



Effect of Basicity on Electrochemical Corrosion Behaviour of *Enantia chlorantha* on the Corrosion of Mild Steel in Acid Environments

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Authors' contributions

This work was carried out in collaboration between both authors. Both authors read and approved the final manuscript.

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ABSTRACT

The effects of *Enantia chlorantha* (ET) stem bark ethanoic extract on the corrosion of Mild steel in acids environment and acid basicity to concentration ratio on the electrochemical corrosion behavior of *Enantia chlorantha* on mild steel in acid environments was studied using electrochemical techniques. The results showed that ET is a good inhibitor of Mild steel corrosion acids media. The Potentiodynamic polarization results showed *Enantia chlorantha* (ET) stem bark ethanoic extract to act as a mixed-type corrosion inhibitor while the Electrochemical Impedance results showed the extract increased the charge transfer resistance and increased the double layer capacitance, attributing the corrosion inhibition process of *Enantia chlorantha* (ET) stem bark ethanoic extract to adsorption of its molecules on the Mild steel/acid interface. However, it was concluded that the basicity of the acid is an important factor on the inhibition performance. Hence need to balance it in order to achieve desired corrosion inhibition targets.

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1. INTRODUCTION

Environmental degradation occasioned by chemical pollution has become the bane of many climes. An estimate of about 18.3 % of global GDP is lost to air pollution alone [1-3]. A major consequence of chemical-aided environmental degradation is electrochemical corrosion. The consequences of electrochemical corrosion include deterioration of environmental aesthetics with great negative economic impact. Also, the industry suffers a huge economic loss due to chemical-aided corrosion. A typical example is the material loss due to acid pickling of petroleum pipelines. Though corrosion is thermodynamically inevitable, they have been appreciable progress in mitigation measures [4-7]. The application of corrosion inhibitors is a good example of a corrosion mitigation technique. Most synthetic inhibitors are toxic to humans and the environment [6-7].

However, a major undesirable impact of some synthetic corrosion inhibitors is the negative environmental consequences when they finally end up in the environment and are expensive and non-renewability. These have led to the search into the application of natural resources such as Phyto-substances as corrosion inhibitors [4-5]. Plant extracts are majorly green, cheap, and renewable. These extracts have varying degrees of corrosion inhibition performance depending on the corrosive environment's physical and chemical environmental characteristics. Most municipal and industrial environments are acidic in nature because their effluents are acidic in nature ranging from acidic gaseous products of combustion - carbon dioxide, carbon monoxide, and sulfur dioxide, and also discharges such from pipeline acid pickling [8,9,10].

The choice of acid when the need for its application arises must be based on scientific insight into the efficacy of the corrosion inhibitor to chosen acid as well as acid efficacy. The two common types of acids are sulphuric acid and hydrochloric acid [11]. A major difference between acids is their basicity, which is a determinant of their acidic strength. Hence the need to investigate basicity's impact on green corrosion inhibitors' corrosion inhibition potentials. This will equally contribute to the baseline guiding the application of acids in industrial operations such as acid pickling.

Interestingly, Phyto green corrosion inhibitor's corrosion inhibition potentials have been attributed to the adsorption of natural product chemicals to the metallic substrate [3-7]. These classes of the chemical have been severally reported to also have medicinal properties. *Enantia chlorantha* is one medicinal plant with potential corrosion-inhibiting chemicals. Some of the phytochemicals in *Enantia chlorantha* are Phenolics, Flavonoids, Alkaloids, Glycosides, Sponins, Phlobatannins, Steroids These compounds have adsorption active functionalities with potential corrosion inhibition characteristics.

Hence, this paper reports the studies on electrochemical corrosion characteristics of *Enantia chlorantha* on the corrosion of mild steel in a mono basic hydrochloric acid and a dibasic tetraoxosulphate vi acid.

2. MATERIALS AND METHODS

2.1 Material Preparation

2.1.1 Extract

The bark of *Enantia chlorantha* was obtained from traditional medicine dealers and characterized by the Plant science department, University of Port Harcourt, Nigeria. They were cut into the smallest possible pieces and allowed to dry under the sun for three days. The dry stems were further broken down with a sterile sharp knife before being pulverized in a blender. About 500 g blended *Enantia chlorantha* stem bark was packed in a 1000 ml volumetric flask and 95 % ethanol was added to sufficiently cover the substrate surface. The set-up was allowed to stabilize, soak and extract for 60 hours. After which, it was decanted and filtered. The ethanol solvent was separated from the extract using a rotary evaporator. The extract was further dried using a thermo-stated water bath at 30 °C to a thick paste. The extracts were then used to prepare serial diluents of extract in 0.5 M H₂SO₄ and 1.0 M HCl solutions.

2.1.2 Metal coupons

The metal coupons were obtained from the Engineering workshop, at the University of Port Harcourt. They were mechanically cut into 1 × 1 cm² shapes, and polished with 200 – 2000 grade SiC paper, under distilled water. They were thereafter rinsed with absolute ethanol, acetone and dried in warm air. The ready coupons were

stored in an active desiccator till, it was used as working electrode in the electrochemical set-up. The preparation was according to Ngobiri et al. [12].

2.1.3 Solution preparation

The corrosive medium was prepared as serial diluents of 0.0 to 2.0 g/L BL extract in 0.5 and 1.0 M, H₂SO₄ and HCl respectively.

2.2 Electrochemical Experiments

The electrochemical studies were conducted with a VersaSTAT 400 complete DC voltameter and corrosion system with V3 studio software from Princeton applied research. The set up comprised a three-electrode system. The prepared mild steel coupon was the Working electrode facing the rectangular 2 X 2 cm² platinum foil that served as the Counter electrode, while a Saturated calomel electrode was used as the Reference electrode. The working electrode was encapsulated with epoxy resin to expose only 1 cm². The experiments were conducted in an open, aerated, and unperturbed cell. The experiments were carried at open circuit potential (OCP) after 30 minutes at a temperature of 303 ± 1⁰ K. The determinations were repeated to triplicate reproducible results and the mean value was recorded for further analysis.

2.2.1 Potentiodynamic polarization (PDP) determination

The potentiodynamic polarization (PDP) experiments were done at a cathodic potential of - 250 mV to an anodic potential of + 250 mV vs OCP at a scan rate of 0.333 mV s⁻¹. The PDP parameters were extrapolated to obtain the corrosion current density (I_{corr}), equilibrium corrosion potential (E_{corr}), and other Tafel parameters. The Corrosion Inhibition efficiency (ηE) was evaluated using I_{corr} values by applying the equation 1: -

$$\eta E (\%) = \frac{I_{corr}^0 - I_{corr}^i}{I_{corr}^0} \times 100 \quad (1)$$

I_{corr}⁰ and I_{corr}ⁱ are corrosion current densities in the uninhibited and inhibited cells respectively.

2.2.2 Electrochemical impedance spectroscopy (EIS) determinations

The electrochemical impedance spectroscopy (EIS) experiments were conducted at open circuit

potential over a frequency range of 100 kHz to 10 mHz using a signal of 5 mV amplitude. The corrosion inhibition efficiency was determined using the charge transfer resistance (R_{ct}) with the equation:

$$\eta E (\%) = \frac{R_{cti} - R_{ct}}{R_{cti}} \times 100 \quad (2)$$

R_{cti} and R_{ct} are the charge transfer resistance with and without BL extract respectively.

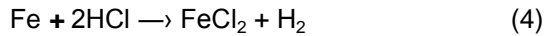
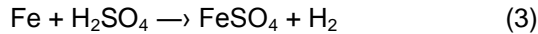
3. RESULTS AND DISCUSSION

3.1 Potentiodynamic Polarization (PDP) Determination of the Effects of *Enantia chlorantha* (ET) Stem Ethanoic Extract (ET) on the Corrosion of Mild Steel in 0.5 M H₂SO₄ and 1.0 M HCl Environments

The electrochemical potentiodynamic polarization experiments of the effects of *Enantia chlorantha* (ET) stem ethanoic extract (ET) on the corrosion of mild steel in 1.0 M HCl and 0.5 M H₂SO₄ environments are presented in Fig. 1, i and ii respectively. While Table 1 presents the electrochemical corrosion parameters in both environments. In order to compare the effects of acid strength on the corrosion inhibition process, 0.5 and 1.0 molar solutions of sulfuric and hydrochloric acids were used. This is to balance their basicity and theoretically balance their strength for a good comparison. ET exhibited significant and comparable inhibition of the corrosion of mild steel in both acids by decreasing the corrosion current density. This observation was more manifest at the lower concentration of 0.5 g/L ET. The inhibitor affected both the anodic and cathodic arms at the same acid strength. Consequently, *Enantia chlorantha* can be described as a mixed-type corrosion inhibitor [13] irrespective of the basicity or strength of the acid.

The values of the calculated corrosion inhibition efficiency were 37.7 % and 89.5 % in 1.0 M HCl, 41.9 % and 89.1 % in 0.5 M H₂SO₄ when 0.5 g/L and 2.0 g/L ET were introduced into both systems respectively. There was an increase in corrosion inhibition efficiency with an increase in the concentration of the inhibitor in both acids. This trend has been severally reported [12,14,9]. Interestingly, both acids showed comparable efficiencies with no clear difference at varying concentrations of the additive and the same acid basicity. This is attributable to balancing the acid

strength of a monobasic and a dibasic acid by doubling the concentration of the monobasic HCl. The blank cells showed active dissolution and consequent evolution of hydrogen gas, there was no indication of a passive region within the studied region in Figs. 1 and 2.



From the above results, it can be assumed that that basicity rather than the type of acid affects corrosion. In other words, the cation in the acid affects corrosion and its inhibition more than the anionic component of an acid.

3.2 Electrochemical Impedance Spectroscopy (EIS) Determination of the Effects of *Enantia chlorantha* (ET) Stem Ethanoic Extract (ET) on the Corrosion of Mild Steel in 0.5 M H₂SO₄ and 1.0 M HCl Environments

“Researchers have applied the electrochemical impedance of corrosion inhibitors to detect the formation of surface films on a metallic surface. This is evident when the solution resistance increases and the double-layer capacitance decrease” [12,9,15]. The electrochemical corrosion characteristics of *Enantia chlorantha* (ET) stem bark ethanoic extract (ET) on the corrosion of mild steel in 1.0 M HCl and 0.5 M H₂SO₄ environments are presented in Fig. 2 (i) and (ii) respectively, on the acid-mild steel interface for the corrosion of mild steel in mono and dibasic acid environments. Fig. 2 is Nyquist

plot, with depressed capacitive semicircles in the high-frequency region corresponding to a single time constant. The depression at the center of the real axis is characteristic of solid electrodes that exhibit frequency depression. Researchers have severely reported this observation [5, 16-17]. It is noteworthy that, the shape of capacitive loops is similar both in the cell with ET and without ET, suggesting that the presence of ET does not alter the corrosion mechanism. The cell has two resistances, solution resistance (R_s) and charge transfer resistance (R_{ct}). Since the semicircles are similar in shape with different solution resistance. It could be inferred that the corrosion inhibition process is controlled by the solution resistance. If the transfer function is represented by the solution resistance shorted by a capacitor C which is parallel to charge transfer resistance, equation 5. This applies primarily to homogenous systems with one time constant and the center of the semicircle lying on the abscissa, unable to explain the depression of the semicircular capacitive loop. If a non-ideal frequency response occurs, the capacitor is exchanged with a constant phase element (CPE) with impedance Z_{CPE} , equation 6 [5,18,19].

$$z(\omega) = R_s + \left(\frac{1}{R_{ct}} + j\omega C \right)^{-1} \quad (5)$$

$$Z_{CPE} = Q^{-1}(j\omega)^{-n} \quad (6)$$

Where Q and n represents constant phase element and exponent respectively while $j = (-1)^{1/2}$ is an imaginary number, ω is the angular frequency in rad s^{-1} ($\omega = 2\pi f$, where f is frequency in Hertz).

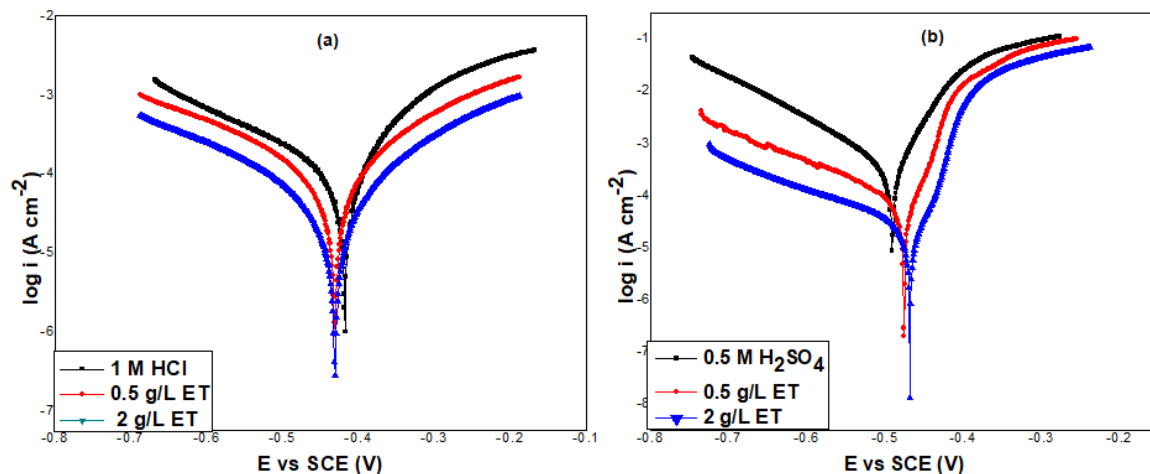


Fig. 1. Potentiodynamic polarization curves of mild steel in: (i) 1 M HCl and (ii) 0.5 M H₂SO₄ solutions without and with ET extract

Table 1. Potentiodynamic polarization parameters for mild steel in 1 M HCl and 0.5 M H₂SO₄ in the absence and presence of BL extract

System	E _{corr}	I _{corr}	IE (%)
1 M HCl	-566.4	183	
0.5 g/L ET	-454.9	125.1	31.7
2 g/L ET	-456.9	19.3	89.5
0.5 M H ₂ SO ₄	-496.4	1340	
0.5 g/L ET	-478.6	778.9	41.9
2 g/L ET	-489.2	115.4	89.1

It is noteworthy that, *Enantia chlorantha* (ET) stem bark ethanoic extract (ET) raised the charge transfer resistance from the uninhibited to the inhibited cell and consequent decrease in C_{dl} values. As earlier stated, this observation has been previously reported [12]. A physical observation reveals an increase in the diameter of the Nyquist semicircles translating to higher impedance in the inhibited cell by ET. This reveals the obvious corrosion inhibition character of *Enantia chlorantha* (ET) stem bark ethanoic extract (ET). "While the decrease in the C_{dl} value indicates decrease in dielectric constant or increase double layer thickness caused by adsorption of inhibitor molecules at the metal/acid interface" [15].

The corrosion electrochemical impedance spectroscopic parameters of ET ethanoic extract on Mild steel in multi-basic solutions are presented in Table 2. The values of the corrosion inhibition efficiency were calculated from equation 2, and presented in Table 2. The values obtained showed an increase as the

concentration of ET was increased. The trend has been severally reported [20,21].

4. ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY

The Corrosion inhibition efficiency increased from 77.7 % to 87.0 % when the concentration of ET increased from 0.5 to 2.0 g/L in 1 M HCl while 0.5 M H₂SO₄ the inhibition efficiency increased from 48.3 % to 82.2 %. This trend was similar to that of the PDP experiments and that of HCl in EIS experiments, except for the H₂SO₄ experiment. This could be attributed to the greater adsorption of molecules of ET on the Mild steel surface.

Importantly, the basicity of acids determines their corrosion ferocity independent of the acid type. So, whether HCl or H₂SO₄ is used for an industrial operation like Oil pipeline pickling. A similar result is expected, in as much the basicity to concentration ratio is balanced.

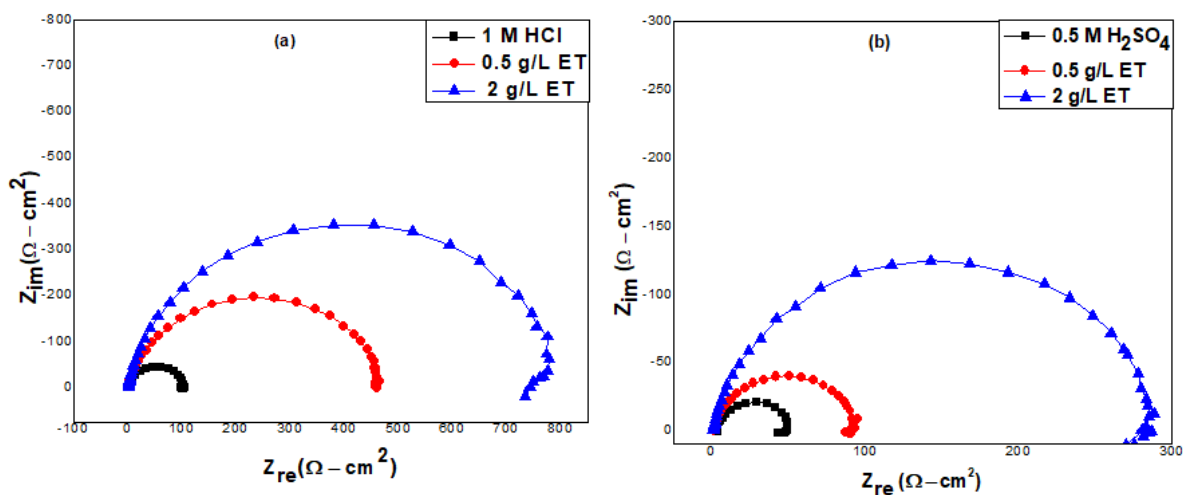
**Fig. 2. Electrochemical impedance spectroscopy for Mild steel in (i) 1 M HCl and (ii) 0.5 M H₂SO₄ in the absence and presence of ET extract**

Table 2. Electrochemical Impedance Spectroscopy EIS, results for mild steel corrosion in 1 M HCl and 0.5 M H₂SO₄ in the Absence and Presence of ET extract

System	R _s (Ω cm ²)	R _{ct} (Ω cm ²)	N	C _{dl} (F cm ⁻²)	IE (%)
1 M HCl	1.659	100.2	0.89	6.918E-5	
0.5 g/L ET	2.001	451.3	0.88	7.094E-5	77.7
2 g/L ET	1.823	762.2	0.88	7.075E-5	87.0
0.5 M H ₂ SO ₄	2.173	50	0.89	3.649E-5	
0.5 g/L ET	3.439	96.2	0.89	2.556E-5	48.3
2 g/L ET	4.16	278.4	0.88	2.178E-5	82.2

5. CONCLUSION

This study examined the corrosion inhibition efficacy as well as the effect of basicity to acid concentration ratio, to corrosion and corrosion inhibition efficiency of ET ethanoic extract on the corrosion of Mild steel in a multi-basic acids environment. The results showed that ET exhibited a good corrosion inhibition of steel corrosion acids media. However, the basicity of the acid is an important factor on the corrosion inhibition performance. Therefore, they is need to balance the basicity to acid concentration ratio, in order to achieve desired inhibition targets. The ET extract exhibited mixed inhibition characteristics, while the mechanism of corrosion inhibition was attributed to adsorption of the molecules of *Enantia chlorantha* (ET) stem bark ethanoic extract on the metal/acid interface.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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