JCSE The Journal of Corrosion Science and Engineering
ISSN 1466-8858 Volume 17, Preprint 6 submitted 28 January 2014

Controlled dissolution of Aluminum 2024 in acidic medium

N.V.Lakshmi[1], S.Karthikeyan[1], N.Arivazhagan[2]*

[1] Surface Engineering Research lab, CNBT, VIT University, Vellore – 632014, India

[2]Manufacturing Division, School of Mechanical and building Sciences, VIT University, Vellore –632014, India

Abstract

The effect of Roxithromycin (RZ) on corrosion of aluminium in 0.1N Hydrochloric acid was investigated using weight loss measurements, potentiostatic polarization techniques and scanning electron microscopy The results showed that RZ is an effective inhibitor for aluminium in 0.1N HCl and inhibition efficiency is >90% at inhibitor concentration of 450ppm beyond this concentration its efficiency decreases. Polarization studies showed that RZ behaves as a mixed inhibitor. Electrochemical impedance studies were used to investigate mechanism of corrosion. Quantum chemical calculations were performed on roxithromycin and different quantum chemical properties were calculated and discussed

Keywords: Corrosion inhibitor, Roxithromycin, Polarization, Quantum chemical

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

Keywords: Al 2024, corrosion, impedance,quantum

1. Introduction

Aluminium and its alloys find wide range of technological applications because of their particular properties such as low density good

ISSN 1466-8858 Volume 17, Preprint 6 submitted 28 January 2014

appearance and corrosion resistance [1-4]. The corrosion resistance is due to the initial film formation of a compact and adherent passive film on the exposed surfaces But the protective film readily dissolve in presence of chloride ions. Usually hydrochloric acid is used for pickling, chemical and electrochemical etching of Al. Various methods are used to reduce the rate of corrosion of metals in acids, and among those methods use of inhibitor is most common. Numerous organic compounds were reported as corrosion inhibitor [5-7]. In recent years antibiotics have been used as corrosion inhibitors because there are environment friendly. Heterocyclic compounds containing hetro atoms such as sulphur, nitrogen and oxygen atoms containing multiple bonds adsorb on the metal surface and thus act as effective corrosion inhibitor for aluminium in acidic medium [8-12]. A systematic investigation was carried out on inhibition properties of roxithromycin. The corrosion inhibiting ability of these antibiotics could be due to its structure. All the above investigation demonstrates that roxithromycin is potential corrosion inhibitor. Roxithromycin is an effective antibiotic used for treating respiratory and urinary tract infections which comes under the class of lactone with 14 members of lactone moiety and an N-Oxime group is attached as side chain with lactone ring.

2. Experimental

Aluminium specimens of compositions, Cu= 4.3%, Mn = 0.5%, Mg = 1.3%,traces of Si, Zn, Ni, Cr and Al remainder, and of size 4 x 1 x 3 cm was used for weight loss. An aluminium plate of same composition as mentioned above and embedded in araldite resin with an exposed area of

ISSN 1466-8858 Volume 17, Preprint 6 submitted 28 January 2014

1cm^2 were employed for potentiodynamic polarization and AC impedance measurements.

The inhibitor was initially screened by a weight loss method [13]. Both cathodic and anodic polarization curves were measured potentiodynamically (1 mVs^{-1}) using corrosion measurement system. Model: CH Instruments 660E computerized electrochemical analyzer. A platinum wire, Ag/AgCl/KCl $_{(sat)}$ were used as auxiliary and reference electrodes, respectively [14]. Double layer capacitance (C_{dl}) and charge transfer resistance values (R_{ct},) were obtained using AC impedance measurements as described in a prior journal [15]. The surfaces of corroded and corrosion inhibited aluminium samples were examined by scanning electron microscopy, Model: S-3000H, Hitachi, Japan.

3. RESULTS AND DISCUSSION

3.1 Mass loss and Gasometric Studies

The values of inhibition efficiency (IE %) and the corrosion rate from mass loss method at different concentrations of Roxithromycin are summarized in table 1. It exhibits that the compound effectively inhibits the corrosion of aluminium in acidic medium. Maximum inhibition efficiency and decreased corrosion rate might be due to the increased adsorption and increased coverage of inhibitor on aluminium surface with increase in the inhibitor concentration.

The structure of the compound is given in Figure 1.

JCSE The Journal of Corrosion Science and Engineering
ISSN 1466-8858 Volume 17, Preprint 6 submitted 28 January 2014

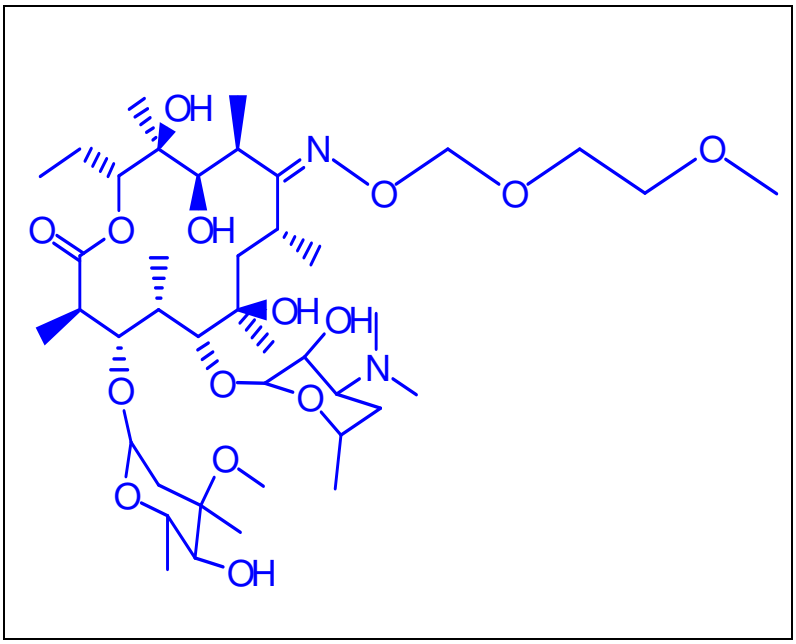


Figure 1. Structure of Roxithromycin.

The corrosion inhibition by roxithromycin can be due to the following interactions:

1. The interaction between the lone pairs of electrons of the nitrogen atoms of the N-Oxime moiety and oxacyclotetradecan groups and the positively charged Aluminium surface.

2. The interactions between the electrons donating $-CH_3$ groups in lactone rings and the positively charged metal surface.

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

JCSE The Journal of Corrosion Science and Engineering
ISSN 1466-8858 Volume 17, Preprint 6 submitted 28 January 2014

3.2 Potentiodynamic polarization studies

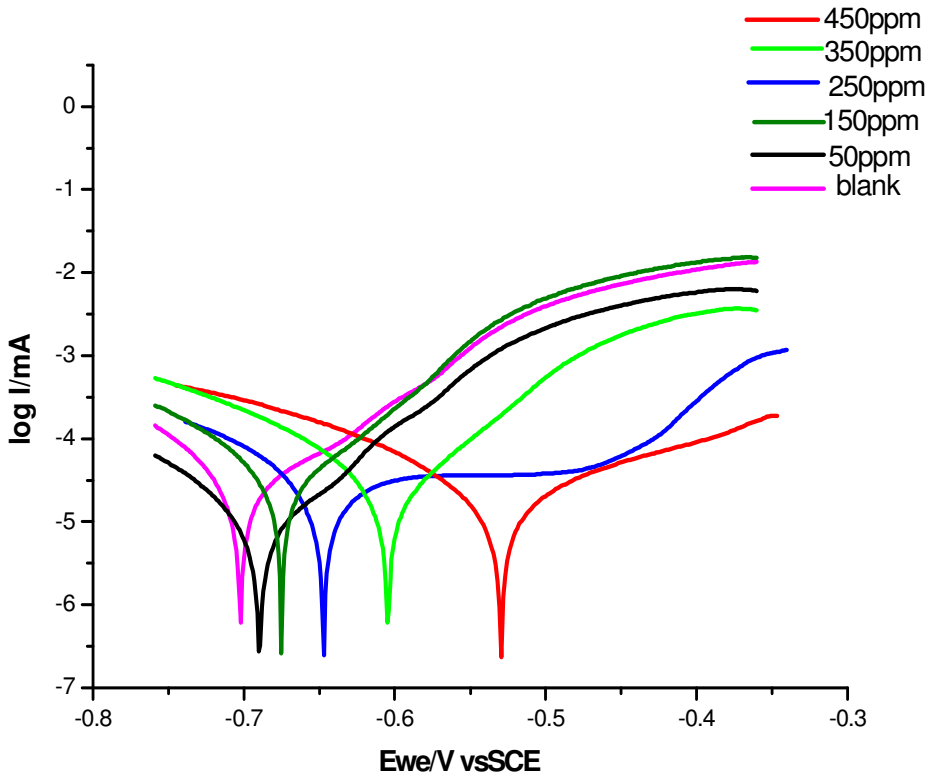


FIG 2 Polarization curves of Aluminium in 0.1M HCl at different concentrations of Roxithromycin

Polarization curves for aluminum in 0.1 N HCl at different concentrations of roxithromycin are shown in curve figure 2. The values of corrosion potential (E_{corr}), current densities (I_{corr}), anodic tafel slopes (β_a) and cathodic tafel slopes (β_c) and inhibition efficiency were calculated from potentiodynamic polarization curves of different concentrations of

ISSN 1466-8858 Volume 17, Preprint 6 submitted 28 January 2014

inhibitor are shown in table 2. It can be seen from this table that values of Tafel slopes and I_{corr} are very much reduced in comparison with uninhibited metal surface. Further it is demonstrated that increasing concentrations of roxithromycin enhances the values of both β_a and β_c in irregular fashion confirming that the inhibition of corrosion of Al in acidic medium is under mixed control [16-17]. Values of E_{corr} are shifted to less negative values in the presence of different concentrations of RZ. This could be the reason for forming firmly adherent adsorbed layer of RZ on the Al metal. It evident that most of the values of inhibition efficiency obtained by mass loss measurements and potentiodynamic polarization studies are with good agreement.

3.4 Impedance studies

The Nyquist representations of impedance behavior of aluminium in 0.1 N HCl with and without addition of different concentrations roxithromycin is shown in the fig 3, from which charge transfer resistance (R_t)and double layer capacitance (C_{dl}) values were calculated (table 3). It can be seen that the values of R_{ct} were found to increase at the expense of double layer capacitance with increase in concentration RZ [13-14]. This can be attributed to increased adsorption of the RZ drug on the Al surface with increase in its concentration.

A graph of surface coverage (ø) versus log C showed a straight line plot confirming that that the adsorption of RZ on Al surface from acid medium obeyed Temkins adsorption isotherm. This is main support to corrosion inhibition by this compound, as a result of its adsorption on the metal surface.

JCSE The Journal of Corrosion Science and Engineering
ISSN 1466-8858 Volume 17, Preprint 6 submitted 28 January 2014

3.5 Quantum chemical studies:

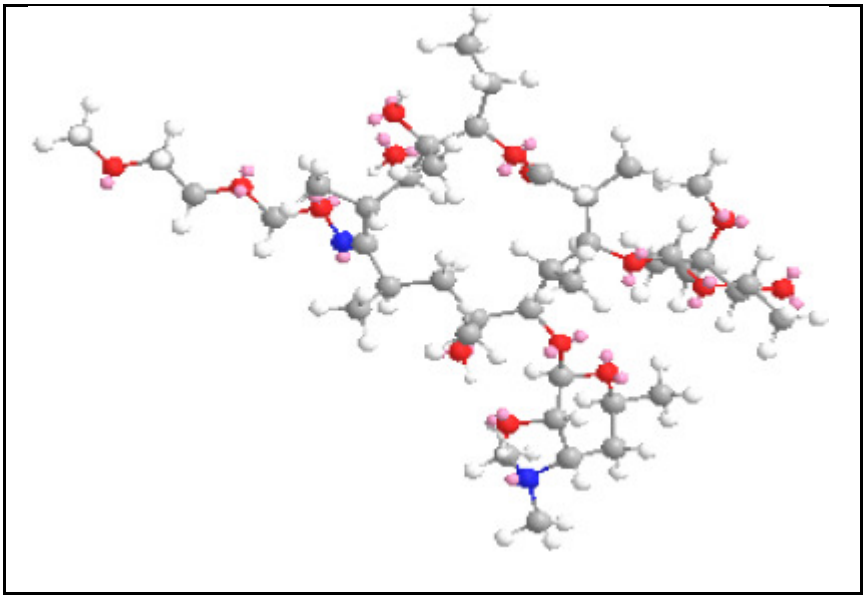


FIG 2 Optimized structure of roxithromycin

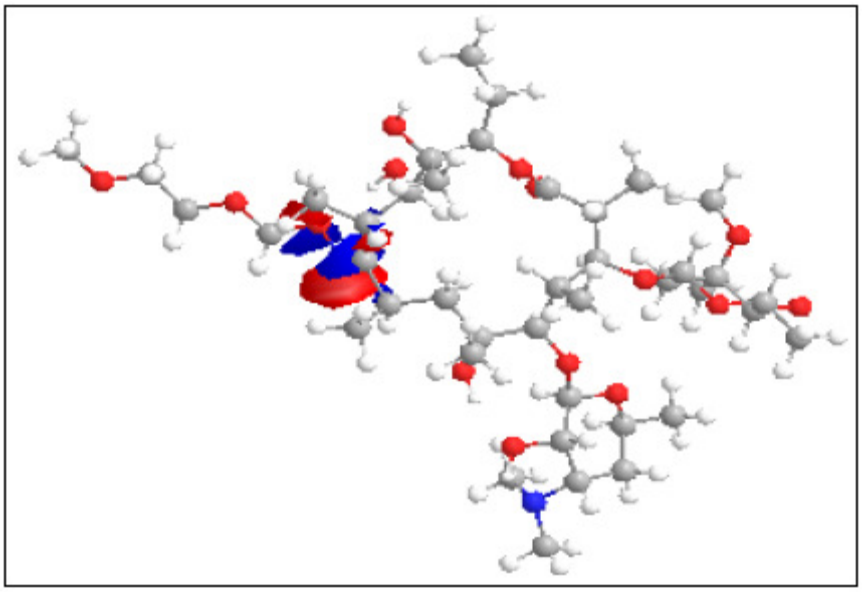
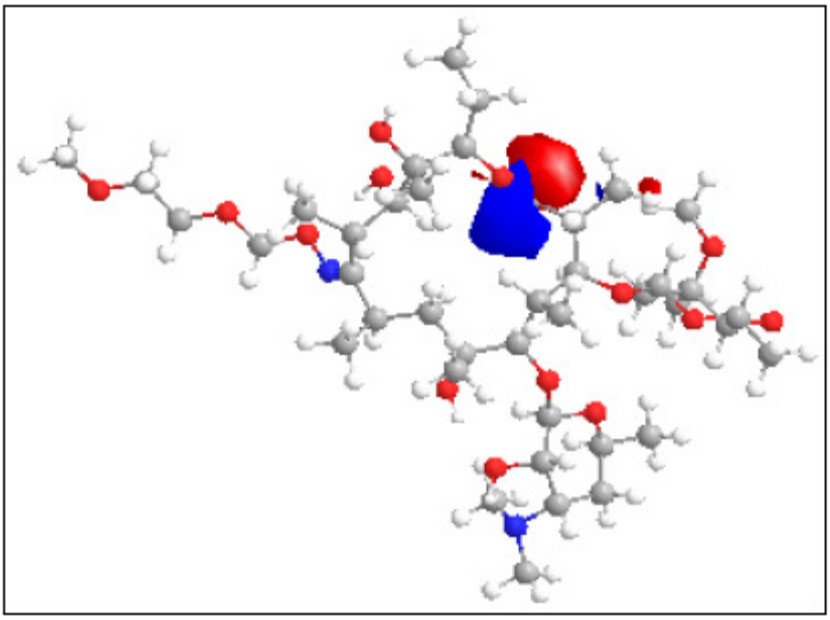


FIG 3 HOMO of Roxithromycin

JCSE The Journal of Corrosion Science and Engineering
ISSN 1466-8858 Volume 17, Preprint 6 submitted 28 January 2014



LUMO

FIG 4

The calculated quantum chemical factors such as highest occupied molecular orbital (E_{HOMO}) energy, lowest unoccupied molecular orbital (E_{LUMO}) energy, LUMO- HOMO, energy gap (ΔE), dipole moment (μ),[18-21] are précised in table 4.

Roxithromycin showed higher inhibition efficiency due to the increased softness values by the presence of electron donating lactones and N-Oxime groups with unshared electron pairs on nitrogen .The ionization potential (I) and electron affinity (A) were derived as per Koopmans theorem

$$A = -E_{LUMO} \quad I = -E_{HOMO}$$

JCSE The Journal of Corrosion Science and Engineering
ISSN 1466-8858 Volume 17, Preprint 6 submitted 28 January 2014

The absolute hardness (η) and absolute electronegativity (x) of the inhibitor molecules were calculated from the following equations

$$X=\frac{I+A}{2}$$

$$\eta = \frac{I-A}{2}$$

The softness (σ) can also be indicated as

$$\sigma= \frac{1}{\eta}$$

Where, hardness and softness are the characteristics of an inhibitor to determine its stability and reactivity. A hard molecule exhibits large energy gap and a small gap existing in soft molecule. Soft inhibitors are more reactive than hard molecule because the ease of donation of electrons to metal is high for former. For the simplest transfer of electrons, adsorption could occur at the part of the molecule where σ which is a local property, has the highest value.

3.6 Scanning electron microscopy:

SEM images are expressive of the changes that supplement both corrosion and protection of the Aluminium surface [22]. Figure (5) displays the SEM of Al in dilute hydrochloric acid, which shows micro cracks, zig zag grooves indicating the damage caused to the surface by hydrochloric acid. Figure (6) displays SEM images of aluminium surface treatment with hydrochloric acid containing 450pm of RZ, showing the appearance of layered surface along with absence of random grooves manifest the adsorption of inhibitor on Al metal.

JCSE The Journal of Corrosion Science and Engineering
ISSN 1466-8858 Volume 17, Preprint 6 submitted 28 January 2014

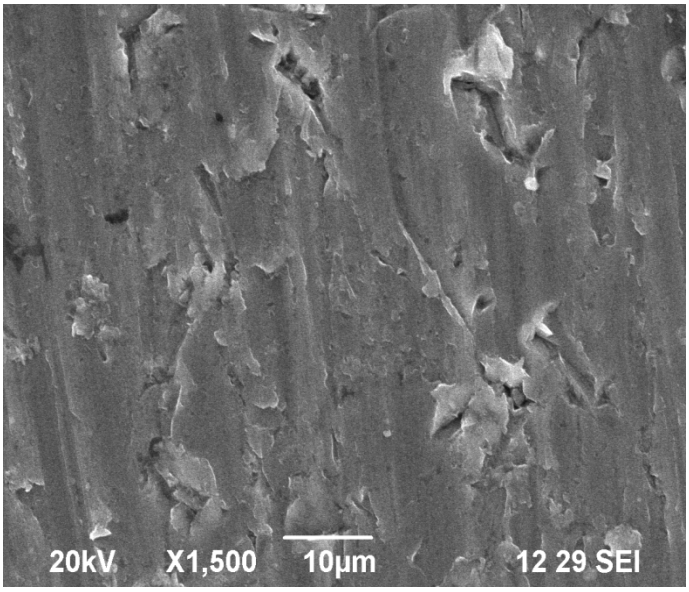


FIG 5 SEM micrograph of Al immersion in 0.1N HCl

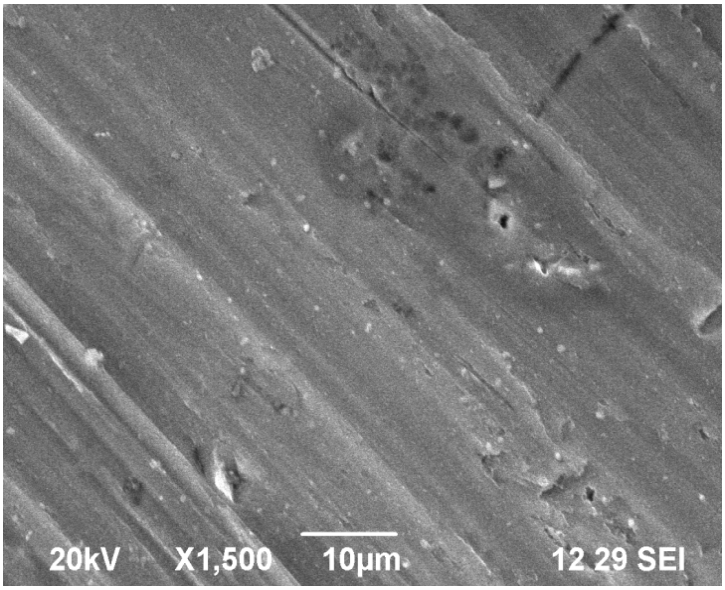


FIG 6 SEM micrograph of Al immersion in 0.1N HCl with 450 ppm RZ

ISSN 1466-8858 Volume 17, Preprint 6 submitted 28 January 2014

4. Conclusions

1. Roxithromycin acts as good inhibitor for corrosion inhibition of aluminium in 0.1N HCl.

2. Potentiodynamic studies show that roxithromycin is a mixed type of inhibitor.

3. The performance of Roxithromycin as effective inhibitor was evidenced from increased R_{ct} and decreased C_{dl} values.

5. SEM images confirmed the formation of protective layer of RMZ on Al.

6. The values of HOMO, LUMO, ΔE and μ derived from quantum chemical calculations substantiated the results of chemical and electrochemical studies.

References:

1. Factors affecting the corrosion behaviour of aluminium in acid solutions. I. Nitrogen and/or sulphur-containing organic compounds as corrosion inhibitors for Al in HCl solutions, S.M. Abd El Haleem, S. Abd El Wanees, E.E. Abd El Aal, A. Farouk, Corrosion science, 2012

2. Antifungal drugs as corrosion inhibitors for aluminium in 0.1 M HCl I.B. Obot , N.O. Obi-Egbedi , S.A. Umoren, Corrosion science, volume 51, pp. 1868-1875, 2009

3. Schiff bases as corrosion inhibitor for aluminium in HCl solution Serpil Safak , Berrin Duran , Aysel Yurt, Gulsen Turkoglu, Corrosion science, volume 54, pp. 251-259, 2012

4. The inhibitive effect of some tetrazole derivatives towards Al corrosion in acid solution: Chemical, electrochemical and theoretical studies, K.F.

ISSN 1466-8858 Volume 17, Preprint 6 submitted 28 January 2014

Khaleda,b, M.M. Al-Qahtanib, Materials chemistry and physics, volume 113, pp. 150-158, 2009

5. Effect of some organic inhibitors on the corrosion behavior of Cu-Fe and Cu-Al-Fe alloys in sulphuric acid solution, N.H. Hela, H.E. El-fifky, M.R. Negem, Journal of Corrosion Science &Engineering, Vol.10, 2006

6. 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

7. Inhibition of acidic corrosion of pure aluminum by some organic compounds, A.K. Maayta , N.A.F. Al-Rawashdeh, Corrosion science, volume 46, pp. 1129-1140, 2004

8. Experimental and theoretical studies of cloxacillin on the corrosion of mild steel in 1M H_2SO_4 S. Harikumar and S. Karthikeyan, Journal of corrosion science and engineering, Vol.16, 2013

9. Corrosion Inhibition performance of cetirizine on mild steel in 1m H_2SO_4, R.S.Dubey, K.U.Singh, Journal of Corrosion Science &Engineering, Vol.14, 2011

10. Antibacterial drugs as corrosion inhibitors for corrosion of aluminium in hydrochloric solution, M. Abdallah, Corrosion science, volume 46, pp 1981-1996, 2004

11.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

ISSN 1466-8858 Volume 17, Preprint 6 submitted 28 January 2014

12. Corrosion inhibition of aluminum 6063 using some pharmaceutical compounds, A.S. Fouda , A.A. Al-Sarawy , F.Sh. Ahmed c, H.M. El-Abbasy, Corrosion science, volume 51, pp. 485-492, 2009

13. 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

14. Mechanism of corrosion and its inhibition, K. Madhavan, PhD Thesis, Alagappa University, India, June 1996

15. The Structure of the Electrical Double Layer at the Metal Solution Interface, M.A. Devanathan, B. Tilak, Chem.Revs, 65, pp635, 1965

16. Adsorption Characteristics and Corrosion Inhibitive Properties of Clotrimazole for Aluminium Corrosion in Hydrochloric Acid, I.B. Obot, N.O. Obi-Egbedi, S.A. Umoren, Int. J. Electrochem. Sci, Vol. 4, pp. 863-877, 2009

17.The effect of inhibitor on the corrosion of aluminum alloys in acidic solutions, R.Rosliza,W.Wan Nik, H.Senin, Materials chemistry and physics, volume 107, pp. 281-288, 2008

18. Gu Hough, Zhou Zhongbai, Tao Yingachu , Yao Luaw, Wahan Dauxe Xuebao, Ziran Kexuebaw, 2, pp57, 1982

19. G. Trabanelli and Zucchui F.Revon, Corrosion and coatings, 1, pp47, 1973

20. A.K. Lahiri, N.G. Banerjee, NML. Tech. Journal, 5, pp33, 1963

21. The use of quantum chemical methods in corrosion inhibitor studies, Gokhan Gece, corrosion science, volume 50, pp 2981-2992, 2008

ISSN 1466-8858 Volume 17, Preprint 6 submitted 28 January 2014

22. Corrosion Inhibition of Mild Steel in 1M H2SO4 by Ampicillin as an Inhibitor, S. Harikumar and S. Karthikeyan, Journal of Corrosion Science &Engineering, Vol.16, 2013

JCSE The Journal of Corrosion Science and Engineering
ISSN 1466-8858 Volume 17, Preprint 6 submitted 28 January 2014

Table 1. Values of inhibition efficiency, corrosion rate and surface coverage for the corrosion of aluminium in 0.1N in presence of different concentrations of roxithromycin obtained from mass loss studies

Concentration (ppm)	Corrosion rate ($mgcm^{-2}h^{-1}$)	Inhibition efficiency (IE %)	Surface coverage (□)
Blank	0.01728	–	–
50	0.00864	50	0.5000
150	0.00672	61	0.6111
250	0.00576	67	0.6701
350	0.00371	78	0.7858
450	0.00190	89	0.8900

JCSE The Journal of Corrosion Science and Engineering
ISSN 1466-8858 Volume 17, Preprint 6 submitted 28 January 2014

Table 2. Electrochemical parameters of aluminium in 0.1N HCl in the presence of different concentrations of roxithromycin from potentiodynamic polarization studies.

Concentration of Inhibitor (ppm)	E_{corr} (mV)	Tafel slopes in mV in dec^{-1}		I_{corr} mA cm^{-1}	Inhibition efficiency (%)
		β_a	β_c		
Blank	-705	68	120	0.734	-
50	-690	72	123	0.389	47
150	-678	75	126	0.301	59
250	-647	71	124	0.256	65
350	-612	76	131	0.186	75
450	-533	73	129	0.096	87

JCSE The Journal of Corrosion Science and Engineering
ISSN 1466-8858 Volume 17, Preprint 6 submitted 28 January 2014

Table 4.Electrochemical parameters and its inhibition efficiency for the corrosion of aluminium in 0.1N HCl in the presence of different concentrations of roxithromycin by impedance method.

Concentration of Inhibitor (ppm)	Charge Transfer resistance (R_{ct}) Ohm.cm^2	Double layer capacitance (C_{dl}) μF.cm^{-2}	Inhibition efficiency (%)
Blank	1.25	2.769×10^{-4}	–
50	2.50	1.0615×10^{-4}	50
150	3.21	7.655×10^{-5}	61
250	3.75	5.0551×10^{-5}	67
350	5.34	2.7108×10^{-5}	77
450	8.72	1.1511×10^{-5}	86

Table 5: Quantum chemical parameters for Roxithromycin

Compound	LUMO (eV)	HOMO (eV)	ΔE (Cal.Mol^{-1})	Dipole moment (Debye)	Hardness (η)	Softness (σ)
Roxithromycin	0.306	8.539	8.233	4.4282	4.4225	0.2261