Neolamarckia cadamba alkaloids as eco-friendly corrosion inhibitors for mild steel in 1 M HCl media

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1. Introduction

In recent days, studies on steel corrosion phenomena have become an industrial and academic topic, especially in acid media [1]. This is because of the increasing industrial applications of acid solutions. The most important fields of applications are acid pickling, industrial cleaning, acid descaling, oil-well acidizing in oil recovery and the petrochemical processes. Aqueous solutions of acids are among the most corrosive media. So, the rate of corrosion at which metals are destroyed in acidic media is very high, especially when soluble corrosion products are formed. Therefore, investigating and exploring corrosion inhibitors for steel corrosion in acid solutions are not only important from an academic point of view but also for its practical applications [2,3].

Most of the reported acid corrosion inhibitors are synthetic organic compounds containing heterocyclic atoms (nitrogen, sulfur, oxygen and phosphorous), aromatic rings or triple bonds [4–6]. Even though, these synthesized molecules have shown high corrosion inhibitive effect, they pollute the environment during the process of their synthesis and applications [7].

Currently, research in corrosion is focused on “green corrosion inhibitors”, that show good inhibition efficiency with low risk of environmental pollution [8]. The term “green inhibitor” or “eco-friendly inhibitor” refers to substances that are biocompatible such as plant extracts since they are of biological origin [9]. Thus natural products (derived from plant materials) are being studied for their corrosion inhibition potential as they are showing good corrosion protection and are more environment friendly [10–14]. We have successfully reported many green corrosion inhibitors for metals in acid media from various plant sources like mangrove tannins [15], Kopsia singapurensis [16], Xylopia ferruginea [17] and catechins [18].

Although, there are numerous successful reports on plant extracts as corrosion inhibitors [7], the phytochemical investigation is rarely carried out on the extract and efforts are seldom made on the pure compounds present in the plant extract. The aim of the present work is to evaluate the corrosion inhibition effect of Neolamarckia cadamba (bark and leaves) crude alkaloid extracts and also that of the major compound from both extracts; 3β-isodihydrocadambine. The crude extracts and 3β-isodihydrocadambine were tested for MS corrosion in 1 M HCl medium by using the following techniques; potentiodynamic polarization, electrochemical impedance spectroscopy, scanning electron microscopy (SEM) and FTIR analysis.

N. cadamba species belongs to Rubiaceae family which is known as Laran in Malaysia and reported to have various medicinal properties such as antidiuretic [19], astringent and antihypertotoxic [20]. Previous phytochemical studies of this plant by various investigations have led to the isolation and identification of indole alkaloids; aminocadambines A and B [21], cadamine, cadambine, isocadambine [22] while neolamarckines A and B [23] have been reported from our laboratory. In continuation of alkaloid isolation from N. cadamba species, we have isolated and structurally...
identified 3β-isodihydrocadambine as a major compound and tested this compound for its corrosion inhibitive potential.

2. Experimental

2.1. Material

The leaves and bark of *N. cadamba* were collected at Sg. Suda Dam, Jeli, Kelantan in 2008. The botanical identification was made by Mr. Teo Leong Eng., Faculty of Science, University of Malaya. The voucher specimen (Herbarium No.: KL5604) was deposited at the Herbarium of the Department of Chemistry, University of Malaya.

2.2. Extraction and isolation of inhibitor

Dried and ground leaves/bark of *N. cadamba* (2.0 kg) were separately extracted with hexane. Defatted plant material was dried and then moistened in 25% NH₄OH for 2 h. They were then soaked and macerated with CH₂Cl₂ (15 L and 17 L respectively) twice over a period of 3 days. The supernatant obtained were concentrated to a period of 3 days. The supernatant obtained were concentrated to give dichloromethane crudes from leaves (30.5 g) and from bark (29.9 mg) which showed an orange spot on TLC upon spraying with Dragendorff reagent. Structural elucidation of this compound, 3β-isodihydrocadambine (Fig. 1) was established by systematic spectral analysis of ¹H and ¹³C NMR, 2D NMR, FTIR, UV and MS data values and comparison with the literature values [25–27].

All the isolated green inhibitors (crude bark, leaf extracts and 3β-isodihydrocadambine) were dried separately and prepared in different concentrations (mg L⁻¹) by using AR grade HCl and double distilled water for the corrosion analysis.

2.3. Characterization of 3β-isodihydrocadambine (Supporting information)

UV (MeOH) λₘₐₓ (log ε) 201 (4.40), 225 (4.51), and 275 (3.84) nm; IR (KBr) νₘₐₓ 3418, 2917, 1666, 1620, 1582, 1487, 1460 and 1161 cm⁻¹. HRESITOFMS gave a pseudo-molecular ion peak at m/z 547 (M+H)+. ¹H NMR (500 MHz, CDCl₃/CD₃OD) δ: 7.45 (1H, s, H-17), 7.37 (1H, d, J = 7.8 Hz, H-9), 7.25 (1H, d, J = 7.8 Hz, H-12), 7.04 (1H, t, J = 7.8 Hz, H-11), 6.97 (1H, t, J = 7.8 Hz, H-10), 5.38 (1H, d, J = 9.1 Hz, H-21), 4.74 (1H, d, J = 7.9 Hz, H-1*), 4.25–4.31 (1H, m, H-19), 3.75–3.87 (1H, m, H-3), 3.73 (3H, s, OMe), 3.62–3.71 (2H, m, H-6*), 3.35–3.45 (2H, m, H-3* and H-4*), 3.32 (1H, t, J = 7.9 Hz, H-2*), 3.15–3.24 (2H, m, H-18 and H-5*), 3.02–3.10 (2H, m, H-5 and H-18), 2.95–3.02 (2H, m, H-5 and H-15), 2.82–2.91 (1H, m, H-6*), 2.68 (1H, br d, J = 14.9 Hz, H-6*). 2.18 (1H, d, J = 14.4 Hz, H-14), 1.91–2.00 (1H, m, H-20), 1.64–1.74 (1H, m, H-14). ¹³C NMR (125 MHz, CDCl₃/CD₃OD) δ: 168.9 (22-C = O), 153.2 (C-17), 136.9 (C-13), 134.8 (C-2), 127 (C-8), 121.7 (C-11), 119.3 (C-10), 118.2 (C-9), 111.4 (C-12), 109.7 (C-16), 108.3 (C-7), 100.1 (C-1*), 96.5 (C-21), 77 (C-5*), 76.8 (C-3*), 73.2 (C-2*), 69.4 (C-4*), 64.9 (C-19), 63.6 (C-3), 61 (C-6*), 58.7 (C-18), 55.4 (C-5), 51.8 (22-OCH₃), 43.4 (C-20), 36.8 (C-14), 33.3 (C-15), 22.9 (C-6).

2.4. Specimen preparation

Mild steel (MS) specimens (C = 0.205 wt%, Si = 0.06 wt%, Mn = 0.55 wt%, S = 0.047 wt%, P = 0.039 wt% and Fe remaining) with an exposed area of 3.14 cm² were used for the electrochemical study and specimens of size 2.3 cm were used for the SEM analysis. The surface preparation of the mechanically abraded specimens was carried out using different grades (350, 500, 800, 1000, 1200 and 1500) of emery papers.

2.5. Electrochemical studies

Electrochemical studies were carried out using Gamry Instruments reference 600 (potentiostat/galvanostat/ZRA). A conventional three electrode system was used for this purpose. MS specimen was used as a working electrode, Pt electrode and saturated calomel electrode (SCE) served as auxiliary and reference electrode.

Fig. 1. Structure of 3β-isodihydrocadambine.
electrodes, respectively. All polarization and impedance curves were recorded at room temperature (30 ± 2 °C) at pH range of 0.7–0.8. The working electrode was immersed in the test solution for 30 min until a steady state open-circuit potential was attained. GAMRY Echem Analyst software package 5.50 was used for fitting impedance data in an equivalent circuit as well as for extrapolating Tafel slopes. Experiments were carried out in duplicate to ensure reproducibility of results.

2.6. Electrochemical impedance study (EIS)

AC impedance measurements were carried out at potential amplitude of 10 mV, peak-to-peak (AC signal) in open-circuit, with 10 points per decade and the frequency ranging from 10,000 Hz to 0.1 Hz. The impedance results obtained are represented as Nyquist plots. Inhibition efficiency \( \eta (\%) \) is calculated from the charge transfer resistance \( R_{ct} \) values by using the following equation:

\[
\eta (\%) = \left(1 - \frac{R_{ct(o)}}{R_{ct(i)}}\right) \times 100
\]

where \( R_{ct(o)} \) is the charge transfer resistance of MS without inhibitor, \( R_{ct(i)} \) is the charge transfer resistance of MS with inhibitor.

2.7. Potentiodynamic polarization study

Potentiodynamic polarization measurements were carried out by scanning the electrode potential from −800 mV to −200 mV (vs SCE) with a scan rate of 0.5 mV s⁻¹. The linear Tafel segments were chosen (approximately 50–100 mV from the corrosion potential, \( E_{corr} \), of the anodic and cathodic curves) and were extrapolated to \( E_{corr} \) several times to obtain reproducible corrosion current density \( i_{corr} \) values. Eq. (2) shows the calculation of \( \eta (\%) \) from the \( i_{corr} \) values:

\[
\eta (\%) = \left(1 - \frac{i_{corr(o)}}{i_{corr(i)}}\right) \times 100
\]

where \( i_{corr(o)} \) is the corrosion current density of MS without inhibitor, \( i_{corr(i)} \) is the corrosion current density of MS with inhibitor.

2.8. Scanning Electron Microscope (SEM) analysis

SEM LEO SUPRA 50VP – Scanning Electron Microscope was used at an accelerating voltage of 15 kV for monitoring the surface morphological changes. For this study, MS plates were carefully polished to a 2500 grit surface finish using silicon carbide paper and immersed in 1 M HCl medium in the presence and absence of 5 mg L⁻¹ of inhibitors for 6 h. Then the specimens were cleaned with distilled water, dried in cold air blaster and used for the SEM analysis.

![Fig. 2. Nyquist plots for MS in 1 M HCl medium in the presence and absence of N. cadamba, (a) bark extract, (b) leaves extract, and (c) 3β-isodihydrocadambine.](image)

![Fig. 3. The electrical equivalent circuit for AC impedance measurement.](image)

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<th>Table 1 Corrosion inhibition effect of N. cadamba extract on MS in HCl medium (impedance studies).</th>
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2.9. FTIR analysis

The isolated inhibitor (3β-isodihydrocadambine), as well as the protective film formed over the MS surface by the inhibitor molecule was analyzed separately by FTIR spectroscopy using the KBr pellet method. For this purpose, MS specimens were immersed in the corrosive medium consisting of 5 mg L\(^{-1}\) of 3β-isodihydrocadambine for 120 h which resulted in the formation of a fine protective film over the MS surface. Further, the film was carefully scratched out from the MS surface and analyzed. The study was carried out by using the Perkin Elmer System 2000 FTIR instrument.

2.10. Molecular modelling

The structure optimization of pure alkaloid (3β-isodihydrocadambine) as well as the molecular orbitals calculations viz., Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO) was performed using Gaussian 03 program [28]. The global minimum energy structure of inhibitor was obtained by using density functional theory (DFT) with Becke 3-Parameter combined with Lee, Yang and Parr functional (B3LYP) method with 6-31G(d,p) basis set. The same level of theory (B3LYP/6-31G(d,p)) was used to compute the molecular orbitals of different oxidation states of Fe (0, +2 and +3). The molecular orbitals were visualized using Gassview (4.2) program.

3. Results and discussion

3.1. Electrochemical impedance study (EIS)

EIS measurements were carried out to study the concentration effect on MS in 1 M HCl in the absence and presence of N. cadamba barks, leaves extracts and 3β-isodihydrocadambine; results obtained are depicted as Nyquist plots in Fig. 2a–c respectively. An equivalent circuit (Fig. 3) was used to consider all the processes involved in the electrical response of the system. The first element in the circuit is a resistance (R\(_s\)) which corresponds to the ohmic resistance of the system. A constant phase element (CPE) represents the double layer capacity. A resistance R\(_ct\) represents the inhibitor’s resistance to the charge transfer upon oxidation of the metal. The different elements were evaluated by a fitting procedure. The data obtained after the fitting procedure are shown in Table 1.

Analysis of the Nyquist plots (Fig. 2) showed a depressed capacitive loop which arises from the time constant of the electrical double layer and charge transfer resistance. This could be attributed to different physical phenomena such as roughness and inhomogeneities of the solid surfaces, impurities, grain boundaries and distribution of the surface active sites [29]. All the curves obtained are approximated by a single capacitive semicircle, showing that the corrosion process was mainly charge-transfer controlled [30]. The general shape of the curves is very similar for all samples; the shape is maintained throughout the whole test period, indicating that almost no change in the corrosion mechanism occurred either due to the immersion time or to the inhibitor addition [31].

The various impedance parameters such as charge transfer resistance (R\(_ct\)), CPE, n, goodness of fit (chi square) and η (%) calculated are depicted in Table 1. The value of “n” seems to be associated with the non-uniform distribution of current as a result of roughness and possible oxide surface defects. When n = 1, CPE is an ideal capacitor. A true capacitive behavior is rarely obtained. The “n” values close to 1 (Table 1) represent the deviation from the ideal capacitor. A constant phase element (CPE) is utilized for data fitting instead of an ideal capacitor, since the “n” values obtained were in the range of 0.9, the value obtained from the data fitting instead of an ideal capacitor, since both extracts contain similar types of alkaloid phytoconstituents that has enabled us to isolate the pure alkaloid (3β-isodihydrocadambine) as a major compound.

At lower concentrations (1 and 2 mg L\(^{-1}\)), 3β-isodihydrocadambine showed less η (%) values compared with that of the bark and leaf extracts. The presence of other alkaloid constituents (besides...
the pure alkaloid) in the crude extracts, may have been involved in the corrosion inhibition process or synergistically enhance the adsorption of crude alkaloids over the MS surface.

3.2. Potentiodynamic polarization study

Fig. 4a–c displays the potentiodynamic polarization curves of MS in 1 M HCl medium which were obtained before and after the introduction of various doses of *N. cadamba* inhibitors (bark, leave extracts and 3β-isodihydrocadambine). Various corrosion parameters viz., corrosion current density (i<sub>corr</sub>), corrosion potential (E<sub>corr</sub>) and Tafel slope values (b<sub>a</sub> and b<sub>c</sub>) derived from these figures are given in Table 2.

Precise evaluation of Tafel slopes by Tafel extrapolation is often impossible, simply because an experimental polarization curve does not exhibit linear Tafel regions [33–37]. Most of the polarization curves obtained in our studies, especially the blank sample, do not display the expected log/linear Tafel behavior but both anodic and cathodic branches exhibited curvature over the complete applied potential range. Bandy and Jones [36] attributed this to a number of aspects including a change in the nature of the metal surface as liberated corrosion products or impurities in the steel (e.g., Fe<sub>3</sub>C) deposit to form a non-passivating, conducting surface film [33]. At both cathodic and anodic branches, since the solution is stationary, diffusion of H<sup>+</sup> ions and Fe ions will be slow, and concentration polarization can act to shorten the cathodic and anodic linear Tafel regions.

In aerated acidic solution, along with dissolved oxygen, only one anodic (metal dissolution) and two cathodic (hydrogen evolution and dissolved oxygen reduction) reactions are expected. Thus, the composite cathodic branch may also exhibit no linearity or a short Tafel region [33]. In the extreme case, linearity may disappear altogether such as in ours, with the cathodic and anodic reactions now under combined activation and diffusion control at E<sub>corr</sub>. Therefore, at cathodic and anodic overpotentials, the marked curvature in the experimental Tafel plot is roughly mimicked by the calculated plots (Fig. 5) and extrapolated by using Gamry Echem Analyst software version 5.50, according to the procedure described in Section 2.7. Lack of linear Tafel regions has given rise to an uncertainty and source error in the numerical values of i<sub>corr</sub> as shown in Table 2.

From Table 2, it could be observed that the presence of different concentrations of green inhibitors molecules cause a decrease of the current density (i<sub>corr</sub>) when the concentration of the inhibitor is increased. It is also observed that addition of *N. cadamba* leaves and bark extract slightly shifted E<sub>corr</sub> values (±10 mV) in both anodic and cathodic directions while the pure alkaloid showed E<sub>corr</sub> shift (15 mV) in the cathodic direction. But, analysis of both anodic (b<sub>a</sub>) and cathodic (b<sub>c</sub>) Tafel slope values indicated that both anodic and cathodic reactions were suppressed during the addition of all green inhibitors, which suggested that all inhibitors reduced anodic dissolution and also retarded the hydrogen evolution reaction [38]. Thus, Tafel slope values confirmed that *N. cadamba* leaves and bark extract as well...
as pure alkaloid reduced corrosion rate through mixed type of inhibition. The obtained \( \eta \) values showed similar trend with the impedance results and reached maximum of above 87% at concentrations of 4–5 mg L\(^{-1}\) but were slightly deviated at lower concentrations (1–2 mg L\(^{-1}\)). The shorter experimental duration for the impedance study in comparison with the polarization measurement may reduce the adsorption of inhibitor molecules at lower concentrations. Consequently, less inhibitor molecules were adsorbed onto the MS surface and were not sufficient to form a time-resistant layer [39], leading to low \( R_{ct} \) values which caused a decrease in \( \eta \) values at low concentrations of inhibitors.

3.3. Adsorption isotherm

It is generally assumed that the adsorption of the inhibitors on the metal surface is the essential step in the inhibition mechanism [40]. To establish the adsorption mode, the fraction of the surface covered by adsorbed molecules (\( \theta \)) was calculated from Eqs. (3) and (4) for impedance and polarization studies respectively [41]:

\[
\frac{C}{\theta} = \frac{1}{K_C} + \frac{1}{K_D} C \quad \text{(Impedance)}
\]

\[
\frac{C}{\theta} = \frac{1}{K_{D,2}} + \frac{1}{K_{D,2}} C \quad \text{(Polarization)}
\]
\[ \theta = \left( \frac{R_{ct(1)} - R_{ct(0)}}{R_{ct(1)}} \right) \]  

\[ \theta = \left( \frac{i_{corr(1)} - i_{corr(0)}}{i_{corr(0)}} \right) \]  

Data were tested graphically by fitting to various isotherms. The plot of concentration \( C \) against \( C/\theta \) resulted in a straight line (Fig. 6a–c) accordingly with Langmuir adsorption isotherm, which can be expressed as:

\[ \frac{C}{\theta} = \frac{1}{K_{ads}} + C \]  

where \( K_{ads} \) is the adsorption equilibrium constant which can be calculated from the intercept of the straight line on the \( C/\theta \)-axis. In all 3 cases, the linear regression coefficients \( R^2 \) are almost equal to 1 and the slopes are very close to 1, indicating that these green inhibitors were adsorbed on the MS surface according to Langmuir adsorption isotherm [42]. \( K_{ads} \) values found for leaves extract are
2500 L g$^{-1}$ for both impedance and polarization studies; bark extract showed 2500 L g$^{-1}$ for impedance and 5000 L g$^{-1}$ for polarization studies while 3β-isodihydrocadambine showed 527 L g$^{-1}$ for impedance and 1360 L g$^{-1}$ for polarization studies. Higher values of $K_{ads}$ showed that the inhibitor adsorbed more strongly on MS surface [43].

3.4. SEM analysis

To establish whether corrosion inhibition is due to the formation of green inhibitor’s protective film on the metal surface, SEM images were taken. Fig. 7 shows the results of the surface morphology of SEM analysis of the samples (MS) examined. Fig. 7b presents the micrograph of MS obtained after exposure to 1 M HCl medium while Fig. 7c–e represents the surface morphology of MS specimens immersed in 1 M HCl medium containing 5 mg L$^{-1}$ of corrosion inhibitors viz., N. cadamba bark, leaves and 3β-isodihydrocadambine respectively. Parallel features on the polished MS surface before exposure to the corrosive solution, which are associated with polishing scratches (Fig. 7a) were observed.

Fig. 7b shows the SEM image after immersion, which revealed a severe damage on the MS surface due to metal dissolution. It appeared that material dissolution began on grain boundaries between ferrite and perlite. It is well known that grain boundaries are active sites where dislocations and other lattice defects are accumulated, so that iron oxide/oxyhydroxide deposition is likely to be initiated on grain boundaries to be later spread to the whole surface. Fig. 7c–e shows the protected MS surface after addition of green inhibitors, whereby the surface damage has diminished in comparison to the blank material. This is attributed to the formation of a good protective film on the MS surface.

3.5. FTIR studies

The FTIR spectra were taken for the characterization of the pure alkaloid, 3β-isodihydrocadambine as well as the scratched protective film formed over the MS surface and are given in Fig. 8a and b, respectively. FTIR spectra (Fig. 8a) of 3β-isodihydrocadambine showed peaks which may be assignable to O–H, N–H bending (3418 cm$^{-1}$), carbonyl of a methyl ester (1666 cm$^{-1}$) and aromatic C=C stretches (indole moiety) at 1582 cm$^{-1}$, 1487 cm$^{-1}$ and 1460 cm$^{-1}$ [27]. In Fig. 8b, the carbonyl peak (1666 cm$^{-1}$ Fig. 8a) that has shifted and merged with the N–H bending peak (1620 cm$^{-1}$ Fig. 8a) and with aromatic C=C

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<th>Table 3</th>
<th>Calculated quantum chemical parameters for pure alkaloid (3β-isodihydrocadambine) and iron (Fe, Fe$^{2+}$ and Fe$^{3+}$).</th>
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<tr>
<td>Compound</td>
<td>$E_{HOMO}$ (eV)</td>
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<tr>
<td>Pure alkaloid</td>
<td>$-0.188$</td>
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<tr>
<td>Fe</td>
<td>$-0.201$</td>
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<tr>
<td>Fe$^{2+}$</td>
<td>$-1.001$</td>
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<td>Fe$^{3+}$</td>
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Fig. 11. Electron density distribution on Iron, (a) Fe (HOMO and LUMO together), (b) Fe$^{2+}$ (HOMO), (c) Fe$^{2+}$ (LUMO), (d) Fe$^{3+}$ (HOMO), (e) Fe$^{3+}$ (LUMO).

Fig. 12. Possible mode of interaction of 3β-isodihydrocadambine on MS surface in 1 M HCl medium.
peak (1582 cm$^{-1}$ Fig. 8a) to give a broad absorption band centred at 1628 cm$^{-1}$ (Fig. 8b) is observed. Further, aromatic C=C peaks at 1460 cm$^{-1}$ and 1487 cm$^{-1}$ were merged, broadened and shifted to 1455 cm$^{-1}$ (Fig. 8b). These observations suggested that aromatic indole moiety and carbonyl groups of 3β-isodihydrocadambine may be involved in the corrosion inhibition process by coordinating with the iron metal.

3.6. Molecular modelling studies

Molecular modelling study was carried out to determine the electron rich groups/atoms in a molecule as well as calculation of the highest molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) will give further insights on the possibility of electron transfer between the inhibitor and metal. The optimized geometry of 3β-isodihydrocadambine is given in Fig. 9 and their corresponding Frontier molecular orbitals (HOMO and LUMO) are shown in Fig. 10a and b respectively. Fig. 11 shows the molecular orbitals of iron (Fe, Fe$^{2+}$ and Fe$^{3+}$) while the energy levels viz., $E_{\text{HOMO}}$, $E_{\text{LUMO}}$ and $\Delta E$ calculated are depicted in Table 3. From Fig. 10, it is evident that electron density (HOMO) is located within the vicinity of the aromatic indole moiety while that of LUMO is located on carbonyl group (C=O). An ideal corrosion inhibitor has a greater tendency to donate electrons, receive electrons or bind strongly to the metal surface [44] which suggests that 3β-isodihydrocadambine may donate electrons to the metal surface through HOMO (indole moiety) and accept electrons from the metal surface through LUMO (carbonyl group). These observations are in agreement with the FTIR results that suggested these two groups (aromatic indole moiety and carbonyl group) are involved in coordination with the MS surface. Further, $E_{\text{HOMO}}$ value for 3β-isodihydrocadambine was found to be $-0.188$ eV, which was higher (less negative) than that of iron values ($-0.201, -1.001$ and $-1.765$ eV). The literature shows that $E_{\text{HOMO}}$ is often associated with the electron donating ability of the molecule and the $\eta$ (%) increases with increase in the values of $E_{\text{HOMO}}$ [45]. A higher value of $E_{\text{HOMO}}$ for 3β-isodihydrocadambine than of iron [45] clearly suggests that it has a greater potential to donate electrons. Moreover, higher energy gap values ($\Delta E$) will prevent the interelectron transfer and prefer the electron donation to MS.

From Table 3, it is clear that the energy gap values follow the order, Fe > 3β-isodihydrocadambine > Fe$^{2+}$ > Fe$^{3+}$, which suggested that 3β-isodihydrocadambine has an ability to donate electrons preferably to Fe$^{2+}$ and Fe$^{3+}$. Thus, molecular modelling studies supported well the corrosion inhibition potential of 3β-isodihydrocadambine while its possible mode of interaction with metal surface is given in Fig. 12.

3.7. Mechanism of corrosion inhibition

The inhibition of MS corrosion in acidic solutions by crude alkaloid extract and 3β-isodihydrocadambine can be explained on the basis of an adsorption process. From the polarization results, it is evident that these compounds inhibit the corrosion by controlling both the anodic and cathodic reactions. In acidic solutions the compounds may exist as protonated species. These protonated species adsorb on the cathodic sites of the MS and decrease the evolution of hydrogen. Adsorption on anodic sites occurs through the π-electrons of aromatic rings and the lone pair electrons of nitrogen and oxygen atoms, which decreases anodic dissolution of mild steel [46]. The inhibitory properties are very similar thus implying that 3β-isodihydrocadambine is the major contributor to the activity. However its inhibitory value is slightly lower than the crude which may suggest that other alkaloids in the crude extract may have additional contribution to the corrosion inhibition effects.

4. Conclusion

In this study, corrosion inhibition efficiency of N. cadamba leaves and bark extract, 3β-isodihydrocadambine on MS in 1 M HCl medium was determined by polarization, impedance and SEM analysis. Results evidenced that all these green inhibitors showed excellent performance (more than 80% at 5 mg L$^{-1}$) as corrosion inhibitors. They inhibit corrosion through adsorption process and were found to follow Langmuir adsorption isotherm. Impedance studies revealed that the inhibitors reduced the corrosion rate by increasing the resistance of the system, and the equivalent circuit was found to fit well with CPE. Potentiodynamic polarization studies confirmed that all the inhibitors acted through mixed type of corrosion inhibition mechanism. SEM studies supported that green inhibitors formed protective layer on MS surface during the inhibition process. FTIR analysis suggested that aromatic indole ring and carbonyl group of 3β-isodihydrocadambine are involved in coordination with the MS surface. Molecular modelling studies supported well the FTIR findings and evidenced the possibility of electron transfer from inhibitor to metal surface. The findings from this study suggest that the alkaloids of N. cadamba, in particular 3β-isodihydrocadambine, are potential eco-friendly corrosion inhibitors which may be beneficial to related industries.

Acknowledgments

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.corsci.2012.11.042.

References
