Caulerpin—A bis-Indole Alkaloid As a Green Inhibitor for the Corrosion of Mild Steel in 1 M HCl Solution from the Marine Alga *Caulerpa racemosa*

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Ⓢ *Supporting Information*

ABSTRACT: A marine alga *Caulerpa racemosa* was tested for its anticorrosion potential against mild steel in 1 M HCl solution by weight loss and electrochemical methods such as potentiodynamic polarization and electrochemical impedance spectroscopic studies at various temperatures viz., 303, 313, and 323 K. The results showed that inhibition efficiency increased with increase of extract concentration and decreased with increase of temperature. The adsorption of the molecules of the extract on the mild steel surface was in accordance with the Temkin adsorption isotherm. Polarization studies showed that the extract inhibits mild steel corrosion through mixed mode and electrochemical impedance spectroscopy (EIS) results confirm the adsorption of the extract at mild steel/acid interface. The major phytoconstituent caulerpin, a bis-indole alkaloid isolated and characterized using UV, IR and NMR spectroscopic studies, was tested for anticorrosion activity using polarization, impedance, and atomic force microscopy (AFM) studies. The AFM results confirmed the formation of a protective layer by caulerpin over mild steel surface. Thus the anticorrosion potential of *C. racemosa* can be correlated to the presence of caulerpin.

INTRODUCTION

The acidization of petroleum oil wells is one of the well-known simulation methods for oil exploration which involves the use of hydrochloric acid solution. In order to reduce the aggressive attacks of acid on tubing and casting materials, inhibitors are usually incorporated to acid solutions during acidization processes.[1] Corrosion inhibitors act by adsorption of ions or molecules over metal surfaces. They reduce the corrosion rate mainly by increasing or decreasing the anodic and/or cathodic reactions, decreasing the diffusion rate for reactants to the surface of the metal and increasing the electrical resistance of the metal surface. Several reports have been documented on the use of many synthetic organic compounds such as 2-mesityl-1*H*-imidazo-[4,5-f][1,10]-phenanthroline,[2] 2-acetylpyridine-*N*(4)-morpholine thiosemicarbazone,[3] some vinylimidazolium ionic liquids,[4] some diamine derivatives,[5] and some piperidin-4-one oximes[6−8] as effective corrosion inhibitors for acid media. For industrial and large scale use, cost of the inhibitor, its toxicity, availability, and environment friendliness are very important.[9] Nevertheless, the known hazardous effects of these synthetic organic inhibitors and the need to develop cheap, nontoxic, and eco-friendly processes have now made researchers focus on the use of natural products.[10−16] There have been reports on the corrosion inhibition potential of plant extracts from our laboratory which showed that *Solanum nigrum*,[17] *Rauvolfia serpentina*,[18] *Solanum tuberosum*,[19] *Calotropis procera*,[20] *Piper nigrum*,[21] *Strychnos nux-vomica*,[22] *Datura stramonium*,[23] *Datura metel*,[24,25] and *Spirulina platensis*[26] served as efficient corrosion inhibitors for mild steel in acid media. Plant extracts from *Shinopsis lorentzii*,[27] *Aloe vera*,[28] *Punica granatum*,[29] and *Zenthoxylum alatum*[30] have also been found to be effective corrosion inhibitors for metals in acid media. The use of natural products as corrosion inhibitors has been well-documented.[31]

Caulerpa racemosa (*C. racemosa*) is a Chlorophyta of the order Bryopsidales belonging to the family Caulerpaceae. The marine alga is commonly known as sea grapes and is predominantly distributed along the Indian coastal region. *C. racemosa* contains sesquiterpenes, caulerpin—an alkaloid present to the extent of 2%, and reducing sugars such as galactose, glucose, arabinose, xylose, mannose, and rhamnose along with amino acids.[32,33] It has been reported to have anti-inflammatory, antinociceptive, antihypertensive, antiviral, cytotoxic properties, etc.[34,35] In the present work, *Caulerpa racemosa*, the marine alga found in the corrosive environment of seawater, has been tested for its corrosion inhibition potential in acid medium using mild steel. Further, the alkaloid present in this marine alga has also been investigated for its corrosion inhibition activity by potentiodynamic polarization, electrochemical impedance spectroscopy, Fourier transform infrared (FT-IR) analysis, and atomic force microscopy (AFM).

EXPERIMENTAL SECTION

Isolation and Characterization of Phytoconstituent. Caulerpin (Figure 1) is a bis-indole alkaloid reported as the major constituent of *C. racemosa*.[31] The residue obtained after evaporation of the methanolic extract of *C. racemosa* was chromatographed on a column of silica gel (60−120 mesh) and was eluted successively with various percentages of solvent mixtures containing petroleum ether, chloroform, and methanol. The fractions eluted with petroleum ether−chloroform (1:1) afforded a red crystalline substance which was
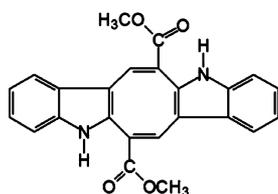
Figure 1. Structure of caulerpin.

characterized using UV, IR, and NMR spectroscopic techniques.[36]

Preparation of *C. racemosa* Extract for Corrosion Inhibition Studies. The marine alga collected from the Indian coastal region was washed thoroughly in running water to remove unwanted impurities, then dried, and powdered. The 300 g of powdered material was refluxed with methanol for about 6 h. The resulting solution was concentrated and evaporated to get a residue which was powdered and used for the study of the corrosion inhibition properties. An appropriate amount of the powdered residue was dissolved in 1 M HCl (AR grade) solutions to get desired concentrations of inhibitor solution ranging from 20 to 100 ppm. Mild steel specimens of the following percentage of composition C = 0.07%, Mn = 0.34%, P = 0.08%, and the remaining percentage Fe were used for the entire study. Prior to use, the specimens were abraded successively with fine grades (1/0, 2/0, 3/0, 4/0, 5/0, 6/0, and 7/0) of emery papers. The specimens were thoroughly washed with doubly distilled water, degreased with acetone, and then dried at room temperature.
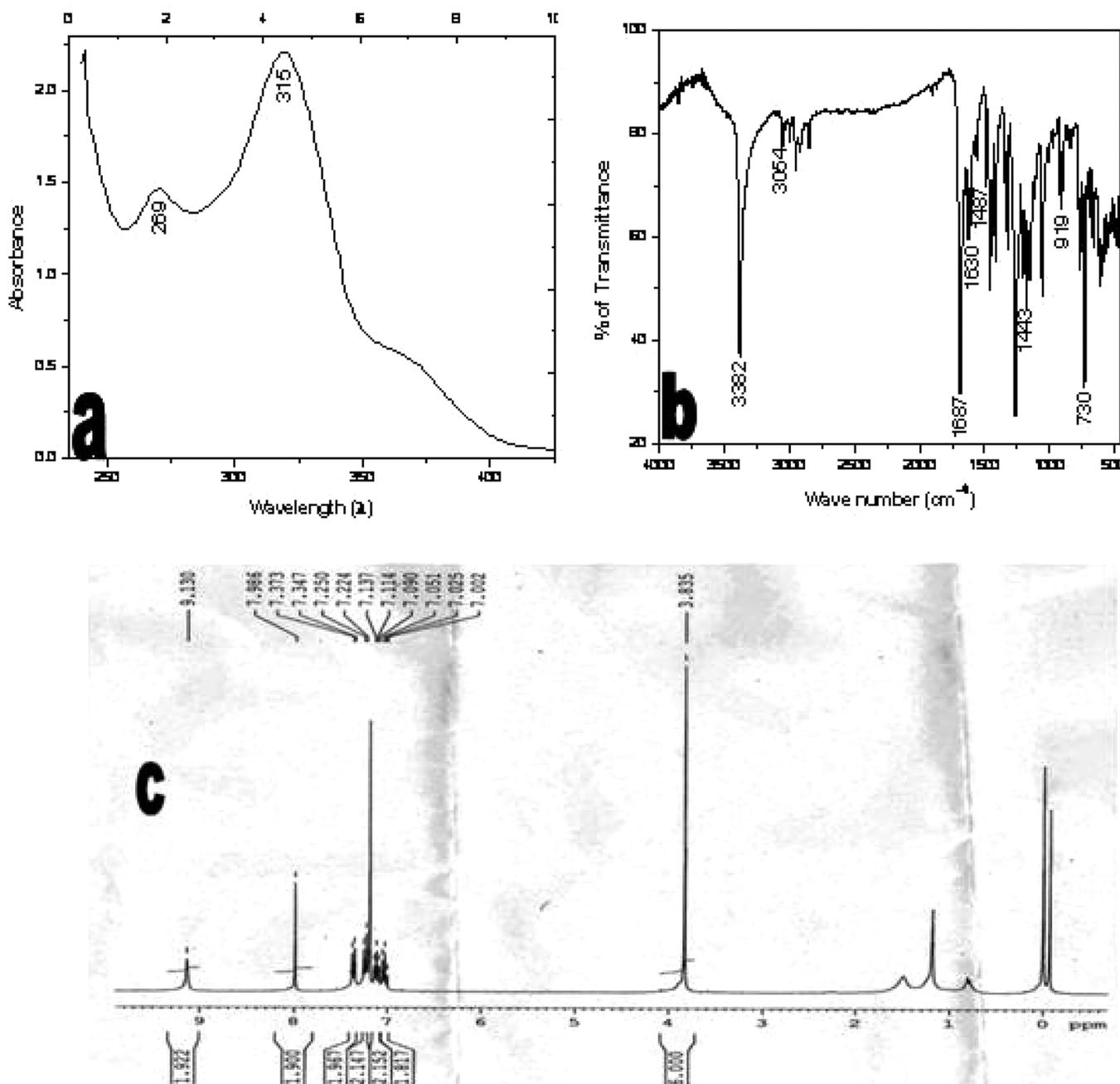

Figure 2. (a) UV spectrum of caulerpin. (b) IR spectrum of caulerpin. (c) ^{1}H NMR spectrum of caulerpin.

Weight Loss Method. The weight loss method was carried out on the preweighed mild steel specimens of regular form of dimension 4 cm × 1 cm × 0.2 cm in 100 mL of 1 M HCl solutions without and with addition of different concentrations viz., 20, 40, 60, 80, and 100 ppm of the extract at three different temperatures viz., 303, 313, and 323 K to study the anticorrosion properties. The specimens were immersed for about 2 h in test solutions. After the immersion period, the specimens were removed from test solutions carefully, washed with distilled water, dried, and again weighed in order to calculate the surface coverage, inhibition efficiency, and corrosion rate using following equations,

$$IE(\%) = \frac{W_0 - W_i}{W_0} \times 100 \tag{1}$$

where, W_0 and W_i are the weight loss values in the absence and presence of inhibitor, respectively.

$$CR = \frac{\text{weight loss of specimen}}{\text{immersion period} \times \text{surface area}} \tag{2}$$

Electrochemical Method. The electrochemical experiments viz., potentiodynamic polarization and electrochemical impedance spectroscopy, were carried out using CHI Electrochemical analyzer model 760 D with operating software CHI 760D. The analyzer had a three electrode cell setup (CHI-Corrosion Cell Kit) having a mild steel working electrode embedded in a Teflon holder with exposed surface area in corrosive environment of 0.785 cm², a saturated calomel electrode as reference electrode, and a platinum wire as counter electrode. All the electrochemical experiments were conducted for mild steel in 1 M HCl without and with different concentrations (20, 40, 60, 80, and 100 ppm) of *C. racemosa* extract at three different temperatures viz., 303, 313, and 323 K using 100 mL of test solutions in an electrical water bath fitted with temperature controller. Electrochemical experiments for mild steel in 1 M HCl in absence and presence of various concentrations of caulerpin at room temperature was also carried out. Before each potentiodynamic polarization and electrochemical impedance study, the electrode was allowed to corrode freely and its open circuit potential (OCP) was recorded as a function of time up to 30 min. After this time, the steady state OCP, corresponding to the corrosion potential of the working electrode, was obtained. The potentiodynamic Tafel measurements were started from cathodic to the anodic direction (OCP ± 300 mV) with a scan rate of 2 mV s⁻¹ and the parameters such as i_{corr}, E_{corr}, b_a, and b_c were calculated. From i_{corr}, the inhibition efficiency was calculated using the following relation,

$$IE(\%) = \frac{i_{corr}^0 - i_{corr}'}{i_{corr}^0} \times 100 \tag{3}$$

where, i_{corr}^0 and i_{corr}' are the corrosion current densities in absence and presence of inhibitor, respectively.

Electrochemical impedance spectroscopy measurements were carried out using ac signals of amplitude 5 mV peak to peak in the frequency range of 0.1 to 10 000 Hz. The electrochemical parameters such as R_{ct} and C_{dl} were calculated from EIS studies. Inhibition efficiency using R_{ct} was calculated using the following equation,

$$IE(\%) = \frac{R_{ct(i)} - R_{ct(b)}}{R_{ct(i)}} \times 100 \tag{4}$$

where, $R_{ct(i)}$ and $R_{ct(b)}$ are the charge transfer resistances in presence and absence of inhibitor, respectively.

FT-IR Analysis. FT-IR spectra were recorded with a frequency ranging from 4000 to 400 cm⁻¹ for the extract as well as the extract adsorbed on mild steel in 1 M HCl solution in KBr matrix using FT-IR JASCOW 460 plus model instrument.

AFM Analysis. For AFM analyses, mild steel specimens with dimension of 1 cm × 1 cm × 0.2 cm were immersed in test solution without inhibitor as well as in test solution containing 25 ppm of inhibitor for 2 h at room temperature. Then, the samples were properly washed with doubly distilled water and dried in warm air. The exposed mild steel specimens were subjected to AFM analysis using a Nanosurf Easyscan2 instrument.

■ RESULTS AND DISCUSSION

Structure of Phytoconstituent—Caulerpin. The red solid (mp 308 °C) obtained from the petroleum ether–chloroform (1:1) showed maximum absorption at λ_{max} 269 and 315 (Figure 2a) which suggested the presence of carbonyl functions in conjugation with aromatic ring system. This was supported by the IR (Figure 2b) absorption bands at 1687 and 1630 cm⁻¹ in the IR spectrum. The bands at 3382 and 1612 cm⁻¹ are responsible for the stretching and bending frequencies of the —N—H group, respectively. The strong aromatic character is indicated by the bands at 3054, 1487, and 1443 cm⁻¹, and bands at 730 and 919 cm⁻¹ could be correlated to the presence of aromatic ring system. The ¹H NMR (Figure 2c) spectrum showed the presence of 18 protons. The chemical shift values are at δ 3.8 ppm (6H, s, 2 × —OCH₃), δ 7.0−7.6 ppm (8H, m, Ar H), δ 8.04 ppm (2H, s, 2 × =CH—) and δ 9.1 ppm (2H, s, 2 × —NH). The δ values at δ 7.0−7.6 ppm and 8.04 ppm suggested the presence of two identically condensed aromatic rings. From the results observed from spectroscopic investigations, the isolated compound was characterized as caulerpin. The spectral data are in good agreement with the previous reports on caulerpin.[34,36]

Weight Loss Studies. The corrosion rate and inhibition efficiency of mild steel exposed to 1 M HCl at 303 K as a function of concentration of *C. racemosa* is shown in Figure 3. It is observed that at 303 K, the corrosion rate of mild steel decreased and inhibition efficiency increased on increasing the extract concentration. This behavior could be attributed to the increase in adsorption of the extract at the mild steel/acid interface while increasing the concentration of *C. racemosa*. The extract showed maximum inhibition efficiency of 83% in HCl medium at an optimum concentration of 100 ppm at 303 K. Further increase in extract concentration did not produce significant changes in inhibition efficiency. To study the effect of temperature on the corrosion inhibition properties, mild steel specimens were exposed to the acid solution containing various concentrations of the extract at three different temperatures such as 303, 313, and 323 K. The calculated corrosion rate and inhibition efficiencies are shown in Figure 3. The corrosion rate values increased and the inhibition efficiency decreased with increase in temperature. This is due to the fact that, at higher temperatures, the metal dissolution process is enhanced and the adsorbed inhibitor molecules are partially desorbed from the surface of metal.[13]
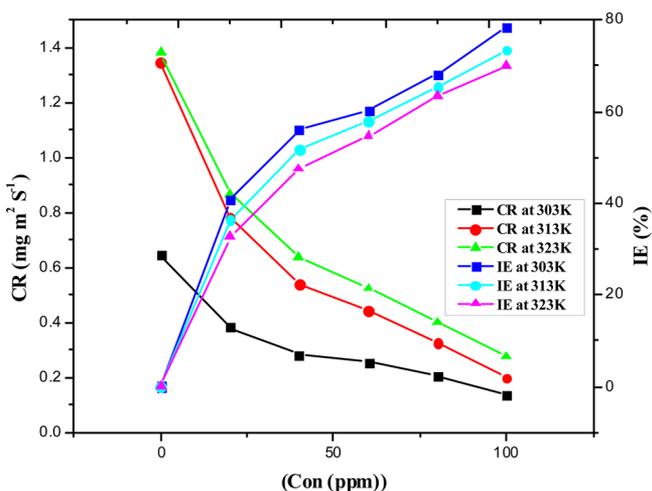
Figure 3. Concentration of *C. racemosa* extract vs corrosion rate and percent of IE.

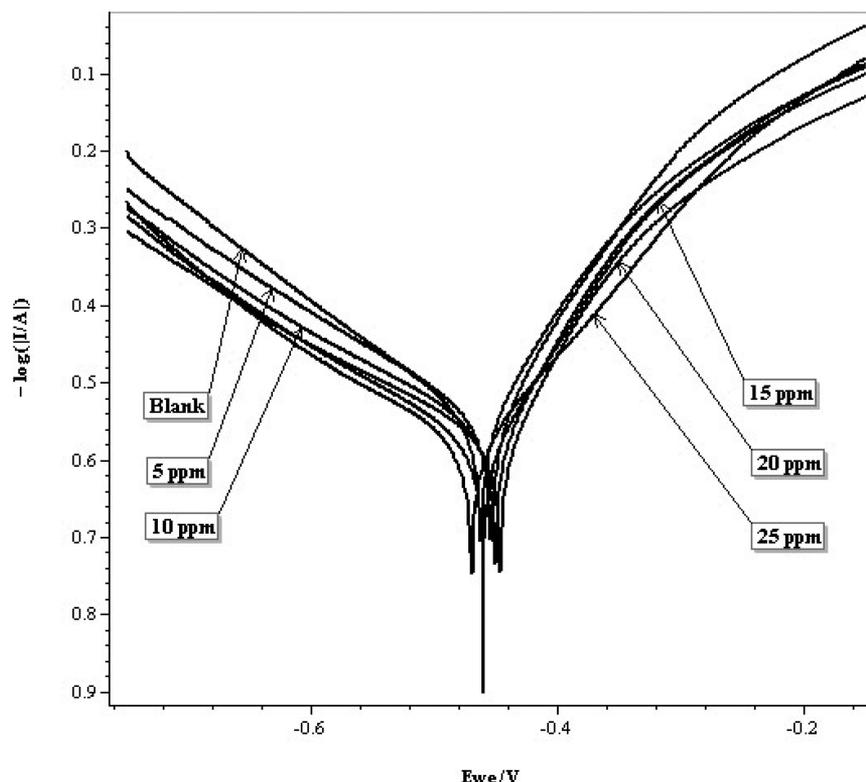**Electrochemical Studies.** *Potentiodynamic Polarization.* The anodic and cathodic polarization curves for the corrosion of mild steel in 1 M HCl with different concentrations of *C. racemosa* extract at three different temperatures viz., 303, 313, and 323 K are depicted in Figure S1 in the Supporting Information. The values of corrosion current density (i_{corr}), the corrosion potential (E_{corr}), the anodic Tafel slopes (b_a), the cathodic Tafel slopes (b_c), and the inhibition efficiency (IE) as a function of the extract concentrations at temperatures (303, 313, and 323 K) are listed in the Supporting Information (Table S1).

The addition of *C. racemosa* extract diminishes the corrosion current density values significantly at all temperatures. At increasing concentrations of extract, the i_{corr} values decreased whereas IE values increased. Maximum IE was obtained for 100 ppm of the extract concentration at 303 K. At higher temperatures, the IE values were found to decrease with increase in temperature, which could be due to weakening of adsorption process at higher temperatures.

From the Figure S1 (Supporting Information), it can be seen that, the cathodic domain decreased with increase in extract concentration. But at 323 K, there was a small change observed, which may be due to high temperature of reaction medium, indicating the inhibition of hydrogen evolution reaction. Further, the parallel cathodic Tafel curves indicated that the hydrogen evolution reaction is activation controlled and the reduction mechanism is not affected by the addition of *C. racemosa* extract.[37,38] The unchanged cathodic domain curves also indicated the inhibitive action of the extract by simply blocking the active sites of the metal surface. In the anodic region, the curves are parallel, but in some cases, the acceleration of anodic reactions could also be observed. But the addition of extract did not change both cathodic and anodic slope values significantly indicating the mixed mode behavior of inhibitor. Further, the E_{corr} values were also not shifted to any particular region supporting the mixed mode action of inhibitor. Similar results have also been observed for mild steel in 1 M HCl in absence and presence of various concentrations of caulerpin (Figure 4) at 303 K. Maximum IE of 80% (Table 1) was obtained for 25 ppm of caulerpin. The result revealed the anticorrosion ability of caulerpin. Thus from the results of the above study, it is certain that anticorrosion property of *C. racemosa* could be influenced by caulerpin.

Electrochemical Impedance Spectroscopy. In order to find information about the kinetics of mild steel corrosion in the presence of extract, the electrochemical process taking place at


Figure 4. Tafel plots of mild steel in 1 M HCl without and with different concentrations of caulerpin.

Table 1. Electrochemical Parameters of Mild Steel Obtained by Potentiodynamic Polarization Method in 1 M HCl Containing Different Concentrations of Caulerpin

S. no.	conc (ppm)	b_a mV dec^{-1}	b_c mV dec^{-1}	$-E_{corr}$ mV	i_{corr} μA cm^{-2}	% of IE
1.	0	87	135	453	245	
2.	5	92	157	461	149	39
3.	10	86	165	451	105	57
4.	15	74	153	461	86	65
5.	20	92	170	446	59	76
6.	25	88	154	470	48	80

the open-circuit potential was studied by electrochemical impedance spectroscopy (EIS). The recorded spectrum for mild steel at 1 M HCl in the presence of different concentrations of the extract at various temperatures viz., 303, 313, and 323 K are shown in Figure S2 in the Supporting Information. The diameter of Nyquist plots increased with increase in extract concentration indicating the strengthening of protected layer formed by inhibitor molecules. The impedance diagram (Nyquist) contained a depressed semicircle with the center under the real axis. Such a behavior is characteristic for solid electrode which may be the result of surface roughness, dislocations, distribution of the active sites, or adsorption of the inhibitor molecules.[39] An equivalent circuit was introduced to explain the EIS data as shown in Figure 5. For the iron/acid
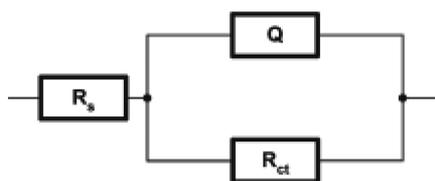
Figure 5. Equivalent circuit model.

interface model, this circuit is generally used to describe EIS data. In this circuit, R_s is solution resistance, R_{ct} is charge transfer resistance, and CPE is a constant phase element. The impedance function of the CPE is as follows:

$$Z_{CPE} = Y^{-1}(j\omega)^{-n} \tag{5}$$

where, Z_{CPE} is impedance of CPE, Y is proportional factor, ω is angular frequency, and n is surface irregularity. The CPE, which is considered as surface irregularity of the electrode, causes greater depression in the Nyquist semicircle, where the metal−solution interface acts as a capacitor with an irregular surface. If the electrode surface is homogeneous and planar, the exponential value (n) becomes equal to 1 and the metal−solution interface will behave as a capacitor with a regular surface.

The simulation of the observed results with Randle's model containing constant CPE instead of capacitance and charge transfer resistance (R_{ct}) showed good agreement with experimental data. The calculated parameters from EIS data for the corrosion of mild steel in 1 M HCl in presence of *C. racemosa* extract at various temperatures are listed in the Supporting Information (Table S2). The R_{ct} values increased and C_{dl} values decreased with increase in extract concentration which revealed the decrease of the corrosion of mild steel with increase of extract concentration. Decrease in C_{dl} values could be attributed to decrease in local dielectric constant/increase in

the thickness of the protective layer formed by inhibitor molecules. This observation supported the adsorption of inhibitor at mild steel/solution interface. The lesser value of n for 1 M HCl shows the surface inhomogeneity and roughening of metal surface caused by corrosion. The reduction of n values with addition of inhibitor indicated the reduction of surface inhomogeneity due to the adsorption of extract molecules over the surface of mild steel.

EIS experiments conducted with different concentrations of *C. racemosa* at various temperatures (303, 313, and 323 K) showed a decrease of inhibition performance with rise of temperature. Decrease of charge transfer resistance (R_{ct}) values and increase of double layer capacitance (C_{dl}) values result in a decrease in inhibition efficiency. The decrease in IE at higher temperatures agreed well with the results of weight loss and potentiodynamic polarization studies.[40] The same trend in results were observed for mild steel in 1 M HCl medium in the absence and presence of various concentrations of caulerpin also (Figure 6). Maximum IE of 85% (Table 2) was shown by caulerpin at a concentration of 25 ppm. Thus the results of EIS confirmed the corrosion inhibition potential of *C. racemosa* and caulerpin.

Adsorption Isotherm. The adsorption isotherm can provide adequate information about the interaction of inhibitor molecules with metal. Organic corrosion inhibitors decrease the corrosion of metal through the adsorption on the surface of the metal followed by the formation of protective layer. The adsorption is usually regarded as a substitution process between the organic molecules present in the inhibitor and water molecules adsorbed at the metal−solution interface.[41] To study adsorption behavior of *C. racemosa* extract, various isotherms were used, and it was found that the Temkin isotherm fitted with the experimental data well. Figure S3 in the Supporting Information shows the Temkin isotherm of mild steel in 1 M HCl solution with various concentrations of the inhibitor at various temperatures. The free energy of adsorption values (ΔG_{ads}) were calculated using Temkin isotherm by the following equation.

$$\Delta G = -RT \ln(55.5)K \tag{6}$$

In the above equation, 55.5 is molar concentration of water. The value of $-\ln K$ was calculated from the slope of the Temkin isotherm. The calculated ΔG_{ads} values are listed in Table S3 (Supporting Information). The negative sign of ΔG_{ads} values indicated the spontaneity of adsorption. The ΔG_{ads} around -30 kJ mol.$^{-1}$ confirmed the physisorption of the extract over the surface of mild steel. The physisorption may occur due to the interaction of π electrons of the inhibitor and metal.[42]

Activation Parameter. From weight loss measurements carried out at three different temperatures viz., 303, 313, and 323 K, Arrhenius plots were drawn (Figure S4 in the Supporting Information). The activation energy of corrosion of mild steel in 1 M HCl in absence and presence of the inhibitor was calculated from the slope of the Arrhenius plots using following equation,

$$\ln CR = \frac{-E_a}{RT} + \ln A \tag{7}$$

The E_a values calculated from the equation were listed in the Supporting Information (Table S4). As can be seen from the table, E_a values increased with the increase in the concentration of inhibitor. This is due to the fact that, after the addition of
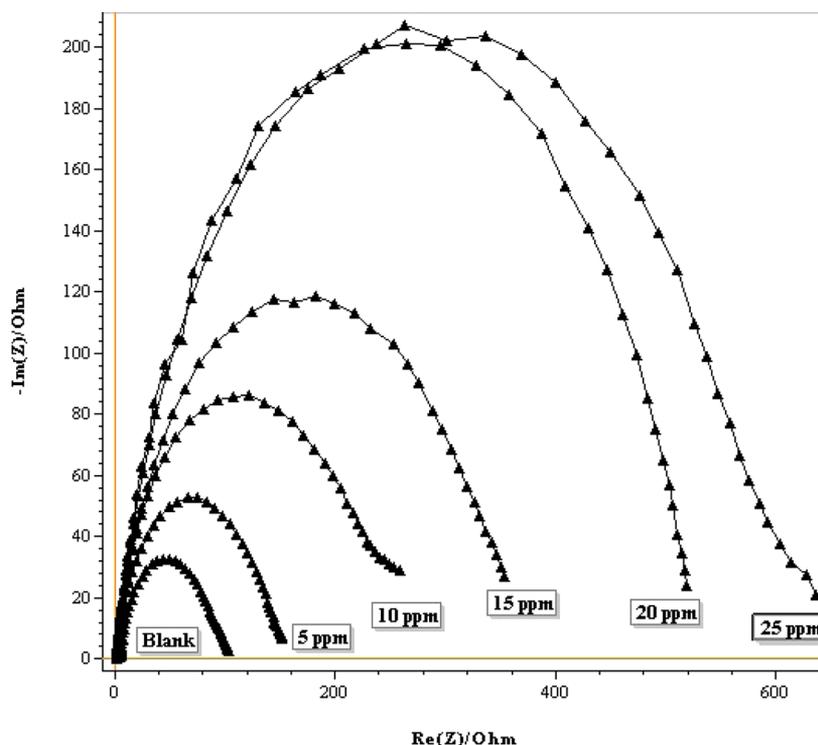
Figure 6. Nyquist plots of mild steel in 1 M HCl without and with different concentrations of caulerpin.

Table 2. Electrochemical Parameters of Mild Steel Obtained by EIS Method in 1 M HCl Containing Different Concentrations of Caulerpin

S. no.	conc (ppm)	R_{ct} Ω cm^{-2}	C_{dl} μF cm^{-2}	n	% of IE
1.	blank	98	82.3	0.803	
2.	5	149	73.6	0.794	34
3.	10	255	56.2	0.789	62
4.	15	353	53.3	0.777	72
5.	20	519	47.4	0.765	81
6.	25	635	44.5	0.758	85

inhibitor, the energy barrier of corrosion reaction increased which resulted in the inhibitive action of *C. racemosa* extract.[43]

FT-IR Analysis. Figure 7 shows the comparison of the IR spectra of the *C. racemosa* extract with that of extract adsorbed
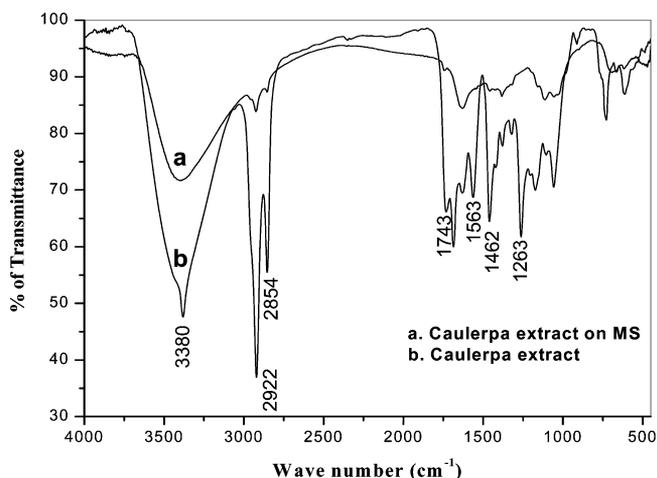

Figure 7. IR spectra of *C. racemosa* extract and extract on mild steel.

on mild steel, which showed a shift from 3380 to 3398 cm^{-1} (N—H stretching of indole nucleus). The band corresponding to C=C at 1461 cm^{-1} disappeared due to the interaction of π electrons of aromatic rings with metal. The band at 1563 cm^{-1} of N—H bending disappeared in spectral line b, which confirmed the interaction of N—H group with metal. The shift of C=O and C—O stretching frequency from 1743 to 1740 cm^{-1} and from 1263 to 1056 cm^{-1}, respectively, confirmed the adsorption of organic molecules of *C. racemosa* on mild steel.

AFM Analysis. AFM is a dynamic tool to examine the surface morphology at nano to micro scale level and has become a new choice to study the nature of protective layer formed over the surface of mild steel.[11] Figure 8a–c, showed the AFM 3D images of polished mild steel, mild steel in 1 M HCl without inhibitor, and mild steel in 1 M HCl with 25 ppm of inhibitor, respectively. As can be seen from the AFM images, the surface is very clear for polished mild steel specimen (Figure 8a) whereas in mild steel immersed in 1 M HCl (Figure 8b) the surface is severely damaged by aggressive acid solution. In Figure 8c, the surface is protected from acid attack by the protective layer formed by the inhibitor molecules. From the AFM images, the average roughness factor (Sa) was calculated as 74.59, 558.34, and 131.89 nm for polished mild steel, mild steel in 1 M HCl without inhibitor, and mild steel in 1 M HCl with 25 ppm of inhibitor respectively which clearly indicated that the surface of mild steel has been protected by inhibitor molecules. From the results, it is clear that the inhibition of mild steel corrosion in 1 M HCl is mainly due to the formation of protective layer by adsorption of inhibitor molecules over the surface of mild steel.

Mechanism of Inhibition. The increase in inhibition efficiency of *C. racemosa* extract with increase in concentration showed that, the inhibitor molecules are adsorbed on the mild steel surface at higher concentration, leading to greater surface

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dx.doi.org/10.1021/ie3010379 | *Ind. Eng. Chem. Res.* 2012, 51, 10399–10407
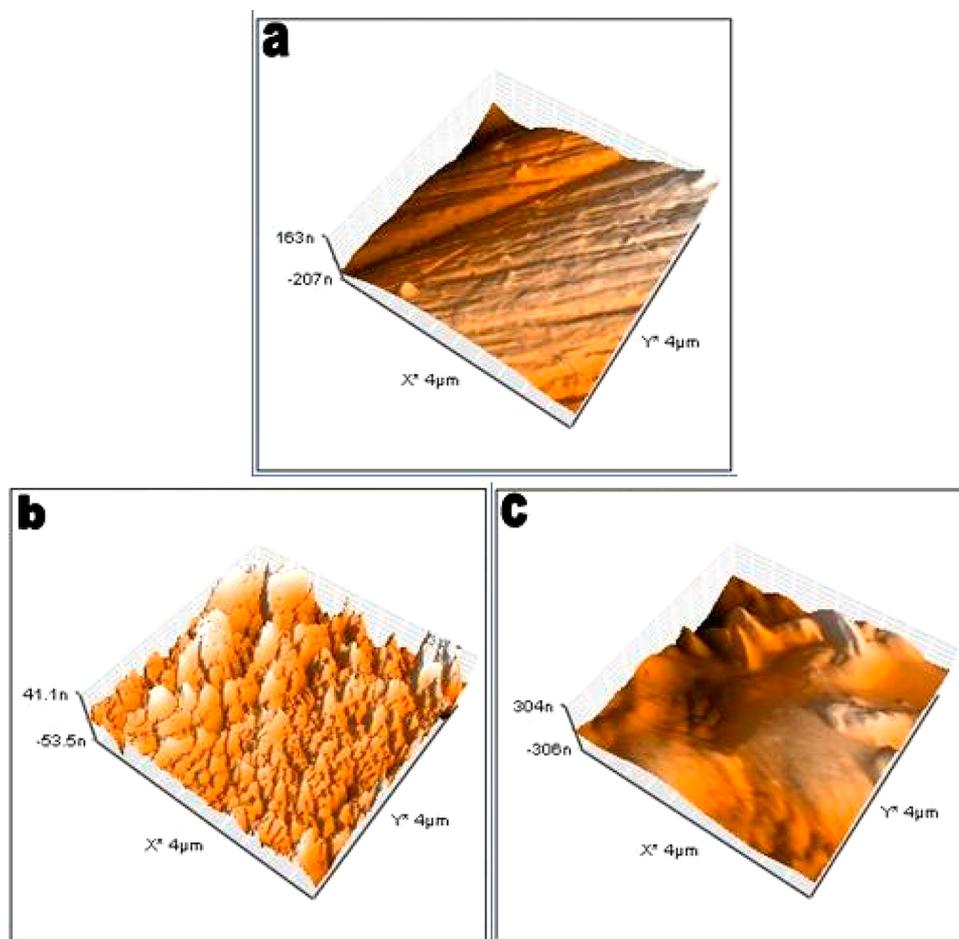
Figure 8. AFM 3D images of (a) polished mild steel, (b) mild steel in 1 M HCl without caulerpin, and (c) mild steel in 1 M HCl with 25 ppm of caulerpin.

coverage (θ). It is a well-known fact that, the first step in the adsorption of an organic inhibitor over mild steel involves the replacement of water molecules from metal surface by inhibitor molecules.

The mixed inhibition mechanism suggested by the polarization data is in accordance with the findings of Oguzie et al.[44] and those of El Azar et al.[45] on the adsorption behavior of organic molecules containing N atoms. In acid solutions, organic inhibitors may interact with the corroding metal and then retard the corrosion reaction in more than one way, sometimes simultaneously. It is therefore often difficult to assign a single general mechanism, since the mechanism may change with experimental conditions. Nitrogen containing compounds tend to favor physisorption.[46]

It is likely that, the groups such as −NH, ester, and aromatic moiety present in the *C. racemosa* extract are readily protonated in HCl solutions. Both molecular and protonated species can be adsorbed on the metal surface. The adsorption of protonated −NH group can occur on the preadsorbed chloride ions on metal surface. Adsorption of protonated −NH group on the cathodic sites on mild steel surface retards hydrogen evolution reaction. Adsorption on the anodic sites of mild steel surface occurs via aromatic (π electrons) and ester groups to retard mild steel dissolution process. Adsorption of inhibitor molecules on mild steel surface is assisted by hydrogen bond formation between the extract and metal, which is evident from IR spectra (Figure 7). This type of adsorption is more prevalent

for protonated inhibitors, because the positive charge on the N atoms is conducive to the formation of hydrogen bonds.[47] *C. racemosa* thus has the ability to influence both the cathodic and anodic partial reactions, giving rise to the mixed mode of inhibition.

■ CONCLUSION

From the results, it is obvious that *C. racemosa* acts as a good inhibitor for corrosion of mild steel in the 1 M HCl solution. The inhibitor prevents the corrosion in a dose dependent manner. Inhibition efficiency of *C. racemosa* extract decreased with the increase in temperature, which is due to the physisorption. Adsorption of *C. racemosa* on mild steel obeyed the Temkin isotherm. The results of Arrhenius plots revealed the inhibition potential of *C. racemosa*. From the electro-chemical studies, it is evident that *C. racemosa* and also its major chemical consituent caulerpin act as a mixed type inhibitors in 1 M HCl solution. AFM and IR spectra results supported the surface film formation over the surface of mild steel by inhibitor. The study carried out with caulerpin clearly revealed that the corrosion inhibitive effect of *C. racemosa* could be correlated to the presence of caulerpin along with synergistic influence of other phytoconstituents.

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dx.doi.org/10.1021/ie3010379 | *Ind. Eng. Chem. Res.* 2012, 51, 10399−10407

■ ASSOCIATED CONTENT

ⓢ Supporting Information

Results of electrochemical investigations (potentiodynamic polarization and a.c. impedance spectroscopy), adsorption isotherm, and Arrhenius plots for mild steel in 1 M HCl without and with different concentrations of *C. racemosa* extract at various temperatures are given here. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

■ REFERENCES

(1) Ekanem, U. F.; Umoren, S. A.; Udousoro, I. I.; Udoh, A. P. Inhibition of mild steel corrosion in HCl using pineapple leaves (*Ananas comosus* L) extract. *J. Mater. Sci.* **2010**, *45*, 5558.

(2) Obot, I. B.; Obi-Egbedi, N. O.; Eseola, A. O. Anticorrosion Potential of 2-Mesityl-1H-imidazo[4,5-f][1,10]-phenanthroline on Mild Steel in Sulfuric Acid Solution: Experimental and Theoretical Study. *Ind. Eng. Chem. Res.* **2011**, *50*, 2098.

(3) Loganathan, S.; Kumar, Ashok; Gopiraman, M.; Saravana Kumar, M.; Sreekanth, A. 2-Acetylpyridine-N(4)-Morpholine Thiosemicarbazone (HAcpMTSc) as a Corrosion Inhibitor on Mild Steel in HCl. *Ind. Eng. Chem. Res.* **2011**, *50*, 7824.

(4) Guzman-Lucero, D.; Olivares-Xometl, O.; Martínez-Palou, R.; Likhanova, N. V.; Domínguez-Aguilar, M. A.; Garibay-Febles, V. Synthesis of Selected Vinylimidazolium Ionic Liquids and Their Effectiveness as Corrosion Inhibitors for Carbon Steel in Aqueous Sulfuric Acid. *Ind. Eng. Chem. Res.* **2011**, *50*, 7129.

(5) Yurt, A.; Bereket, G. Combined Electrochemical and Quantum Chemical Study of Some Diamine Derivatives as Corrosion Inhibitors for Copper. *Ind. Eng. Chem. Res.* **2011**, *50*, 8073.

(6) Senthilkumar, A. N.; Tharini, K.; Sethuraman, M. G. Steric Effect of Alkyl Substituted Piperidin-4-one Oximes for Corrosion Control of Mild Steel in H_2SO_4 Medium. *Acta Phys. Chim. Sin.* **2012**, *28*, 399.

(7) Senthilkumar, A. N.; Sethuraman, M. G. Studies on Few Substituted Piperidin-4-one oximes as Corrosion Inhibitor for Mild Steel in HCl. *J. Mater. Eng. Perform.* **2011**, DOI: 10.1007/s11665-010-9719-9.

(8) Senthilkumar, A. N.; Tharini, K.; Sethuraman, M. G. Corrosion inhibitory effect of few Piperidin-4-one oximes on mild steel in hydrochloric medium. *Surf. Rev. Lett.* **2009**, *16*, 141.

(9) ji, G.; Shukla, S. K.; Dwivedi, P.; Sundaram, S.; Prakash, R. Inhibitive Effect of *Argemone mexicana* Plant Extract on Acid Corrosion of Mild Steel. *Ind. Eng. Chem. Res.* **2011**, *50*, 11954.

(10) Obot, I. B.; Obi-Egbedi, N. O. An interesting and efficient green corrosion inhibitor for aluminium from extracts of *Chlomolaena odorta* L. in acidic solution. *J. Appl. Electrochem.* **2010**, *40*, 1977.

(11) Satapathy, A. K.; Gunasekaran, G.; Sahoo, S. C.; Kumar, Amit; Rodrigues, P. V. Corrosion inhibition by *Justicia gendarussa* plant extract in hydrochloric acid solution. *Corros. Sci.* **2009**, *51*, 2848.

(12) Oguzie, E. E. Evaluation of the inhibitive effect of some plant extracts on the acid corrosion of mild steel. *Corros. Sci.* **2008**, *50*, 2993.

(13) Singh, A.; Ahamad, I.; Singh, V. K.; Quraishi, M. A. Inhibition effect of environmentally benign Karanj (*Pongamia pinnata*) seed extract on corrosion of mild steel in hydrochloric acid solution. *J. Solid State Electrochem.* **2011**, *11*, 1087.

(14) Behpour, M.; Ghoreishi, S. M.; Khayatkashani, M.; Soltani, N. Green approach to corrosion inhibition of mild steel in two acidic solutions by the extract of *Punica granatum* peel and main constituents. *Mater. Chem. Phys.* **2012**, *131*, 621.

(15) Bouyanzer, A.; Hammouti, B.; Majidi, L. Pennyroyal oil from *Mentha puligium* as corrosion inhibitor for steel in 1 M HCl. *Mater. Lett.* **2006**, *60*, 2840.

(16) El-Etre, A. Y. Khillah extract as inhibitor for acid corrosion of SX 316 steel. *Appl. Surf. Sci.* **2006**, *252*, 8521.

(17) Raja, P. B.; Sethuraman, M. G. *Solanum nigrum* as natural source of corrosion inhibitor for mild steel in sulphuric acid medium. *Corros. Eng. Sci. Tech.* **2010**, *45*, 455.

(18) Raja, P. B.; Sethuraman, M. G. Studies on the Inhibition of Mild Steel Corrosion by *Rauvolfia serpentina* in Acid Media. *J. Mater. Eng. Perform.* **2010**, *19*, 761.

(19) Raja, P. B.; Sethuraman, M. G. *Solanum Tuberosum* as an Inhibitor of Mild Steel Corrosion in Acid Media. *Iran. J. Chem. Chem. Eng.* **2009**, *28*, 77.

(20) Raja, P. B.; Sethuraman, M. G. Inhibition of Corrosion of mild steel in Sulphuric acid medium by *Calotropis procera*. *Pig. Res. Tech.* **2009**, *38*, 33.

(21) Raja, P. B.; Sethuraman, M. G. Inhibitive effect of black pepper extract on the sulphuric acid corrosion of mild steel. *Mater. Lett.* **2008**, *62*, 2977.

(22) Raja, P. B.; Sethuraman, M. G. *Strychnos nux-vomica* - an eco-friendly corrosion inhibitor for mild steel in 1M sulfuric acid medium. *Mater. Corros.* **2008**, *60*, 22.

(23) Raja, P. B.; Sethuraman, M. G. Studies on the inhibitive effect of *Datura stramonium* extract on the acid corrosion of mild steel. *Surf. Rev. Lett.* **2007**, *14*, 1457.

(24) Raja, P. B.; Sethuraman, M. G. Atropine sulphate as corrosion inhibitor for mild steel in sulphuric acid medium. *Mater. Lett.* **2008**, *62*, 1602.

(25) Raja, P. B.; Sethuraman, M. G. Corrosion inhibition of mild steel by *Datura metel* (leaves) in acidic medium. *Pig. Res. Tech.* **2005**, *34*, 327.

(26) Kamal, C.; Sethuraman, M. G. *Spirulina platensis* — A novel green inhibitor for the acid corrosion of mild steel. *Arab. J. Chem.* **2012**, *5*, 155.

(27) Gerengi, H.; Sahin, H. I. *Schinopsis lorentzii* as a green corrosion inhibitor for low carbon steel in 1M HCl solution. *Ind. Eng. Chem. Res.* DOI: 10.1021/ie20176q.

(28) Abiola, O. K.; James., O. A. The effects of *Aloe vera* extract on the corrosion and kinetics of corrosion process of Zn in HCl solution. *Corros. Sci.* **2010**, *52*, 661.

(29) Chidiebere, M. A.; Ogukwe, C.; Oguzie, K.; Eneh, C.; Oguzie, E. E. Corrosion inhibition and adsorption behavior of *Punica granatum* extract on mild steel in acidic environments — Experimental and theoretical studies. *Ind. Eng. Chem. Res.* **2012**, *51*, 668−677.

(30) Chauhan, L. R.; Gunasekaran, G. Corrosion inhibition of mild steel by plant extract in dilute HCl medium. *Corros. Sci.* **2007**, *49*, 1143.

(31) Raja, P. B.; Sethuraman, M. G. Natural Products as corrosion inhibitor for metals in corrosive media - A review. *Mater. Lett.* **2008**, *62*, 113.

(32) Ghosh, P.; Adhikari, U.; Ghosal, P. K.; Pujol, C. A.; Carlucci, M. J.; Damonte, E. B.; Ray, B. In vitro anti-herpetic activity of sulfated polysaccharide fractions from *Caulerpa racemosa*. *Phytochem.* **2004**, *65*, 3151.

(33) Anjaneyulu, S. R.; Prakash, C. V. S.; Mallavadhani, U. V. Two Caulerpin analogues and a sesquiterpene from *Caulerpa racemosa*. *Phytochem.* **1991**, *30*, 3041.

10406

dx.doi.org/10.1021/ie3010379 | *Ind. Eng. Chem. Res.* 2012, 51, 10399−10407

(34) Tenório de Souza, E.; Pereira de Lira, D.; Cavalcanti de Queiroz, A.; Costa da Silva, D. J.; Bezerra de Aquino, A.; Campessato Mella, E. A.; Lorenzo, V. P.; Emmanuel C. de Miranda, G.; Xavier de Araújo-Júnior, J.; Célia de Oliveira Chaves, M.; Barbosa-Filho, J. M.; Filgueiras de Athayde-Filho, P.; Viviana de Oliveira Santos, B.; Alexandre-Moreira, M. S. The Antinociceptive and Anti-Inflammatory Activities of Caulerpin, a Bisindole Alkaloid Isolated from Seaweeds of the Genus Caulerpa. *Mar. Drugs* **2009**, *7*, 689.

(35) Rocha, P. D.; Soares, A. R.; Houghton, P. J.; Pereira, R. C.; Kaplan, M. A. C.; Teixeira, V. L. Potential Cytotoxic Activity of Some Brazilian Seaweeds on Human Melanoma Cells. *Phytother. Res.* **2007**, *21*, 170.

(36) Ayyad, S. E. N.; Badria, F. A. Caulerpin, an antitumor índole alkaloid from *Caulerpa racemosa*, *Alex. J. Pharm. Sci.* **1994**, *8*, 217.

(37) Fu, J. J.; Li, S. N.; Cao, L. H.; Wang, Y.; Yan., L. H.; Lu, L. D. L-Tryptophan as green corrosion inhibitor for low carbon steel in hydrochloric acid solution. *J. Mater. Chem.* **2010**, *45*, 979.

(38) Aljourani, J.; Raeissi, K.; Golozar, M. A. Benzimidazole and its derivatives as corrosion inhibitors for mild steel in 1M HCl solution. *Corros. Sci.* **2009**, *51*, 1836.

(39) Shukla, S. K.; Quraishi, M. A. 4-Substituted anilinomethylpropionate: New and efficient corrosion inhibitors for mild steel in hydrochloric acid solution. *Corros. Sci.* **2009**, *51*, 1990.

(40) Ehteshamzadeh, M.; Shahrabi, T. Innovation in acid pickling treatments of copper by characterizations of a new series of Schiff bases as corrosion inhibitors. *Anti Corros. Meth. Mater.* **2006**, *53*, 296.

(41) Oguzie, E. E.; Njoku, V. O.; Enenebeaku, C. K.; Akalezi, C. O.; Obi, C. Effect of hexamethylpararosaniline chloride (crystal violet) on mild steel corrosion in acidic media. *Corros. Sci.* **2008**, *50*, 3480.

(42) Abdeli, M.; Parvini-Ahmadi, N.; Khosroshahi, R. A. Corrosion inhibition of mild steel in hydrochloric acid by 6-aminohexanoic acid. *Mater. Corros.* **2010**, *61*, 147.

(43) Abdeli, M.; Parvini-Ahamadi, N. Khosroshahi. Nile blue and indigo carmine dyes as corrosion inhibitor of mild steel in hydrochloric acid. *J. Solid State Electrochem.* **2010**, *14*, 1317.

(44) Oguzie, E. E.; Onuoha, G. N.; Onuchukwu, E. I. Inhibitory mechanism of mild steel corrosion in 2 M sulphuric acid solution by methylene blue dye. *Mater. Chem. Phys.* **2004**, *89*, 305.

(45) El Azar, M.; Mernari, B.; Traisnel, M.; Bentiss, F.; Lagrenee, M. Corrosion inhibition of mild steel by the new class of inhibitors [2,5-bis(n-pyridyl)-1,3,4-thiadiazoles] in acidic media. *Corros. Sci.* **2001**, *43*, 2229.

(46) Fragnani, A.; Trabanelli, G. Influence of Organic Additives on the Corrosion of Iron-Based Amorphous Alloys in Dilute Sulfuric Acid Solution. *Corrosion* **1999**, *55*, 653.

(47) Khaled, K. F.; Amin, M. A. Computational and electrochemical investigation for corrosion inhibition of nickel in molar nitric acid by piperidines. *J. Appl. Electrochem.* **2008**, *38*, 1609.