

Corrosion Inhibition of Mild Steel in Hydrochloric Acid by Acid Extracts of *Eichhornia Crassipes*

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Abstract Acid extracts from leaves and roots of *Eichhornia crassipes* (water hyacinth) were tested as corrosion inhibitors for mild steel in hydrochloric acid solutions using a gasometric technique. The effects of temperature and concentration on the inhibition performance of the extracts have been studied. The results show that both the leaf and root extracts functioned as effective corrosion inhibitors, with the leaf extracts exerting a greater effect. Fitting of the experimental data to the Arrhenius and transition state equations revealed that the organic constituents of the extracts were physically adsorbed on the corroding mild steel surface. The adsorption characteristics of selected extract constituents were theoretically evaluated by molecular dynamics simulations in the framework of the density functional theory and confirm distinct adsorption of the extract organic matter on the mild steel surface. Our findings provide ready eco-friendly application for the problematic fresh water weed *Eichhornia crassipes*.

Keywords Acid Corrosion Inhibition, Gasometric Technique, Mild Steel, *Eichhornia Crassipes*, Molecular Dynamics Simulation

1. Introduction

Iron and its alloys are used as materials of choice in diverse industrial and structural applications. Acid solutions are often used in drilling operations in oil and gas exploration, as well as for cleaning, decaling and pickling of steel structure; processes which are normally accompanied by considerable dissolution of the metal and it is very important to add corrosion inhibitors to decrease the corrosion rate in such situations. Organic heterogeneous compounds containing these elements have been reported to be efficient corrosion inhibitors[1-8]. These compounds contain nitrogen, oxygen, sulphur and aromatic ring in their molecular structures and function via adsorption of the molecules on the metal surface creating a barrier to corrosive attack.

The use of natural products of plant origin as corrosion inhibitors has been widely reported by several authors[9-19]. Such interest derives from their inexpensive and eco-friendly nature, easy availability and wide variety. Also the use of these biomass products is justified by the phytochemical compounds present therein with molecular and electronic structures bearing close similarity to conventional organic

inhibitor molecules[11]. The yield of these compounds as well as the corrosion inhibition abilities vary widely depending on the part of the plant and its geographical location[13].

E. crassipes is noted as one of the most important and noxious freshwater weeds[20], ranked 8th in the list of the world's ten most serious weeds according to[21]. It is a floating aquatic plant with inflated petioles and native to tropical America[22]. It is believed that the weed originated in Brazil[23] but found its way into Nigerian waters from a lagoon in the Port Novo area of the Republic of Benin which opens into the Badagry creek enroute to the Atlantic ocean [22]. Since then *Eichhornia crassipes* has become a major weed in Nigeria, having successfully invaded and established itself on the entire Badagry Creek, the Yewa Lagoon, Ologe Lagoon, the Lagos Lagoon and the waterways of Okitipupa, it was reported in 1982 in local newspapers as a weed that is spreading fast and paralyzing the fishing industry[22]. Despite its long list of harmful effects, in recent years it has been found useful in animal feeds, compost, paper, energy (from biogas), biological waste water treatment and heavy metals uptake[20].

In recent times, studies have been carried out to identify more useful applications of this abundant noxious weed and certain active compounds with antioxidant activities such as chlorophylls and carotenoids, phenols, alkaloids and terpenoids have been successfully obtained from *E.*

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Crassipes extracts[24]. The antioxidants showed corrosion inhibition efficiency on magnesium alloy and it may be due to the presence of a great number of double bonds, amine and hydroxyl groups known for their oxygen scavenging and hydrogen donating antioxidant activities[24]. However, to the best of our knowledge, the plant has not been studied for corrosion inhibition abilities on mild steel. The present study investigates the inhibitive effect of leaves (ELV) and roots (ERT) extracts of *Eichhornia crassipes* on mild steel corrosion in HCl solutions using gasometric technique and its modelled structures provides additional insight into the mechanism of inhibitory action.

2. Materials and Methods

2.1. Metal Specimen

The mild steel sheets used in this present work have the composition presented in Table 1. Before measurements, the mild steel coupons were mechanically polished with series of emery paper of variable grades starting with the coarsest and proceeding in steps to the finest (1200) grade, degreased with absolute ethanol, dipped into acetone and air dried. All experiments were conducted on mild steel coupons of dimension 2.0 x 0.08 x 5.0 cm (with a surface area of 21.12 cm²).

Table 1. Chemical composition of the mild steel

C	Si	Mn	S	P	Ni	Cr	Mo	Cu
0.19	0.26	0.64	0.05	0.06	0.09	0.08	0.02	0.27

2.2. Preparation of Plant Extracts

Leaves and roots of *E. crassipes* were collected from a water dam in the University of Ibadan, Nigeria. They were cleaned from epiphytes, washed, dried to a constant weight, ground and kept in labelled glass jars till use. Stock solutions of the leaves and roots extracts were prepared by soaking 4.0 g of the dried and ground leaves and roots in 1000 ml of 5 M HCl solution. The resultant solution was kept for 24 hours, filtered and stored. From the stock solution (4.0 g/l), inhibitor test solutions (concentrations of 0.1, 0.5, 1.0 and 2.0g/l) were prepared.

2.3. Gasometric Experiments

Gasometric measurements were carried out as previously described[25, 26]. Experiments were conducted at 30, 40, 50 and 60 °C. Gasometric technique is based on the principle that corrosion reactions in aqueous acidic media are characterized by the evolution of gas resulting from the cathodic reaction of the corrosion process, which is proportional to the rate of corrosion[27]. The rate of evolution of the gas (R_H) is determined from the slope of the graph of volume of gas evolved (V) versus time (t) and the degree of surface coverage (θ) and hence inhibition efficiency ($\eta\%$) determined using equations (1) and (2), respectively.

$$\theta = (1 - R_{Hi} / R_{Ho}) \quad (1)$$

$$\eta\% = (1 - R_{Hi} / R_{Ho}) \times 100 \quad (2)$$

where R_{Ho} and R_{Hi} are the rates of hydrogen evolution in the absence and presence of the inhibiting molecules, respectively. Results obtained using the gasometric technique have been corroborated by other well established corrosion rate determination techniques, including weight loss, thermometric and electrochemical techniques[3, 28, 29].

2.4. Quantum Chemical Calculations

All theoretical calculations were performed using the density functional theory (DFT) electronic structure programs Forcite and DMol³ as contained in the Materials Studio 4.0 software (Accelrys, Inc.). We modeled the molecular electronic structures of the compounds, including the distribution of frontier molecular orbitals and Fukui indices in order to establish the active sites as well as the local reactivity of the molecules. The calculations were performed by means of the DFT electronic structure program DMol³ using a Mulliken population analysis[30,31]. Electronic parameters for the simulation include restricted spin polarization using the DND basis set and the Perdew Wang (PW) local correlation density functional. Geometry optimization was achieved using COMPASS force field and the Smart minimize method by high-convergence criteria.

Forcite quench molecular dynamics was used to sample many different low energy adsorption configurations of the different molecules on Fe[32,33]. The Fe crystal was cleaved along the (110) plane. Calculations were carried out in a 12 x 8 supercell using the COMPASS force field and the Smart algorithm with NVE (microcanonical) ensemble, a time step of 1 fs and simulation time 5 ps. Temperature was fixed at 350 K.

3. Results and Discussion

We have employed gas-volumetric measurements to investigate mild steel corrosion in 5 M HCl solutions in the absence and presence of ELV and ERT extracts, which are studied herein for corrosion-inhibiting efficacy.

3.1. Corrosion Rates

Figure 1 shows the representative hydrogen evolution plots for mild steel in uninhibited 5 M HCl at 30 – 60 °C. The data presented are means of triplicate determinations, with standard deviation ranging from 0 to 0.003. Hydrogen gas evolution can be seen to increase with increase in temperature resulting in degradation of the mild steel.

Figure 2 illustrates the hydrogen gas evolution rates of the mild steel specimen in 5 M HCl in the presence of different concentrations of ELV (Figure 2a) and ERT (Figure 2b) at different temperatures. The plots indicate that the extracts actually retarded mild steel corrosion at all concentrations in 5 M HCl and the inhibiting effect becomes more pronounced at higher extract concentrations. The data in Figures 1 and 2

also indicate that the rates of steel corrosion in absence and presence of the extracts increased with rise in temperature. This is because an increase in temperature usually accelerates corrosive processes, particularly in media in which H_2 gas evolution accompanies corrosion, giving rise to higher dissolution rates of the metal.

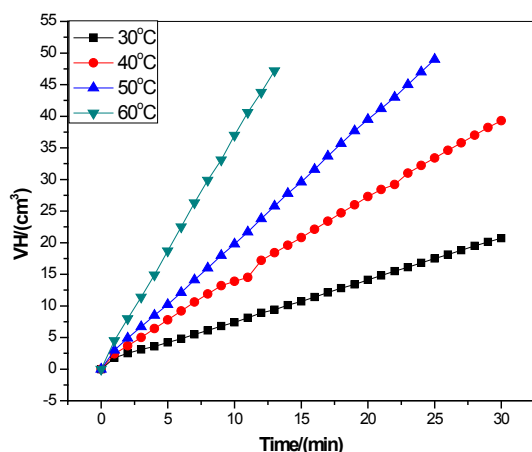


Figure 1. Hydrogen evolution plots for mild steel in uninhibited 5 M HCl at 30 – 60 °C

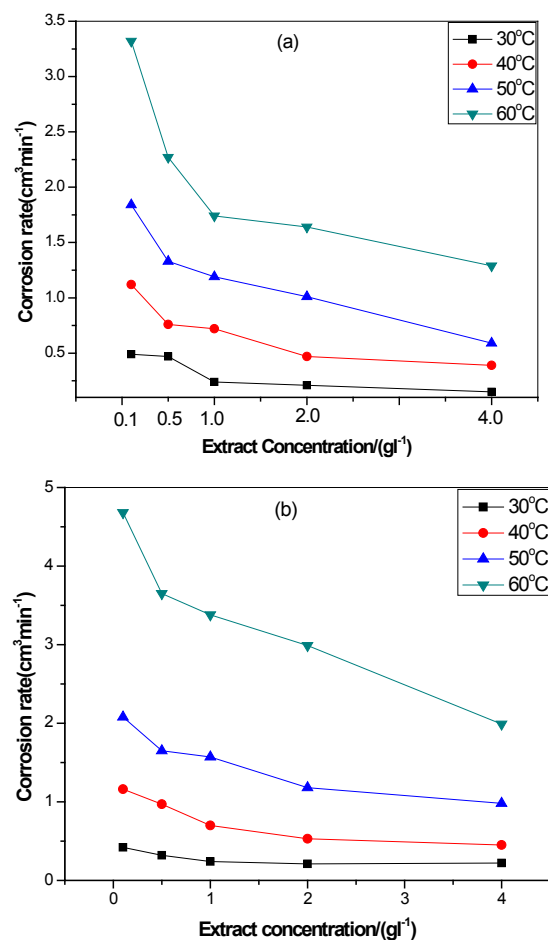


Figure 2. Variation of corrosion rates with extracts concentration for mild steel in 5 M HCl containing (a) ELV and (b) ERT

3.2. Inhibition Efficiency and Adsorption Considerations

Quantitative characterization of the inhibiting effect of PNG extract on the free corrosion of mild steel was carried out by an assessment of the inhibition efficiency (IE %) defined by Eq. 2 above. Figures 3a and 3b show the variation of inhibition efficiency with extract concentration and temperature in 5 M HCl. Inhibition efficiency increased steadily with increasing extract concentration and decreases with rise in temperature. The increase in efficiency of inhibition with extract concentration indicates that more of the extract constituents are adsorbed on the metal surface at higher concentration, leading to greater surface coverage. Declining efficiency with rise in temperature suggests a possible shift of the adsorption-desorption equilibrium towards desorption of adsorbed inhibiting species, since the interface becomes increasingly agitated due to higher rates of hydrogen gas evolution, thus perturbing the adsorbed species. Additionally, the roughening of the metal surface as a result of enhanced corrosion could also reduce the ability of the inhibitor to be adsorbed on the metal surface at high temperatures.

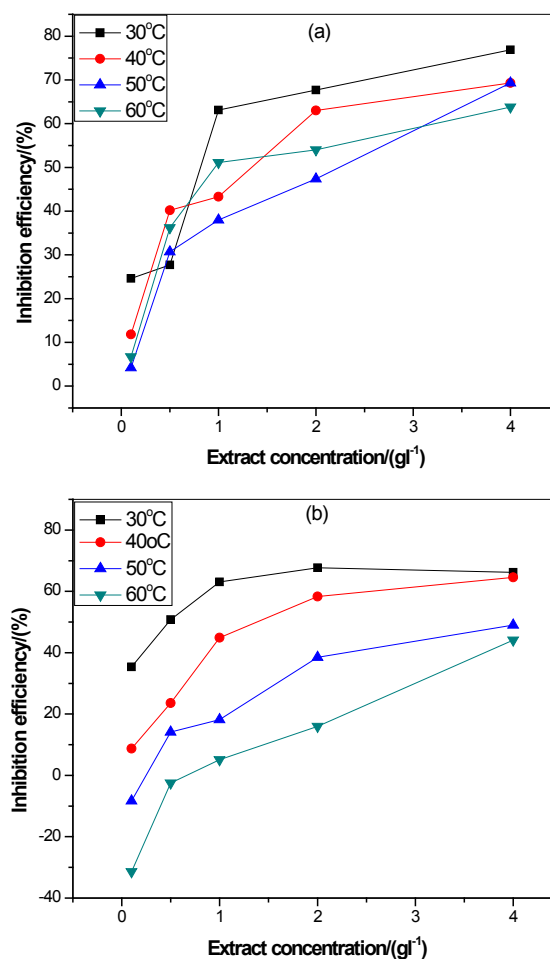


Figure 3. Variation of inhibition efficiency with extracts concentration for mild steel in 5 M HCl containing (a) ELV (b) ERT

In accounting for the observed protective effect, it should be noted that the extracts comprise a mixture of organic and resinous matter. Some of which are known to exhibit good

corrosion inhibiting abilities. The complex chemical compositions make it rather difficult to assign the inhibiting action to a particular constituent. Nevertheless, the net adsorption of the extract organic matter on the metal surface creates a barrier to charge and mass transfer, thus protecting the metal surface from corrosive attack [8].

Interestingly, Shanab et al.[24] isolated, characterized and assessed the corrosion inhibiting efficacies of different active antioxidant fractions of *E. Crassipes* extracts on magnesium corrosion in saline environments. The obtained fractions include the alkaloid (18,19-Secoyohimban-19-oic acid, 16, 17,20, 21-tetradehydro-16-(hydroxymethyl)-methyl ester) and several phthalate derivatives ((i) Methyl dioctyl phthalate, 1,2-Benzene dicarboxylic acid, mono-(2-ethylhexyl ester) (ii) 1,2 Benzene dicarboxylic acid, dioctyl ester (iii) Methyl dioctyl phthalate, (iv) 1,2 Benzene dicarboxylic acid, diisooctyl ester).

The results indicate that all the different fractions inhibited the corrosion reaction under the studied conditions, which was attributed to the chemical structure with many double bonds, hydroxyl and amine groups which have high oxygen scavenging activity leading to oxygen reduction in the corroding system and consequently reduces the rate of metal corrosion by forming an adsorbed layer on the metal surface.

The often complex processes associated with metal-inhibitor interactions can be theoretically investigated at the molecular level using computer simulations of suitable models in the framework of the density functional theory (DFT). We have performed such calculations to model the electronic and adsorption structures of above mentioned phytochemical constituents of *E. Crassipes*.

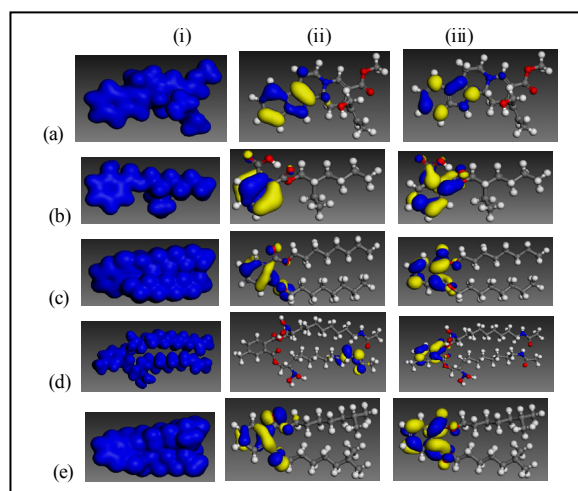


Figure 4. (COLOUR ONLINE) Electronic properties of (a) (18,19-Secoyohimban-19-oic acid,16,17,20,21-tetradehydro-16-(hydroxymethyl)-, methyl ester, (15 beta,16 E); (b) 1,2-Benzene dicarboxylic acid, mono-(2-ethylhexyl ester); (c) 1,2 Benzene dicarboxylic acid, dioctyl ester; (d) Methyl dioctyl phthalate; (e) 1,2 Benzene dicarboxylic acid, diisooctyl ester: (i) total electron density (ii) HOMO orbital (iii) LUMO orbital. (Atom legend: white = H; gray = C; red = O; blue = N)

Figure 4 depicts the highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO) and the total electron density, all of which bear close

resemblance to those of conventional organic corrosion inhibitors[34-38].

The corresponding optimized (lowest energy) adsorption structures for the different molecules on Fe (110) surface are presented in Figures 5 a-e and show that all the molecules maintain a flat-lying adsorption orientation on the Fe surface. The motivation for the computational studies is not so much to provide in depth explanation of the adsorption of the extract, but rather to provide some insight into the nature of their individual interactions with the mild steel surface and their possible contributions to the overall inhibiting effect. The high negative values of the corresponding adsorption energies [$E_{\text{ads}} = E_{\text{total}} - (E_{\text{mol}} + E_{\text{Fe}})$]; where E_{mol} , E_{Fe} and E_{total} correspond respectively to the total energies of the molecule, Fe (110) slab and the adsorbed Mol/Fe (110) couple, point towards strong interaction of the molecules with the metal surface and is responsible for the observed corrosion inhibiting effect of the extracts.

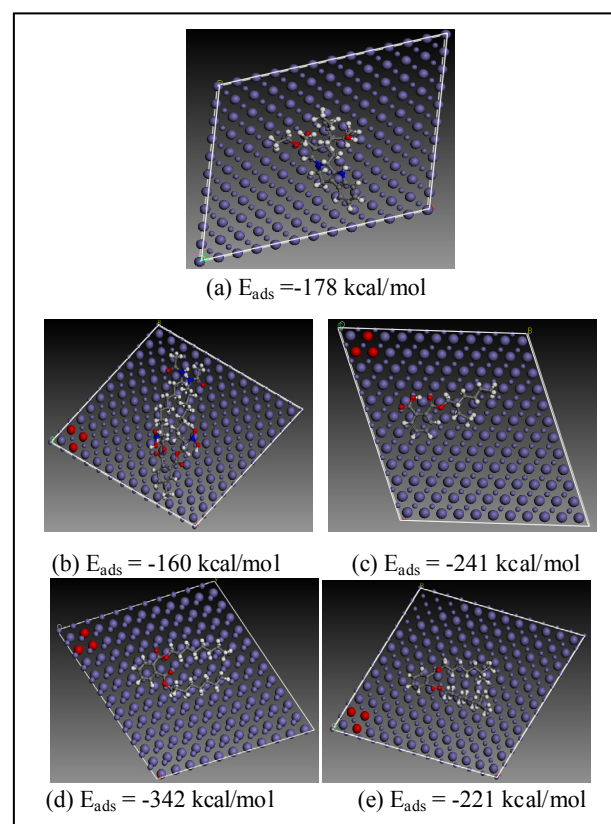


Figure 5. Molecular dynamics models of adsorption of the different extract constituents on Fe (110) surface; (a) (18,19-Secoyohimban-19-oic acid,16,17,20,21-tetradehydro-16-(hydroxymethyl)-methyl ester, (15 beta,16 E); (b) 1,2-Benzene dicarboxylic acid, mono-(2-ethylhexyl ester); (c) 1,2 Benzene dicarboxylic acid, dioctyl ester; (d) Methyl dioctyl phthalate; (e) 1,2 Benzene dicarboxylic acid, diisooctyl ester

3.3. Thermodynamics Parameters

The Arrhenius-type relationship between the corrosion rate (k) of mild steel in acidic media and temperature (T) as often expressed by the Arrhenius equation was used to determine the activation energies (E_a):

$$k = A \exp(-E_a/RT) \quad (3)$$

A is the preexponential factor and R the universal gas constant. The variation of logarithm of corrosion rate with reciprocal of absolute temperature is shown in Figure 6 and Figure 7 for mild steel corrosion in 5 M HCl containing ELV and ERT respectively. The calculated values of E_a are given in Table 2. Addition of the extracts can be seen to increase E_a for the corrosion reaction, implying that the extracts would be more effective at lower temperatures, which in agreement with the observed trend of inhibition efficiency with temperature as well as the proposed physisorption mechanism for the adsorption of the extract organic matter.

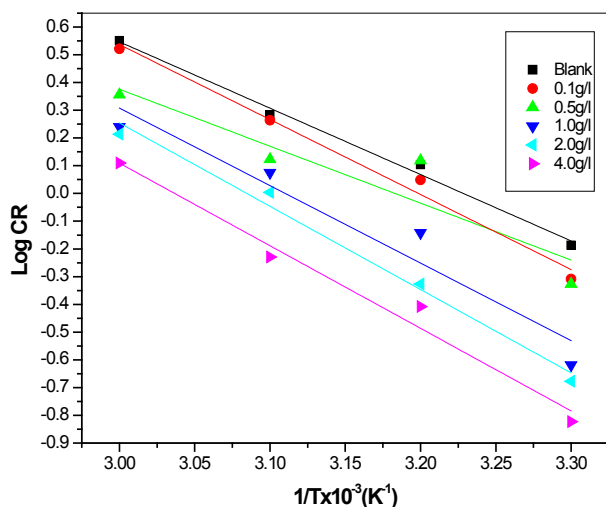


Figure 6. Arrhenius plots for mild steel corrosion in 5 M HCl in the absence and presence of different concentrations of ELV

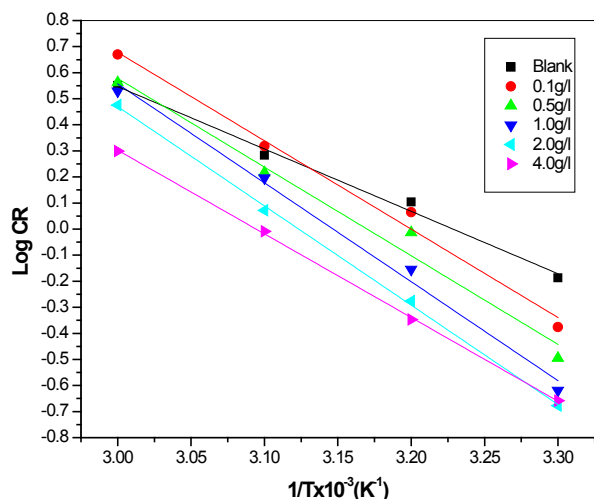


Figure 7. Arrhenius plots for mild steel corrosion in 5 M HCl in the absence and presence of different concentrations of ERT

Some other activation parameters such as the enthalpy change of activation (ΔH^*) and entropy change of activation (ΔS^*) were obtained from the Eyring transition state equation[39]:

$$CR = \frac{RT}{N_h} \exp\left(\frac{\Delta S^*}{R}\right) \exp\left(\frac{-\Delta H^*}{RT}\right) \quad (4)$$

where R is molar gas constant; T is absolute temperature, N is Avogadro's number, h is Planck's constant.

Table 2. Calculated values of activation energy, activation enthalpy and activation entropy for mild steel in 5 M HCl containing ELV and ERT

System	Conc. (g l ⁻¹)	E _a (KJmol ⁻¹)	ΔH° (KJmol ⁻¹)	ΔS° (Jmol ⁻¹ K ⁻¹)
Blank	0	46.27	43.63	-104.50
	0.1	52.42	49.78	-86.23
	0.5	44.28	41.64	-85.22
ELV	1.0	54.43	51.79	-84.56
	2.0	58.29	55.65	-74.04
	4.0	57.70	55.06	-78.61
ERT	0.1	65.65	63.01	-43.85
	0.5	65.86	63.22	-45.14
	1.0	73.47	70.83	-22.71
	2.0	73.52	70.88	-24.25
	4.0	61.93	59.29	-62.23

Straight lines were obtained from the Eyring plots (Figures 8 and 9) with slope $\Delta H^* / R$ and intercept $[\ln(R/NAh) + \Delta S^*/R]$. The calculated values of ΔH^* and ΔS^* obtained from these plots are also given in Table 2. The positive values of ΔH^* both in absence and presence of inhibitor reflect the endothermic nature of the steel dissolution process. It is also clear that the activation enthalpies vary in the same manner as the activation energies, supporting the proposed inhibition mechanism. Large and negative values of entropies imply that the activated complex in the rate determining step represents an association rather than a dissociation step, meaning that a decrease in disordering takes place on going from reactants to the activated complex.

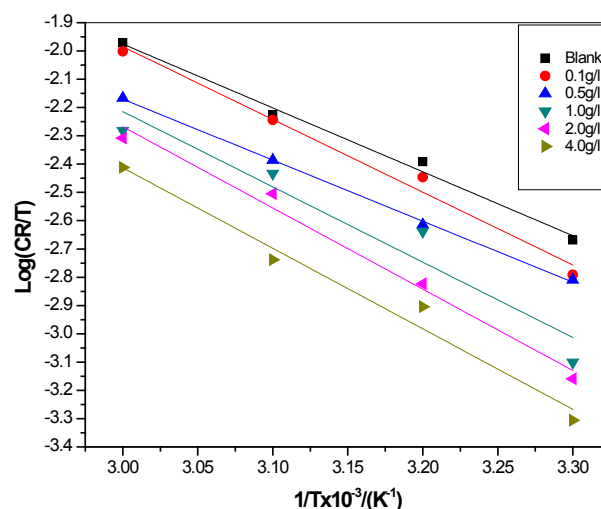


Figure 8. Eyring plots for mild steel corrosion in 5 M HCl without and with ELV

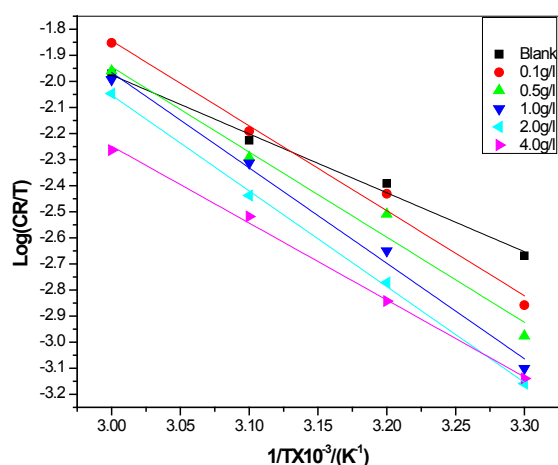


Figure 9. Eyring plots for mild steel corrosion in 5 M HCl without and with ERT

4. Conclusions

The aim of this research was to determine the feasibility of exploiting the bothersome weed (*Eichhornia crassipes*) for materials corrosion control.

Our findings show that the leaf (ELV) and root extracts (ERT) of *E. crassipes* effectively inhibited mild steel corrosion in 5 M HCl. At higher concentrations and lower temperatures, the extracts performed better, whereas at low concentrations and high temperature, their inhibition efficiency decreased. ELV inhibited better than ERT at ordinary temperature and highest concentration of 4 g/l. The inhibiting potential of the extracts were theoretically confirmed via, DFT based quantum chemical computations of parameters associated with the electronic and adsorption structures of selected phytochemical components of the extract.

These results propose a ready industrial application for the problematic fresh water weed for the control of the acid corrosion of mild steel.

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