



ORIGINAL ARTICLE

Corrosion inhibition by leaves and stem extracts of *Sida acuta* for mild steel in 1 M H₂SO₄ solutions investigated by chemical and spectroscopic techniques



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Abstract Corrosion inhibition of mild steel in 1 M H₂SO₄ by leaves and stem extracts of *Sida acuta* was studied using chemical (weight loss and hydrogen evolution) and spectroscopic (AAS, FTIR and UV-V) techniques at 30–60 °C. It was found that the leaves and stem extracts of *S. acuta* inhibited the acid induced corrosion of mild steel. The inhibition efficiency increases with increase in concentration of the extracts but decrease with rise in temperature. Inhibitive effect was afforded by adsorption of the extracts' components which was approximated by Freundlich adsorption isotherm. Inhibition mechanism is deduced from the temperature dependence of the inhibition efficiency and also from spectroscopic results.

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1. Introduction

Pure metals and alloys react chemically/electrochemically with corrosive medium to form a stable compound, in which the loss of metal occurs. The compound so formed is called corrosion product and metal surface becomes corroded. Corrosion involves the movement of metal ions into the solution at active areas (anode), passage of electrons from the metal to an accep-

tor at less active areas (cathode), an ionic current in the solution and an electronic current in the metal. The cathodic process requires the presence of an electron acceptor such as oxygen or oxidizing agents or hydrogen ions (Bentiss et al., 2000; Hukovic-Metikos et al., 2002; Lagrenee et al., 2001; Sinko, 2001; Raja and Sethuraman, 2008). Corrosion of metals is a major problem that must be confronted for safety, environment, and economic reasons. It can be minimized by suitable strategies which in turn stifle, retard or completely stop the anodic or cathodic reactions or both (Raja and Sethuraman, 2009a). Among the several methods of corrosion control and prevention, the use of corrosion inhibitors, is very popular. Most of the efficient inhibitors are organic compounds that contain in their structures mostly nitrogen, sulfur or oxygen atoms.

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Unfortunately, the use of some chemical inhibitors have been limited because of some reasons namely their synthesis is very often expensive and they can be toxic and hazardous for human beings environment as well (Halambek et al., 2010). This has prompted the search for eco-friendly corrosion inhibitors as an alternative to replace inorganic and organic inhibitors to foster sustainable greenness to the environment. These nontoxic, benign, inexpensive, renewable and readily available alternative corrosion inhibitors have been found in different parts of plant extracts (Okafor et al., 2008, 2010; Oguzie, 2008). The use of plant products as corrosion inhibitors are justified by the phytochemical compounds present therein, with molecular and electronic structures bearing close similarity to those of conventional organic inhibitor molecules (Oguzie et al., 2010).

Scientific corrosion literature has descriptions and lists of numerous plant products that exhibit inhibitive properties for mild steel in acidic solutions. However, the latest reports include the inhibitive effect of *Andrographis paniculata* (Singh et al., 2010a), *Spirulina platensis* (Kamal and Sethuraman, 2012), *Jasminum nudiflorum* L. (Li et al., 2010), *Pongamia pinnata* (Singh et al., 2010b), *Bridelia retusa* (Patela et al., 2010), *Dacryodis edulis* (Oguzie et al., 2010), aqueous extracts of mango, orange, passion fruit and cashew peels (da Rocha et al., 2010), *Artemisia pallens* (Kalaiselvi et al., 2010), *Gongronema latifolium* (Eddy and Ebenso, 2010), *Murraya koenigii* (Quraishi et al., 2010), *Azadirachta indica* [(Okafor et al., 2010; Nahlé et al., 2010; Sharma et al., 2010), *Ananas comosus* L. (Ekanem et al., 2010), *Heinsia crinata* (Eddy and Odiongenyi, 2010), *Garcinia kola* and *Cola nitida* (Eddy, 2010), *Kopsia singaporensis* (Raja et al., 2010), *Fenugreek* seeds extract (Bouyanzer et al., 2010)], *Ocimum gratissimum* (Eddy et al., 2010), *Nauclea latifolia* (Uwah et al., 2013), *Salvia aucherii mesatlantica* essential oil (Znini et al., 2012) *Ocimum sanctum* (Kumpawat et al., 2010) and *Embllica officinalis* (Saratha and Vasudha, 2010).

Sida acuta Brum. f (*Malvaceae*) is a shrub indigenous to pantropical areas, widely distributed in these regions and widely used in traditional medicine. The aerial part of the plant is the most frequently used part. In central America, the plant is used to treat asthma, renal inflammation, colds, fever, headache, ulcers and worms (Caceres et al., 1987; Coe and Anderson, 1996). In Colombia the plant is used to treat snake bites. The ethanolic extract of the plant have an effective moderate activity against the venom of *Bothrox atherox* (Otero et al., 2000a,b). Among the compounds isolated from *S. acuta*, its alkaloids appeared to be of great interest in pharmacological studies. For example, Cryptolepine 5-méthylindolo (2-3b)-quinolic and Quindoline, two main alkaloids from the plant have been isolated, characterized and well investigated for its various biological properties and has been reported to enhance antibacterial activity in Burkina Faso (Karoul et al., 2006). In Nigeria, the leaves and stem of the plant are used by the local populace for the treatment of whitlow and other skin diseases (Ekpo and Etim, 2009). Preliminary phytochemical screening of the ethanolic extracts of *S. acuta* in our laboratory and reports of other authors (Edeoga et al., 2005; Akaneme, 2007) have revealed that the extracts is a complex mixture of various phytochemical components like saponins, flavanoids, tannis, alkaloids, organic acid and anthraquinones in the leaves and tannins, alkaloids, and anthraquinones only present in the stem extract.

The present work continues to focus on the application of plant extracts for metallic corrosion control and reports on the inhibiting effects of the leaves and stem extracts of *S. acuta* for mild steel (1005 AISI Grade) corrosion in acidic solution at 30–60 °C using weight loss, hydrogen evolution and atomic absorption spectrophotometry techniques. UV–Vis spectroscopy together with FTIR was further employed to provide additional insights into the mechanism of inhibitory action.

2. Experimental

2.1. Materials

The mild steel sheets used for this study were sourced locally. Each sheet was 0.04 cm in thickness and has the following composition (wt.%): C = 0.13; Si = 0.18; Mn = 0.39; P = 0.40; S = 0.04; Cu = 0.025 and the balance Fe. It was mechanically press cut into 5 × 4 cm coupons. They were abraded with different grades (#400, 600, 800 and 1000) silicon carbide paper, degreased in absolute ethanol, dried in acetone and stored in a moisture-free desiccator prior to use. The corrosive medium was 1 M H₂SO₄ prepared from 98% analytical grade supplied by Sigma–Aldrich. Deionised water was used for the preparation of all reagents.

2.2. Preparation of the *S. acuta* extracts

The leaves and stem of *S. acuta* were collected from Ikot Osong Iman, Etinan, Akwa Ibom, Nigeria, rinsed with distilled water, sun dried and ground to powder using a manual blender. One kilogram of the dry powered samples was extracted using absolute ethanol for 48 h. The extract was concentrated initially using vacuum evaporator and finally by evaporation to dryness on a steam bath to obtain a solid residue devoid of ethanol. From the solid residue, different concentrations (0.1–0.5) g were weighed and then dissolved in 1.0 L of 1 M H₂SO₄ solution for weight loss and hydrogen evolution measurements.

2.3. Weight loss measurements

Experiments were conducted under total immersion in stagnant aerated condition using 250 mL capacity beakers containing 200 mL test solution at 30–60 °C maintained in a thermostated water bath. The mild steel coupons were weighed and suspended in the beaker with the aid of rod and hook. The coupons were retrieved at 2 h interval progressively for 10 h, appropriately cleaned, dried as previously reported (Umoren et al., 2010) and reweighed. The weight loss, (in grams), was taken as the difference in the weight of the mild steel coupons before and after immersion in different test solutions. The tests were performed in triplicate to guarantee the reliability of the results, and the mean value of the weight loss is reported. The reproducibility of the experiment was higher than 95%. From the weight loss values, corrosion rates were computed accordingly using the expression:

$$v = \frac{\Delta W}{At} \quad (1)$$

where v is the corrosion rate, ΔW is the weight loss, A is the sectional area and t is the exposure time of the mild steel coupon.

The inhibition efficiency ($\eta\%$) of the *S. acuta* extracts was evaluated from the following equation:

$$\eta\% = \frac{v_{(\text{blank})} - v_{(\text{inh})}}{v_{(\text{blank})}} \times 100 \quad (2)$$

where $v_{(\text{blank})}$ and $v_{(\text{inh})}$ are the corrosion rates of the mild steel coupons in the absence and presence of inhibitor, respectively.

2.4. Hydrogen evolution measurements

The technique involves the measurement of the volume of hydrogen gas evolved from the surface of a corroding metal-solution system. The measurements were performed using gasometric assembly; its detailed description and procedure has been reported elsewhere (Umoren and Ekanem, 2010). The test solution was kept at 100 mL. The progress of corrosion in the absence and presence of test inhibitor (plant parts' extract) was monitored by careful measurements of the volume of hydrogen gas evolved at fixed time intervals. The experiment was performed for the blank solution (1 M H₂SO₄) and inhibited solutions containing different concentrations (0.1–0.5 g/L) of the plant parts' extracts at 30–60 °C were maintained with a thermostated water bath. Hydrogen evolution rate (ρ_{H}) which can be correlated to the mild steel corrosion rate was computed based on the volume of H₂ evolved using the expression:

$$\rho_{\text{H}} = \frac{V_t - V_i}{T_t - T_i} \quad (3)$$

where V_t and V_i are volumes of hydrogen evolved at time T_t and T_i , respectively. The inhibition efficiency ($\eta\%$) was computed using the equation:

$$\eta\% = \frac{\rho_{\text{H}(\text{blank})} - \rho_{\text{H}(\text{inh})}}{\rho_{\text{H}(\text{blank})}} \times 100 \quad (4)$$

where $\rho_{\text{H}(\text{blank})}$ and $\rho_{\text{H}(\text{inh})}$ are the rate of hydrogen evolution in the absence and presence of extracts, respectively.

2.5. Spectrophotometric analysis

The amount of iron dissolved in solution for both uninhibited and inhibited samples was determined using Perkin–Elmer AA spectrophotometer (Lambda 35 model) after a 72 h immersion of the mild steel in 1 M H₂SO₄ (blank) solution and solutions containing 0.5 g/L of each of the leaves and stem extracts. The inhibition efficiency was computed using the equation:

$$\eta\% = \frac{C_0 - C}{C_0} \times 100 \quad (5)$$

where C_0 (mg L⁻¹) and C (mg L⁻¹) are iron concentrations after immersion in solution without and with inhibitor, respectively.

The film formed on the metal surface after 72 h immersion of the steel in a solution containing each of 0.5 g/L of the leaves and stem extracts was carefully removed, mixed thoroughly with potassium bromide (KBr), and made as pellets. The FTIR spectra (KBr pellet) of the film formed on the mild steel samples were recorded with a Perkin–Elmer FTIR

spectrophotometer (100 series). FTIR analysis was also performed for the leaves and stem extracts of *S. acuta*.

UV–Visible absorption spectrophotometric method was carried out on the prepared mild steel samples after immersion in 1 M H₂SO₄ with and without addition of 0.5 g/L of leaves and stem extracts of *S. acuta* at 30 °C for 72 h. The UV–Visible spectra measurements were carried out using a UV–Visible Jenway 5305 model spectrophotometer.

3. Results and discussion

3.1. Weight loss, corrosion rates and inhibition efficiency

The weight loss method has found broad practical application (Fomin and Zhigalova, 1986). The rate of corrosion can be defined as the ratio of the loss in weight of the sample ΔW to its area A and the time length over which the test was undertaken as given in Eq. (1). A major advantage of this method is its relative simplicity and availability. In addition, the method uses a direct parameter for the quantitative evaluation of corrosion, i.e., the loss in mass of the metal. The data obtained for the corrosion behaviour of mild steel in 1 M H₂SO₄ solution containing leaves and stem extracts of *S. acuta* within the concentration range of 0.1–0.5 g/L from weight loss measurements are presented in Figs. 1 and 2, respectively, as well as Table 1. Fig. 1 shows the weight loss–time curves for mild steel in 1 M H₂SO₄ without and with different concentrations of leaves (LV) of *S. acuta* extract at different temperatures (30–60 °C). Similar plots for the stem (ST) of the plant extract are depicted in Fig. 2 at the same temperatures. It is seen from the plots that the amount of material loss (g cm⁻²) decreases significantly in the presence of the extracts compared to the blank acid solution and was also found to be dependent on the concentration of the extracts. This indicates that the two additives inhibit the corrosion of mild steel in 1 M H₂SO₄ solution. Also the amount of material loss increases with increase in temperature and greater loss in mass of the mild steel specimen was recorded at 60 °C both in the absence and presence of the studied plant extracts.

The values of corrosion rate and inhibition efficiency in the absence and presence of different extract concentrations are listed in Table 1. Results in the table indicate that the extracts act as good corrosion inhibitor for mild steel in 1 M H₂SO₄ solution given that the corrosion rate was reduced in the presence of the extracts compared to their absence. Further inspection of Table 1 reveals that corrosion rate increases with increase in temperature with the highest values obtained at 60 °C for all the systems investigated. The inhibition efficiency increases with increasing extracts concentration and is more pronounced for the leaves compared to the stem extract. For instance the % inhibition efficiency values of 85% and 52% were obtained at the highest extract concentration (0.5 g/l) for leaves and stem, respectively, at 30 °C. Examination of the table reveals a decreasing trend in inhibition efficiency with increasing experimental temperatures for all the system studied. This suggests possible desorption of some of the adsorbed inhibitor from the metal surface at higher temperatures. Such behaviour shows that the additives were physically adsorbed on the metal surface (Oguzie, 2007).

The corrosion-inhibiting effect of LV and ST extracts of *S. acuta* can be attributed to phytochemical constituents

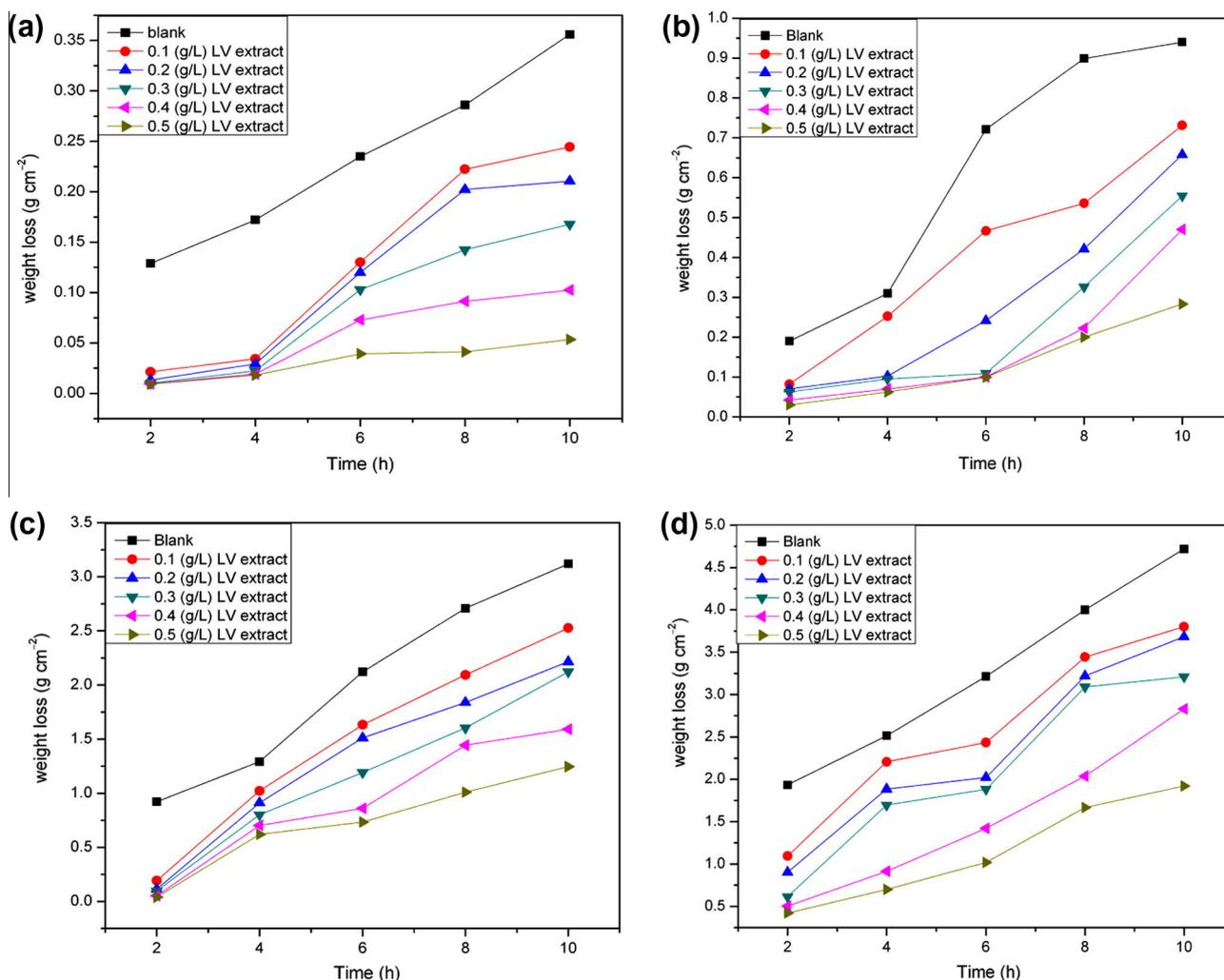


Figure 1 Plot of weight loss against time for mild steel in 1 M H₂SO₄ without and with *Sida acuta* LV extract at (a) 30 °C, (b) 40 °C, (c) 50 °C and (d) 60 °C.

including saponins, flavanoids, tannis, alkaloids, organic acid and anthraquinones in the leaves and tannins, alkaloids, and anthraquinones only in the stem extracts. The different constituents may react with freshly generated Fe²⁺ ions on a corroding metal surface forming organometallic [Fe–Inh] complexes. The inhibiting effect of such complexes then depends on their stability and solubility in the aqueous corrodent, which from our results is a function of the extracts concentration. Corrosion inhibition process is complex in nature. This complexity is increased by several orders of magnitude when one considers plant extracts with their complicated chemical compositions. This makes it difficult to assign the inhibitive effect to adsorption of any particular constituent, since some of these constituents, including tannins, organic and amino acids, alkaloids, proteins, flavonoids, and organic pigments and their acid hydrolysis products are known to exhibit inhibiting action (Zucchi and Omar, 1985; Martinez and Stern, 2001; Quraishi, 2004; Kliskic et al., 2000). Zucchi and Omar (1985) attributed the inhibiting effect of acid extracts of some plant materials to protonated species resulting from protein hydrolysis products.

3.2. Hydrogen evolution measurements

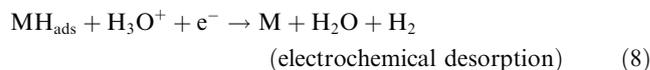
Hydrogen can enter into the metal during various industrial operations like melting, heat treatment, or pickling and electrochemical processes such as cathodic cleaning and electrolytic machining. Of the various sources of entry of hydrogen into the metal, pickling is one of the basic steps in electroplating processes in which mineral acids are used for the removal of rust and scale. The main reactions in acidic solutions are as follows (Muralidharan et al., 2000):



where M is the cathodic metal surface. This discharge step is followed by either



or



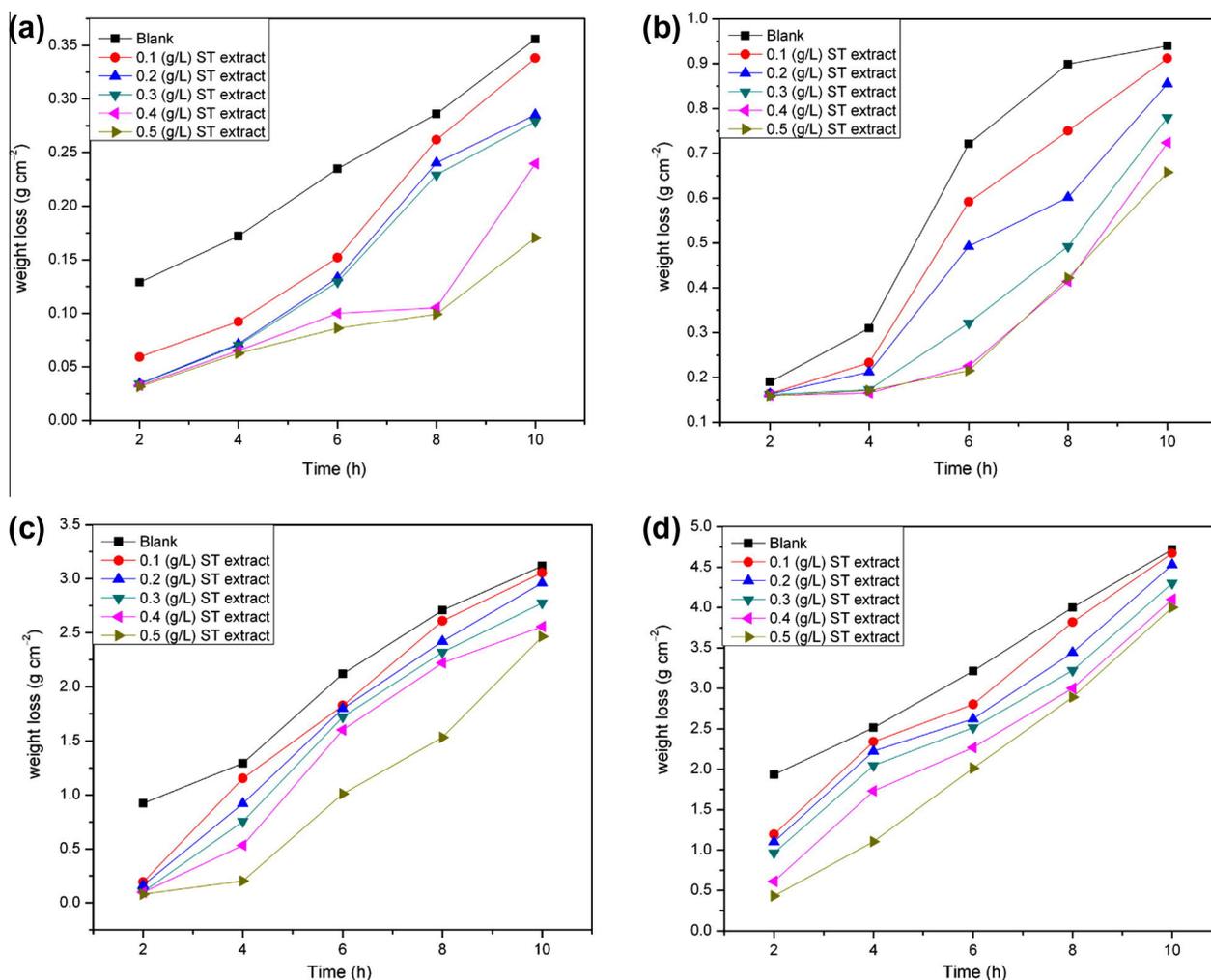


Figure 2 Plot of weight loss against time for mild steel in 1 M H₂SO₄ without and with *Sida acuta* ST extract at (a) 30 °C, (b) 40 °C, (c) 50 °C and (d) 60 °C.

Table 1 Calculated values of corrosion rate and inhibition efficiency for mild steel in 1 M H₂SO₄ in the absence and presence of LV and ST extracts of *Sida acuta* at 30–60 °C from weight loss measurements.

Systems/concentration	Corrosion rate (g cm ⁻² h ⁻¹)				Inhibition efficiency (η%)			
	30 °C	40 °C	50 °C	60 °C	30 °C	40 °C	50 °C	60 °C
Blank	1.78	4.70	15.60	23.60				
0.5 g/L LV extract	0.27	1.41	6.22	9.60	85	69	60	59
0.4 g/L LV extract	0.51	2.35	7.96	14.16	71	50	49	40
0.3 g/L LV extract	0.84	2.77	10.61	16.05	53	41	35	32
0.2 g/L LV extract	1.05	3.29	11.08	18.41	41	32	29	22
0.1 g/L LV extract	1.22	3.66	12.64	20.19	31	22	19	15
0.5 g/L ST extract	0.85	3.29	12.32	20.00	52	30	21	15
0.4 g/L ST extract	1.19	3.62	12.79	21.00	33	23	18	11
0.3 g/L ST extract	1.39	3.90	13.88	21.50	22	17	11	09
0.2 g/L ST extract	1.43	4.28	14.82	22.66	19	09	05	04
0.1 g/L ST extract	1.69	4.56	15.29	23.36	05	03	02	01

A part of the atomic hydrogen liberated during the pickling process enters the metal, and the remainder is evolved as hydrogen gas. Organic compounds are generally added to pickling baths in order to minimize the base metal attack

and limit the hydrogen liberated. However, the fraction of hydrogen atoms that enters the metal produces some detrimental effects (Subramanyan et al., 1970) on the mechanical properties of iron/steel, such as reduction in ductility, lowering of

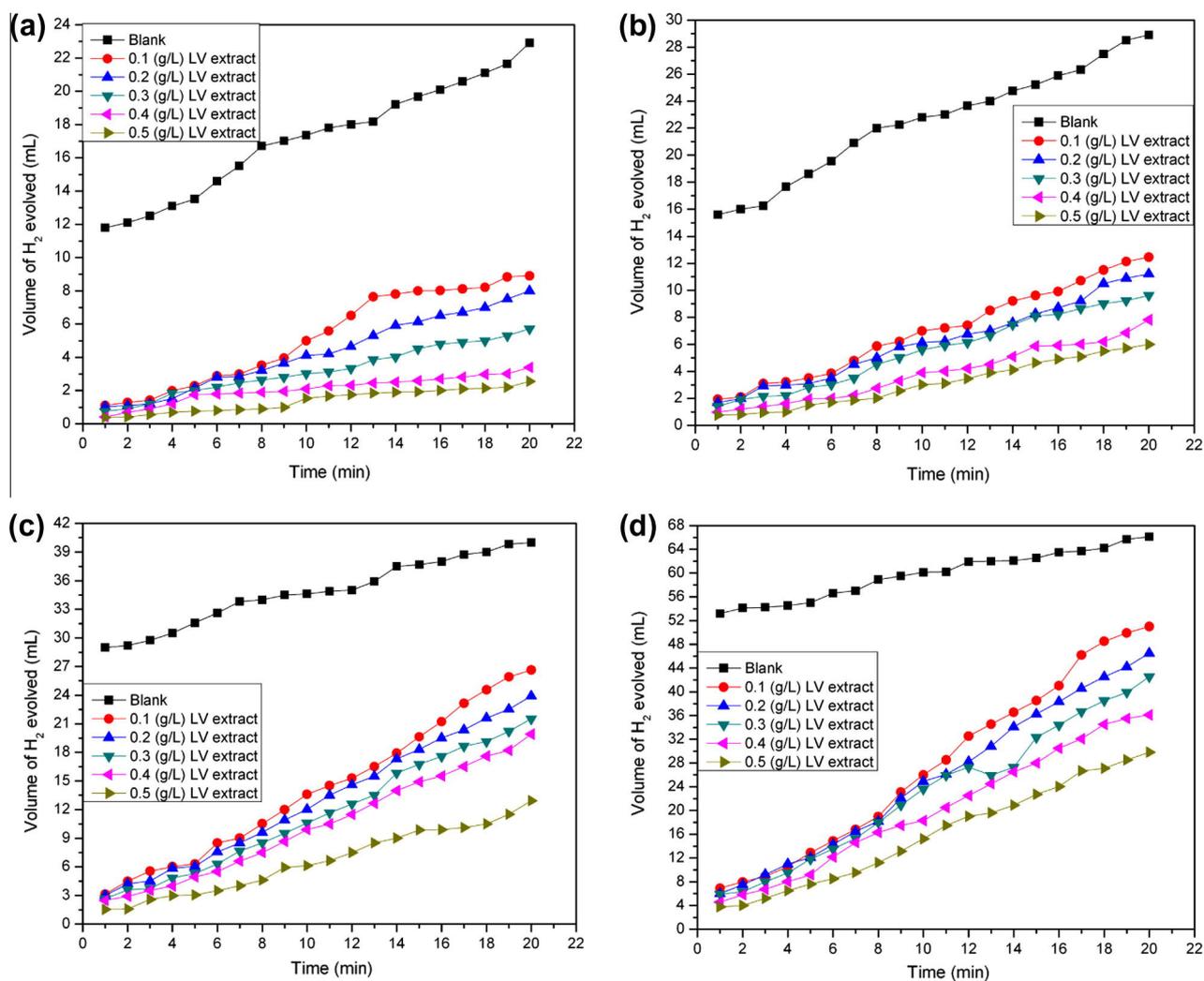


Figure 3 Plot of volume of H₂ evolved against time for mild steel in 1 M H₂SO₄ without and with *Sida acuta* LV extract at (a) 30 °C, (b) 40 °C, (c) 50 °C and (d) 60 °C.

fracture stress and loss in mechanical strength leading to embrittlement. It has been already pointed out that hydrogen evolution measurements can be a useful tool for evaluating inhibitors from the point of view of predicting the extent of hydrogen evolution inhibition (Aytac et al., 2005). In the present study the volume of hydrogen gas evolved are determined in H₂SO₄ in the absence and presence of inhibitors with an idea of screening leaves and stem extracts of *S. acuta* with regard to their effectiveness on the reduction of hydrogen gas evolved on corroding mild steel surface.

The volume of hydrogen evolved during the corrosion of mild steel in 1 M H₂SO₄ solutions in the absence and presence of *S. acuta* LV extracts at 30–60 °C measured as a function of time is shown in Fig. 3. Similar plots for the uninhibited and inhibited solutions containing different concentrations of the ST extract are depicted in Fig. 4. Inspection of the figures reveals that the volume of hydrogen evolved increases with time, probably due to the constant attack of the active ion in the corrosion reaction on the surface of the metal. Introduction of both plant parts extracts into the corrodent results in a progressive decrease deflection in the volume of

hydrogen evolved showing that the extracts actually afforded corrosion inhibition of mild steel in the acidic environment. The volume of hydrogen gas evolved was observed to increase with increase in temperature in the absence and presence of the extracts. Also the volume of H₂ evolved was dependent on extract concentration, decreasing with increasing extract concentration.

The values of hydrogen evolution rate which can be correlated to the corrosion rate of mild steel coupons in the absence and presence of the extracts as well as the inhibition efficiency at different temperatures are given in Table 2. From the table, it is clearly seen that hydrogen evolution rates were reduced in the presence of the extracts compared to the blank acid solution. Inspection of the table further reveals that hydrogen evolution rate of mild steel in the presence of the extract decreases with increase in concentration but increases with temperature rise. Results presented in Table 2 also show that inhibition efficiency increases with increase in the concentration of the extract but decreases with increase in temperature. Increase in inhibition efficiency with decreases in temperature is suggestive of physical

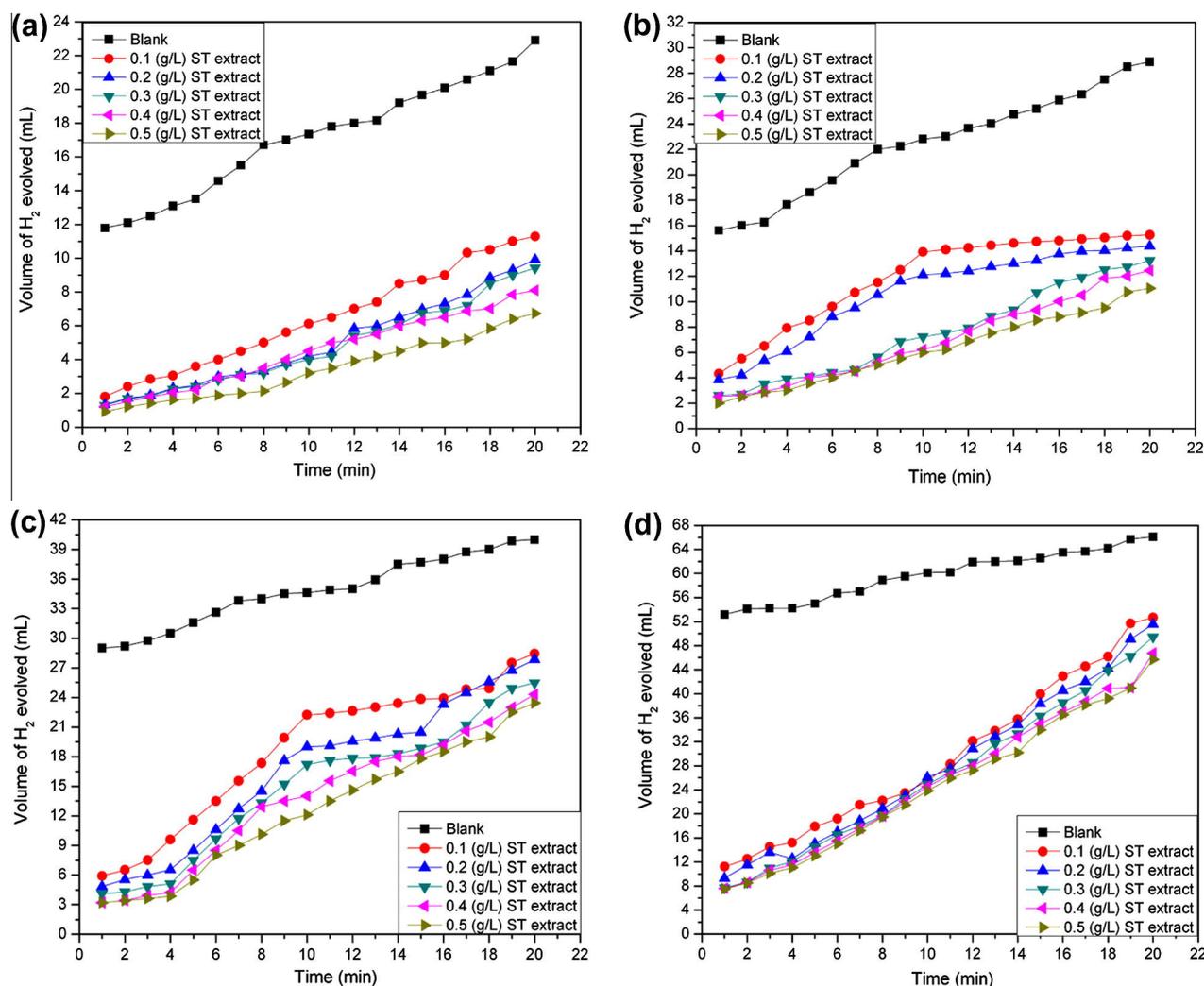


Figure 4 Plot of volume of H₂ evolved against time for mild steel in 1 M H₂SO₄ without and with *Sida acuta* ST extract at (a) 30 °C, (b) 40 °C, (c) 50 °C and (d) 60 °C.

Table 2 Calculated values of hydrogen evolution rate and inhibition efficiency for mild steel in 1 M H₂SO₄ in the absence and presence of LV and ST extracts of *Sida acuta* at 30–60 °C from hydrogen evolution measurements.

Systems/concentration	Hydrogen evolution rate (mL min ⁻¹)				Inhibition efficiency ($\eta\%$)			
	30 °C	40 °C	50 °C	60 °C	30 °C	40 °C	50 °C	60 °C
Blank	0.59	0.78	1.45	2.66				
0.5 g/L LV extract	0.12	0.31	0.68	1.51	80	60	53	43
0.4 g/L LV extract	0.19	0.39	0.99	1.89	69	49	31	29
0.3 g/L LV extract	0.30	0.53	1.14	2.26	49	32	21	15
0.2 g/L LV extract	0.41	0.56	1.23	2.42	31	28	15	09
0.1 g/L LV extract	0.44	0.66	1.33	2.51	25	16	08	06
0.5 g/L ST extract	0.34	0.55	1.17	2.28	43	29	19	14
0.4 g/L ST extract	0.41	0.62	1.22	2.34	31	20	16	12
0.3 g/L ST extract	0.47	0.67	1.27	2.47	20	16	12	07
0.2 g/L ST extract	0.49	0.72	1.39	2.58	16	08	04	03
0.1 g/L ST extract	0.57	0.76	1.42	2.63	04	02	02	01

adsorption of the *S. acuta* leaves and stem extracts components onto the mild steel surface. The inhibition efficiency obtained from this method follows the same trend observed from the weight loss technique.

3.3. Atomic absorption spectrophotometry

Acid is widely used in various industries for the pickling of ferrous alloys and steels. Because of the aggressive nature of

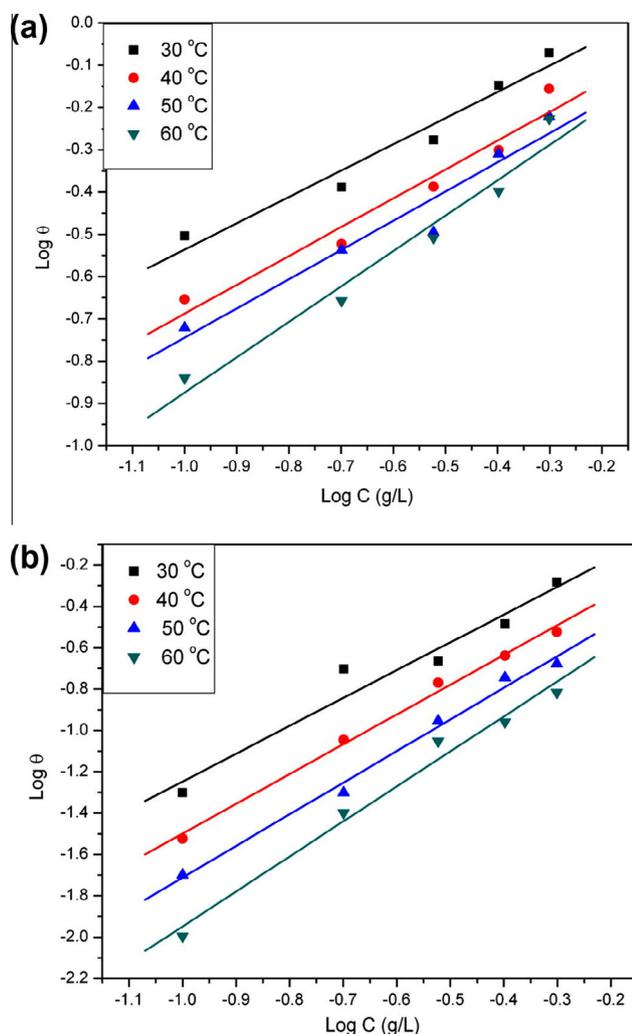


Figure 5 Freundlich adsorption isotherm plot for mild steel in 1 M H₂SO₄ with *Sida acuta* extracts for (a) LV and (b) ST at different temperatures.

the acid medium, the metal corrodes. On corrosion, atoms of the metal are reduced and passed into the solution as ions. The amount of ions in the solution will increase with the concentration of the acid media and with temperature, in the absence of inhibiting species. Inhibitors are commonly used to reduce acid attack on the substrate metal and then, reduce the amount of metal ions being passed into the solution. Experiments were undertaken using AAS to determine the amount of the iron from the bulk of the metal into the electrolyte in the absence and presence of the highest concentration (0.5 g/L) of both LV and ST extracts of *S. acuta* after 72 h of immersion period. Results obtained indicate that there was a decrease in the amount of dissolved iron in the presence of the inhibitors (plant extracts) compared to the blank solution. In the blank acid solution (1 M H₂SO₄) the concentration of dissolved Fe was found to be 70 mg/L. This value was reduced to 20 and 30 mg/L on introduction of 0.5 g/L of leaves and stem extract of *S. acuta*, respectively. This may be attributed to the adsorption of components of the extracts on the steel surface, producing a barrier, which isolates the surface from the corrosion environment. Inhibition efficiency values

obtained from AAS determination were 71% and 57% for leaves and stem extracts, respectively. The result is consistent with the observed trend from other techniques (weight loss and hydrogen evolution) and also clearly shows that the LV extract is a better inhibitor than the ST extract within the limit of the concentration and temperature range studied.

3.4. Adsorption isotherm and thermodynamics parameters

The mechanism of the interaction between inhibitor and the metal surface can be explained using adsorption isotherms. The degree of surface coverage, θ , was computed for the different concentrations of the extracts from weight loss measurements as follows: $\eta\% = \theta \times 100$, assuming direct relationship between surface coverage and inhibition efficiency. The surface coverage values obtained were applied to various adsorption isotherm models and correlation coefficient (R^2) was a useful means of determining the best fit isotherm. By far, the best result was obtained for Freundlich adsorption isotherm, which may be formulated as:

$$\theta = K_{\text{ads}} C^n \quad (9)$$

or

$$\log \theta = \log K_{\text{ads}} + n \log C \quad (10)$$

where $0 < n < 1$; θ is the surface coverage, C is the inhibitor concentration and K_{ads} is equilibrium constant of adsorption–desorption process. Fig. 5 shows the plot of $\log \theta$ against $\log C$ for (a) LV (b) ST extracts at 30–60 °C. Linear plots were obtained for the different systems studied indicating that the experimental results relating the adsorption of the plant extracts can be approximated by Freundlich adsorption isotherm. The adsorption parameters derived from the plot are listed in Table 3. Results in the table indicate that K_{ads} values whose values indicate the binding power of the inhibitor to the metal surface (Tebbjji et al., 2007) are seen to decrease with increasing temperature. Such behaviour can be interpreted on the basis that an increase in temperature results in the desorption of some adsorbed components of the extracts on the metal surface and is consistent with the proposed physisorption mechanism. The values of free energy of adsorption indicate that the inhibitors function by physically adsorbing on the metal surface. Generally, values of free energy of adsorption up to -20 kJ mol^{-1} are consistent with electrostatic interaction between charged molecules and a charged metal (which indicates physical adsorption) while those more negative than -40 kJ mol^{-1} involves charge sharing or transfer from the inhibitor molecules to the metal surface to form a co-ordinate type of bond (which indicates chemisorption). Result presented in the table indicate that the values of free energy of adsorption for all the systems studied lie between -9.5 and $-10.6 \text{ kJ mol}^{-1}$ signifying spontaneous adsorption of the additives via physisorption mechanism.

Thermodynamic model is very useful to explain the adsorption phenomenon of inhibitor molecule. The enthalpy of adsorption could be calculated according to the Van't Hoff equation (Tang et al., 2003; Zhao and Mu, 1999):

$$\ln K_{\text{ads}} = \frac{-\Delta H_{\text{ads}}^{\circ}}{RT} + \text{constant} \quad (11)$$

Table 3 Freundlich adsorption parameters for LV and ST extracts of *Sida acuta* at different temperatures.

Plant part	Temperature (°C)	$\Delta G_{\text{ads}}^{\circ}$ (kJ mol ⁻¹)	K_{ads} (g L ⁻¹)	n	R^2
LV	30	-10.6	1.22	0.62	0.98
	40	-10.4	0.99	0.68	0.98
	50	-10.5	0.87	0.69	0.97
	60	-10.9	0.92	0.84	0.98
ST	30	-10.7	1.24	1.03	0.97
	40	-10.1	0.88	1.04	0.99
	50	-9.7	0.66	1.05	0.99
	60	-9.5	0.56	1.06	0.99

where $\Delta H_{\text{ads}}^{\circ}$ and K_{ads} are the enthalpy of adsorption and adsorptive equilibrium constant, respectively.

Fig. 6 shows the plot of relationship between $\ln K_{\text{ads}}$ and $1/T$ for the LV and ST extract of *S. acuta*. Straight line plots were obtained and the enthalpy of adsorption was obtained from the slope of the linear plot.

The enthalpy of adsorption (ΔH) can be approximately regarded as the standard enthalpy of adsorption ($\Delta H_{\text{ads}}^{\circ}$) under the experimental conditions (Zhao and Mu, 1999; Mu et al., 2004) and the values obtained were -22.5 and -11.1 kJ mol⁻¹ for the LV and ST extracts, respectively. The standard adsorption free energy ($\Delta G_{\text{ads}}^{\circ}$) listed in Table 3 was obtained using the relation ship (Noor, 2009):

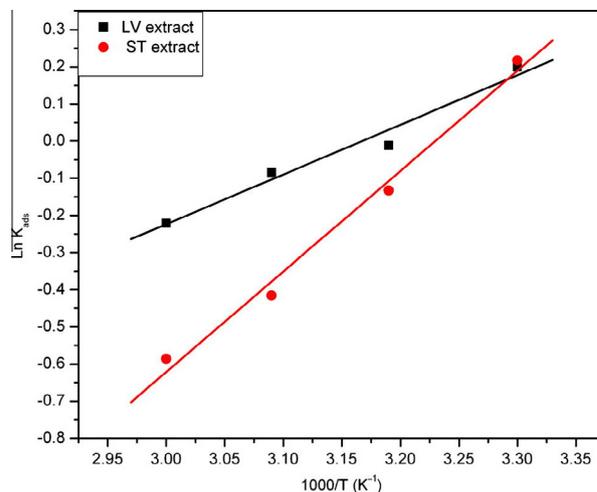
$$\log K_{\text{ads}} = -\log C_{\text{H}_2\text{O}} - \frac{\Delta G_{\text{ads}}^{\circ}}{2.303RT} \quad (12)$$

where $C_{\text{H}_2\text{O}}$ is the concentration of water expressed in g L⁻¹ (the same as that of inhibitor concentration), R is the molar gas constant and T is the absolute temperature. The standard entropy of adsorption ($\Delta S_{\text{ads}}^{\circ}$) was obtained from the basic thermodynamic equation:

$$\Delta G_{\text{ads}}^{\circ} = \Delta H_{\text{ads}}^{\circ} - T\Delta S_{\text{ads}}^{\circ} \quad (13)$$

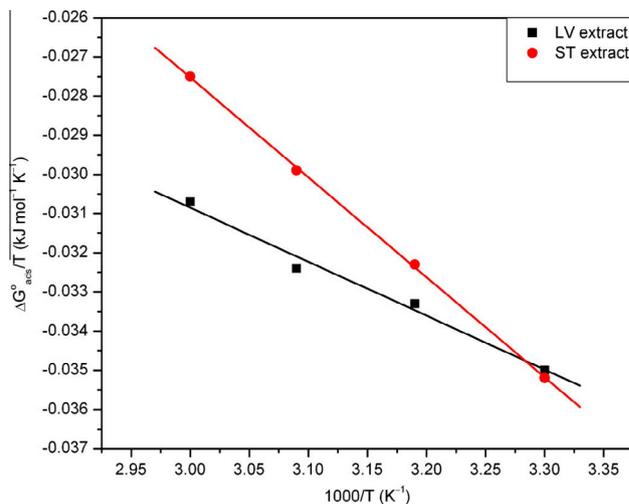
The calculated values of $\Delta S_{\text{ads}}^{\circ}$ were -0.039, -0.039, -0.037 and -0.035 J mol⁻¹ K⁻¹ at 30, 40, 50 and 60 °C, respectively, for the LV extract. Values of -6.6×10^{-4} , -3.2×10^{-3} , -4.3×10^{-3} and -4.8×10^{-3} J mol⁻¹ K⁻¹ were obtained for ST extract correspondingly. The values of thermodynamic parameters for the adsorption of inhibitors can provide valuable information about the mechanism of corrosion inhibition. The endothermic adsorption process ($\Delta H_{\text{ads}}^{\circ} > 0$) is attributed unequivocally to chemisorption (Durnie et al., 1999) while generally, an exothermic adsorption process ($\Delta H_{\text{ads}}^{\circ} < 0$) may involve either physisorption or chemisorption or a mixture of both processes. In the present case; the negative sign of $\Delta H_{\text{ads}}^{\circ}$ indicates that the adsorption of components of the extracts is an exothermic process (Gomma and Wahdan, 1995). The negative values of $\Delta S_{\text{ads}}^{\circ}$ indicate that the adsorption process is accompanied by a reduction in entropy. The negative values of $\Delta S_{\text{ads}}^{\circ}$ might be explained as follows: before the adsorption of components of the extracts onto the mild steel surface, components of the extracts might freely move in the bulk solution (the components of the extracts were chaotic), but with the progress in the adsorption, components of the extracts were orderly adsorbed onto the mild steel surface, resulting in a decrease in entropy (Tang et al., 2003).

Standard enthalpy of adsorption ($\Delta H_{\text{ads}}^{\circ}$) can also be deduced from the Gibbs-Helmholtz equation expressed by (Emregul and Hayval, 2006):

**Figure 6** Plot of $\ln K_{\text{ads}}$ against $1/T$ for LV and ST extracts of *Sida acuta*.

$$\frac{\Delta G_{\text{ads}}^{\circ}}{T} = \frac{\Delta H_{\text{ads}}^{\circ}}{T} + \text{constant} \quad (14)$$

Fig. 7 shows the variation of $\Delta G_{\text{ads}}^{\circ}/T$ with $1/T$ which gives a straight line with a slope that equals $\Delta H_{\text{ads}}^{\circ}$. It can be seen from the figure that $\Delta G_{\text{ads}}^{\circ}/T$ decreases with $1/T$ in a linear fashion.

**Figure 7** Plot of $\Delta G_{\text{ads}}^{\circ}/T$ against $1/T$ for LV and ST extracts of *Sida acuta*.

The calculated $\Delta H_{\text{ads}}^{\circ}$ values using the Gibbs–Helmholtz equation are -22.6 and -10.9 kJ mol^{-1} for LV and ST extracts, respectively, confirming the exothermic behaviour of adsorption on the mild steel surface, therefore, the values of $\Delta H_{\text{ads}}^{\circ}$ obtained by both methods are in good agreement.

3.5. Kinetic parameters

Temperature has a great effect on the rate of metal electrochemical corrosion. Some authors (Popova et al., 2003; Obi-Egbedi and Obot, 2011) opined that for corrosion in a neutral solution (oxygen depolarization) the increase in temperature has a favourable effect on the overpotential of oxygen depolarization and the rate of oxygen diffusion but leads to a decrease of oxygen solubility, whereas for corrosion in acidic medium (hydrogen depolarization), the corrosion rate increases exponentially with temperature increase because the hydrogen evolution overpotential decreases. Effect of temperature on the corrosion and inhibition process of mild steel in 1 M H_2SO_4 in the absence and presence of different concentrations of the *S. acuta* extracts after 10 h of immersion was studied at 30–60 °C using weight loss measurements. The results of the effect of temperature on corrosion rate as presented in Table 4 are in agreement with earlier reports of studies involving plant extracts (Ekanem et al., 2010) increasing as temperature increases. The dependence of corrosion rate on temperature can be expressed by the Arrhenius equation:

$$\log v = \log A - \left(\frac{E_a}{2.303RT} \right) \quad (15)$$

where t is the corrosion rate, E_a is the apparent activation energy of the mild steel dissolution, R is the molar gas constant, T is the absolute temperature, and A is the frequency factor. Fig. 8 depicts Arrhenius plot as log of corrosion rate ($\log v$) against the reciprocal of temperature ($1/T$) for mild steel in 1 M H_2SO_4 in the free acid solution and the acid containing different concentrations of *S. acuta* extracts for (a) LV and (b) ST. The plots obtained are straight lines and the activation energy was evaluated from the slope of the straight line plots. The calculated values of activation energy are listed in Table 4. It can be seen in the table that E_a is higher in the presence of the inhibitors than in their absence. The modification in the values of E_a may be attributed to the geometric blocking effect of adsorbed inhibitive species on the metal surface (Tebji et

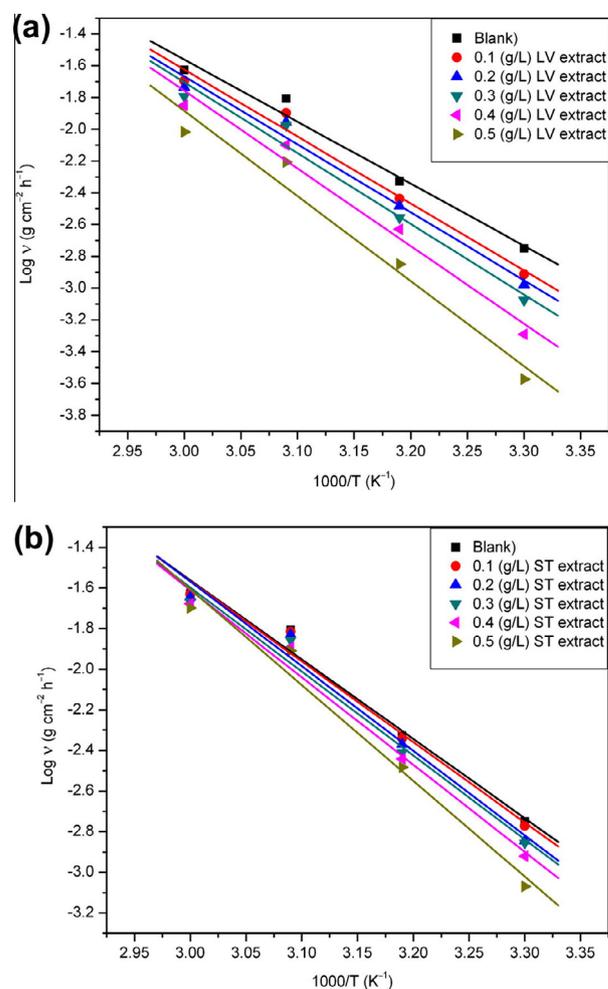


Figure 8 Arrhenius plot for mild steel in 1 M H_2SO_4 without and with different concentrations *Sida acuta* extract for (a) LV and (b) ST.

al., 2007). This observation further supports the proposed physisorption mechanism as reports (Fu et al., 2010; Solomon et al., 2010; Ahamad et al., 2010) show that lower values of E_a in the presence of inhibitors in comparison to the free acid solution are indicative of chemical adsorption mechanism, whereas the opposite suggests a physical adsorption

Table 4 Activation parameters for mild steel corrosion in 1 M H_2SO_4 in the absence and presence of different concentrations of LV and ST of *Sida acuta* extracts.

Systems/concentration	E_a (kJ mol^{-1})	Q_{ads} (kJ mol^{-1})	ΔH^* (kJ mol^{-1})	ΔS^* ($\text{J mol}^{-1} \text{K}^{-1}$)
Blank	74.6	–	71.9	–59.3
0.1 g/L LV extract	80.6	–26.5	78.0	–42.9
0.2 g/L LV extract	81.9	–22.8	79.2	–40.1
0.3 g/L LV extract	85.3	–26.4	82.7	–30.5
0.4 g/L LV extract	93.6	–33.5	90.9	–17.8
0.5 g/L LV extract	102.5	–38.1	99.9	–6.9
0.1 g/L ST extract	74.8	–44.2	73.3	–56.0
0.2 g/L ST extract	75.9	–50.2	77.1	–44.6
0.3 g/L ST extract	79.7	–30.2	76.5	–46.9
0.4 g/L ST extract	79.1	–36.5	79.7	–37.7
0.5 g/L ST extract	82.3	–49.2	87.6	–13.7

mechanism. Further inspection of Table 4 also revealed that E_a increases with increase in extracts concentration for both plant parts. Similar observation has been reported by Singh et al. (2010a) in their studies of the inhibition of corrosion of mild steel in hydrochloric acid solution by the extract of Kalmegh (*A. paniculata*) leaves extract.

In order to calculate the enthalpy, ΔH^* and entropy, ΔS^* of activation for the corrosion process, the alternative formulation of Arrhenius equation, also called transition state equations (16), was used:

$$\log\left(\frac{v}{T}\right) = \left[\log\left(\frac{R}{Nh}\right) + \left(\frac{\Delta S^*}{2.303R}\right) \right] - \frac{\Delta H^*}{2.303RT} \quad (16)$$

where h is the Planck's constant, N is the Avogadro's number, ΔS^* is the entropy of activation, T is the absolute temperature and R is the universal gas constant. The linear plots of $\log(v/T)$ against $1/T$ deduced from Eq. (16) was applied in the computation of ΔH^* and ΔS^* from the slope of $(-\Delta H^*/2.303R)$ and an intercept of $(\log(R/Nh) + \Delta S^*/2.303R)$ as shown in Fig. 9 for (a) LV and (b) ST extracts of *S. acuta*. The values of ΔH^* and ΔS^* are given in Table 3. The positive values of ΔH^* both in the absence and presence of additives reflect the

endothermic nature of the steel dissolution process and it indicates that the dissolution of steel is difficult (Zerga et al., 2010). It is also seen in Table 4 that E_a and ΔH^* vary in the same manner but however, the values of ΔH^* are lower than that of E_a . This has been reported (Ekanem et al., 2010; Noor, 2007) to indicate that the corrosion process must involve a gaseous reaction, simply hydrogen evolution reaction associated with decrease in total reaction volume. The values of ΔS^* in the absence and presence of the extracts are negative (Table 4). This indicates that the activated complex in the rate determining step represents an association rather than dissociation meaning that a decrease in disordering takes place on going from reactants to activated complex. Similar observations have been reported in the literature for mild steel dissolution in the absence and presence of inhibitors in H₂SO₄ solution (Zerga et al., 2010; Noor and Al-Moubaraki, 2008). Also the ΔS^* values tend to more negative values as the extract concentration increases showing more ordered behaviour leading to increase inhibition efficiency.

Heat of adsorption (Q_{ads}) was evaluated from the kinetic thermodynamic model to further gain insight into the adsorption mechanism using the expression (Solmaz et al., 2008; Avic, 2008):

$$\log\left(\frac{\theta}{1-\theta}\right) = \log A + \log C - \left[\frac{Q_{ads}}{2.303RT}\right] \quad (17)$$

where A is a constant, C is the inhibitor concentration, θ is the occupied, and $(1 - \theta)$ is the vacant site not occupied by the inhibitor. Fig. 10 depicts the plot of $\log(\theta/1 - \theta)$ as a function of $1/T$ for the different concentrations of the extract for (a) LV and (b) ST. The values of heat of adsorption were estimated from the slope of the linear plots and are listed in Table 4. The values are negative and increases with increase in concentration of the extracts. Negative values of Q_{ads} (as obtained in this study) have been reported to indicate that the inhibitor adsorption and, hence, inhibition efficiency decreases with rise in temperature, while positive values mean the opposite effect (Oguzie et al., 2008). The negative values of heat of adsorption obtained also support the physical adsorption mechanism proposed.

3.6. UV-Vis and FTIR analyses

In order to confirm the possibility of the formation of LV/ST extract-Fe complex, UV-Visible absorption spectra obtained from 1 M H₂SO₄ solution containing 0.5 g/L extracts of *S. acuta* before and after 3 days of mild steel immersions are shown in Fig. 11 for (a) LV and (b) ST. From the figures, a deviation is shown in absorbance values and their intensities. There is an increase in absorbance after mild steel immersion for the LV and ST extracts. This reveals the formation of a complex between the Fe²⁺ and the phytoconstituents of the plant extracts. Formation of this complex may be responsible for the observed deviation in the absorbance and its intensity value and this may be responsible for *S. acuta* anti-corrosion activity. Similar assertion has been reported by Raja and Sethuraman (2009a,b). It is also noted that there was no significant difference in the shape of the spectra before and after the immersion of both plant parts' extracts showing a possibility of weak interaction between the extracts and mild steel (physisorption).

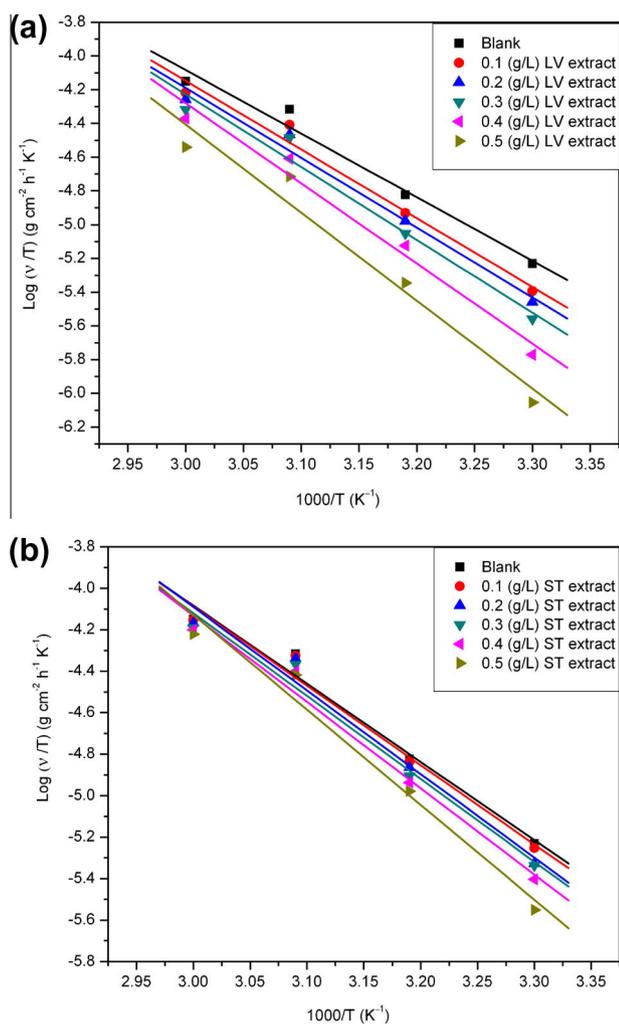


Figure 9 Transition state plot for mild steel in 1 M H₂SO₄ without and with different concentrations *Sida acuta* extract for (a) leaves and (b) stem.

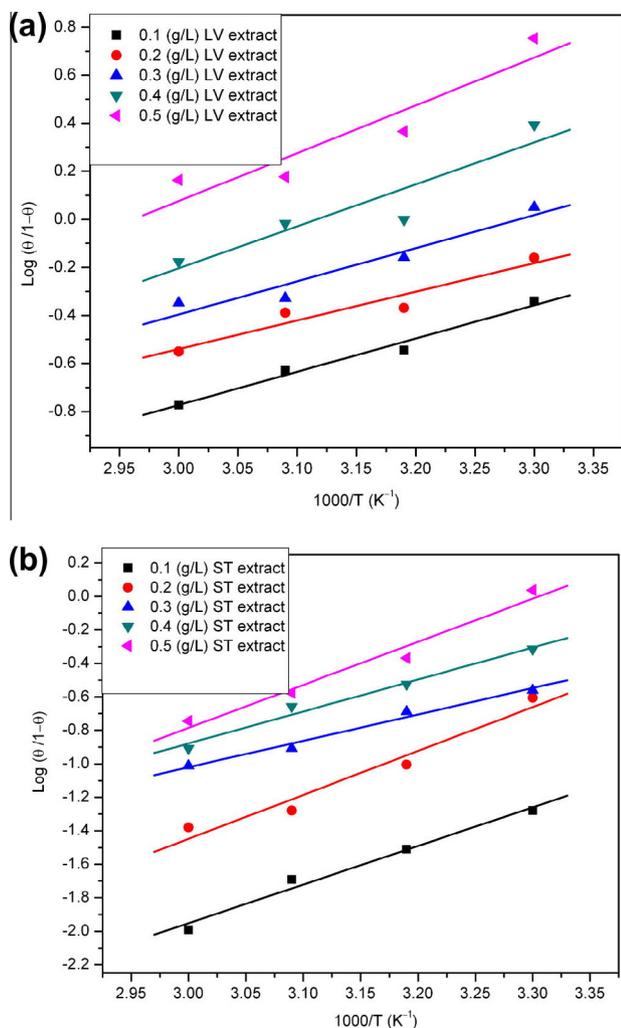


Figure 10 Plot of $\log(\theta/(1-\theta))$ vs $1/T$ for mild steel in 1 M H_2SO_4 containing different concentrations of *Sida acuta* extracts for (a) LV and (b) ST.

It is well established that FTIR spectrophotometer is a powerful tool that can be used to identify the type of bonding particularly functional group(s) present in organic compounds. Since extracts contained organic compounds and these organic compounds were adsorbed on the metal surface providing protection against corrosion. So, FTIR analyses of metal surface can be useful for predicting whether organic inhibitors are adsorbed or not adsorbed on the metal surface (Singh et al., 2010a). In the present study, FTIR spectra were used to support the fact that corrosion inhibition of mild steel in acid medium is due to the adsorption of inhibitor molecules on the mild steel surface as well as providing new bonding information on the steel surface after immersion in inhibited H_2SO_4 solution.

Fig. 12(a) shows the IR spectrum of the *S. acuta* LV extract while the FTIR spectrum of the protective film formed on the surface of the metal after immersion in the solution containing 0.5 g/L LV extract is shown in Fig. 12(b). Similar plots involving the *S. acuta* ST extract are depicted in Fig 13(a) and (b), respectively. Original absorption at 3429.96 cm^{-1} (associated hydroxyl) was overlapped by the strong stretching mode of N-H. The 1634.71 cm^{-1} band is assigned to the N-H bend. The peak at 1078.62 cm^{-1} can be assigned to stretching

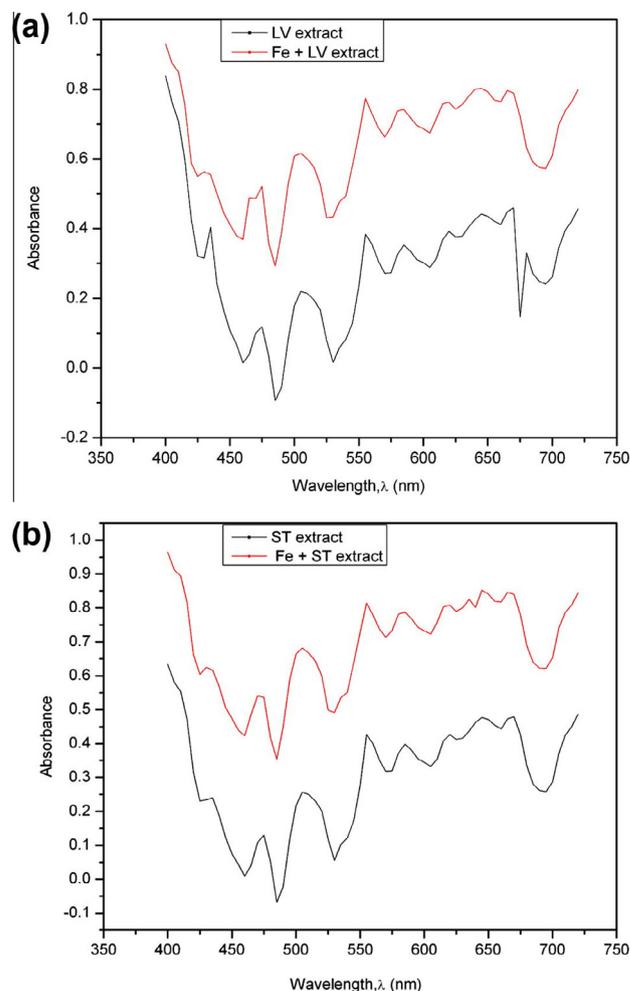


Figure 11 UV-Visible spectra of the 1 M H_2SO_4 solution containing 0.5 g/L *Sida acuta* extract before and after 72 h of mild steel immersion for (a) leaves and (b) stem.

mode of C-O group. The bands at 1402.75 cm^{-1} are attributed to C-C in ring (for aromatic). The absorption bands in the range above 600 cm^{-1} are assigned to the $-C\equiv C-H:C-H$ bending vibration. This shows that this plant extracts contain mixtures of compounds, i.e., alkaloids, flavonoids and organic acids (Satapathy et al., 2009).

The FTIR spectra of adsorbed protective layer formed on mild steel surface after 72 h immersion in 1.0 M H_2SO_4 containing 0.5 g/L LV and ST extracts of *S. acuta* shown in Figs. 12(b) and 13(b), respectively, revealed that the -OH stretching at 3429.96 cm^{-1} shifted to 3430.08 cm^{-1} and from 3429.77 to 3433.53 cm^{-1} for both LV and ST. 1634.71 cm^{-1} is identified as an N-H bending and was found to shift to 1635.98 cm^{-1} on the adsorbed film of the LV spectra and from 1634.26 to 1635.91 cm^{-1} shift on the stem's adsorbed film. The C-O stretch at 1078.62 and 1078.80 cm^{-1} for the LV and ST spectra, respectively, was found to shift to higher values of 1099.48 and 1098.82 cm^{-1} . Also, a shift from 674.06 to 631.17 cm^{-1} due to a $-C\equiv C-H:C-H$ bending for the leaves only, and a rare shift from 1402.75 to 1498.01 cm^{-1} was observed due to a C-C stretching (in ring) for the ST only. These progressive shifts in the wavelength of absorption are indica-

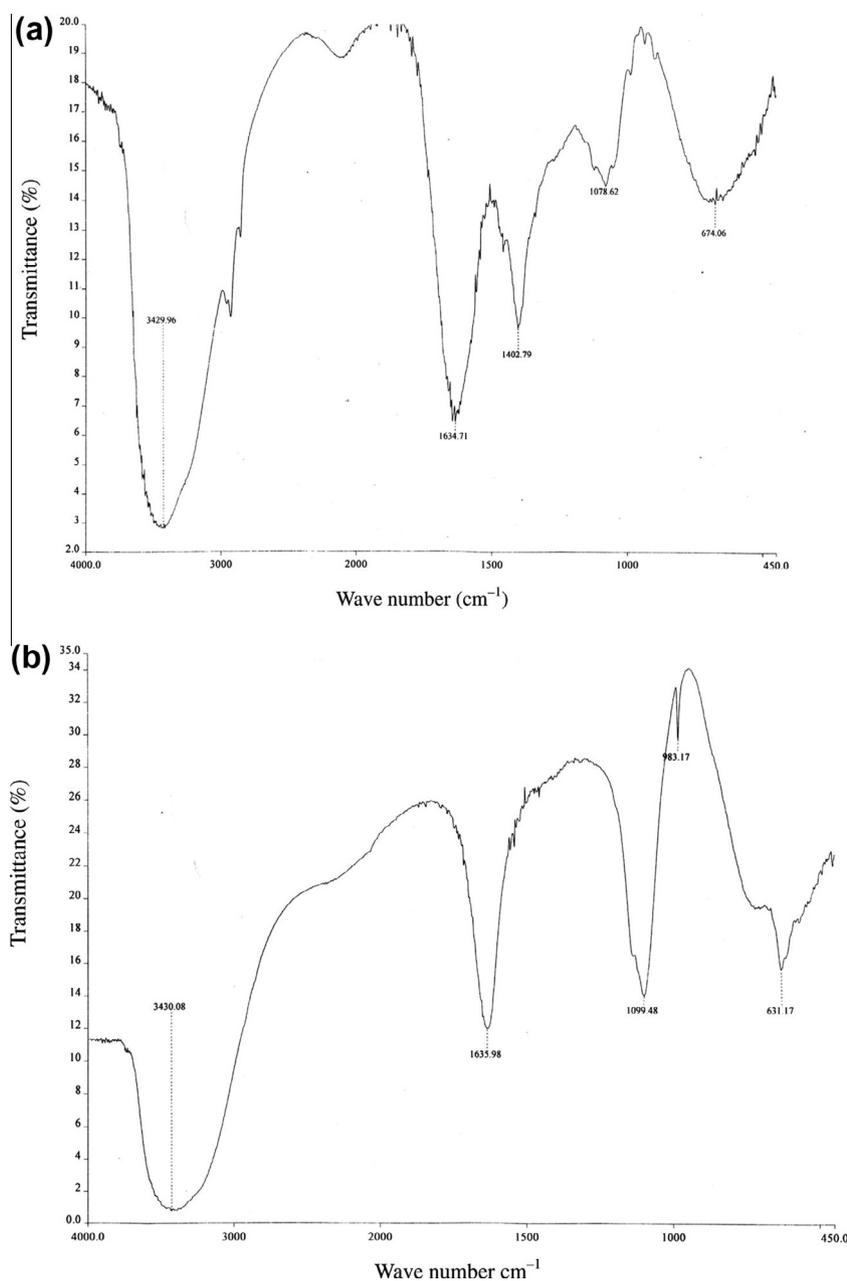


Figure 12 FTIR spectra of (a) *Sida acuta* LV extract (b) film on mild steel surface after immersion in 1 M H₂SO₄ containing 0.5 g/L LV extract after 10 h of immersion.

tive of the interactions between the extracts of *S. acuta* and the surface of mild steel. While a =C-H bending is found at 983.17 cm⁻¹, a N-O asymmetric stretching is seen at 1542.01 cm⁻¹ on the protective films of LV and ST spectra, respectively, indicating likely products of these interactions, since they were not originally present in the *S. acuta* plant parts' spectra. Also C-C stretching (in ring) was missing in the spectrum of the LV protective layer, indicating that this functional group was not used for bonding/interaction. Therefore, we proposed that the adsorption of the inhibitors took place via -OH stretching, N-H bending, C-O stretching for both extracts, and -C≡C-H:C-H bending only in the LV, and C-C stretching (in ring) only in the ST.

3.7. Mechanism of corrosion inhibition

The inhibitive action of *S. acuta* leaves and stem extracts towards the acid corrosion of steel can be attributed to the adsorption of the leaves and stem extracts components onto the steel surface. FTIR results also show that LV and ST extracts of *S. acuta* contain oxygen and nitrogen atoms in functional groups (O-H, N-H, C-N, C-O) and aromatic ring, which meet the general consideration of typical corrosion inhibitors. In aqueous acidic solutions, the components of the plant parts extracts exist either as neutral molecules or in the form of cations (protonated species). In general, two modes of adsorption could be considered. The neutral species

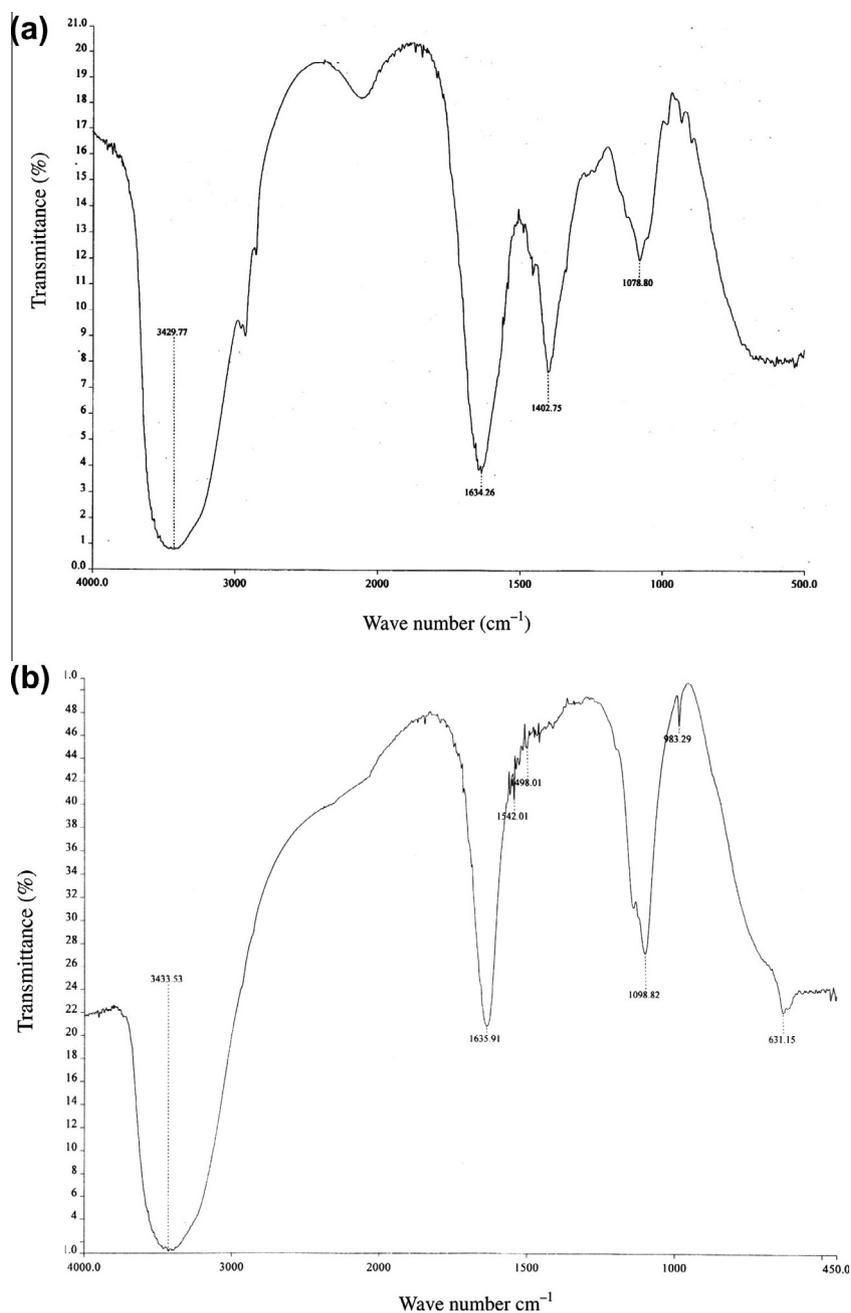
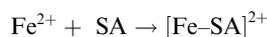
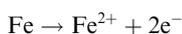


Figure 13 FTIR spectra of (a) *Sida acuta* ST extract (b) film on mild steel surface after immersion in 1 M H₂SO₄ containing 0.5 g/L ST extract after 10 h of immersion.

may adsorb on metal surface via the chemisorption mechanism, involving the displacement of water molecules from the metal surface and the sharing electrons between the N and O atoms and Fe. The *S. acuta* extracts components can also adsorb on the surface of the metal on the basis of donor-acceptor interactions between π -electrons of aromatic ring and vacant d-orbitals of Fe. The large number of different chemical compounds for plant extracts of *S. acuta* (SA) may react with the iron, which is firstly dissolved from the metal surface, forming organo-metallic complex such as Fe-plant extract [Fe-SA] according to the following mechanism (El-Etre et al., 2005; Abdel-Gaber et al., 2006):



These complexes might get adsorbed onto steel surface by van der Waals force to form a protective film to isolate mild steel from corrosion. This assumption could be further confirmed by the FTIR results.

4. Conclusions

The results presented in this work show that the LV and ST extracts from *S. acuta* inhibit the corrosion of mild steel in H₂SO₄ solutions to an appreciable extent. The inhibition efficiencies of the plant extracts increased with increase in extract concentration but decreases with increase in temperature. The

LV is found to be a better inhibitor compared to the ST which could be attributed to the presence of highest concentration of the phytoconstituents in the LV than the ST extracts of *S. acuta*. The adsorbed species formed insoluble [Fe-SA] complex due to their interactions with the dissolved iron ions. UV-Vis and FT-IR show that the compounds present in plant extracts form corrosion inhibitive layer by reacting with iron ions present on the mild steel surface. Based on the trend of inhibition efficiency with temperature and from the obtained values of activation energy and heat of adsorption, the corrosion inhibition is attributed to physical adsorption of the phytochemical components of the plant on the surface of the mild steel. The experimental data fit into the Freundlich adsorption isotherm model. The inhibition mechanism was further corroborated by the values of thermodynamic and kinetic parameters obtained from the experimental data.

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