Corrosion studies of Copper powder coated mild steel parts in salt water

S.Karthikeyan, K.Raja, A.S.S.Balan, P.A.Jeeva*

School of Mechanical and Building Sciences, VIT University, Vellore – 632014, India.
(*Corresponding author: p.a.jeeva@gmail.com)

Abstract

The corrosion inhibition of copper powder coated mild steel sheets in 5% NaCl with Ticarcillin (TCN) as non-toxic inhibitor has been reported by Weight loss, potentiodynamic polarization, electrochemical impedance spectroscopy, hydrogen permeation studies and quantum mechanical studies. All these techniques indicate that the TCN inhibits the corrosion of copper coated steel in 5% NaCl medium to great extent. Polarization studies confirmed that the mode of inhibition follows mixed type. The adsorption of the compounds on copper coated steel surface obeys Langmuir adsorption isotherm.

Introduction

Copper powder coated mild steel is widely used in the applications such as electric wires, circuits, automotive metal parts and house hold fashion materials because of its excellent corrosion resistance in moisture and sea water media[1-6]. However, several reports on failure of copper coated pipes and tanks have been studied as being due to corrosion processes in chloride environment, which is evident from the formation of rust in those systems that lead to severe damage to industrial components [7].

Numerous reports were available for the resistance of corrosion of copper coated mild steel in acidic medium, but the use of inhibitors is an important one [8-10].

The usage of inhibitors is inexpensive and real method to reduce electrochemical corrosion. Numerous organic compounds which have π bonds and contain hetero atoms were reported as corrosion inhibitors by several investigators [11-16] for dissolution of iron metal in acid medium. Research findings in recent times are stimulated towards emerging the cheap, non-toxic drugs as environment responsive corrosion inhibitors [17-24].

The literature review indicates that few antibiotics have been reported as corrosion inhibitors for the corrosion of steel and aluminium in acidic and alkaline media [25]. Very Recently, Ampicilin drug [26] was reported as inhibitor for the corrosion of mild steel in 1 M HCl. Nevertheless, no concrete results have been published for the corrosion inhibition of

1

copper coated mild steel sheet in 5% NaCl with use of Ticarcillin (TCN) as inhibitor and hence the present study.

The inhibition efficacies of the compound were calculated using mass loss, electrochemical techniques. Rarely, the usage of hydrogen permeation measurement studies for this green inhibitor established the prominent performance of the inhibitors. This inhibitor is big enough, amply planar and could be able to block more galvanized steel surface area .

Experimental Section

Materials

Copper powder coated specimens of size 1×4 cm^2 were used for mass loss and electrochemical studies. The aggressive solution of 5% NaCl [AR Grade] is used for all the studies. The antibiotic namely Ticarcillin (Mol.Weight = 384.42 g/Mol) was procured from medical shop and then purified using chromatographic techniques. The structure of the green inhibitor is given in the fig.1 Electrochemical experiments were performed with a three electrode cell assembly with copper powder coated samples as working electrode, platinum as counter electrode and saturated calomel [SCE] as the reference electrode.

Weight Loss Studies

Weight loss and hydrogen permeation studies were carried out as described earlier [27]. The concentrations of green compound used for weight loss and electrochemical study were from 10 PPM to 100 PPM. Copper coated metal specimens of size 1×4 cm^2 were abraded with different grade emery papers and then degreased with acetone. The cleaned surfaces were washed with double distilled water, air dried and preserved in the desiccator. The mass loss study was followed at room temperature for three hours in 5% NaCl. The inhibition efficiency (IE%) was calculated by the following equation ,

$$\text{Inhibition Efficiency (IE\%)} = (W_a - W_p / W_a) \times 100 \qquad (1)$$

where W_a & W_p are the weight loss values in absence and presence of the green inhibitor.

Potential-Current Measurements by Electrochemical Studies

Potentiodynamic polarization measurements were monitored in a conventional three electrode cylindrical glass cell, using CH electrochemical analyzer at a scan rate of 5 mV s^{-1}. Before carrying out the polarization measurements the solution was deaerated for 20 min. and the working electrode was maintained at its corrosion potential for 20 minutes until a steady state was obtained. The Copper metal surface was put in to various concentrations of inhibitors in 100 mL of 5% NaCl at room temperature. The inhibition efficiency (IE%) was calculated using the equation,

Inhibition Efficiency (IE%) $=$ $(I_a - I_p / I_a) \times 100$ (2)

where I_a and I_p are the corrosion current density without and with the green inhibitor respectively.

The potentiodynamic current–potential curves were recorded by changing the electrode potential automatically from −950 mV to +900 mV versus the open circuit potential. The corresponding corrosion current (I_{corr}) was recorded. Tafel plots were made by plotting E versus log I. Corrosion Potential (E_{corr}), corrosion current density (I_{corr}) and cathodic and anodic slopes (β_c and β_a) were calculated according to known procedures.

Impedance measurements were done in the frequency range from 0.1 to 10000 Hz by means of amplitude of 20 mV and 10 mV peak to peak with an AC signal at the open–circuit potential. Charge transfer resistance (R_{ct}) and double layer capacitance (C_{dl}) values were got from Nyquist plot [28–30]. The percentage inhibition efficiency was calculated from the equation,

Inhibition Efficiency (IE%) $=$ $(C_{dl}{}^a - C_{dl}{}^p / C_{dl}{}^a) \times 100$ (3)

where $C_{dl}{}^a$ and $C_{dl}{}^p$ are the charge transfer resistance of copper coated sheets without and with green inhibitor respectively.

Results and Discussion

Weight Loss Studies

The values of inhibition efficiency (IE%) and surface coverage (θ) calculated for green inhibitor at different concentrations for the corrosion reaction of copper coated mild steel sheets in 5% NaCl from the weight loss data is summarized in the Table 1. It is proven that inhibition efficiency increases with increase in the inhibitor concentration. It was also ostensible that corrosion rate decreases with increase in green inhibitor concentration. It was ascertained that inhibitors retard the copper coated metal corrosion at all the concentrations used in the study. Maximum inhibition efficiency is observed at 100 ppm concentrations of the Ticarcillin

Potential–Current Measurements by Electrochemical Studies

Polarization results such as the values of corrosion potential [E$_{corr}$], corrosion current densities (I_{corr}), anodic tafel slope (β_a) ,cathodic tafel slope (β_c) surface coverage (θ) and inhibition efficiency (IE%) were calculated using polarization curves for the corrosion of copper coated sheets in 5% NaCl are shown in Table 2.

It can also be evident from the table that corrosion current (I_{corr}) value declines with increase in the concentration of the antibiotics. Further it is established that increasing concentrations of green inhibitor enhance the values of both β_a and β_c, in a random fashion. Hence the inhibition of corrosion by Ticarcillin compound is chiefly under mixed type. The

inhibition efficiency (IE%) and surface coverage (θ) increases with increase in TCN dosage in the experiment. The maximum inhibition efficiency was obtainable at 100 ppm concentration. A definite correlation occurs between the results obtained from weight loss and potential-current studies for the above inhibitor.

Electrochemical Impedance Studies

The Nyquist representations of impedance behavior of copper powder coated mild steel in 5% NaCl with and without addition of various concentrations of Ticarcillin molecules are given in table 3. The table also contained the values of charge transfer resistance (R_{ct}) and double layer capacitance (C_{dl}) calculated from Nyquist plots for the dissolution of copper power coated mild steel in sea water. It can be envisaged that the values of R_{ct} was observed to increase with increase in concentration of inhibitor in the sea water. It was also found that values of C_{dl} are brought down by enhancing concentrations of Ticarcillin in the sea water medium. This can be accredited to the increasing adsorption of the inhibitor on the metal surface with increase in its concentration [33].

Adsorption Isotherm

The degree of Surface Coverage (θ) for different concentrations of Ticarcillin in 5% NaCl has been calculated from weight loss, Polarization and Electrochemical Impedance studies. The obtained data was tested graphically for fitting suitable isotherm [34- 36]. A straight line was observed by plotting log (C/θ) Vs log C which ratifies that the adsorption of this green inhibitor follows Langmuir adsorption isotherm.

The Langmuir isotherm for the adsorbed layers is given by the equation [37],

$$C_{inh}/\theta = 1/K_{ads} + C_{inh} \tag{4}$$

where K_{ads} is the equilibrium constant of the adsorption/desorption process. Adsorption equilibrium constant (K_{ads}) and free energy of adsorption [ΔG^{o}_{ads}] were calculated using the equation [38]

$$K_{ads} = 1/C_{inh} \times \theta/1-\theta \tag{5}$$

$$\Delta G^{o}_{ads} = -2.303RT \log [55.5 K_{ads}] \tag{6}$$

where 55.5 is the molar concentration of water in solution [38-39]. R is the gas constant, T is the temperature. The values of adsorption equilibrium constant (K_{ads}) and free energy of adsorption (ΔG^{o}_{ads}) are given in Table 4. The negative values of (ΔG^{o}_{ads}) showed

that adsorption of Ticarcillin on copper coated mild steel   surface in chloride environment is a spontaneous process. It is well-known that values of (ΔG^{o}_{ads}) is of order 20 kJmol^{-1} or lower indicates a physisorption, those of order of -40 kJmol^{-1} or higher involve charge sharing or transfer from the inhibitors to the metal surface to form a co-ordinate bond, the process known as chemisorption. The values of free energy of adsorption (ΔG^{o}_{ads}) in this study lies in the range -28 to -32 kJmol^{-1}, demonstrating that the adsorption is not a simple physisorption but it may include some other interactions [40-43].

Mechanism of Inhibition
In Ticarcillin , the presence of lone pairs of electrons of nitrogen and sulfur atoms of both benzamino and sulfoxide groups along with oxygen atom   which favour the adsorption of Ticarcillin on oxidized copper surfaces by virtue of donating electrons to the positively charged Fe atoms when exposed to chloride environment.

Mechanism of Inhibition
In Ticarcillin , the presence of lone pairs of electrons of nitrogen and sulfur atoms of both thienyl acetamino and oxa thia groups along with oxygen atom of azabiccyclo heptane moiety which favour the adsorption of Ticarcillin on oxidized copper surfaces by virtue of giving electrons to the positively charged Fe atoms when exposed to chloride environment.

Quantum Mechanical Studies
Quantum mechanical calculations were carried out to explore the adsorption and inhibition mechanism of the Ticarcillin compound on the corrosion of copper coated mild steel surfaces in 5% NaCl. Figure 2 & 3 indicate HOMO and LUMO structure of Ticarcillin inhibitor. 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) etc. are presented in table-5. E_{HOMO} is related to the electron-releasing capability of the inhibitor molecule while E_{LUMO} is explained for electron with drawing capacity of inhibitor molecule. In the present investigation, the adsorption of a Ticarcillin on copper surface acquired on the basis of donor-acceptor interactions between the π-electrons of nitrogen and sulphur atoms of thienyl acetyl amino and oxa thia groups along with oxygen atom of azabiccyclo heptane moiety is responsible for its coverage on mild steel surfaces evidenced from the   dense electrons cloud in HOMO and LUMO structure wherein the electronic cloud is similar in both orbitals. It is well understood that if both HOMO and LUMO structures are resembling each other, the resultant adsorption of inhibitor will be better on metal surface. The gap between HOMO-LUMO energy levels of molecules was another important factor that needs to be considered. Higher the value of ΔE of an inhibitor,

higher is the inhibition efficiency of that inhibitor. It has been reported that, large values of the dipole moment will improve corrosion inhibition. Based on the values of ∆E and dipole moment, the compound TCN has strongly been adsorbed on copper steel surface immersed in 5% NaCl .

Conclusions

The controlled dissolution of Copper coated mild steel surfaces were monitored and controlled in 5% NaCl solutions at different temperatures (313–333 K) without and with various concentrations of Ticacillin, a green inhibitor by adapting chemical and electrochemical methods. The main conclusions are:

(i) Ticarcillin antibiotic exhibited inhibiting properties for copper powder coated mild steel corrosion in 5% NaCl effectively.

(ii) Tafel polarization plots designated that inhibitor was showing mixed mode of inhibition.

(iii) Rates of corrosion obtained from the impedance measurements were in good agreement with those recorded using the Potentiodynamic polarization. This confirms the validity of the corrosion rates measured by the potentiodynamic polarization.

(iv) Adsorption of the Ticarcillin on copper coated surfaces obeyed Langmuir isotherm.

(v) Apparent activation energies in the presence of Ticarcillin for the corrosion of copper coated steel in chloride medium lie in the range 28 to –32 kJmol^{-1}, demonstrating that the adsorption is not a simple physisorption.

(vi) Quantum mechanical results confirm the remarkable performance of Ticarcillin green inhibitor through its real adsorption on copper surfaces immersed in 5% NaCl.

References

[1]   Rhodanine azosulpha drugs as corrosion inhibitors for corrosion of 304 stainless steel in hydrochloric acid solution, M. Abdallah, Corros. Sci,44, pp728, 2002

[2]   Antifungal drugs as corrosion inhibitors for aluminium in 0.1 M HCl, I.B. Obot, N.O. Obi-Egbedi, S.A. Umoren, Int. J. Electrochem. Sci, Vol. 4,2009

[3]   Torsemide and Furosemide as Green Inhibitors for the Corrosion of Mild Steel in Hydrochloric Acid Medium, S. Harikumar and S. Karthikeyan, Industrial and Engineering Chemistry Research, 52(22), pp. 7457-7469, 2013

[4]   Adsorption characteristics and corrosion inhibitive properties of clotrimazole for Aluminium corrosion in hydrochloric acid, I. Obot,N.Umoren, Int. J. Electrochem. Sci, Vol. 4, pp. 863-877, 2009

[5]   Inhibition of mild steel corrosion in hydrochloric acid solution by cloxacillin drug, S. Harikumar and S. Karthikeyan, Journal of Materials and Environmental Studies, Vol.5, pp. 925-934, 2012

[6]   Influence of some thiazole derivatives on corrosion of mild steel in hydrochloric acid, M.A. Quraishi, M.A.W. Khan, M. Ajmal, Anti-Corros. Methods Mater, 43, 5, 1996

[7]   The inhibitive action of cyclohexyl thiourea on corrosion and hydrogen permeation through mild steel in acidic solutions, S. Karthikeyan, S.Harikumar, G. Venkatachalam, S.Narayanan, R. Venckatesh, International Journal of ChemTech Research, 4(3), pp. 1065-1071, 2012

[8]   Electrochemical studies of two corrosion inhibitors for iron in HCl, Al-Andis, N.Khamis, E. Al-Mayouf, H. Aboul b Enicm, Corros. Prev. Cont rol, 42, 13,1995

[9]   L-Methionine methyl ester hydrochloride as corrosion inhibitor of iron in 1 M HCl, B. Hamm outi, M. Aouniti, M. Taleb, M. Bri ghli, S. Kertit, Corrosion, 51,441, 1995

[10]   Influence of anions on corrosion inhibition and hydrogen permeation through mild steel in acidic solutions in the presence of p-tolyl thiourea, K. Madhavan, S. Karthikeyan, S.V.K. Iyer, Ind. J.Chem. Tech, 9, pp68, 2002

[11]   The Structure of the Electrical Double Layer at the Metal Solution Interface, M.A. Devanathan, B. Til ak, Chem.Revs, 65, pp.635, 1965

[12]   Surface coordination chemistry of monometallic and bimetallic eletrocatalysts, Soriaga, Chem.Revs, 90, pp77, 1990

[13]   The inhibition of sulphuric acid corrosion of 410 stainless steel by thioureas, Reeta Agarwal, T.K.G. Namboodri, Corros.Sci, 30, pp37, 1990

[14]   Mechanism of corrosion and its inhibition, K. Madhavan, PhD Thesis, Alagappa Uni versity, India, June 1996

[15]   W.Waiter Voss, J.Chemistry of Amides, Zabersky Edition, Interscience, Newyork, 187, 1997

[16] A.K. Lahiri, N.G. Banerjee, NML. Tech. Journal, 5, pp33, 1963

[17] Gu Hough, Zhou Zhongbai, Tao Yingachu , Yao Luaw, Wahan Dauxe Xuebao, Ziran Kexuebaw, 2, pp57, 1982

[18] G. Trabanelli and Zucchui F.Revon, Corrosion and coatings, 1, pp47, 1973

[19] The use of Quantum chemical methods in corrosion inhibitor studies, G. Gece, Corrosion Science, pp.2981-2992, 2008

[20] Inhibition Effect of Amoxicillin drug on the Corrosion of Mild Steel in 1N Hydrochloric acid Solution, S. Hari Kumar, S. Karthikeyan, S.Narayanan and K.N.Srinivasan, International Journal of ChemTech Research, 4(3), pp. 1077-1084, 2012

[21] The retardation of dissolution of Al-Sic composites in acidic medium – A green approach, V. Umasankar, S. Karthikeyan, M. Anthony Xavier, Journal of Corrosion Science and Engineering, 16, pp47, 2013

[22] Ethane-2- thioamido-4-amino-N-(5-methylisoxazol-3-yl)-benzene sulfonamide: A novel inhibitor for the corrosion of mild steel in 1N HCl , S. Karthikeyan, N. Arivazhagan, S. Narayanan, Journal of Corrosion Science &Engineering, Vol.16, 2013

[23] Performance characteristics of 1, 3-diorthotolyl thiourea on the corrosion of mild steel in 5% NaCl, S. Karthikeyan, N. Arivazhagan, D.Ramkumar, S. Narayanan, Journal of Corrosion Science &Engineering, Vol.16, 2013.

[24] Eddy NO, Odoemelam SA, Mbaba AJ (2008) Afri J Pure Appl Chem 2:132

[25] Roberta de Oliveira Ramos, Alice Battistin, Reinaldo Simoes Goncalves (2012)) J Solid State Electrochem 16:747

[26] Corrosion inhibition of mild steel in 1M H2SO4 by Ampicillin as an inhibitor, S. Hari Kumar, S. Karthikeyan, P.A. Jeeva, Journal of Corrosion Science and Engineering, Vol16, 2013

[27] Gokhan Gece (2011) Corros Sci 53:3873

[28] HariKumar S, Karthikeyan S (2012) International Journal of Current Research and Review, 4:96

[29] Muralidharan S, Madhavan K, Karthikeyan S & Venkatakrishna Iyer S (2002) Indian J chem technol 9 : 68

[30] Bentiss F, Lagrenee M, Traisnel M, Hornez JC (1999) Corros Sci 41:789

[31] Ashassi-Sorkhabi H, Shaabani B, Seifzadeh D (2005) Electrochim Acta 50:344

[32] Karthikeyan S , Neelakandan MA (2006) J Electrochem Soc India 56:84

[33] Devanathan MAV, Stachurski Z (1962) Proc Roy Soc 270:90

[34] Shukla SK, Quraishi MA (2009) Corros Sci 51:1990

[35] Madhavan K, Quaraishi MA, Karthikeyan S & Venkatakrishna Iyer S (2000) J Electrochem Soc India 49:183

[36] Madhavan K,Karthikeyan S & Venkatakrishna Iyer S (2001) J Electrochem Soc India 50:37

[37] Eddy NO and Ebenso EE (2010) E-J Chem 7 : S442
[38] Eddy NO, Odoemelam SA and Mbaba AJ (2008) African Journal of Pure and Applied Chemistry 2:132
[39] Lebrini M, Traisnel M, Lagrenee M, Mernari B, Bentiss F (2008) Corros Sci 50: 473
[40] Morad MS, Kamal El-Dean AM (2006) Corros Sci 48:3398
[41] Tang L, Mu G, Liu G (2003) Corros Sci 45:2251
[42] Khamis E, Bellucci F, Latanision RM, El-Ashry ESH (1991) Corrosion 47:677
[43] Geler E, Azambuja DS (2000) Corros Sci 42:631

Table 1 Values of Inhibition Efficiency and Surface coverage for the dissolution of copper coated metal in 5% NaCl in presence of different concentrations of Ticarcillin obtained from mass loss measurements

Inhibitor Conc.	Inhibition efficiency (IE) (%)	Surface coverage (θ)
Ticarcillin		
Blank	–	–
10 ppm	75.42	0.75
50 ppm	87.87	0.88
100 ppm	98.32	0.98

Table 2 Electro kinteic parameters and Inhibition Efficiency for corrosion of copper coated steel in 5% NaCl obtained by Polarization method in presence of Ticarcillin

Inhi. Con. (ppm)	E_{corr} (mV vs SCE)	I_{corr} (µA cm^{-2})	βa (mV dec^{-1})	βc (mV dec^{-1})	IE (mV dec^{-1})	θ (%)
Blank	−395.0	160.0	98.2	110.5	–	–
Ticarcillin						
10	−382.55	44.8	81.4	104. 2	72.0	0.72
50	−380.42	18.08	86.3	108.4	88.7	0.88
100	−381.62	2.56	74.2	96.2	98.4	0.98

Table 3 Electrochemical impedance parameters for dissolution of copper coated steel in 5% NaCl with and without Ticarcillin compound

Inhibitor Conc. (ppm)	R_{ct} (Ω cm^2)	C_{dl} (F cm^{-2})	IE (%)	Surface coverage (θ)
Blank	65.5	0.280	–	–
Ticarcillin				
10	87.45	0.0789	71.80	0.75
50	109.58	0.0310	88.70	0.87
100	330.32	0.0045	98.40	0.98

Table 4 Gibbs free energy parameters and adsorption equilibrium constant (K_{ads}) of green inhibitor (TCN) at different temperatures evaluated by mass loss method

Temperature [K]	K_{ads} Green inhibitor	$-\Delta G^{o}_{ads}$ [kJmol^{-1}] Green inhibitor
313	931	28.33
323	1164	29.82
333	1341	31.17

Table 5: Quantum mechanical parameters for Ticarcillin for the corrosion of copper surfaces

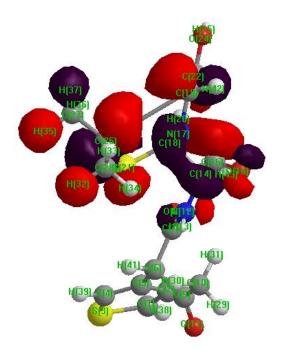| Inhibitor	LUMO (eV)	HOMO (eV)	ΔE (Cal.Mol^{-1})	Dipole moment (Debye)
Ticarcillin	−2.3928	−5.4584	3.0656	3.8

Figure 1.Structure of Ticarcillin

Fig 2.Highest molecular orbital of Ticarcillin molecules during the adsorption on Copper coated steel surfaces
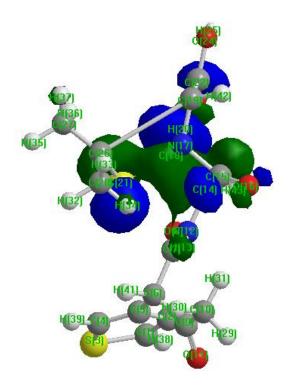
Fig 3. Lowest unoccupied molecular orbital of Ticarcillin molecules during the adsorption on copper coated surfaces