ (softness) etc. are summarized in table-5.

E_{HOMO} is associated with the electron-donating ability of the molecule. Several researchers have shown that the adsorption of an inhibitor on metal surface can occur on the basis of donor-acceptor interactions between the π -electrons of heterocyclic atoms and the vacant d-orbitals of the metal surface atoms [19–21]. A high value of E_{HOMO} indicates a tendency of a molecule to donate electrons to acceptor molecules with low energy empty molecular orbital. Increasing values of E_{HOMO} facilitates the adsorption and increases the inhibition efficiency by influencing the transport process through the adsorbed layer [20]. E_{LUMO} indicates the ability of the molecule to accept the electrons, hence these are acceptor states.

The lower the value of E_{LUMO} , the more probable is that the molecule can accept electrons and increase the inhibition efficiency. Regarding ΔE ($E_{\text{LUMO}} - E_{\text{HOMO}}$) lower values of energy difference will cause higher inhibition efficiency because energy to release electron from last occupied orbital will be low. When dipole moment is concerned higher values of μ , will favours a strong interaction of inhibitor molecule with the metal surface [22].

Other indicators are absolute electro negativity (χ), absolute hardness (η). Absolute electro negativity is a chemical property that describes the ability of a molecule to attract electron towards itself in a covalent bond. Absolute hardness is measured by the energy gap between E_{HOMO} and E_{LUMO} . Absolute softness σ is the reciprocal of the hardness. χ , η , σ are calculated using the energies of HOMO and LUMO orbital's of the inhibitor molecules are related to the ionization potential (I), electron affinity (A) by the following relations

$$\chi = I + A / 2, \eta = I - A / 2, \sigma = 2 / I - A$$

$$\text{Where } I = -E_{\text{HOMO}}, A = -E_{\text{LUMO}}$$

The results deduced indicate that the electron flow will happen from the molecule with low electro negativity towards that of higher value until the chemical potentials are same. In our studies the best inhibition effect is shown by Carbenicillin with low electro negativity.

The higher value of dipole moment and lower total energy for Carbenicillin(CBN) indicates the strong interaction of inhibitor with metal that leading to improved adsorption. The halogen atom exerts +M effect on Carbenicillin, leads to enhanced corrosion inhibition.

From figure 2 it can be observed that the energy highly occupied molecular orbital's (HOMO) are localized on hetero atoms for Carbenicillin. From Figure 3 it is observed that lowest unoccupied molecular orbital's (LUMO) of CBN, which is responsible for the better adsorption.

4. Conclusions

1. Carbenicillin(CBN) inhibits the corrosion of mild steel in both acids, but shows a better performance in 0.5M H₂SO₄.
2. The inhibition of corrosion of mild steel in both the acids, by the compound is under cathodic control.
3. The presence of CBN 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 Temkin's adsorption isotherm.

References:

- [1]. I.Singh ,. *Corrosion* , **49**(1993) 473.
- [2]. R.Agrawal, T.K.G Namboodhri , *Corr. Sci.* 30(1990)37.
- [3]. I.A. Sekine, A. Masuko Senoo . *Corr. Sci.* 43(1987)553.
- [4]. M. A. Quraishi, F. A. Ansari ,D.Jamal, *Materials Chemistry and Physics*,
30(2003) 687.
- [5]. M. A. Quraishi, M.A.W. Khan, M. Ajmal,. *Anti-Corros. Methods Mater*,
43(1996) 5.
- [6]. S. Murlidharan, S.V.K. Iyer, *Anti-Corros. Methods Mater*, 44(1997)100.
- [7]. N. Al-Andis, E. Khamis, H. Al-Mayouf, Aboulb Enicm. *Corros. Prev. Control*,
43(1995)13.
- [8]. B. Hammouti, M. Aouniti, Taleb, M. Brighli, S. Kertit,. *Corrosion*,
51(1995)441.
- [9]. K. Madhavan ,S. Karthikeyan, S.V.K Iyer,.*Ind.J.Chem.Tech*, 9(2002) 68.

- [10]. M.A.V Devanathan, B. Tilak, Chem.Revs, 65(1965)635.
- [11]. Soriaga, Chem.Revs, 90(1990)77.
- [12]. Reeta Agarwal, T.K.G. Namboodri, Corros.Sci,30(1990)37.
- [13]. K.Madhavan,. PhD Thesis, Alagappa University,India,June (1996)
- [14].W. Waiter, J. Voss, Chemistry of Amides, Zabersky
Edition,Interscience,Newyork,1970,p-187.
- [15].T.JLane, A. Yamaguchi, J.V Quachano, Ryan,J.Am.Chem.Soc,81(1959)382
- [16]. Gu Hough;Zhou Zhongbai ;Tao Yingachu and Yao Luaw.Wahan Dauxe
Xuebao Ziran

Kexuebaw, 2(1982)57
- [17]. G. Trabanelli and F. Zucchui ,Rev.on Corrosion and coatings, 1(1973),47.
- [18]. A.K. Lahiri, N.G Banerjee,. NML Tech.Journal,5(1963)33 .

- [19] Issa R M, Awad M K and Atlam F M, *Appl.Surf.Sci.*, **255** pp2433–2441, 2008.
 [20]. Khaled K F and Al-Qahtani M M, *Mater. Chem. Phys.*, **113**,pp150–158, 2009.
 [21]. Laarej K, Bouachrine M, Radi S, Kertit S and Hammouti B, *E-Journal of Chemistry*, **7**, **2**, pp419–424, 2010.
 [22]. Ambrish Singh, Quraishi M A, Avyaya J N, and Eno. E. Ebenso, *Res Chem Intermed.*, DOI 10.1007/s11164-012-0577-y, 2012.

Table 1. Values of inhibition efficiency for the corrosion of mild steel in 1M HCl and 0.5 M H₂SO₄ in the presence of different concentrations of Carbenicillin(CBN) obtained from weight loss and gasometric measurements.

Concentration of Inhibitor (mM)	Inhibition efficiency (%)			
	HCl		H ₂ SO ₄	
	Weight loss Studies	Gasometric measurements	Weight loss studies	Gasometric measurements
2	83.5	83.4	93.2	93.0
10	85.6	85.1	94.5	94.7
18	90.4	90.4	96.6	96.4
26	98.5	98.4	99.2	99.1

Table 2.a Corrosion kinetic parameters of mild steel in 1M HCl in the presence of different concentrations of Carbenicillin(CBN) obtained from galvanostatic polarization studies.

Concentration of Inhibitor (mM)	E_{corr} (mV)	Tafel slopes in mV in dec^{-1}		I_{corr} mA cm^{-1}	Inhibition efficiency (%)
		b_a	b_c		
Blank ---	-512	65.2	120.3	2.80	
2 83	-495	73.1	126.2	0.48	
10 85.3	-487	76.3	136.6	0.41	
18 90.7	-476	78.1	140.3	0.26	
26 98.4	-471	83.2	146.6	0.04	

Table 2.b Corrosion kinetic parameters of mild steel in 1M H₂SO₄ in the presence of different concentrations of Carbenicillin(CBN) obtained from galvanostatic polarization studies.

Concentration of Inhibitor (mM)	E _{corr} (mV)	Tafel slopes in mV in dec ⁻¹		I _{corr} mA cm ⁻¹	Inhibition efficiency (%)
		b _a	b _c		
Blank ---	-909	71	131	2.35	
2 93.0	-895	71	137	0.164	
10 94.2	-886	77	138	0.136	
18 96.4	-881	80	141	0.08	
26 98.9	-876	81	151	0.02	

Table 3 Values of permeation current for the corrosion of mild steel in 1M HCl and 0.5 M H₂SO₄ in the presence of different concentrations of Carbenicillin(CBN) .

Concentration of Inhibitor (mM)	Steady state permeation current (μA)	
	1M HCl	0.5M H ₂ SO ₄
Blank	22.4	11.5
2	25.2	12.7
10	23.3	13.6
18	24.1	14.7
26	24.7	15.4

Table 4. Impedance parameters for the corrosion of mild steel in 1M HCl and 0.5 M H₂SO₄ in the presence of different concentrations of Carbenicillin(CBN) .

Concentration of Inhibitor (mM)	HCl		H ₂ SO ₄	
	Charge Transfer resistance (R _t) Ohm.cm ²	Double layer capacitance (C _{dl}) μF.cm ⁻²	Charge Transfer resistance (R _t) Ohm.cm ²	Double layer capacitance (C _{dl}) μF.cm ⁻²
Blank	43.8	243.2	6.6	183.8
2	31.2	171.6	32.2	177.2
10	42.7	135.7	44.7	130.9
18	71.4	121.9	77.9	108.7
26	89.4	102.3	91.3	97.9

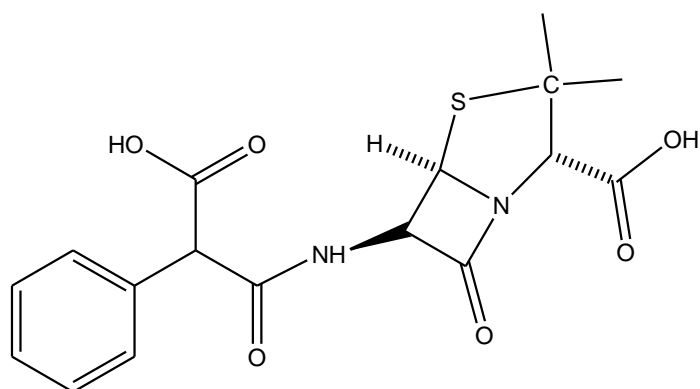


Fig 1.Optimized structure of Carbenicillin

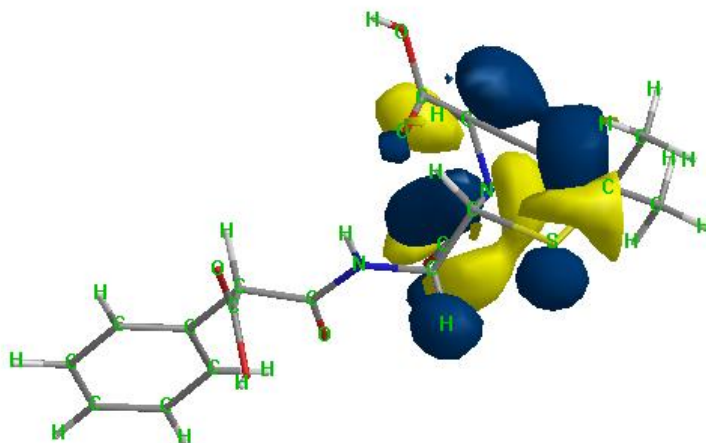


Fig 2.HOMO of Carbenicillin

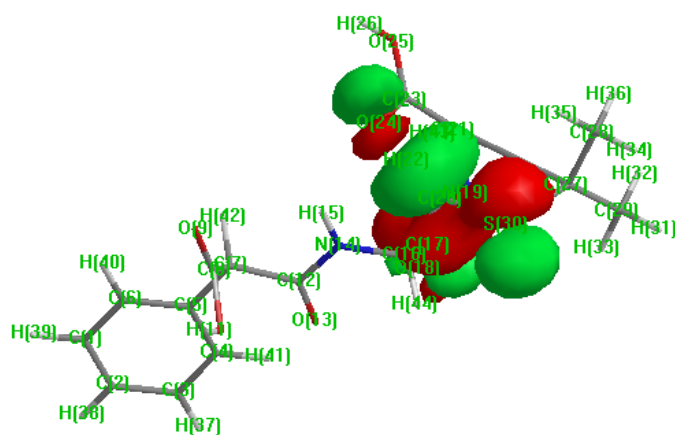


Fig 3. LUMO of Carbenicillin