# Inhibitive Effect of *Siparuna Guianensis* Extracts on the Corrosion of Low Carbon Steel in Acidic Media

A. Lecante., F. Robert<sup>\*</sup>, M. Lebrini, C. Roos

Laboratoire Matériaux et Molécules en Milieu Amazonien, UAG-UMR ECOFOG, Campus Trou Biran, Cayenne 97337, French Guiana. \*E-mail: <u>florent.robert@guyane.univ-ag.fr</u>

Received: 6 May 2011 / Accepted: 15 June 2011 / Published: 1 November 2011

The present study examines the effect of alkaloids extract from *Siparuna guianensis* leaves and stems on corrosion of C38 steel in 0.1 M HCl using electrochemical impedance spectroscopy (EIS), potentiodynamic polarization technique and Raman spectroscopy. The protection efficiency is better with stems alkaloids extract. The inhibition was assumed to occur via adsorption of inhibitor molecules on the metal surface. The influence of stems alkaloids extract concentration on corrosion of low carbon steel in 0.1 M HCl was studied. The inhibition efficiency obtained from impedance and polarization measurements was in a good agreement and was found to increase with increasing concentration of alkaloids extract up to 50 mg/L for stems extract. The adsorption of the extract on the low carbon steel surface obeys the Langmuir adsorption.

Keywords: Alkaloids extract, corrosion inhibition, C38 steel, EIS, raman spectroscopy

## **1. INTRODUCTION**

Acidic solutions are used in many industrial areas. The most important applications are acid pickling, industrial acid cleaning, acid descaling, and oil well acidizing [1,2].

Corrosion inhibitors are used to prevent unexpected metal dissolution and excess acid consumption in the process of acid cleaning of metal [3]. The most effective inhibitors are organic compounds that have  $\pi$  bonds and heteroatoms (especially N, S, O, P) [4], and inorganic compounds such as chromate, dichromate, nitrite, etc. [5]. At the same time, these products are environment friendliness and they present a toxic effect on human beings and other living species. An alternative of organic and inorganic compounds is the use of natural products as anticorrosion agents, which are eco-friendly and harmless. Thus, in the recent times, several authors reported the use of natural products as corrosion inhibitors [6-16]. Lebrini et al. [17] have studied harmane and norharmane as corrosion inhibitors for

C38 steel in molar hydrochloric acid and in sulfuric acid [18]. Among natural products tested, alkaloids act as good inhibitors for mild steel in acidic media. The present study is on *Siparuna guianensis. Siparuna* is the largest genus of the family *Monimiaceae* is widely spread in the Southern Hemisphere, mainly in tropical and subtropical regions of the Americas [19,20]. These plants are considered by local people as tonic, stimulant, digestive and carminative [21-24]. The aporphines are the largest group of alkaloids isolated from *Siparuna* [25]. The oxoaporphinoid alkaloids have a marked occurrence in this genus, being reported in *Siparuna guianensis* [26]. Furthermore, liriodenine and cassamedine isolated from *Siparuna guianensis* leaves are presented in Fig. 1 [26]. This group of alkaloids possesses  $\pi$  bonds and N and O atoms; that are regarded as important parameters for a good inhibitor. In this article, we investigated the inhibition behaviour of the *Siparuna guianensis* alkaloids extract from the leaves and the stems for C38 steel in 0.1 M HCl solutions.



Figure 1. Chemical structure of two alkaloids present in Siparuna guianensis leaves.

#### 2. EXPERIMENTAL

## 2.1. Preparation of plant extracts

S. guianensis leaves and stems were collected in French Guiana. The typical alkaloid extraction was performed [27]. Air-dried plant material was powdered and 100 g of it was treated with aqueous 5% NH<sub>4</sub>OH. The alkalized raw material was refluxed with dichloromethane ( $3\times200$  mL) for 10 min. The extract was collected by filtration and the combined dichloromethane fractions were washed with water ( $3\times100$  mL). Then, the organic layer was extracted with 3% aqueous HCl ( $3\times100$  mL). The combined aqueous fractions were combined and washed with dichloromethane ( $3\times80$  mL) and the pH of the aqueous solution was adjusted to 9 with 25% aqueous NH<sub>4</sub>OH. The neutralized solution was then extracted with dichloromethane ( $3\times100$  mL), dried over Na<sub>2</sub>SO<sub>4</sub> and collected by filtration. The organic layer consisting of basic compounds was evaporated and an orange amorphous solid was obtained. The yields of total

alkaloids extractions were about 0.07% (wt. %) and 0.09% (wt. %) for the stems and the leaves, respectively. Several concentrations of the plant extract were prepared by dissolving the known quantity of the resultant alkaloids extract in acidic solution.

## 2.2. Electrodes and solutions

Experiments were performed on cylindrical C38 working electrodes of the following composition (wt. %): 0.36% C, 0.66% Mn, 0.27% Si, 0.02% S, 0.015% P, 0.21% Cr, 0.02% Mo, 0.22% Cu, and 0.06% Al and the remainder iron. The specimens were embedded in epoxy resin leaving a working area of 0.785 cm<sup>2</sup>. The surface of the working electrode was subsequently abraded by using a range of emery papers from 180 grit to 1200 grit, cleaned with distilled water and ethanol. The corrosive medium was 0.1 M HCl solution prepared from analytical reagent grade 37% hydrochloric acid using distilled water. All tests were realized in non-aerated solution. The temperature was controlled at  $25^{\circ}$ C.

## 2.3. Electrochemical measurements

The electrochemical experiments were carried out using VSP Biologic model VMP3 operated with EC-Lab software, in conventional electrolytic cell with three electrodes. Platinum wire and saturated calomel electrode were counter and reference electrodes, respectively. After 3 h of immersion of working electrode in the test solution, electrochemical impedance spectroscopy measurements were performed at corrosion potentials,  $E_{corr}$ , at the frequency range from 10 mHz to 100 kHz, with a signal amplitude perturbation of 10 mV peak to peak. Impedance data were analyzed using ZSimpWin 3.22d software. Polarization studies were performed with scan 20 mV.min-1 in the potential range -300 to +300 mV relative to the corrosion potential. The above procedures were repeated 2 times for each concentration of the two alkaloids extracts.

## **3. RESULTS AND DISCUSSION**

#### 3.1. Inhibition efficiencies of two parts of the plant in 0.1 M HCl solutions

In the first time, the influence of the alkaloids extracted from two parts of the *S. guianensis* plant (leaves and stems) was studied on the inhibition effect for low carbon steel corrosion in 0.1 M HCl solutions. Two concentrations of alkaloids extract (50 and 150 mg/L in 0.1 M HCl solutions) were selected for the electrochemical tests. Fig. 2 represent the polarization curves for low carbon steel in 0.1 M HCl containing two concentrations of alkaloids extract from the leaves and the stems. As can be seen from Fig. 2, both anodic and cathodic reactions of C38 steel electrode corrosion are affected by alkaloid extracts in 0.1 M HCl solutions, suggesting that that the addition of alkaloids extracts reduce anodic dissolution and also retard the hydrogen evolution reaction. The determination of the corrosion

currents from polarisation curves by Tafel extrapolation is often impossible; simply because an experimental polarization curve does not exhibit linear Tafel regions (Our experimental polarization curves presented here do not display the expected log/linear Tafel behavior). The values of associated electrochemical parameters obtained from polarisation curves can be expressed simply in terms of polarization resistance. The polarization resistances ( $R_p$ ) were calculated from the linear *I-E* plots in the potential range ±20 mV from the corrosion potential. The corresponding  $R_p$  values of steel in 0.1 M HCl solutions in the absence and presence of alkaloids extracts are given in Table 1. Inhibition efficiency ( $IE_I$ ) calculated from polarization resistance is:

$$IE_1 = \frac{R_p - R_p^0}{R_p} \times 100 \tag{1}$$

where  $R_p$  and  $R_p^0$  are the polarization resistances of low carbon steel with and without alkaloids extract, respectively. It is found that,  $R_p$  increases with increasing of alkaloids extract concentration for both leaves and stems parts. Nevertheless, the increase seems to be more pronounced for stems alkaloids extract. In the case of the stems, corrosion potential shifted slightly to positive direction; although there was not a specific relation between  $E_{corr}$  and inhibitors concentration. No trend of corrosion potential was observed in the presence of leaves extract.  $IE_I(\%)$  increase with extract concentrations for both leaves and stems parts. It's found that, alkaloids extracted from stems present a slightly better performance than alkaloids extracted from leaves.



**Figure 2.** Potentiodynamic polarization curves for low carbon steel in 0.1 M HCl containing two concentrations of alkaloids extract from the leaves (LE) and the stems (SE).

As the studies on the phytochemical constituents of the total alkaloids extract from *S*. *guianensis* leaves shows that it contains the oxoaporphinoid alkaloids as liriodenine and cassamedine [26]. These molecules can play an important role on the inhibition efficiency of the extract and thus, the difference in inhibition efficiency can only discussed in terms of the proportion of these molecules in the extract. The stems may be contains more of these molecules than the leaves. This can be used to explain the higher inhibition efficiency obtained for alkaloids extracted from stems. On the other hand, a difference of the composition in the different parts of the plant may lead also differences in inhibition efficiencies [28], it means that the stems may be contains more constituents than the leaves. We can conclude that the ability of the extract to adsorb on the steel surface was dependent on the source of alkaloids extract.

Plant Part	[Conc.]	$-\mathbf{E}_{corr}$	R <sub>p</sub>	$IE_1$
	(mg/L)	(mV vs. SCE)	$(\Omega \text{ cm}^2)$	(%)
Blank	0	542	81	
Lagyag	50	544	386	79
Leaves	150	540	642	87
Stome	50	531	626	87
Stellis	150	539	691	88

**Table 1.** Kinetic parameters for the corrosion of low carbon steel in 0.1 M HCl solutions containing two concentrations of alkaloids extract from leaves and stems.

The corrosion behaviour of C38 steel in the acidic solution in the absence and presence of inhibitor was also investigated by EIS method at corrosion potential after 3 h of immersion. Fig. 3 and Fig. 4 present, respectively, the complex-plane impedance obtained for the low carbon steel in 0.1 M HCl solutions with and without various concentrations of alkaloids extracts, at corrosion potential at 25°C. The Nyquist plots in the absence of inhibitor consist of a depressed capacitive loop at high frequencies followed by an inductive loop at low frequencies. The inductive loop at low-frequency regions may be attributed to the relaxation process obtained by adsorption species as  $Cl_{ads}$  and  $H_{ads}^+$  on the electrode surface [30-32]. The capacitive loop originates from the time constant of charge transfer resistance and the electric double-layer capacitance. The corresponding electrical equivalent circuit model for low carbon steel in the absence of alkaloids extract is given in Fig. 5a. The double-layer capacitance is in parallel to the charge transfer resistance  $(R_{ct})$ , which is in series with the inductive elements L and  $R_L$ . In presence of alkaloids extract, one can notice that the shape of Nyquist diagrams is more complex. In the presence of alkaloids extract, the Nyquist diagrams are composed of two depressed capacitive semicircles at high and low frequencies, respectively. The low frequency impedance modulus Zmod can be easily used to compare corrosion resistance of different samples. Thus, impedance modulus increases notably with inhibitor content, indicating an anticorrosion activity of alkaloids extract [33].



**Figure 3.** Nyquist plots for low carbon steel in 0.1 M HCl solutions in the absence and presence of two concentrations of alkaloids extract from the leaves (LE) and the stems (SE) obtained from experimental and fit data.





**Figure 4.** The experimental data in the Bode format obtained for low carbon steel in 0.1 M HCl solutions at 25°C without and with two concentrations of alkaloids extract from the leaves (LE) and the stems (SE) and the relative fit obtained with the circuit model of Fig. 5.

The experimental impedance spectra in the presence of alkaloids extract are described better by the equivalent circuit which consists of two time constants as shown in Fig. 5b. This model indicates two consecutive processes. The time constant in the high frequency region ( $CPE_{ct}$  and  $R_{ct}$ ) is attributed to the charge transfer reactions [34]. The second time constant in the low frequency region ( $CPE_f$  and  $R_f$ ) results from the film formation at the steel surface [34]. The additional time constant may be explained by the more complicated structure of the double layer in the presence of large adsorbed molecules [35,36]. Often a constant phase element (CPE) is used in a model in place of a capacitor to compensate for non-homogeneity of the metal surface that causes a greater depression in Nyquist semicircle diagram. Its impedance is described by the expression [37,38]:

$$Z_{CPE} = A^{-1} (j\omega)^{-n}$$
<sup>(2)</sup>

where Z(CPE), impedance of CPE; A, a proportional factor;  $\omega$ , angular frequency; j, (-1)1/2; n, surface irregularity. If the electrode surface is homogeneous and plane, the exponential value (*n*) becomes equal to 1 and the metal – solution interface acts as a capacitor with regular surface, i. e., when n = 1,  $Z_{CPE} = (j\omega C)^{-1}$  where C is the capacitance. The factor *n* is an adjustable parameter that usually lies between 0.50 and 1.00 [39]. The capacitances were calculated from A and R, using the equation [40-42]:

$$C = (A.R_{ct}^{1-n})^{1/n}$$
(3)

The inhibition efficiencies (IE) are calculated as follows:

$$IE_{2} = \frac{R_{\rm p} - R_{\rm p}^{0}}{R_{\rm p}} \times 100 \tag{4}$$

where  $R_p$  and  $R_p^0$  are the polarization resistances of low carbon steel with and without alkaloids extract, respectively. In the absence of inhibitor molecules,  $R_p$  values consist of only charge transfer resistance ( $R_{ct}$ ), whereas in the presence of plant extract,  $R_p$  is the sum of charge transfer resistance ( $R_{ct}$ ) and inhibitor film resistance ( $R_f$ ) [43].

The relaxation time of the surface state can be calculated by the following equation [34]:

$$\tau = (A.R)^{1/n} \tag{5}$$

The time constant gives information about charge and discharge of the double electrochemical layer in the metal-solution interface. In fact, the relaxation time corresponds to the time required for returning of charge distribution to equilibrium after an electric perturbation. If the inhibitor adsorption needs a short time to reach equilibrium, Bode plots exhibit only one time constant for double-layer charging. The fact that the systems need some more time to reach equilibrium can be explained by the appearance of a second time constant [44]. The parameters of adequate equivalent circuit were evaluated using the simple least squares fit procedure and are presented in Table 2. A good correlation between experimental and simulated data was obtained. The error of the fitted parameters is done by the chi-square  $\chi^2$ . As it can be seen from Table 2, when concentration of extract increases,  $C_{dl}$  values tend to decrease while the charge transfer resistance values increase for both parts of plant. Decrease in the  $C_{dl}$ , which can result from a decrease in local dielectric constant and/or an increase in the thickness of the electrical double layer, suggesting that the alkaloids molecules function by adsorption at the metal solution/interface.



Figure 5. The equivalent circuit model used to fit the impedance data for low carbon steel in the absence; (a) and the presence of alkaloids extracts; (b) (c).

**Table 2.** Fitting results of EIS data for low carbon steel in HCl solutions with pH 1 in the absence and the presence of two concentrations of alkaloids extract from leaves and stems.

Plant part	[Conc.]	<b>R</b> <sub>ct</sub>	$A_{dl} \times 10^{-4}$	n <sub>dl</sub>	C <sub>dl</sub>	$\tau_{dl} \times 10^{-3}$	$\mathbf{R}_{\mathbf{f}}$	$A_f \times 10^{-4}$	$\mathbf{n}_{\mathbf{f}}$	IE <sub>2</sub>
	(mg/L)	$(\Omega \text{ cm}^2)$	$(s^n \Omega^{-1} cm^{-2})$		$(\mu F \text{ cm}^{-2})$	(s)	$(\Omega.cm^2)$	$(s^n \Omega^{-1} \operatorname{cm}^{-2})$		(%)
	0	78.7	11.14	0.86	742	59.0	-	-	-	-
Leaves	50	199.1	2.55	0.73	85	16.9	172.1	124.9	0.67	79
	150	356.8	3.63	0.65	120	43.1	139.0	250.2	0.81	84
Stome	50	293.3	2.30	0.70	72	21.2	272.8	87.06	0.69	86
Stellis	150	345.3	2.99	0.67	96	33.1	218.3	84.04	0.83	86

The  $R_f$  values show a marked tendency to decrease with concentration in the aggressive solution. It is obvious from Table 2 that the time constant, connected with double-layer charging, raises with the concentration of plant extract. The inhibition efficiencies calculated by both methods show the same trend. However, IE(%) increase with extract concentrations for both parts. The excellent behaviour of alkaloids extract previously evidenced in the polarisation curves was again confirmed by AC impedance study. The highest efficiency values were calculated for stems alkaloids extract, due to the similar raison given in the polarisation curves paragraph. Therefore, simply the influence of the stems alkaloids extract concentration on the inhibition efficiency was studied.

#### 3.2. Influence of the alkaloids extract concentration on the inhibition efficiency

#### 3. 2.1. Potentiodynamic polarization results



**Figure 6.** Potentiodynamic polarization curves for low carbon steel in 0.1 M HCl solutions containing different concentrations of stems alkaloids extract from *S. guianensis*.

250

1				
	[Conc.]	-E <sub>corr</sub>	$\mathbf{R}_{\mathbf{p}}$	IE <sub>1</sub>
	(mg/L)	(mV vs. SCE)	$(\Omega \text{ cm}^2)$	(%)
	-	542	81	-
	10	530	356	77
	25	517	533	85
	50	531	626	87
	150	539	691	88

541

712

**Table 3.** Fitting results of EIS data for low carbon steel in 0.1 M HCl solutions in the absence and the presence of variation of concentrations of alkaloids extract from stems.

The effect of stems extract concentrations on the potentiodynamic polarization curves of low carbon steel in 0.1 M HCl solutions for 3 h of immersion is shown in Fig. 6. The electrochemical parameters obtained by polarization resistance method are listed in Table 3. As seen from Fig. 6, addition of *S. guianensis* alkaloids extract affects both anodic dissolution of steel and cathodic reactions, indicating that the inhibition mechanism occurred by simple blocking of the available cathodic and anodic sites of the metal surface. However, the cathodic current was reduced more significantly than the anodic current. Increasing *S. guianensis* alkaloids extract concentration does not affect significantly the values of corrosion potential ( $E_{corr}$ ). As a result, the displayed data confirm the previous results and this extract could be classified as mixed-type inhibitor.

## 3.2.2. Electrochemical impedance spectroscopy results

Nyquist plots for C38 steel in 0.1 M HCl solutions in the absence and presence of different alkaloids extract concentrations are shown in Fig. 7. The recorded EIS spectrum of low carbon steel in 0.1 M HCl solution with 10 mg/L alkaloids extract showed one single depressed capacitive loop indicating that a protective film is not formed. The equivalent circuit (EC) given in Fig. 5c was used to fit the experimental spectra. Starting from 25 mg/L of plant extract, an additional time constant becomes visible, very well expressed in the Bode presentation (Fig. 8). Nyquist plots have two capacitive loops: one loop in the high frequency region (HF) and one loop at the low frequency region. In the case of two time constants, Fig. 5b represents the equivalent circuit design used to fit the experimental EIS data for low carbon steel in 0.1 M HCl solutions in the presence of alkaloids extract. The values of the corresponding fitted parameters are given in Table 4. The results show that the charge-transfer resistances,  $R_{ct}$ , increased with increasing of the plant extract, from 25 mg/L to 250 mg/L. In addition, the value of  $C_{dl}$  is always smaller in the presence of plant extract than in its absence, suggesting that alkaloids extracts act via adsorption at metal/solution interface. Low values of  $n_f$  and  $n_{dl}$  indicate an energy dissipation in the adsorption layer and a certain heterogeneity of metal surface [45].

89

The variations of  $R_f$  did not show a clear trend but the results are in the same order of magnitude. Globally, inhibition efficiency increased with increasing alkaloids extract concentration up to 50 mg/L. This result followed the same general trend of inhibition efficiency obtained from linear polarization resistance method.



**Figure 7.** Nyquist plots for low carbon steel in HCl solutions with pH 1 in the absence and presence of different concentrations of alkaloids stems extract from *S. guianensis* and the relative fit obtained with the circuit model of Fig. 5.

**Table 4.** Fitting results of EIS data for low carbon steel in 0.1 M HCl solutions in the absence and the presence of different concentrations of alkaloids extract from stems.

[Conc.]	<b>R</b> <sub>ct</sub>	$A_{dl} \times 10^{-4}$	$\mathbf{n}_{dl}$	$C_{dl}$	$\tau_{dl} \times 10^{-3}$	$\mathbf{R}_{\mathbf{f}}$	$A_f \times 10^{-4}$	$\mathbf{n}_{\mathrm{f}}$	$IE_2$
(mg/L)	$(\Omega \text{ cm}^2)$	$(s^n \Omega^{-1} cm^{-2})$		$(\mu F \text{ cm}^{-2})$	(s)	$(\Omega.cm^2)$	$(s^n \Omega^{-1} cm^{-2})$		(%)
-	78.7	11.14	0.86	750	59.0	-	-	-	-
10	290.3	6.54	0.65	267	77.6	-	-	-	73
25	166.6	2.87	0.78	119	20.2	183.2	27.8	0.74	78
50	293.3	2.30	0.70	72	21.2	272.8	87.06	0.69	86
150	345.3	2.99	0.67	96	33.1	218.3	84.04	0.83	86
250	402.8	2.23	0.68	71	29.0	209.4	87.68	0.71	87



**Figure 8.** The experimental data in the Bode format obtained for low carbon steel in 0.1 HCl at 25°C without and with various concentrations of stems alkaloids extracts and the relative fit obtained with the circuit model of Fig. 5.

#### 3.2.3. Fourier transform Raman spectroscopy

Raman spectra were obtained from a solid sample of the alkaloids extract and from the low carbon steel surface after 3 hours of immersion in 0.1 M HCl solution containing 150 mg/L plant extract, in order to characterize the adsorbed compounds. The Fourier transform Raman spectrum of alkaloids extract is shown in Fig. 9a. The weak bands at 3344 cm<sup>-1</sup> and 3133 cm<sup>-1</sup> are attributed to N-H vibrations [45,46]. The band at 2910 cm<sup>-1</sup> is due to C-H asymmetric stretching vibrations. The band at 1679 cm<sup>-1</sup> can be reasonably assigned to C=N and C=O stretching vibrations. The weak bands at 1526 cm<sup>-1</sup> and 1343 cm<sup>-1</sup> are assigned to C=C stretching vibrations in benzene and CH<sub>2</sub> wagging vibrations [47], respectively. C-C stretching vibrations are noticed at 1140 cm<sup>-1</sup>. The strong band at 1007 cm<sup>-1</sup> is due to benzene ring in-plane breathing vibrations [48]. The band at about 846 cm<sup>-1</sup> can be assignable to benzene out-of-plane deformations. Moreover, the band at 660 cm<sup>-1</sup> corresponds probably to out-of-plane C-H deformations. The peak at 534 cm<sup>-1</sup> involves benzene in-plane bending vibrations. In Fig. 9b, Raman spectrum of the low carbon steel electrode immersed in 0.1 M HCl solution containing 150 mg/L alkaloids extract during 3 hours reveals the presence of major characteristic functional group peaks of alkaloids plant extract. The Raman results provide direct evidence of the adsorption of alkaloids extract onto the steel surface thus strongly supporting the model invoking the blocking its active sites and preventing it from being corroded easily.



**Figure 9.** Raman spectra obtained for; (a) the solid alkaloids extract; (b) the low carbon steel surface after 3 hours of immersion in 0.1 M HCl + 150 mg/L plant extract.

#### 3.2.4. Adsorption Isotherm

Adsorption isotherms provide some basic information about adsorption mechanism of the inhibitor molecules. The degree of surface ( $\theta$ ) of the metal surface by an adsorbed plant extract is estimated using equation:

$$\theta = \frac{R_{\rm p} - R_{\rm p}^{0}}{R_{\rm p}} \tag{6}$$

The variation of surface coverage with concentration of *S. guianensis* extracts are shown in Fig. 10. This curve is characterized by an initial rapid increase in surface coverage followed by a plateau over which an increase in extract concentration has little effect on the inhibition efficiency. The plot of  $C_{inh}/\theta$  versus  $C_{inh}$  (Fig. 11) yields a straight line with a correlation coefficient of 0.999, supporting the assumption that adsorption of alkaloids extract in 0.1 M HCl solutions on the low carbon steel surface at 25°C obeys a Langmuir adsorption isotherm, which is represented by the equation (7). The Langmuir isotherm is based on assumption that all adsorption sites are equivalent and that particle binding occurs independently from nearby sites being occupied or not [49].

$$\frac{C_{inh}}{\theta} = C_{inh} + \frac{1}{K_{ads}}$$
(7)

where  $C_{inh}$  is the alkaloids extract concentration, and  $K_{ads}$  is the equilibrium constant of the adsorption/desorption process. The slope of the linear regression between  $C_{inh}/\theta$  and  $C_{inh}$  is close to unity (1.140) and the intercept permit the calculation of  $K_{ads}$  which is about 0.404 L.mg<sup>-1</sup>. The determination of the standard free energy of value ( $\Delta G_{ads}$ ) is not possible because the molecular mass of the extract components is not known.

#### 3.2.5. Inhibition mechanism

Due to the complexity of the alkaloids mixture, it is difficult to attribute the inhibiting action to a particular constituent or group of constituents. However, a synergistic or antagonistic effect of these molecules may play an important role on the inhibition efficiency of *S. guianensis* extracts. From the polarization an impedance measurements, it is found that the alkaloids extracts inhibit the corrosion processes by blocking the available cathodic and anodic sites of the metal through adsorption of the alkaloids on the metal surface. This phenomenon could be explained via [50]:

1 – Electrostatic attraction between the protonated nitrogen atom of the alkaloids (cationic form of the oxoaporphinoid alkaloids as liriodenine, cassamedine) and negatively charged low carbon steel surface (anodic sites).

2 – Interaction between unshared electron pairs of oxygen and nitrogen atoms and interaction between  $\pi$ -electrons of the aromatic cycles with the vacant, low energy d-orbitals of Fe atoms surface;

## **4. CONCLUSION**

*S. guianensis* leaves extract seem to be less efficient than stems extract. Maximum inhibition efficiency was about 87%. Excellent agreement between the inhibition efficiencies calculated using both techniques was obtained. Polarization studies showed that alkaloids extracts act as mixed-type inhibitor without affecting corrosion potential. Also, the Raman spectrum of the low carbon steel electrode immersed in a test solution probed that the adsorption proves took place. Adsorption of inhibitor molecules on low carbon steel surface was found to obey Langmuir isotherm. The results obtained for inhibitive action of *S. guianensis* alkaloids extract show that this extract can be proposed as a good, ecologically acceptable candidate for low carbon steel corrosion inhibition.

#### **ACKNOWLEDGEMENTS**

This work was supported by European Union through DEGRAD framework (European Regional Development Funds, PRESAGE 30070).

#### References

- 1. D. Chebabe, Z. Ait Chikh, N. Hajjaji, Corros Sci. 45 (2003) 309.
- 2. KF. Kalhed, N. Hackerman, Mater Chem Phys. 82 (2003) 949.
- 3. JM. Br. Sykes, Corros. 25 (1990) 175.
- 4. Jr. Riggs OL, Corrosion Inhibitors, second edn. C. C. Nathan, Houston, TX (1973).
- 5. M.G. Fontana, Corrosion Engineering, third edn. McGrawHill, Singapore (1986).
- 6. P.B. Raja, M.G. Sethuraman, Mat Lett. 62 (2008) 113.
- 7. P.C. Okafor, E.E. Ebenso, U.J. Ekpe, Int. J. Electrochem. Sci. 5 (2010) 978.
- 8. I.B. Obot, N.O. Obi-Egbedi, S.A. Umoren, E.E. Ebenso, Int. J. Electrochem. Sci. 5 (2010) 994.
- 9. M. Dahmani, A. Et-Touhami, S.S. Al-Deyab, B. Hammouti, A. Bouyanzer, *Int. J. Electrochem. Sci.* 5 (2010) 1060.
- 10. M. Lebrini, F. Robert, C. Roos, Int. J. Electrochem. Sci. 5 (2010) 1698.
- 11. M. Lebrini, F. Robert, A. Lecante, C. Roos, Corros. Sci. 53 (2011) 687.
- 12. M. Lebrini, F. Robert, C. Roos, Int. J. Electrochem. Sci. 6 (2011) 847.
- 13. L. Vrsalovic, M. Kliškic, S. Gudic Int. J. Electrochem. Sci. 4 (2009) 1568.
- 14. I.B. Obot, N.O. Obi-Egbedi, Int. J. Electrochem. Sci. 4 (2009) 1277.
- 15. E.A. Noor, Int. J. Electrochem. Sci. 2 (2007) 996.
- 16. A.Lecante, F.Robert, P.A. blandinières, C. Roos, Curr. Appl. Phys. 11 (2011) 714.
- 17. M. Lebrini, F. Robert, H. Vezin, C. Roos, Corros. Sci. 52 (2010) 3367.
- 18. M. Lebrini, F. Robert, H. Vezin, C. Roos, Int. J. Electrochem. Sci., 6 (2011) xx .
- 19. J. Hutchinson, The Genera of Flowering Plants, Vol. II. Oxford University Press, London, (1976) 110.
- 20. W.R.Philipson, The Families and the Genera of Vascular Plants Vol. II. Springer-Verlag, Berlin, (1993) 426.
- G. Peckolt, P. Peckolt, História das Plantas Medecinais e Úteis do Brasil, 8a Ed. São Paulo, (1920) 146.

- 22. M.P. Corrêa, Dicionário das Plantas Úteis do Brasil e das Exóticas Cultivadas, Vol. I. Imprensa Nacional, (1926) 660.
- 23. M.P. Corrêa, Dicionário das Plantas, Úteis do Brasil e das Exóticas Cultivadas, Vol. IV. Inst. Brasileiro de Desenv. Florestal, (1978) 41, 158, 646, 650, 656.
- 24. A.Occhioni, M.E.M Lyra, In: Arquivos do Jardim Botanicos Vol. VIII. Contribuição ao Estudo das Monimiaceas, Medicinais Brasileiras, (1948) 253.
- 25. G.G. Leitão, N.K. Simas, S.S.V. Soares, A.P.P. de Britos, B.M.G Claros, T.B.M Brito, F Delle Monache, *J Ethnopharm*. 65 (1999) 87.
- R. Braz-Filho, S.J. Gabriel, O.R. Gottlieb, M.G.A.E Bichara, J.G.S Maia *Phytochemistry*. 15 (1976) 1187.
- 27. H. Wagner, S. Bladt, V. Rickl, Plant Drug Analysis. Springer-Verlag, Berlin-Heidelberg (2009).
- 28. P.C. Okafor, E.E. Ebenso, Pigm. Res. Technol. 36 (2007) 134.
- 29. G. Lyberatos, L. Kobotiatis, Corros. 47 (1991) 820.
- 30. H.J.W. Lenderink, M.V.D. Linden, J.H.W. De Wit, *Electrochim Acta*. 38 (1993) 1989.
- 31. H.H. Hassan, E. Abdelghani, M.A. Amin, *Electrochim Acta*. 52 (2007) 6359.
- 32. [32] M.A. Amin, S.S. Abd El Rehim, E.E.F El-Sherbini, R.S. Bayoumi, *Electrochim. Acta* 52 (2007) 3588.
- 33. S.V. Lamaka, M.L. Zheludkevich, K.A. Yasakau, R. Serra, S.K. Poznyak, M.G.S. Ferreira, *Prog. Org. Coat.* 58 (2007) 127.
- 34. A.Popova, M. Christov, Corros. Sci. 48 (2006) 3208.
- 35. I.Dehri, M. Erbil, Corros Sci. 42 (2000) 969.
- 36. M. Özcan, I. Dehri, M. Erbil, Appl Surf. Sci. 236 (2004) 155.
- 37. J. Cruz, T. Pandiyan, E.G. Ochoa, J. Electroanal. Chem. 583 (2005) 8.
- 38. D.A. Lopez, S.N. Simison, S.R. de Sanchez, Corros Sci. 47 (2005) 735.
- 39. (a)B.A. Boukamamp, *Solid State Ionics* (1980) 20:32;(b) International Report CT 89/214/128. University of Twente, Eindhoven, The Netherlands (1989).
- 40. S. Martinez, M. Metiko-Huković, J. Appl. Electrochem. Soc. 33 (2003) 1137.
- 41. X. Wu, H. Ma, S. Chen, Z. Xu, A. Sui, J Electrochem Soc. 146 (1999) 1847.
- 42. H. Ma, X. Cheng, G. Li, S. Chen, Z. Quan, S. Zhao, L. Niu, Corros. Sci. 42 (2000) 1669.
- 43. G. Avci, Colloids and Surfaces A: Physicochem. Eng. Aspects, 317 (2008) 730.
- 44. A.Popova, M. Christov, A. Vasilev Corros. Sci. 49 (2007) 3290.
- 45. T. Frosch, M. Schmitt, K. Schenzel, J.H. Faber, G. Bringmann, W. Kiefer, *J. Popp. Biopolymers* 82 (2006) 295.
- 46. S.J. Oh, D.C. Cook, H.E. Townsend, Hyperfine Interactions 112 (1998) 59.
- 47. S. Gunasekaran, G. Sankari, S. Ponnusamy, Spectrochimica Acta part A 61 (2005) 117.
- 48. L. Fengting, L. Suiqing, L. Xuefei, Spectroscopy Lett. 33(2000) 901.
- 49. A.M. Abdel-Gaber, B.A. Abd-El Nabey, I.M. Sidahmed, A.M. Zayady, S. Saadawy, *Corros.* 42 (2006) 293.
- 50. D. Schweinsgberg, G. George, H. Nishihara, J. Electrochem. Soc. 137 (1990) 1354.

© 2011 by ESG (<u>www.electrochemsci.org</u>)