

Corrosion characterization of a synthesized novel 1,5-dimethyl-4-((2-methylbenzylidene) amino)-2-phenyl-1*H*-pyrazol-3(2*H*)-one (DMPO) derivative on aluminium alloy in hydrochloric acid solution

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ABSTRACT

1,5-Dimethyl-4-((2-methylbenzylidene)amino)-2-phenyl-1*H*-pyrazol-3(2*H*)-one (DMPO) was synthesized to be evaluated as a corrosion inhibitor. The corrosion inhibitory effects of DMPO on Aluminum alloy in 1.0 M HCl were investigated using electrochemical impedance spectroscopy (EIS), potentiodynamic polarization, open circuit potential (OCP) and electrochemical frequency modulation (EFM). The results showed that DMPO inhibited Aluminium Alloy corrosion in acid solution and indicated that the inhibition efficiency increased with increasing inhibitor concentration. Changes in the impedance parameters suggested an adsorption of DMPO onto the Aluminum Alloy surface, leading to the formation of protective films. The novel synthesized corrosion inhibitor was characterized using UV-Vis and FT-IR spectral analyses.

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KEYWORDS

Corrosion inhibitor;
Electrochemical impedance spectroscopy (EIS);
Potentiodynamic polarization;
Open circuit potential (OCP) and electrochemical frequency modulation (EFM);
DMPO.

INTRODUCTION

Corrosion inhibitors are of considerable practical importance, as they are extensively employed in reducing metallic waste during production and in minimizing the risk of material failure, both of which can result in the sudden shut-down of industrial processes, which in turn leads to added costs^[1]. It is also important to use corrosion inhibitors to prevent metal dissolution and minimize acid consumption^[2-4]. The majority of well-known acid inhibitors are organic compounds that contain nitrogen, sulfur and oxygen atoms. The inhibitory action exercised by organic compounds on the dissolution of metallic

species is normally related to adsorption interactions between the inhibitors and the metal surface^[5,6]. The planarity (*p*) and lone pairs of electrons present on N, O and S atoms are important structural features that control the adsorption of these molecules onto the surface of the metal. The purpose of this work was to verify the previously established results on the corrosion inhibition effect of various Schiff bases on Aluminum Alloy in acidic media^[7]. Many researchers have reported that the inhibition effect depends mainly on some physicochemical and electronic properties of the organic inhibitor related to its functional groups, steric effects, electronic density of donor atoms and orbital character of elec-

trons donor^[8]. Schiff bases are organic compounds that have the general formula R–C=N–R-, where R and R- are aryl, alkyl or heterocyclic groups. Schiff bases are formed by the condensation reaction of a primary amine and a ketone or aldehyde and are potential corrosion inhibitors. The greatest advantage of many Schiff base compounds is that they can be conveniently and easily synthesized from relatively cheap materials. Due to the presence of the imine group (–C=N–) and electronegative nitrogen, sulfur and/or oxygen atoms in the molecule, Schiff bases have been reported to be effective inhibitors for the corrosion of steel in acid media by several authors^[9–12]. Conversely, the surface state and excess charge of the metal have also been reported to affect the adsorption behavior of inhibitor molecules onto the metal surface^[13]. Generally, the tendency to form a stronger coordination bond, consequently resulting in high inhibition efficiency, increases in the order of O < N < S < P^[14]. As a continuation of previous studies^[15–20], we focused on the synthesis of new heterocyclic compounds as novel organic corrosion inhibitors. Herein, we report the synthesis of 1, 5-dimethyl-4-((2-methylbenzylidene) amino)-2-phenyl-1H-pyrazol-3(2H)-one, DMPO, and chemical structure elucidation using spectroscopic techniques (*i.e.*, UV-Vis and IR). Recent studies have shown that organic compounds containing polar functional groups are quite efficient in minimizing the effect of corrosion in addition to heterocyclic compounds containing polar groups and π -electrons. The molecular design of the DMPO molecule is based on the fact that 4-aminoantipyrine consists of amine, methylamine, carbonyl and π -electron bonds, which would effectively contribute towards the inhibition of Aluminium Alloy corrosion in acidic media. Moreover, Schiff bases containing imine groups would contribute more effectively to the inhibition of corrosion of Aluminium alloy in acid medium. The proposed struc-

ture of the synthesized novel corrosion inhibitor is shown in below.

Experimental section

All chemicals used were of reagent grade (supplied by Sigma-Aldrich) and used as supplied without further purification. The FT-IR spectra were measured using a Thermo Scientific Model Nicolet 6700 spectrophotometer and UV-Visible spectra were recorded on a double beam UV-Vis Spectrophotometer UV 5704SS

Synthesis of corrosion inhibitor DMPO

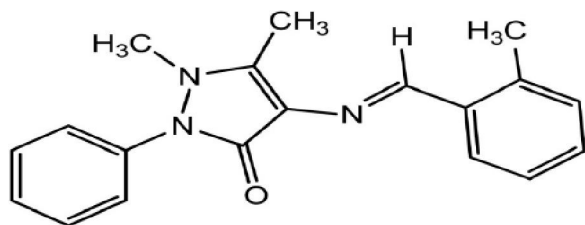
To synthesize the new corrosion inhibitor DMPO, the reaction sequence outlined in was followed, starting from commercially available 4-aminoantipyrine. The synthesis was carried out by refluxing 4-aminoantipyrine with 2-methylbenzaldehyde in the presence of a few drops of acetic acid. The mechanism of this reaction followed the Schiff base mechanism.

A solution of 2-methylbenzaldehyde (0.4 mmol) in 50 mL ethanol was refluxed with 4-aminoantipyrine (0.4 mmol) for 5 h. After cooling to room temperature, a solid mass was separated and recrystallized from ethanol in 87% yield. IR: 3050.0, 3061.6 cm^{-1} (C–H, aromatic), 2910.7, 2945.9 and 2970.0 cm^{-1} (C–H, aliphatic), 1646.6 cm^{-1} (C=O), 1569.4 cm^{-1} (C=C); 1588.6 cm^{-1} (C=N, imine), 1484.4 cm^{-1} (C=C, aromatic); UV-Vis: 250 nm in acetonitrile.

The IR spectrum provided good evidence for the formation of the synthesized DMPO. In the IR spectrum of DMPO, the imine stretching frequency was observed at 1588.6 cm^{-1} . The high value of the C=N wavenumber was due to the high conjugation (resonance effect) of the substituted double bonds, whereas the aromatic carbon-carbon double bond stretching appeared at 1569.4 cm^{-1} . However, two types of tautomers, *i.e.*, amine and imine, could be expected from the DMPO structure.

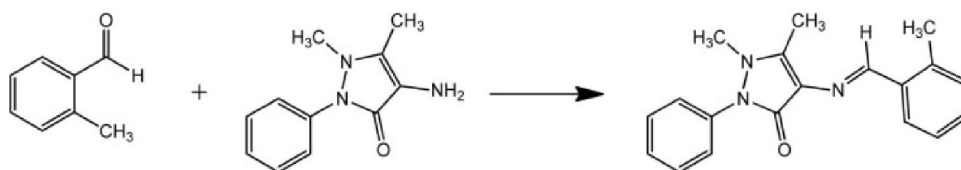
Electrochemical measurements

Aluminium alloy specimens obtained from the Metal Samples Company were used as the working electrodes throughout the study. The composition (wt %) of the aluminium alloy was as follows: Fe, 99.21; C, 0.21; Si, 0.38; P, 0.09; S, 0.05; Al, 0.01.

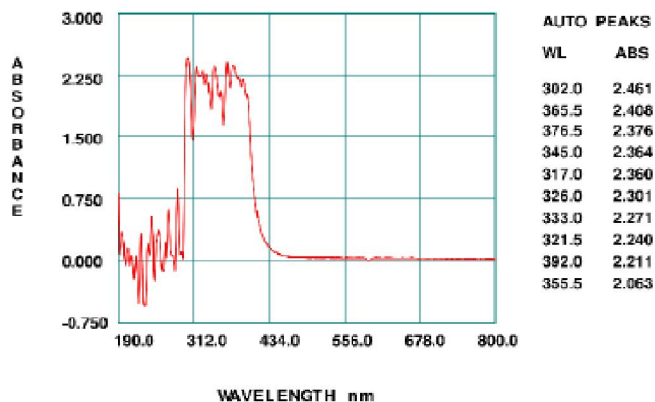


Chemical structure of 1, 5-dimethyl-4-((2-methylbenzylidene) amino)-2-phenyl-1H-pyrazol-3(2H)-one (DMPO)

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EC DoubleBeam UV-VIS Spectrophotometer
 Date : 08/28/15 Time : 15:56:14
 System : ECIL UV 5704ss
 Sample_ID : venkatesh T
 Analyst : DMPO
 File Name : DMPO.abs

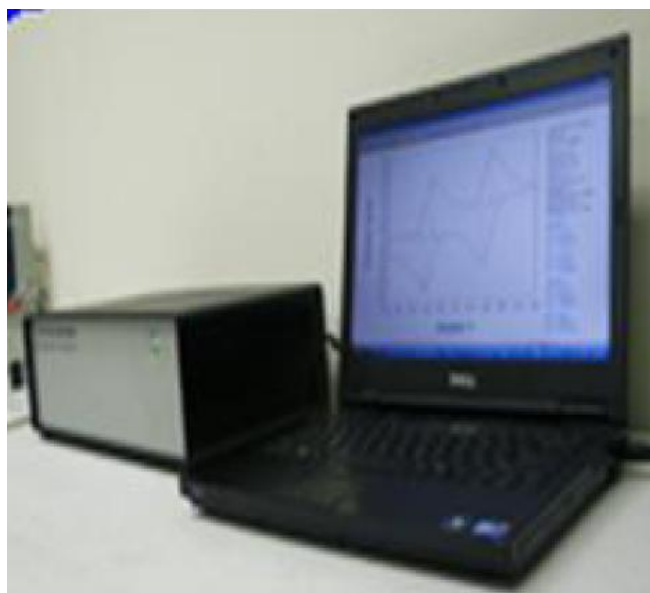


The specimens were cleaned according to ASTM standard G1-03^[46,47]. Measurements were performed in aerated non-stirred 1.0 M hydrochloric acid solutions at 30 °C with a concentration range of 1.25×10^{-4} to 5×10^{-4} M DMPO corrosion inhibitor. Solutions were freshly prepared from analytical grade chemical reagents using distilled water. All measurements were performed in triplicate, and the average values were reported. Measurements were performed using a CH Instrument Potentiostat/Galvanostat/608E Series. The DC105 and EIS300 software were used for potentiodynamic scans and electrochemical impedance spectroscopy (EIS). The potentiodynamic current-potential curves were

swept from -0.25 to $+0.25$ V_{sc} at a scan rate of 0.5 mV·s⁻¹. All impedance data were fitted to appropriate equivalent circuits (EC) using Echem Analyst software. Experiments for electrochemical measurements were initiated approximately 30 min after the working electrode was immersed in the solution to stabilize the steady state potential.

Electrochemical impedance spectroscopy (EIS) measurements

The experimental results obtained from the EIS



measurements for the corrosion of aluminium alloy in the absence and presence of the inhibitor at 30 °C are summarized in TABLE 1. The impedance spectra for the Aluminium alloy samples in 1.0 M HCl in various concentrations of DMPO at 30 °C are presented as Nyquist plots in Figure 1. As shown in Figure 1, a considerable increase in the total substrate impedance was observed with increasing concentration of DMPO inhibitor added to the corrosive solution. In the impedance spectrum of the Aluminium alloy in the presence of DMPO, the Nyquist plots have two loops: one loop in the high frequency region (HF) and one loop at an intermediate frequency (MF), with slight inductive behavior at low

frequencies (LF). The HF and MF loops were attributed to the electrode and the charge-transfer process, respectively. The inductive behavior observed in the LF region was attributed to either the relaxation of the adsorption of corrosion products or the adsorption of the inhibitor molecules on the Aluminium alloy surface in the acid solution in the absence or presence of inhibitor, respectively^[21,22]. The inhibition efficiencies (IE%) were calculated from the charge transfer resistance using the following equation:

$$IE(\%) = \frac{R_{ct} - R_{ct}'}{R_{ct}} \times 100 \tag{1}$$

where R_{ct}' and R_{ct} indicate the values of the charge transfer resistances in the presence or absence of inhibitor, respectively.

Electrochemical impedance spectroscopy (EIS) parameters for aluminium alloy in 1.0 M HCl with various concentrations of 1,5-dimethyl-4-((2-methylbenzylidene)amino)-2-phenyl-1H-pyrazol-3(2H)-one (DMPO) at 30 °C.

From TABLE 1, it can be observed that the R_{ct} and IE% values increase with increasing concentration.

In these cases, the parallel network charge-transfer resistance double-layer capacitance ($R_{ct}-C_{dl}$) is usually a poor approximation, especially for systems in which an efficient inhibitor is present. The corroding surface of the Aluminium alloy in 1.0 M HCl is expected to be inhomogeneous because of its roughness; therefore, the capacitance is presented

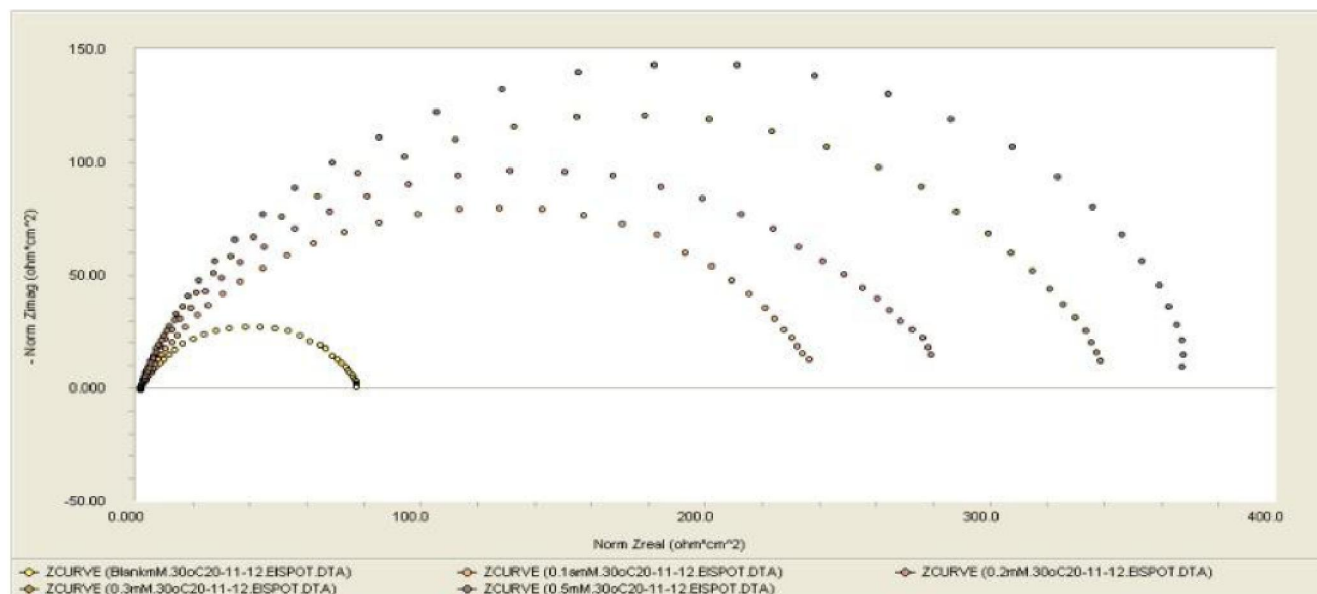


Figure 1 : Nyquist plots for Aluminium alloy in 1.0 M HCl with DMPO at various concentrations

TABLE 1

Conc., $1 \times 10^{-3} \text{M}$	R_s , ohm cm^2	R_{ct} , ohm cm^2	CPE_{dl} ($\text{Y}0 \times 10^{-5}$), $\text{ohm}^{-1} \text{cm}^2 \text{S}^n$	IE (%)
0	–	77	–	0
0.1	1.55	239	39.4	71.08
0.2	1.56	259	22.2	70
0.3	1.63	328	17.7	77
0.5	1.73	376	23.3	80

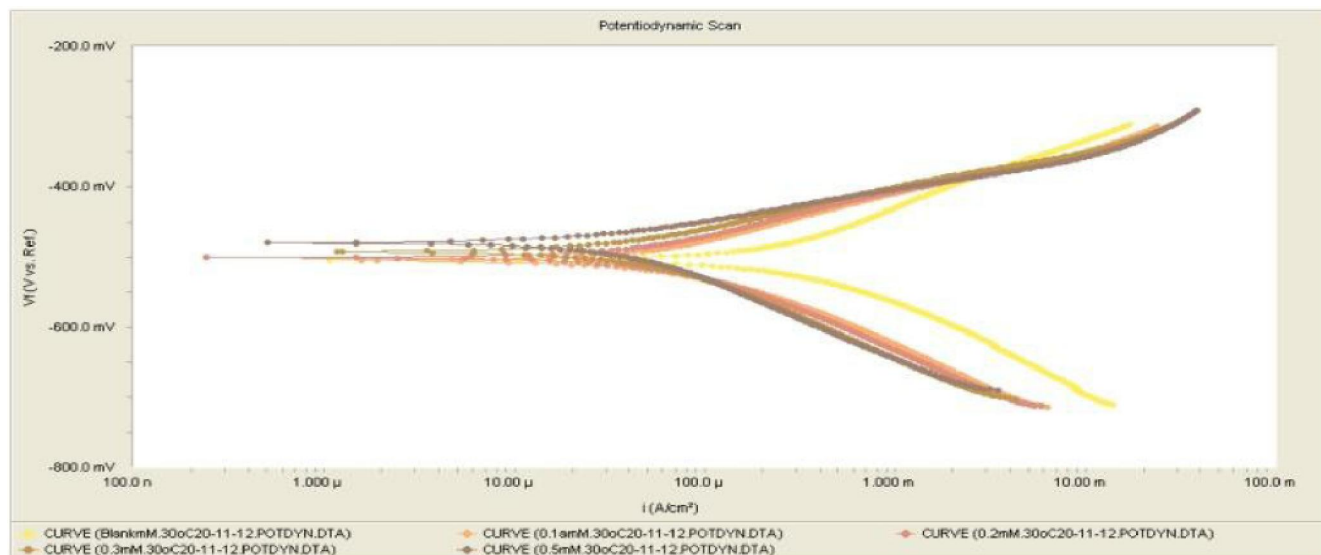


Figure 2 : Potentiodynamic polarization curve for aluminium alloy in 1.0 M HCl with various concentrations of DMPO at 30 °C.

through a constant phase element (CPE).

Potentiodynamic measurements

The numerical values of the variations in corrosion current density (i_{corr}), corrosion potential (E_{corr}), anodic Tafel slope (β_a), cathodic Tafel slope (β_c), the degree of surface coverage (θ) and inhibition efficiency (IE%) with the concentrations of inhibitor DMPO are given in TABLE 1. The surface coverage (θ) is calculated thus^[22]:

$$\theta = \frac{i_{corr}(\text{uninh}) - i_{corr}(\text{inh})}{i_{corr}(\text{uninh})} \quad (2)$$

where $i_{corr}(\text{uninh})$ and $i_{corr}(\text{inh})$ are the corrosion current densities in the absence and presence of the inhibitor, respectively. The inhibition efficiency (IE%) is given by

$$\text{IE\%} = \theta \times 100 \quad (3)$$

The results also indicate that the inhibition efficiencies increased with the concentration of inhibitor. Such behavior can be interpreted on the basis that the inhibitor acts by adsorbing onto the metal surface. In acidic solutions, the anodic reaction of corrosion is the passage of metal ions from the metal surface into the solution, and the cathodic reaction

is the discharge of hydrogen ions to produce hydrogen gas or to reduce oxygen. The inhibitor may affect either the anodic or the cathodic reaction, or both^[23]. Because the anodic Tafel slope (β_a) and cathodic Tafel slope (β_c) of DMPO, were found to change with inhibitor concentration, the inhibitor had thus affected both of these reactions^[24]. DMPO can thus be classified as an anodic- or cathodic-type inhibitor when the change in the E_{corr} value is greater than 85 mV^[25]. Because the largest displacement exhibited by DMPO was 40 mV at 30 °C (TABLE 2), it may be concluded that this molecule should be considered a mixed-type inhibitor, meaning that the addition of DMPO to a 1.0 M HCl solution both reduces the anodic dissolution of aluminium alloy and retards the cathodic hydrogen evolution reaction. The polarization profile of aluminium alloy in 1.0 M HCl at 30 °C in the presence and absence of DMPO is shown in Figure 2. The presence of increasing amounts of DMPO led to a decrease in both the cathodic and anodic current densities. Adsorption is the mechanism that is generally accepted to explain the inhibitory action of organic corrosion

TABLE 2 : Polarization parameters for aluminium alloy in 1.0 M HCl with different concentrations of DMPO at 30 °C

Conc., 1×10^{-3} M	i_{corr} ($\mu\text{A cm}^{-2}$)	$-E_{\text{corr}}$ (mV vs. SCE)	β_a (V dec^{-1})	β_c (V dec^{-1})	IE%
0	298	504	0.119	0.121	0
0.1	60	505	0.07	0.10	79.860
0.2	49	500	0.06	0.10	83.550
0.3	40.5	492	0.06	0.11	86.410
0.5	39.6	479	0.06	0.12	87.700

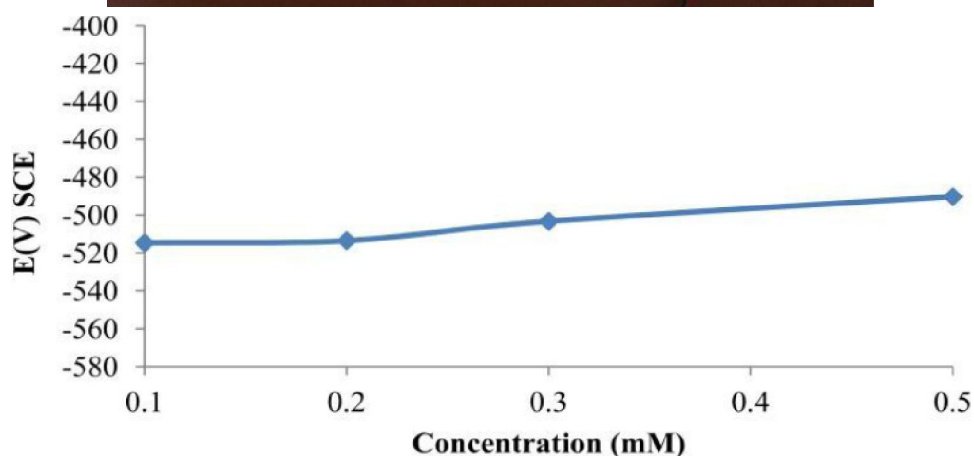


Figure 3 : Open circuit potential (OCP) value for aluminium alloy in an HCl solution with various concentrations of DMPO at 30 °C.

inhibitors. The adsorption of inhibitors can affect the corrosion rate in two ways: (i) by decreasing the available reaction area, *i.e.*, the so-called geometric blocking effect, and (ii) by modifying the activation energy of the cathodic and/or anodic reactions occurring in the inhibitor-free metal in the

course of the inhibited corrosion process. It is a difficult task to determine which aspects of the inhibiting effect are connected to the geometric blocking action and which are connected to the energy effect. Theoretically, no shifts in E_{corr} should be observed after the addition of the corrosion inhibitor if the

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TABLE 3 : Electrochemical frequency modulation (EFM) parameters for aluminium alloy in 1.0 M HCl with various concentrations of DMPO at 30 °C.

Conc, mM	i_{corr} , ($\mu\text{A}\cdot\text{cm}^{-2}$)	β_{as} , ($\text{V}\cdot\text{dec}^{-1}$)	β_{c} , ($\text{V}\cdot\text{dec}^{-1}$)	CR mmpy	IE (%)
0	189.8	24.26e-3	27.00e-3	4.89	0
0.1	501.9	96.88e-3	152.5e-3	1.295	80
0.2	478.5	66.90e-3	173.2e-3	1.234	83
0.3	388.1	105.4e-3	152.4e-3	1.001	86

geometric blocking effect is stronger than the energy effect^[23].

Open circuit potential (OCP) measurements

The OCP of Aluminium Alloy was monitored in the presence of 0 mM, 0.1 mM, 0.2 mM, 0.3 mM and 0.5 mM DMPO. Figure 3 presents the effect of the presence of the DMPO inhibitor on the variation of the OCP of aluminium alloy in 1.0 M HCl solutions. This preliminary result suggests that DMPO can retard both reactions under open circuit conditions, including the oxidation of the oxide-free iron and the discharge of the hydrogen ions to produce hydrogen gas on the surface of the Aluminium Alloy^[26,27].

Electrochemical frequency modulation measurement

Electrochemical frequency modulation (EFM) is a new electrochemical technique for determining the corrosion rate without preliminary knowledge of the Tafel constants. The main advantages of this technique include measuring the corrosion rate, Tafel parameters and causality factors in a single set of data. While using EFM, a potential perturbation signal composed of two sine waves is applied to any corroding specimen to obtain the current response. EFM has been used for different combinations of metals and electrolytes to accurately measure the corrosion parameters. EFM is related to the harmonic method of employing a lower amplitude (20 mV) sinusoidal perturbation signal but is composed of two sine waves instead of one. EFM is superior to the harmonic method in many aspects, including data validation, larger current response and insensitivity to harmonics in the perturbation signal.

The corrosion parameters, including the corrosion efficiency (E_{EFM} %), the corrosion current density ($\mu\text{A}/\text{cm}^2$), the Tafel constant and the causality factors (CF-2 and CF-3), with different concentra-

tions of DMPO in 1.0 M HCl at a constant temperature of 30 °C are listed in TABLE 3.

CONCLUSIONS

In this study, a new 4-aminoantipyrine, *i.e.*, 1,5-dimethyl-4-((2-methylbenzylidene)amino)-2-phenyl-1*H*-pyrazol-3(2*H*)-one (DMPO), was sequentially synthesized and characterized using various spectroscopic methods. Changes in the electrochemical impedance spectroscopy (EIS), open circuit potential (OCP) and potentiodynamic polarization were used to study the corrosion inhibition of aluminium alloy in 1.0 M HCl solutions at 30 °C using different concentrations of DMPO as an inhibitor. This compound exhibited excellent inhibition performance as a mixed-type inhibitor. In general, the acidic corrosion of aluminium alloy was reduced upon the addition of an appropriate concentration of DMPO. The inhibition efficiencies obtained from the EIS data were comparable to those obtained from the polarization measurements in that they were greater for the inhibitory solution than those of the non-inhibitory solution. DMPO acts as an efficient corrosion inhibitor in 1.0 M hydrochloric acid and it exhibits a maximum inhibition efficiency of 87%.

ACKNOWLEDGMENTS

The authors gratefully acknowledge VGST, Govt. of Karnataka for financial support under the project CISEE /2014-15/ GRD No. 325. Also express their gratitude to Management and Principal, RajaRajeswari College of Engineering, Bangalore for providing infrastructural facilities.

REFERENCES

- [1] P.R.Roberge; Handbook of corrosion engineering, McGraw-hill professional publishing, New York, NY,

- USA, 1–3 (1999).
- [2] D.N.Sing, A.K.Dey; Synergistic effects of inorganic and organic cations on inhibitive performance of propargyl alcohol on steel dissolution in boiling hydrochloric acid solution, *Corrosion*, **49**, 594–600 (1993).
- [3] G.Banerjee, S.N.Malhotra; Contribution to adsorption of aromatic amines on aluminium alloy surface from HCl solutions by impedance, UV, and raman spectroscopy, *Corrosion*, **48**, 10–15 (1992).
- [4] S.T.Arab, E.A.Noor; Inhibition of acid corrosion of steel by some S- Alkylisothiuronium, *Corrosion*, **49**, 122–129 (1993).
- [5] F.H.Khaled; Investigation of the inhibitive effect of *ortho*-substituted on corrosion of iron in 0.5 M H₂SO₄ solutions, *Mater.Chem.Phys.*, **82**, 949–960 (2003).
- [6] W.Lin; Inhibiting effect of 2-mercaptopyrimidine on the corrosion of a low carbon steel in phosphoric acid, *Corros.Sci.*, **43**, 1637–1644 (2001).
- [7] H.Shorky, M.Yuasa, I.Sekine, R.M.Issa, H.Y.El-Baradie, G.K.Gomma; Corrosion inhibition of aluminium alloy by schiff base compounds in various aqueous solutions, *Corros.Sci.*, **40**, 2173–2186 (1998).
- [8] M.Abdallah; Rhodanine azosulpha drugs as corrosion inhibitor, *Corros.Sci.*, **44**, 717–728 (2002).
- [9] R.A.Prabhu, T.V.Venkatesha, A.V.Shanbhag, G.M.Kulkarni, R.G.Kalkhambkar; Inhibition effects of some Schiff's bases on the corrosion of aluminium alloy in hydrochloric acid solution, *Corros.Sci.*, **50**, 3356–3362 (2008).
- [10] R.A.Prabhu, A.V.Shanbhag, T.V.Venkatesha; Influence of tramadol [2-[(dimethylamino)methyl]-1-(3-methoxyphenyl)cyclohexanolhydrate] on corrosion inhibition of aluminium alloy in acidic media, *J.Appl.Electrochem.*, **37**, 491–497 (2007).
- [11] M.El-Naggar; Corrosion inhibition of aluminium alloy in acidic medium by some sulfa drugs compounds, *Corros.Sci.*, **49**, 2226–2236 (2007).
- [12] I.B.Obot, Obi N.O.Egbedi, S.A.Umoren; Drugs as corrosion inhibitors for aluminium in 0.1 M HCl, *Corros.Sci.*, **51**, 1868–1875 (2009).
- [13] S.K.Shukla, M.A.Quraishi; 4-Substituted anilinomethylpropionate: New and efficient. Corrosion inhibitors for aluminium alloy, *Corros.Sci.*, **51**, 1007–1011 (2009).
- [14] S.K.Shukla, A.K.Singh, I.Ahamad, M.A.Quraishi; Drug as corrosion inhibitor for aluminium alloy in hydrochloric acid solution, *Mater.Lett.*, **63**, 819–822 (2009).
- [15] A.A.Al-Amiery, Al R.I.Bayati, F.M.Saed, W.B.Ali, A.H.Kadhun, A.B.Mohamad; Novel pyranopyrazoles: Synthesis and theoretical studies, *Molecules*, [PubMed], **17**, 10377–10389 (2012).
- [16] A.A.H.Kadhun, A.Mohamad, A.A.Al-Amiery; Antimicrobial and anti-oxidant activities of new metal complexes derived from 3-aminocoumarin, *Molecules*, [PubMed], **16**, 6969–6984 (2011).
- [17] A.A.H.Kadhun, Al A.A.Amiery, M.Shikara, A.Mohamad, Al R.Bayati; Synthesis, Structure elucidation and DFT studies of new thiadiazoles, *Int.J.Phys.Sci.*, **6**, 6692–6697 (2012).
- [18] Al A.A.Amiery; Synthesis and antioxidant, Antimicrobial evaluation, DFT studies of novel metal complexes derivate from Schiff base, *Res.Chem.Intermediat*, **38**, 745–759 (2012).
- [19] Al A.A.Amiery, A.A.H.Kadhun, A.Mohamad; Antifungal activities of new coumarins, *Molecules*, [PubMed], **17**, 5713–5723 (2012).
- [20] S.Junaedi, A.A.H.Kadhun, Al A.A.Amiery, A.Mohamad., M.Takriff; Synthesis and characterization of novel corrosion inhibitor derived from oleic acid: 2-Amino 5-Oleyl-1,3,4Thiadiazol (AOT) *Int.J.Electrochem.Sci.*, **7**, 3543–3554 (2012).
- [21] A.Y.Musa, A.A.H.Kadhun, A.B.Mohamad, A.R.Daud, M.S.Takriff, S.K.Kamarudin; A comparative study of the corrosion inhibition of aluminium alloy in sulphuric acid by 4,4-dimethyloxazolidine-2-thione, *Corros.Sci.*, **51**, 2393–2399 (2009).
- [22] S.Hleli, A.Abdelghani, A.Tlili; Impedance spectroscopy technique for DNA hybridization, *Sensors*, **3**, 472–479 (2003).
- [23] Z.Wang; The inhibition effect of Bis-Benzimidazole compound for aluminium alloy in 0.5 M HCl solution, *Int.J.Electrochem.Sci.*, **7**, 11149–11160 (2012).
- [24] Ramesh V.Saliyan, A.V.Adhikari; Quinolin-5-ylmethylene-3-[[8-(trifluoromethyl)quinolin-4-yl]thio]propanohydrazide as an effective inhibitor of aluminium alloy corrosion in HCl solution, *Corros.Sci.*, **50**, 55–61 (2008).
- [25] G.F.Liu, M.Du, J.Zhang, M.Qiu; Electrochemical behavior of Q235 steel in saltwater saturated with carbon dioxide based on new imidazoline derivative inhibitor, *Corros.Sci.*, **51**, 102–109 (2009).
- [26] De F.S.Souza; Caffeic acid as a green corrosion inhibitor for aluminium alloy, *Corros.Sci.*, **51**, 642–649 (2009).
- [27] A.A.Hermas, M.S.Morad; A comparative study on the corrosion behaviour of 304 austenitic stainless

Full Paper

- steel in sulfamic and sulfuric acid solutions, *Corros.Sci.*, **50**, 2710–2717 (2008).
- [28] T.Arslan, F.Kandemirli, E.Ebens, I.Love, H.Alemu; Quantum chemical studies on the corrosion inhibition of some sulphonamides on aluminium alloy in acidic medium, *Corros.Sci.*, **51**, 35–47 (2009).
- [29] Obi N.O.Egbedi; Inhibitive properties, thermodynamic and quantum chemical studies of alloxazine on aluminium alloy corrosion in H₂SO₄, *Corros.Sci.*, **53**, 263–275 (2011).
- [30] Al A.A.Amiery, Al R.Bayati, K.Saour, M.Radi; Cytotoxicity, Antioxidant and antimicrobial activities of novel 2-quinolone derivatives derived from coumarins, *Res.Chem.Intermediat.*, **38**, 559–569 (2012).
- [31] Al A.A.Amiery, A.Y.Musa, A.A.H.Kadhum, A.Mohamad; The antioxidant activity of new coumarin derivatives, *Int.J.Mol.Sci.*, **12**, 5757–5761 (2011).
- [32] Al A.A.Amiery, A.A.H.Kadhum, A.Mohamad; Antifungal and antioxidant activities of pyrrolidone-thiosemicarbazone complexes, *Bioinorg.Chem.Appl.*, **2012**, 1–5 (2012).
- [33] Al A.A.Amiery, Al Y.Majedy, H.Abdulreazak, H.Abood; Synthesis, Characterization, Theoretical crystal structure, and antibacterial activities of some transition metal complexes of the thiosemicarbazone, *Bioinorg.Chem.Appl.*, **2011**, 1–6 (2011).
- [34] Al A.A.Amiery; Antimicrobial and antioxidant activities of new metal complexes derived from (*E*)-3-((5-phenyl-1,3,4-oxadiazol-2-ylimino) methyl) naphthalen-2-ol, *Med.Chem.Res.*, **21**, 3204–3213 (2012).
- [35] F.Kandemirli, S.Sagdinc; Theoretical study of corrosion inhibition of amides and thiosemicarbazones, *Corros.Sci.*, **49**, 2118–2130 (2007).
- [36] Al A.A.Amiery, A.Y.Musa, A.A.H.Kadhum, A.Mohamad; The use of umbelliferone in the synthesis of new heterocyclic compounds. *Molecules*, **16**, 6833–6843 (2011).
- [37] J.M.Costa, J.M.Lluch; The use of quantum mechanics calculations for the study of corrosion inhibitors, *Corros.Sci.*, **24**, 924–933 (1984).
- [38] N.Khalil; Quantum chemical approach of corrosion inhibition, *Electrochim.Acta*, **48**, 2635–2640 (2003).
- [39] G.Bereket, C.Ogretir, A.Yurt; Quantum mechanical calculations on some 4-methyl-5-substituted imidazole derivatives as acidic corrosion inhibitor for zinc, *J.Mol.Struct.(Theochem.)*, **571**, 139–145 (2001).
- [40] S.Xia, M.Qiu, L.Yu, F.Liu, H.Zhao; Molecular dynamics and density functional theory study on relationship between structure of imidazoline derivatives and inhibition performance, *Corros.Sci.*, **50**, 2021–2029 (2008).
- [41] A.Y.Musa, A.H.Kadhum, A.B.Mohamad, A.B.Rahoma, H.Mesmari; Electrochemical and quantum chemical calculations on 4,4-dimethyloxazolidine-2-thione as inhibitor for aluminium alloy corrosion in hydrochloric acid, *J.Mol.Struct.*, **969**, 233–327 (2010).
- [42] I.B.Obot, E.E.Ebenso, I.A.Akpan, Z.M.Gasem; Afolabi Ayo S.119 Thermodynamic and density functional theory investigation of sulphathiazole as green corrosion inhibitor at aluminium alloy/hydrochloric acid interface, *Int.J.Electrochem.Sci.*, **7**, 1978–1996 (2012).
- [43] I.B.Obot, Obi N.O.Egbedi; Anti-corrosive properties of xanthone on aluminium alloy corrosion in sulphuric acid: Experimental and theoretical investigations, *Curr.Appl.Phys.*, **11**, 382–392 (2011).
- [44] I.B.Obot, N.O.Obi-Egbedi, A.O.Eseola; Anticorrosion potential of 2-Mesityl-1*H*-imidazo[4,5-*f*][1,10]phenanthroline on aluminium alloy in sulfuric acid solution: Experimental and theoretical study, *Ind.Eng.Chem.Res.*, **50**, 2098–2110 (2011).
- [45] I.B.Obot, Obi N.O.Egbedi; 1171 Theoretical study of benzimidazole and its derivatives and their potential activity as corrosion inhibitors, *Corros.Sci.*, **52**, 657–660 (2010).
- [46] ASTM (American society for testing and materials) Standard practice for preparing, Cleaning, and evaluating corrosion test specimens, ASTM, West Conshohocken, PA, USA, [(accessed on 11 March 2013)], (2003).
- [47] Al A.A.Amiery, A.H.K.Abdul, B.M.Abu, J.Sutiana; A novel hydrazinecarbothioamide as a potential corrosion inhibitor for aluminium alloy in HCl, *Materials*, **6**, 1420–1431 (2013).