Performances of Alkaloid Extract from *Rauvolfia macrophylla* Stapf toward Corrosion Inhibition of C38 Steel in Acidic Media

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Supporting Information

**ABSTRACT:** Alkaloid extract from *Rauvolfia macrophylla* Stapf (AERMS) was studied as the corrosion inhibitor for C38 steel in 1 M HCl and 0.5 M H2SO4 using electrochemistry and surface analysis. The corrosion inhibition was efficient and proceeds via adsorption of AERMS on the steel surface due to the active functional groups present in the molecules. AERMS acts as a mixed inhibitor in HCl and as a cathodic inhibitor in H2SO4. In H2SO4 corrosive medium, the presence of iodides improves the adsorption of the alkaloid molecules by reducing the surface charge of the electrode and thus substantially decreases the corrosion rate. Two pure alkaloids (tetrahydroalastonine (THA) and perakine (PER)) were quantitatively isolated from AERMS, and their anticorrosive properties for C38 steel in 1 M HCl and 0.5 M H2SO4 were evaluated. THA showed the highest efficiency while the performance of PER was less important compared to the extract. This confirms that the efficiency of AERMS was the result of the complementary action of the chemical compounds present in the extract.

1. INTRODUCTION

The pickling process, cleaning and removal of localized deposits (rust, bacterial deposits, calculus, etc.) from pipes and other steel based structures used in industries, are generally performed in concentrated acid solutions.12,13 These aggressive milieus easily corrode metals during the cleaning process. Inhibitors are frequently added to the acidic solution before application to prevent or reduce corrosion. At relatively low concentrations, inhibitors can substantially reduce metal corrosion.13,14 The most commonly used inhibitors in acid medium are organic compounds whose efficiency is attributed to the presence of heteroatoms (O, N, S, and P) in their structures.15,16 These heteroatoms can coordinate with iron(II) resulting from steel corrosion, forming complexes at the metal surface, thereby serving as a barrier to aggressive agents.13,16

Nitrogen-rich compounds are attractive as corrosion inhibitors. The large amount of nitrogen-rich corrosion inhibitors are synthetic compounds.1,12,13 However, it was shown recently that natural compounds extracted from plants also display very interesting properties.6,7,15,24 Moreover, plant extracts have the advantage of being less expensive, easily obtained, renewable, highly biodegradable, available, and especially nontoxic to the environment.25,26 Among these natural nitrogen-rich compounds extracted from plants and used as corrosion inhibitors, alkaloids represent the most important family. The size, functionalities, and geometry of these molecules are determining parameters that explain their efficiencies when used as corrosion inhibitors.27

Alkaloid extract of various origins have been shown to have excellent corrosion inhibition properties toward C38 steel in acidic media, mainly HCl.15,16,28–30 Some other studies also reported that these inhibition properties decrease slightly when the temperature of the corrosive solution was increased.14,31 In general, the activity of these compounds as corrosion inhibitors are explained by the formation of a passive layer at the metal surface, which reduces its accessibility to corrosion agents.15 Although the nature and the chemical composition of this passive layer are not well elucidated yet; it is obvious that it consists mainly of a mixture of the alkaloids and corrosion products.15,16

Cameroon, with its large forest and exceptional biodiversity, is considered as a reservoir of natural substances with interesting pharmacologic applications. Indeed, lots of compounds have been isolated from local plants by organic chemists,32 many of which are alkaloids that are potential corrosion inhibitors. *Rauvolfia macrophylla* Stapf (RMS) is a Cameroonn medicinal plant belonging to the Apocynaceae family. This plant contains huge alkaloid fraction and is highly solicited in traditional medicine, especially in the treatment of various diseases like rheumatism, hepatitis, and malaria. Despite, its high alkaloid content, the use of RMS as a corrosion inhibitor has never been reported to the best of our knowledge.

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The aim of this work is to investigate the corrosion inhibitory properties of alkaloid extract from RMS on C38 steel in 1 M hydrochloric acid and 0.5 M sulfuric acid media. This included the elucidation of the protection mechanism involved and the study of the effect of some external parameters such as the experimentation temperature and the amount of the extract. The use of an additive such as iodide to improve the inhibition efficiency was also scrutinized. The comparative study of the alkaloid extract and the isolated compounds (tetrahydroalstonine (THA) and perakine (PER)) in the extract is performed. For this to be achieved, the alkaloid fraction was first extracted from the RMS bark, and the corrosion inhibition parameters were obtained from electrochemical measurements (polarization and electrochemical impedance spectroscopy curves).

2. RESULTS AND DISCUSSION

2.1. Corrosion Inhibition Effect of AERMS in HCl and H2SO4 Solution. 2.1.1. Electrochemical Impedance Spectroscopy (EIS). EIS curves (Nyquist and Bode representations) of C38 steel in 1 M HCl and 0.5 M H2SO4 obtained in the absence on one hand and presence on the other hand of AERMS at various concentrations are presented in Figure 1.

The Nyquist plots in 1 M HCl and 0.5 M H2SO4 solutions with the AERMS (Figure 1a,d, respectively) display the capacitive loop characteristic of the corrosion process controlled by a charge transfer step on a solid electrode with a heterogeneous and irregular surface. The diameters of the capacitive half-loops of the Nyquist diagrams and the impedance modulus (Figure 1b,e) increased gradually with the AERMS concentration in the corrosive solution. However, this increase is not proportional because as the concentration doubles, the distance between the curves remains approximately equal. The inductive loops at lower frequencies were attributed to the relaxation processes due to ion adsorption (mainly Clads, Hads, and SO4ads) on the electrode surface. The best equivalent circuit that matches the experimental data of the Nyquist plots is presented in the inset of Figure 1a for hydrochloric acid and Figure 1d for sulfuric acid, where Rf (the first intersection of the semicircle with the Z axis) represents the resistance of the corrosive solution; Rct (the second intersection of the semicircle with the Z axis) is the charge transfer resistance, L is the inductance, which is intimately associated with the inductive loop at low frequencies; Rrs is the resistive element; and A is the CPE (constant phase element) constant that accounts for surface inhomogeneity. After the fitting procedure, these electrochemical parameters are recorded in Table 1.

Low values of the goodness of fit (χ2) indicate that the fitted data have good agreement with the experimental data. The values of the charge transfer resistance increases with the amount of the AERMS in solution, while the double layer capacitance (Cdl) decreases at the same time. The formation of a protective layer (due to the reaction of alloy when in contact with oxygen of the solution) by adsorption on the surface of the C38 steel electrode fully explains the trend of the values of Rf and Cdl obtained. These molecules are probably associated to the corrosion products to form a protective layer, which reduces the number of active corrosion sites. The values of deviation from the ideal behavior (n) did not vary significantly, therefore confirming the charge transfer controlled mechanism of C38 steel without and with inhibitor. The thickness of the protective layer depends on the concentration of the inhibitor in solution: for high AERMS concentrations, the rather higher thickness was noticed, substantially increasing the charge resistance transfer and thus the inhibition efficiency. The adsorbed layer also affects the double layer capacitance (Cdl) at the electrode/solution interface by replacing water molecules. The best inhibition efficiency (97%) obtained in the hydrochloric acid solution compared to sulfuric acid (93%) could be due to the beneficial adsorption of chloride ions at the anode surface.

2.1.2. Polarization Curves. The potentiodynamic curves (logarithmic transformation) recorded in hydrochloric acid and in sulfuric acid solutions in the absence and presence of AERMS at various concentrations are presented in Figure 2.

The corrosion parameters (corrosion potential (Ecorr), corrosion current densities (Icorr), cathodic Tafel slope (βc), and anodic Tafel slope (βa)) extracted from Figure 2a,b are presented in Table 2. This table also presents the inhibition efficiencies (IE) based on experimental corrosion current densities.

A shift in corrosion potential is insignificant and cannot be ascribe to the act of the corrosion inhibitor. The cathodic branch (assigned to the proton reduction) and the anodic branch (assigned to the oxidation of iron) of the signal are well defined. In both acids, the current densities recorded in the cathodic part of the curves decrease gradually with the amount of the AERMS added, showing that the extract inhibits the cathodic reaction associated to the corrosion process.
observation was made on the anodic part of the curve recorded in HCl, that is, a decrease in the iron oxidation current with AERMS concentration. In sulfuric acid, the decrease in the oxidation current densities was not clearly observed. AERMS can thus be considered as a cathodic inhibitor in sulfuric acid and a mixed inhibitor with predominant cathodic effectiveness in HCl. The values of the anodic and cathodic ($\beta_a$ and $\beta_c$) slopes in both acids are respectively modified with the addition of the inhibitor. These observations suggest that inhibition is controlled by anodic and cathodic reactions. One can also notice that at high oxidation potentials (> −0.25 mV in HCl and > −0.35 mV in H$_2$SO$_4$), almost no variation of the oxidation current densities was observed even when the extract was present in the corrosive medium.

Table 1. Corrosion Parameters Extracted from Experimental Data and the Corresponding Corrosion Inhibition Efficiency in 1 M HCl and 0.5 M H$_2$SO$_4$ Containing Different Concentrations of AERMS

| Concentration (mg L$^{-1}$) | $R_m$ (Ω cm$^2$) | $10^{-3} A$ (Ω$^{-1}$ s$^{-1}$ cm$^{-2}$) | $n$ | $C_d$ (μF cm$^{-2}$) | $L$ (H cm$^2$) | $R_i$ (Ω cm$^2$) | $\chi^2$ | IE (%) |
|---------------------------|-----------------|-------------------------------|-----|-----------------|----------------|----------------|--------|--------|
| 1 M HCl                   |                 |                               |     |                 |               |               |        |        |
| 0                         | 14.6            | 3.048                         | 0.9792 | 1147            | 3.49           | 1.6            | 0.0050 |        |
| 5                         | 53.2            | 1.413                         | 0.9508 | 457             | 1.69           | 51.1           | 0.0081 | 73     |
| 10                        | 71.1            | 1.027                         | 0.9581 | 453             | 1.04           | 10.1           | 0.0071 | 80     |
| 25                        | 98.0            | 1.118                         | 0.9330 | 329             | 4.56           | 92.3           | 0.0090 | 85     |
| 50                        | 226.7           | 0.394                         | 0.9093 | 188             | 2.10           | 22.6           | 0.0050 | 94     |
| 100                       | 372.0           | 0.177                         | 0.9380 | 87              | 1.55           | 367.4          | 0.0089 | 96     |
| 200                       | 554.0           | 0.142                         | 0.8589 | 77              | 23.04          | 20.0           | 0.0054 | 97     |
| 0.5 M H$_2$SO$_4$         |                 |                               |     |                 |               |               |        |        |
| 0                         | 29.6            | 1.334                         | 0.8425 | 620             | 250.10         | 425.8          | 0.0081 |        |
| 5                         | 40.2            | 1.014                         | 0.8409 | 605             | 364.40         | 334.2          | 0.0089 | 26     |
| 10                        | 79.0            | 0.392                         | 0.8192 | 175             | 399.50         | 1213.0         | 0.0019 | 63     |
| 25                        | 123.4           | 0.302                         | 0.8149 | 149             | 1088.00        | 1293.0         | 0.0058 | 76     |
| 50                        | 189.0           | 0.323                         | 0.8644 | 128             | 2265.00        | 2048.0         | 0.0019 | 84     |
| 100                       | 290.0           | 0.184                         | 0.8779 | 84              | 596.00         | 2900.0         | 0.0079 | 90     |
| 200                       | 428.0           | 0.173                         | 0.8537 | 100             | 2400.00        | 6732.0         | 0.0029 | 93     |

Figure 2. Potentiodynamic polarization curves for C38 steel obtain in (a) 1 M HCl and (b) 0.5 M H$_2$SO$_4$ in the absence and presence of different concentrations of AERMS.

Table 2. Polarization Parameters and the Corresponding Inhibition for the Corrosion of C38 Steel in 1 M HCl and 0.5 M H$_2$SO$_4$ for Various AERMS Concentrations

| Concentration (mg L$^{-1}$) | $E_{corr}$ (mV/SCE) | $J_{corr}$ (μA/cm$^2$) | $-\beta_c$ (mV/decade) | $\beta_a$ (mV/decade) | IE (%) |
|---------------------------|---------------------|------------------------|------------------------|------------------------|--------|
| 1 M HCl                   |                     |                        |                        |                        |        |
| 0                         | −469                | 381                    | 134                    | 88                     |        |
| 5                         | −483                | 143                    | 129                    | 78                     | 63     |
| 10                        | −479                | 114                    | 126                    | 76                     | 70     |
| 25                        | −477                | 85                     | 119                    | 79                     | 78     |
| 50                        | −464                | 47                     | 112                    | 84                     | 88     |
| 100                       | −443                | 34                     | 118                    | 74                     | 91     |
| 200                       | −474                | 30                     | 119                    | 83                     | 92     |
| 0.5 M H$_2$SO$_4$         |                     |                        |                        |                        |        |
| 0                         | −481                | 234                    | 53                     | 44                     |        |
| 5                         | −477                | 192                    | 49                     | 49                     | 18     |
| 10                        | −482                | 101                    | 39                     | 45                     | 57     |
| 25                        | −471                | 71                     | 35                     | 48                     | 70     |
| 50                        | −485                | 36                     | 54                     | 47                     | 85     |
| 100                       | −468                | 22                     | 35                     | 46                     | 91     |
| 200                       | −473                | 16                     | 36                     | 59                     | 93     |
As expected, the corrosion current density greatly decreased as the amount of AERMS in the solution grows from 234 to 16 μAc m⁻² in H₂SO₄ and from 381 to 30 μAc m⁻² in HCl. Consecutively to these, substantial diminishes of \( J_{\text{corr}} \) and high percentages of IE up to 90% were obtained for AERMS concentrations higher than 100 mg/L. One particularly noticeable result was the high efficiency of the inhibitor in HCl at lower concentrations (IE of 63% at 5 mg/L) compared to H₂SO₄ (18% at 5 mg/L). This clearly showed that the counteranion of the acid was inactive during the inhibition process.¹³,²⁶ The corrosion potential has no direct correlation with the composition of the corrosive solution as it varies randomly.¹⁶

Ours results clearly show that the activity of AERMS as an inhibitor proceeds via a step of its adsorption at the surface of the steel electrode, making the accessibility of the metal to protons more difficult. The adsorption of the inhibitor at the surface of the steel electrode was confirmed by FTIR analysis of the thin layer recovered at the electrode surface after its immersion in a corrosive solution containing AERMS for 3 h (Figure 3 and Table 3).

During this adsorption step, the water molecules and other ionic species previously adsorbed on the metal surface are replaced by the inhibitor molecules. In order to assess the spatial distribution of the inhibitor on the metal surface, the coverage (θ) was determined at a given AERMS concentration, and these experimental data fitted with a well-known linearized Langmuir model (eq 1)³⁶,³⁷

\[
\frac{C_{\text{inh}}}{\theta} = \frac{1}{K} + C_{\text{inh}}
\]

\[
\theta = \left(1 - \frac{R_{\text{ct}}}{R_{\text{ct(inh)}}}\right)
\]

(1)

where \( K \) is the Langmuir adsorption equilibrium constant, and \( C_{\text{inh}} \) (mg/L) is the concentration of the inhibitor. Figure 4 represents the results obtained for HCl and H₂SO₄.

| function | AERMS powder | deposit in HCl + AERMS | deposit in H₂SO₄ + AERMS | deposit in HCl | deposit in H₂SO₄ |
|----------|--------------|------------------------|--------------------------|---------------|-----------------|
| H₂O      | 3360         | 3420                   | 3442                     | 3414          | 3430            |
|          | 1630         | 1630                   | 1630                     | 1630          | 1630            |
| C−H      | 3000–2800    | 2980–2800              | 2980–2800                | 2980–2800     | 2980–2800       |
| C=O      | 1730         | 1736                   | 1736                     | 1736          | 1736            |
| SO₄      | 1104         | 1096                   |                          |               |                 |

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\[
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\]

\[
\theta = \left(1 - \frac{R_{\text{ct}}}{R_{\text{ct(inh)}}}\right)
\]

(1)

where \( K \) is the Langmuir adsorption equilibrium constant, and \( C_{\text{inh}} \) (mg/L) is the concentration of the inhibitor. Figure 4 represents the results obtained for HCl and H₂SO₄.

The correlation coefficients (quite close to 1 (\( R^2 > 0.99 \)) both in 1 M HCl and 0.5 M H₂SO₄) tend to show that the Langmuir adsorption isotherm was suitable to describe AERMS adsorption in a single layer on the C38 steel surface.¹⁵

2.1.3. Field Emission Scanning Electron Microscopy (FESEM) Analysis. This surface analysis technique is used to visualize very small topographic details on the surface and to
produce less electrostatically distorted images. Figure 5 shows the surface morphology of C38 steel during FESEM analysis. FESEM micrograph observation of the surface obtained before immersion (Figure 5a) is smooth. After immersion in 1 M HCl and 0.5 M H₂SO₄ solutions in the absence of the inhibitor, a highly damaged steel surface was observed (Figure 5b,c) with the presence of clusters of iron and punctures. This is due to the oxidation of iron in the absence of the inhibitor. In the presence of AERMS (Figure 5c–e), the surface of steel exhibits an absence of rust. By comparing the micrographs...
obtained after immersion in the two solutions without inhibitor, we can conclude that the surface of steel in the presence of AERMS is almost free of corrosion. These observations can be explained by the formation of a film made up of alkaloid molecules on the steel surface preventing the access of aggressive agents.\textsuperscript{1,6,13,15}

2.2. Effect of Temperature. Corrosion inhibitors are used in various environments submitted to noticeable temperature variations. The corrosion mechanism being essentially a surface phenomenon should then be very sensitive to temperature variations.

2.2.1. Polarization Curves. The polarization curves recorded at 30, 40, 50, and 60 °C in 1 M HCl and 0.5 M H$_2$SO$_4$ solutions without and with the optimal concentration of AERMS (100 mg/L) are presented in Figure 6. The electrochemical parameters and the inhibition efficiencies derived from these curves are recorded in Tables 4 and 5.

![Polarization curves for C38 steel at different temperatures in (a) 1 M HCl, (b) 1 M HCl + 100 mg/L AERMS, (c) 0.5 M H$_2$SO$_4$, (d) 0.5 M H$_2$SO$_4$ + 100 mg/L AERMS.](image)

**Figure 6.** Polarization curves for C38 steel at different temperatures in (a) 1 M HCl, (b) 1 M HCl + 100 mg/L AERMS, (c) 0.5 M H$_2$SO$_4$, (d) 0.5 M H$_2$SO$_4$ + 100 mg/L AERMS.

**Table 4.** Corrosion Parameters and the Corresponding Inhibition Efficiency at Different Temperatures in 1 M HCl without and with 100 mg/L AERMS

| Temperature (°C) | $E_{corr}$ (mV/SCE) | $i_{corr}$ (μA/cm$^2$) | $\beta_a$ (mV/decade) | $\beta_c$ (mV/decade) | IE (%) |
|-----------------|----------------------|------------------------|-----------------------|-----------------------|--------|
| 1 M HCl         |                      |                        |                       |                       |        |
| 30              | –469                 | 381                    | 134                   | 88                    |        |
| 40              | –471                 | 769                    | 145                   | 81                    |        |
| 50              | –461                 | 2550                   | 186                   | 96                    |        |
| 60              | –447                 | 4368                   | 192                   | 167                   |        |
| 1 M HCl + AERMS |                      |                        |                       |                       |        |
| 30              | –443                 | 33                     | 118                   | 74                    | 91     |
| 40              | –481                 | 74                     | 147                   | 76                    | 90     |
| 50              | –519                 | 176                    | 192                   | 104                   | 93     |
| 60              | –533                 | 477                    | 177                   | 139                   | 89     |

As expected, the temperature increases with the current densities in the absence of the corrosion inhibitor. The corrosion current densities ($i_{corr}$) follow the same trend, confirming the harmful effect of the temperature increase in the corrosion of C38 steel. This tendency is preserved even in the presence of the inhibitor (100 mg/L). However, in HCl + 100 mg/L AERMS, it is mainly the anodic branch that was strongly affected by the temperature increase, whereas it was the cathodic branch in the case of H$_2$SO$_4$. These results clearly suggest that the mechanism of action of the extract as the corrosion inhibitor of C38 steel is different in the two acid solutions. The decrease in inhibition efficiency in 0.5 M H$_2$SO$_4$ when the temperature was increased suggests the physical adsorption of the inhibitor molecules.\textsuperscript{15}

2.2.2. Thermodynamic Activation Parameters. In order to further the elucidation of these corrosion phenomena, the activation energy and thermodynamic parameters associated to the adsorption of AERMS on the C38 steel surface were determined. This was achieved using current densities obtained from the extrapolation of plots at different temperatures. The activation energy derived from the Arrhenius equation (eq 2)\textsuperscript{38} was obtained by plotting the logarithm of the experimental corrosion current density versus $(1/T)$ (Figure 7).

$$J_{corr} = K \exp \left( -\frac{E_a}{RT} \right)$$

(2)

where $K$ is the Arrhenius pre-exponential constant, $E_a$ (J/mol) is the activation energy, $T$ (K) is the temperature, and $R = 8.314$ J/(mol-K) is the gas constant.

The activation energy ($E_a$) values calculated from the slopes of the straight lines in the absence and presence of AERMS are listed in Table 6.

It is clear that the addition of 100 mg/L AERMS increases the apparent activated energy from 74.58 to 113.74 kJ/mol in 0.5 M H$_2$SO$_4$ and from 70.33 to 73.83 kJ/mol in 1 M HCl. This behavior suggests that AERMS inhibits the corrosion reaction by increasing its activation energy. This could be done by adsorption of the molecule inhibitor on the C38 steel surface, making a barrier to the mass and charge transfer.\textsuperscript{39}

Some other useful thermodynamic parameters such as the standard enthalpy of activation ($\Delta H_a$) and standard entropy of activation ($\Delta S_a$) can be derived from the Arrhenius equation (eq 3) put in a different form:

$$J_{corr} = \frac{RT}{N h} \exp \left( \frac{\Delta S_a}{R} \right) \exp \left( \frac{-\Delta H_a}{RT} \right)$$

(3)

where $h = (6.626 \times 10^{-34}$ J s) is the Planck constant, and $N = (6.022 \times 10^{23}$ mol$^{-1}$) is the Avogadro’s number. By plotting $\ln(J_{corr}/T) = f(1/T)$ (Figure 7c,d), $\Delta H_a$ and $\Delta S_a$ were determined (Table 6).

The positive values of $\Delta H_a$ both in the absence and presence of AERMS confirm the endothermic nature of C38 steel dissolution in acid media.\textsuperscript{15,31,40} By contrast, in the same condition, the values of $\Delta S_a$ are negative. However, $\Delta S_a$ is lower in the presence of the extract, confirming the higher stability of the protective layer when AERMS was added in HCl solution. Indeed, in the presence of the inhibitor, the Fe–inhibitor complex is formed in the place of Fe–H$_2$O. The decrease in the entropy upon inhibitor addition implies that the protecting layer is more ordered in the presence of the inhibitor.\textsuperscript{1}

The strong increase in the value of $\Delta S_a$ in 0.5 M H$_2$SO$_4$ with the addition of alkaloid extract (32.11 kJ/mol) indicates that the activated complex is more disordered in the presence of the
The effect of the anion (Cl\(^{-}\) or I\(^{-}\)) is very crucial on the overall adsorption process.

2.3. Effect of Iodide on the Efficiency of AERMS on the Corrosion Inhibition of C38 Steel. In order to improve the adsorption of AERMS on the steel surface in 0.5 M H\(_2\)SO\(_4\) medium, the halide ions may be used. Iodide is well known for its ability to enhance the efficiency of alkaloid extracts as corrosion inhibitors.\(^{41,42}\) The large size of this highly polarizable anion seems to be the factor responsible for this exceptional efficiency.\(^{43}\) The effect of the concentration of this anion on the efficiency of AERMS was investigated. The study was conducted exclusively in sulfuric acid because of the lower adsorption of the extract in this acid compared to HCl.

Figure 8a compares the Nyquist plots of the effect of 1 mM iodide on the corrosion of C38 steel in H\(_2\)SO\(_4\) without or with AERMS. The curve obtained in the presence of the extract without iodide is also plotted as a reference. The IE determined from \(R_{ct}\) and \(J_{corr}\) reported in Tables 7 and 8 shows that 1 mM iodide offers poor protection of steel against corrosion (IE of 61%). When iodide is associated to AERMS, a net decrease in current densities was observed, and IE moves from 90% without KI to 90% with 100 mg/L AERMS.

Table 5. Corrosion Parameters and the Corresponding Inhibition Efficiency at Different Temperatures in 0.5 M H\(_2\)SO\(_4\) without and with 100 mg/L AERMS

| temperature (°C) | \(E_{corr}\) (mV/SCE) | \(J_{corr}\) (μA/cm\(^2\)) | \(-\beta_{a}\) (mV/decade) | \(\beta_{a}\) (mV/decade) | IE (%) |
|-----------------|-----------------------|-----------------------------|--------------------------|--------------------------|-------|
| 0.5 M H\(_2\)SO\(_4\) | | | | | |
| 30 | -481 | 234 | 53 | 44 |
| 40 | -487 | 460 | 55 | 48 |
| 50 | -488 | 2066 | 56 | 58 |
| 60 | -488 | 2800 | 57 | 56 |
| 0.5 M H\(_2\)SO\(_4\) + AERMS | | | | | |
| 30 | -468 | 22 | 36 | 47 | 90 |
| 40 | -478 | 60 | 32 | 57 | 90 |
| 50 | -490 | 432 | 46 | 47 | 88 |
| 60 | -471 | 1069 | 38 | 74 | 85 |

Figure 7. Arrhenius plots of (a) \(\ln J_{corr}\) vs \(1/T\) and (c) \(\ln(J_{corr}/T)\) vs \(1/T\) in 1 M HCl and (b) \(\ln J_{corr}\) vs \(1/T\) and (d) \(\ln(J_{corr}/T)\) vs \(1/T\) in 0.5 M H\(_2\)SO\(_4\) in the temperature range of 30–60 °C and in the absence and presence of 100 mg/L AERMS.

Table 6. Thermodynamic Activation Parameters of C38 Steel in 1 M HCl and 0.5 M H\(_2\)SO\(_4\) without and with 100 mg/L AERMS

| solution | \(E_a\) (kJ mol\(^{-1}\)) | \(\Delta H_a\) (kJ mol\(^{-1}\)) | \(\Delta S_a\) (J mol\(^{-1}\) K\(^{-1}\)) |
|----------|--------------------------|-----------------------------|--------------------------|
| 1 M HCl  | 70.33 | 72.83 | -70.80 |
| 1 M HCl + 100 mg/L AERMS | 73.83 | 71.08 | -96.61 |
| 0.5 M H\(_2\)SO\(_4\) | 74.58 | 71.83 | -77.60 |
| 0.5 M H\(_2\)SO\(_4\) + 100 mg/L AERMS | 113.74 | 111.24 | 32.11 |
96% in the presence of the anion. These results clearly demonstrate that iodide improves the ability of the extract to protect the metal against the corrosive environment of the acidic solution. As a matter of fact, the IE is equivalent to the value obtained in HCl using identical AERMS concentrations.

The large size and the important polarizability of iodide facilitate the bonding of the anion at the metal surface through chemisorption. This is followed by the adsorption of protonated alkaloids present in AERMS on the first layer of adsorbed halide ions. AERMS adsorption was more homogeneous as it was directed by the first layer of well-adsorbed iodide. This results to a more uniform metal surface coverage and thus good protection. Potentiodynamic analysis (Figure 8b) shows that, in the presence of 1 mM iodide alone in the acidic solution, anodic protection was displayed. Associated to the extract, a mixed-type inhibitor was obtained as both cathodic and anodic protection was obtained. These results confirm once again the synergistic effect of KI toward the corrosion inhibition of C38 steel when added to the alkaloid extract. The corrosion parameters \((J_{corr} \text{ and } E_{corr})\) extracted from these curves confirmed this interpretation (Table 8).

2.4. Isolation of THA and PER and Study of Their Inhibition Efficiency. 2.4.1. Isolation of THA and PER. AERMS contains several alkaloids that can act as corrosion inhibitors. The effect observed with AERMS is certainly the result of the complementary action of the efficient compounds present in the extract. Only two compounds (THA and PER) were quantitatively isolated from AERMS and analyzed using high-resolution \(^{13}\)C and \(^{1}H\) NMR. Following the interpretation of these \(^{1}H\) and \(^{13}C\) NMR chemical shift spectra (see Supporting Information, Tables S1 and S2), the chemical structures of PER and THA were elucidated (Figure 9). These structures correspond to some compounds recently isolated in the alkaloid extract. The corrosion parameters \((J_{corr} \text{ and } E_{corr})\) of these 1H and 13C NMR chemical shift spectra (see Supporting Information, Tables S1 and S2), the chemical structures of PER and THA were elucidated (Figure 9).

Examining the structure of these two indole alkaloids reveals that their adsorption on the metal surface can proceed via the free doublets of basic nitrogen, oxygen atoms, and aromatic rings.

2.4.2. Corrosion Inhibition of C38 Steel in 1 M HCl and 0.5 M H\(_{2}\)SO\(_{4}\) by THA and PER. The corrosion inhibition of THA and PER on C38 steel in 1 M HCl and 0.5 M H\(_{2}\)SO\(_{4}\) was evaluated and compared to the result obtained with the extract (AERMS). A concentration of 10 mg/L was chosen to compare the efficiencies of the inhibitors in the active domain of the process. Indeed, results obtained with AERMS showed that at a concentration of 10 mg/L, the inhibition efficiency was higher than 60%. The polarization curves and Nyquist plots obtained with AERMS, PER, and THA in HCl and H\(_{2}\)SO\(_{4}\) are presented in Figure 10. The constants derived from these plots are summarized in Table S3.

The addition of inhibitors decreases the corrosion current density. However, the cathodic curves are more shifted toward the lower current density, especially in HCl, with THA as the most efficient inhibitor. The Nyquist plots were more effective to distinguish the efficiencies of the three inhibitors. Indeed, the differences are well highlighted on the curves depicted in Figure 10c,d. Based on the \(R_d\) values, THA was confirmed as the most efficient inhibitor followed by AERMS. Surprisingly, AERMS is more efficient than PER, especially in H\(_{2}\)SO\(_{4}\). The poor efficiency of PER compared to THA may be due to the more pronounced steric hindrance of the basic nitrogen atom. This result confirms once again the decisive role played by the availability of the structural basic nitrogen atom on the corrosion inhibition. On the other hand, one can conclude that the constituents of the extract act concomitantly in AERMS; the more powerful compensating the less efficient.

3. CONCLUSIONS

This study puts a major emphasis on the three points: the investigation of the inhibitory properties of AERMS, the improvement of the adsorption of AERMS in H\(_{2}\)SO\(_{4}\) solution by KI, and the comparative study of the inhibitory activity of AERMS and the two isolated compounds. Several interesting points can be highlighted from the obtained results. AERMS strongly adsorbs on the steel surface and thus prevents its corrosion. These surface phenomenon were confirmed by analyses of the metal surface before and after corrosion experiments (FESEM and FTIR). The inhibition of AERMS was improved in the presence of iodide in corrosive solution where it acts as a mixed inhibitor, with the efficiency increasing from 90 to 96% in H\(_{2}\)SO\(_{4}\) medium. The experiment with the two isolated compounds of the extract (PER and THA) confirmed the important role played by the basic nitrogen atom in the process and the variable efficiencies of compounds present in the alkaloid extract. More investigations are still needed to determine whether the action of the compounds is synergetic or just the superimposition of the individual effect.

4. MATERIALS AND EXPERIMENTAL METHODS

4.1. Materials and Solutions. Corrosion tests were performed on a cylindrical C38 steel sample from Tacinas.
Company (France). Its chemical composition (wt %) was 0.360 C, 0.230 Si, 0.680 Mn, 0.016 S, 0.077 Cr, 0.011 Ti, 0.059 Ni, 0.009 Co, 0.160 Cu, and 98.388 Fe according to the French standard. The C38 steel surface was coated in a polytetrafluoroethylene (PTFE) ribbon, leaving a free circular basal working surface of 0.785 cm². To obtain reproducible results, the working electrode was polished with silicon carbide abrasive papers of different grades (100, 1200, 2500, and 4000) from the most abrasive to the least abrasive. Corrosive solutions (1 M HCl and 0.5 M H₂SO₄) were prepared from commercial solutions of 37% HCl (Scharlau) and 98% H₂SO₄ (Scharlau) and distilled water.

4.2. Extraction of Total Alkaloids from Rauvolfia macrophylla Stapf Bark. RMS barks was harvested at the So'o locality, of Nyong and So'o division, in the center region of Cameroon. The samples were cut into tiny pieces, air dried for 15 days, and finely grounded. The resulting powder was macerated at room temperature for 3 days in a dichloromethane/methanol (1:1) mixture. The crude extract was obtained by evaporating the solvent, and the total alkaloid extract was obtained following Pandian’s procedure. The Dragendorff’s test confirmed the high content of alkaloids in the extract.

4.3. Electrochemical Measurements. The electrochemical experiments were performed in a thermostated electrochemical cell with three electrodes: the working electrode was the C38 steel rod, the auxiliary electrode was a platinum wire, and the reference electrode was a saturated calomel electrode (SCE). These electrodes were connected to an Autolab PGSTAT 12 (EcoChemie) potentiostat/galvanostat controlled by the software FRA (Frequency Response Analysis) for electrochemical impedance measurements, and GPES (General Purpose Electrochemical System) for the open circuit and potentiodynamic polarization experiments.

Before recording the polarization and EIS curves, the working electrode was first immersed in the test solution (acidic solution with or without AERMS) for 3 hours (experimental optimum immersion time required to reach constant potential at a steady-state open circuit).

The polarization curves were recorded by scanning the potential from −800 to −200 mV/SCE at a scan rate of 0.5 mV/s. The inhibitory efficiency (IE) was calculated using eq 4

\[
IE = \left(1 - \frac{J_{corr(inh)}}{J_{corr}} \right) \times 100
\]

where \(J_{corr} \) (A cm⁻²) and \(J_{corr(inh)} \) (A cm⁻²) are the corrosion current density in the absence and presence of the inhibitor, respectively.

A voltage amplitude of 10 mV around the open-circuit corrosion potential and a frequency range of 10 kHz to 100 mHz were used for the EIS measurements. The inhibition efficiencies were determined using eq 5

\[
IE = \left(1 - \frac{R_{ct}}{R_{ct(inh)}} \right) \times 100
\]

where \(R_{ct} \) (Ω cm²) and \(R_{ct(inh)} \) (Ω cm²) are the charge transfer resistance in the absence and presence of the inhibitor, respectively.

The capacity of double layer was determined using eq 6:

Table 8. Polarization Parameters of C38 Steel in 0.5 M H₂SO₄ Solutions in the Absence and Presence of KI, AERMS, and KI with AERMS

| concentration (mg L⁻¹) | Ecorr (mV/SCE) | Jcorr (μA/cm²) | βa (mV/decade) | −βc (mV/decade) | IE (%) |
|------------------------|----------------|----------------|----------------|-----------------|--------|
| 0.5 M H₂SO₄            | −481           | 234            | 44             | 53              |        |
| 0.5 M H₂SO₄ + KI       | −473           | 71             | 34             | 49              | 69     |
| 0.5 M H₂SO₄ + AERMS    | −468           | 22             | 46             | 35              | 91     |
| 0.5 M H₂SO₄ + KI + AERMS| −466          | 10             | 43             | 50              | 96     |

Figure 9. Structure of isolated molecules: (a) perakine and (b) tetrahydroalastonine.

Figure 10. Comparison of the polarization curves and Nyquist diagrams for C38 steel in (a, c) 1 M HCl and (b, d) 0.5 M H₂SO₄ in the absence and presence of different inhibitors (10 mg/L).
FESEM analysis was used to investigate the morphology of C38 steel after immersion in 1 M HCl and 0.5 M H$_2$SO$_4$ solutions in the absence and presence of AERMS at the optimum concentration for 3 h. FESEM analysis was performed with a Sopra 5V field emission microscope.

4.4. Fourier Transform Infrared (FTIR) Spectroscopy. The recording of the FTIR spectra of the deposits on the electrode surface after immersion in the corrosive solutions resulted in the formation of the passive layer. The deposit was removed by immersing for 3 h in the acidic solution in the presence of (or absence from) acetone. The passive layer was then gently removed with a spatula, and the resulted powder used for the preparation of the KBr pellets used for the recording of the FTIR spectra.

4.5. Field Emission Scanning Electron Microscopy (FESEM) Analysis. FESEM analysis was used to investigate the surface morphology of C38 steel after immersion in 1 M HCl and 0.5 M H$_2$SO$_4$ solutions in the absence and presence of AERMS at the optimum concentration for 3 h. FESEM analysis was performed with a Sopra 5V field emission microscope.

## ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b01076.

$^1$H and $^{13}$C NMR chemicals shifts of THA and PER, and electrochemical parameters of C38 steel in 1 M HCl and 0.5 M H$_2$SO$_4$ solutions in the absence and presence of PER, AERMS, and THA (PDF)

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### Notes
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## REFERENCES

(1) Mourya, P.; Banerjee, S.; Singh, M. M. Corrosion inhibition of mild steel in acidic solution by Tagetes erecta (Marigold flower) extract as a green inhibitor. *Corros. Sci.* 2014, 85, 352–363.

(2) Zaferani, S. H.; Sharifi, M.; Zaarei, D.; Shishesaz, M. R. Application of eco-friendly products as corrosion inhibitors for metals in acid pickling processes. A review. *J. Environ. Chem. Eng.* 2013, 1, 652–657.

(3) Raja, P. B.; Qureshi, A. K.; Rahim, A. A.; Osman, H.; Awang, K. Neolamarckia cadamba alkaloids as eco-friendly corrosion inhibitors for mild steel in 1M HCl media. *Corros. Sci.* 2013, 69, 292–301.

(4) Garai, S.; Garai, S.; Jaisankar, P.; Singh, J. K.; Elango, A. A. A comprehensive study on crude methanolic extract of Artemisia pallens (Asteraceae) and its active component as effective corrosion inhibitors of mild steel in acid solution. *Corros. Sci.* 2012, 60, 193–204.

(5) Rekkab, S.; Zarrak, H.; Salghi, R.; Zarrourk, A.; Bazzi, L.; Hammouti, B.; Kabouche, Z.; Touzani, R.; Zougagh, M. Green corrosion inhibitor from essential oil of Eucalyptus globulus (Myrtaceae) for C38 steel in sulfuric acid solution. *J. Mater. Environ. Sci.* 2012, 3, 613–627.

(6) Da Rocha, J. C.; Gomes, J. A. D. C. P.; D’Elia, E. Corrosion inhibition of carbon steel in hydrochloric acid solution by fruit peel aqueous extracts. *Corros. Sci.* 2010, 52, 2341–2348.

(7) Singh, A.K.; Mohapatra, S.; Pani, B. Corrosion inhibition effect of Aloe Vera gel: Gravimetric and electrochemical study. *J. Ind. Eng. Chem.* 2016, 33, 288–297.

(8) Aljourni, J.; Rassias, K.; Golozar, M. A. Benzimidazole and its derivatives as corrosion inhibitors for mild steel in 1M HCl solution. *Corros. Sci.* 2009, 51, 1836–1843.

(9) Lebrini, M.; Bentiss, F.; Chihib, N. E.; Jama, C.; Hornez, J. P.; Lagrenée, M. Polyphosphate derivatives of guanidine and urea copolymer: Inhibiting corrosion effect of Armco iron in acid solution and antibacterial activity. *Corros. Sci.* 2008, 50, 2914–2918.

(10) Bentiss, F.; Lebrini, M.; Vezin, H.; Lagrenée, M. Experimental and theoretical study of 3-pyridyl-substituted 1,2,4-thiadiazole and 1,3,4-thiadiazole as corrosion inhibitors of mild steel in acid media. *Mater. Chem. Phys.* 2004, 87, 18–23.

(11) Khanna, A.; Srivastava, M.; Rai, M. P.; Prakash, R. Application of Unsaturated Fatty Acid Molecules Derived from Microalgae toward Mild Steel Corrosion Inhibition in HCl Solution: A Novel Approach for Metal—Inhibitor Association. *ACS Omega.* 2018, 3, 12369–12382.

(12) Haque, J.; Srivastava, V.; Chauhan, D. S.; Lgaz, H.; Quraishi, M. A. Microwave-Induced Synthesis of Chitosan Schiff Bases and Their Application as Novel and Green Corrosion Inhibitors: Experimental and Theoretical Approach. *ACS Omega.* 2018, 3, 5654–5668.

(13) Odewunmi, N. A.; Umoren, S. A.; Gasem, Z. M. Utilization of watermelon rind extract as a green corrosion inhibitor for mild steel in acidic media. *J. Ind. Eng. Chem.* 2015, 21, 239–247.

(14) Bentiss, F.; Lebrini, M.; Lagrenée, M.; Traisnel, M.; Elfarouk, A.; Vezin, H. The influence of some new 2,5-disubstituted 1,3,4-thiadiazoles on the corrosion behaviour of mild steel in 1M HCl solution: AC impedance study and theoretical approach. *Electrochim. Acta* 2007, 52, 6865–6872.

(15) Faustin, M.; Maciu, A.; Salvin, P.; Roos, C.; Lebrini, M. Corrosion inhibition of C38 steel by alkaloids extract of Geissospermum laeve in 1M hydrochloric acid: Electrochemical and phytochemical studies. *Corros. Sci.* 2015, 92, 287–300.

(16) El Hamdani, N.; Fidil, R.; Tourabi, M.; Jama, C.; Bentiss, F. Alkaloids extract of Retama monosperma (L.) Boiss. seeds used as novel eco-friendly inhibitor for carbon steel corrosion in 1 M HCl solution: Electrochemical and surface studies. *Appl. Surf. Sci.* 2015, 357, 1294–1305.

(17) Pereira, S. S. D. A. A.; Pêgas, M. M.; Fernández, T. L.; Magalhães, M.; Schöntag, T. G.; Lago, D. C.; de Senna, L. F.; D’Elia, E. Inhibitory action of aqueous garlic peel extract on the corrosion of carbon steel in HCl solution. *Corros. Sci.* 2012, 65, 360–366.
(18) Ebenso, E. E.; Oguzie, E. E. Corrosion inhibition of mild steel in acidic media by some organic dyes. Mater. Lett. 2005, 59, 2163–2165.

(19) Hu, K.; Zhuang, J.; Ding, J.; Ma, Z.; Wang, F.; Zeng, X. Influence of biomacromolecule DNA corrosion inhibitor on carbon steel. Corros. Sci. 2017, 125, 68–76.

(20) Qiang, Y.; Zhang, S.; Tan, B.; Chen, S. Evaluation of Ginkgo leaf extract as an eco-friendly corrosion inhibitor of X70 steel in HCl solution. Corros. Sci. 2018, 133, 6–16.

(21) Amin, M. A.; Ibrahim, M. M. Corrosion and corrosion control of mild steel in concentrated H2SO4 solutions by a newly synthesized glycine derivative. Corros. Sci. 2011, 53, 873–885.

(22) Bentiss, F.; Jama, C.; Memari, B.; Attari, H. E.; Kadi, L. E.; Lebrini, M.; Traisnel, M.; Lagreneé, M. Corrosion control of mild steel using 3,5-bis-(4-methoxyphenyl)-4-amino-1,2,4-triazole in normal hydrochloric acid medium. Corros. Sci. 2009, 51, 1628–1635.

(23) Pourazarm, S.; Moayed, M. H.; Rahimizadeh, M. In situ inhibitor synthesis from admixture of benzaldehyde and benzene-1,2-diamine along with FeCl3 catalyst as a new corrosion inhibitor for mild steel in 0.5M sulphuric acid. Corros. Sci. 2013, 71, 20–31.

(24) Shaban-Nooshabadi, M.; Ghandchi, M. S. Santolina chamaecyparissus extract as a natural source inhibitor for 304 stainless steel corrosion in 3.5% NaCl. J. Ind. Eng. Chem. 2015, 31, 231–237.

(25) Li, L.; Zhang, X.; Lei, J.; He, J.; Zhang, S.; Pan, F. Adsorption and corrosion inhibition of Osmanthus fragrans leaves extract on carbon steel. Corros. Sci. 2012, 63, 82–90.

(26) Li, X.; Deng, S.; Fu, H. Inhibition of the corrosion of steel in HCl, H2SO4 solutions by bamboo leaf extract. Corros. Sci. 2012, 62, 163–175.

(27) El-Etre, A. Y. Inhibition of acid corrosion of carbon steel using aqueous extract of olive leaves. J. Colloid Interface Sci. 2007, 314, 578–583.

(28) Lebrini, M.; Robert, F.; Roos, C. Alkaloids extract from Paliourea guianensis plant as corrosion inhibitor for C38 steel in 1 M hydrochloric acid medium. Int. J. Electrochem. Sci. 2011, 6, 847–859.

(29) Chevalier, M.; Robert, F.; Amusant, N.; Traisnel, M.; Roos, C.; Lebrini, M. Enhanced corrosion resistance of mild steel in 1 M hydrochloric acid solution by alkaloids extract from Aniba rosaeodora plant: Electrochemical, phytochemical and XPS studies. Electrochim. Acta 2014, 131, 96–105.

(30) Chevalier, M.; Roos, C.; Tomi, F.; Soutour, S.; Lebrini, M. Corrosion inhibition of C38 steel in 1M HCl media by alkaloidic extract from Xylopia frutescens amazonian tree. ECS Trans. 2015, 64, 1–28.

(31) Lebrini, M.; Robert, F.; Leccante, A.; Roos, C. Corrosion inhibition of C38 steel in 1M hydrochloric acid medium by alkaloids extract from Ocandra asbeckii plant. Corros. Sci. 2011, 53, 687–695.

(32) Bruneton, J. Pharmacognosie, Phytochimie et plantes médicinales. 2nd ed.; Techniquet Documentation: Lavoisier, 1993.

(33) Outirite, M.; Lagreneé, M.; Lebrini, M.; Traisnel, M.; Jama, C.; Zevin, H.; Bentiss, F. ac impedance, X-ray photoelectron spectroscopy and density functional theory studies of 3,5-bis(n-pyridyl)-1,2,4-oxadiazoles as efficient corrosion inhibitors for carbon steel surface in hydrochloric acid solution. Electrochim. Acta 2010, 55, 1670–1681.

(34) Dutta, A.; Saha, S. K.; Adhikari, U.; Banerjee, S.; Sukul, D. Effect of substitution on corrosion inhibition properties of 2-(substituted phenyl) benzimidazole derivatives on mild steel in 1 M HCl solution: A combined experimental and theoretical approach. Corros. Sci. 2017, 123, 256–266.

(35) Ossei, C. I.; Boswell, B.; Davies, I. J. Pipeline failures in corrosive environments — A conceptual analysis of trends and effects. Eng. Fail. Anal. 2015, 53, 36–58.

(36) Dieter, L. Corrosion et Chimie de surface des métaux; Alden Press: Oxford, 1993.

(37) Yıldız, R. An electrochemical and theoretical evaluation of 4,6-diamino-2-pyrimidinethiol as a corrosion inhibitor for mild steel in HCl solutions. Corros. Sci. 2015, 90, 544–553.