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ORIGINAL ARTICLE

Synergistic inhibition effects between leaves and stem extracts of *Sida acuta* and iodide ion for mild steel corrosion in 1 M H_2SO_4 solutions

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Synergism

Abstract The synergistic action caused by iodide ions on the corrosion inhibition of mild steel in 1 M H_2SO_4 by leaves and stem extracts of *Sida acuta* was studied using weight loss and hydrogen evolution methods at 30–60 °C. It was found that the leaves and stem extracts of *S. acuta* inhibited the acid induced corrosion of mild steel. Addition of iodide ions enhances the inhibition efficiency to a considerable extent. The inhibition efficiency increases with increase in the iodide ion concentration but decreases with rise in temperature. Adsorption of the extracts alone and in combination of iodide ion was found to obey Freundlich adsorption isotherm at all temperatures studied. Inhibition mechanism is deduced from the temperature dependence of the inhibition efficiency as well as from assessment of kinetic and activation parameters that govern the processes. The synergism parameter (S_1) is defined and evaluated from the inhibition efficiency values. This parameter for the different concentrations of iodide ions from the two techniques employed is found to be greater than unity indicating that the enhanced inhibition efficiency of the extracts caused by the addition of iodide ions is due to synergism.

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1. Introduction

Iron and iron-based alloys of different grades are extensively used in numerous industrial and engineering applications, including construction and designs, where they are deployed in various service environments containing, acids, alkalis and salt solutions. These service environments readily lead to inevitable corrosion of exposed surfaces of the metal because of their aggressive nature. It is a general consensus that the best method to protect the metal deployed in these corrosive environments is to add corrosion inhibitors (Ashassi-Sorkhabi and Nabavi-Amri, 2002; Migahed and Nassar, 2008; Fouda and Ellithy, 2009). To this end, the use of organic and inorganic

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substances to inhibit corrosion of metals in many environments is well established. Unfortunately, most of the organic and inorganic inhibitors are toxic, very expensive and environmentally unfriendly. Due to increasing environmental awareness and adverse effect of some chemicals, an alternative has to be sought 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).

Despite the broad spectrum of organic/naturally occurring compounds as corrosion inhibitors, the final choice of the appropriate inhibitor for a particular application is restricted by several factors. One factor is the vast variety of possible corrosion systems coupled with the specificity of action of most acid inhibitors which often necessitates the use of a combination of additives to provide multiple effects required for effective corrosion inhibition. This has resulted in studies to identify co-operative (synergistic) effects among corrosion inhibiting species. Synergism is an effective method to improve the inhibitive performance, to decrease the amount of usage, to diversify the application of inhibitor in acidic media. It plays an important role not only in theoretical research on corrosion inhibitors but also in practical work (Li et al., 2009). Some authors have reported on synergistic inhibition effects between organic inhibitors and halide ions (Cl^-, Br^-, and I^-) (Feng et al., 1999; Larabi et al., 2004; Okafor and Zheng, 2009; Umoren et al., 2006, 2010), organic inhibitor/metallic ion mixture (Cheng et al., 2007; Li et al., 2007, 2008; Alagta et al., 2007; Morad, 2007) as well as organic inhibitor/organic inhibitor mixture (Qu et al., 2007; Rammelt et al., 2008; Hosseini et al., 2003; Okafor et al., 2010; Ehteshamzadeh et al., 2006) on steel corrosion in acidic solution. However, literature reports on synergistic inhibition effects between plant extracts and halide ions are very scanty. Synergistic corrosion inhibition of mild steel in 2 M HCl and 1 M H_2SO_4 by leaf extracts of *Occimum viridis* (OV) and halide ions has been reported (Oguzie, 2006). The efficacy of *Telfaria occidentalis* extract as a corrosion inhibitor for mild steel in 2 M HCl and 1 M H_2SO_4 solutions and the effect of halide additives on the inhibition efficiency have been reported (Oguzie, 2005). The inhibiting action of the calyx extract of *Hibiscus sabdariffa* on mild steel corrosion in 2 M HCl and 1 M H_2SO_4 and synergistic effect of halide ions have also been studied (Oguzie, 2008). Oguzie et al. as well pointed out synergistic influence of iodide ion on mild steel corrosion inhibition in acid solutions by aqueous extracts from *Garcinia kola* seeds (Oguzie and Onuchukwu, 2007). Eddy et al. observed that addition of Br^- and I^- ions to *Lasianthera africana* (Eddy et al., 2009a) and *Gnetum african (*Eddy et al., 2009b) leaves extract antagonized inhibition while Cl^- exerted synergistic effect for mild steel corrosion in H_2SO_4 solution. Synergistic inhibition effect between I^- ion and *Dacrodyes edulis* (Oguzie et al., 2010) for mild steel in acidic media has also been reported. We have also reported in our laboratory synergistic corrosion inhibition between halide ions and natural exudate gums of *Raphia hookeri* (Umoren et al., 2008) and *Pachylobus edulis* (Umoren and Ekanem, 2010) for mild steel in acidic medium.

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 *Sida acuta*, including the synergistic effect of iodide ion additive for mild steel (1005 AISI Grade) corrosion in 1 M sulphuric acid solution at 30–60 °C using weight loss and hydrogen evolution (via gasometric assembly) techniques.

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 H_2SO_4 prepared from 98% analytical grade supplied by Sigma–Aldrich. Deionized 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 sun dried and ground to powder using a manual blender. One kilogramme of the dry powdered 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 one litre of 1 M H_2SO_4 solution for weight loss and hydrogen evolution measurements.

2.3. Weight loss measurements

Weight loss measurements 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 help of rod and hook. The coupons were retrieved at 2 h interval progressively for 10 h, immersed in a solution of 20% NaOH containing 200 g/L zinc dust at room temperature, scrubbed with bristle brush under running water, dried in acetone and reweighed. The weight loss, in grammes, was taken as the difference in the weight of the mild steel coupons before and after immersion in different test solutions. Tests were performed for the free acid solution, solution of 0.5 g/L leaves and stem extracts of *S. acuta* alone and this concentration of the extracts in combination with different concentrations (0.5–5 mM) KI at different temperatures. The experiments were repeated three times to ensure good reproducibility. The standard deviation values among parallel triplicate experiments were found to be smaller than 5%, indicating good reproducibility. From the weight loss values, corrosion rates were computed using the expression:

$$C_R = \frac{m_1 - m_2}{At} \qquad (1)$$

where m_1 and m_2 are weight losses (mg) of mild steel coupons before and after immersion, respectively, in test solutions, A is the area of specimen (cm^2) and t is the exposure time (h).

The inhibition efficiency (η%) was computed using Eq. (2)

$$\eta\% = \frac{C_{R(\text{blank})} - C_{R(\text{inh})}}{C_{R(\text{blank})}} \times 100 \qquad (2)$$

where $C_{R(\text{blank})}$ and $C_{R(\text{inh})}$ are the corrosion rates in the absence and presence of the inhibitors, respectively, in 1 M H_2SO_4 at same temperature.

2.4. Hydrogen evolution measurements

Hydrogen evolution measurements were performed using gasometric assembly. Detailed description of the assembly has been reported elsewhere (Umoren and Ekanem, 2010). The procedure followed was similar to that reported by other authors (Umoren et al., 2006; Eddy et al., 2009b; Obot et al., 2009; Aytac et al., 2005; Ebenso and Oguzie, 2005). The test solution was kept at 100 mL. The progress of corrosion in the absence and presence of test inhibitor was monitored by careful measurements of the volume of hydrogen gas evolved at fixed time intervals. The experiment was performed for 1 M H_2SO_4 (blank), solution of 0.5 g/L leaves and stem extracts of *S. acuta* alone and this concentration of the extracts in combination of different concentrations (0.5–5 mM) KI at 30–60 °C was maintained using a thermostated water bath.

Hydrogen evolution rate (RV_H) that can be correlated to the mild steel corrosion rate was computed based on the volume of H_2 evolved using the expression:

$$RV_H = \frac{V_t - V_i}{T_t - T_i} \qquad (3)$$

where V_t and V_i are volumes of hydrogen evolved at times T_t and T_i, respectively.

The inhibition efficiency (η%) was computed using the equation:

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

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

3. Results and discussion

3.1. Weight loss, corrosion rates and inhibition efficiency

The weight loss method as a means of evaluating corrosion rates of metals in corrosive environments and inhibiting potentials of studied inhibitors is widely reported in the literature, such that the technique forms the baseline method of measurement in many corrosion monitoring programmes (Afidah and Kassim, 2008). Results of the present investigations involving leaves and stem extracts of *S. acuta* indicate that the inhibition efficiency increases with increase in extracts concentration and the maximum inhibition efficiency was obtained with 0.5 g/L concentration within the range of concentrations studied. This concentration was, therefore, chosen to evaluate the effect of iodide ion additive. Fig. 1 shows the weight loss-time curves for mild steel in 1 M H_2SO_4 without and with 0.5 g/L leaves (LV) of *S. acuta* extract and different concentrations of iodide ion in combination with 0.5 g/L leaves extract of *S. acuta* 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.

Inspection of the figures show that the weight loss of mild steel varies linearly with time and was reduced in the presence of the inhibitor (plant extract) compared to the free acid solution. Further inspection of the figures reveals that weight loss increases with temperature and greater weight loss was obtained at 60 °C for extracts of both plant parts. Also, the extent of reduction in weight increases with the increase in concentration of the iodide ion at all temperatures studied.

The computed values of corrosion rate and the inhibition efficiency for the additives at different temperatures for the two plant parts are given in Table 1. Results in the table show that the corrosion rates of mild steel in 1 M H_2SO_4 are lower in the presence of the plant extracts compared to the blank acid solution. Again corrosion rates are observed to be lower in the inhibiting solutions containing extracts–KI combination than that of the extracts alone. Examination of the table further reveals that the corrosion rate of mild steel in solutions of leaves extract–KI combination is lower than that of the stem extract–KI combination at all the temperatures. This indicates that the LV extract is a better inhibitor than the ST extract of *S. acuta*. Results in Table 1 also show that corrosion rate increases with increase in temperature with the highest values obtained at 60 °C for all the systems investigated. Inhibition efficiency values also presented in Table 1 show a decreasing trend with increasing experimental temperatures for all the systems studied. This suggests possible desorption of some of the adsorbed inhibitors from the metal surface at higher temperatures. Such behavior shows that the additives were physically adsorbed on the metal surface (Oguzie, 2007). The inhibition efficiency was found to be synergistically enhanced in the presence of KI additive and increased with the increase in KI concentration with the most profound effect noted with 5 mM KI concentration. For instance at 30 °C, the inhibition efficiency obtained for 0.5 g/L leaves and stem alone were 85.00% and 52.14%, respectively (Table 1). Addition of 5 mM KI to extracts of both plant parts increased the values to 91.97% and 77.42% for the leaves and stem, respectively.

The inhibitive action of leaves and stem of *S. acuta* extract toward the acid corrosion of mild steel can be attributed to the adsorption of the leaves and stem extract components onto the steel surface. Corrosion inhibition is initiated by the displacement of adsorbed water molecules by the inhibitor species leading to specific adsorption on the metal surface (Solmaz et al., 2008). Some studies (Edeoga et al., 2005; Akaneme, 2007) have shown that extracts of *S. acuta* are a complex mixture of various photochemicals components like saponins, flavanoids, tannis, alkaloids, organic acid and anthraquinones in the leaves and tannins, alkaloids and anthraquinones only present in the stem extract. Some of these components have heteroatoms, such as N and O in their molecules. Thus, the corrosion of mild steel may be attributed to the adsorption of *S. acuta* components through these atoms that are regarded as centers of adsorption onto the metal surface thereby creating a barrier for mass and charge transfer and thus isolating the metal from further attack of the corrosive anions. Decrease

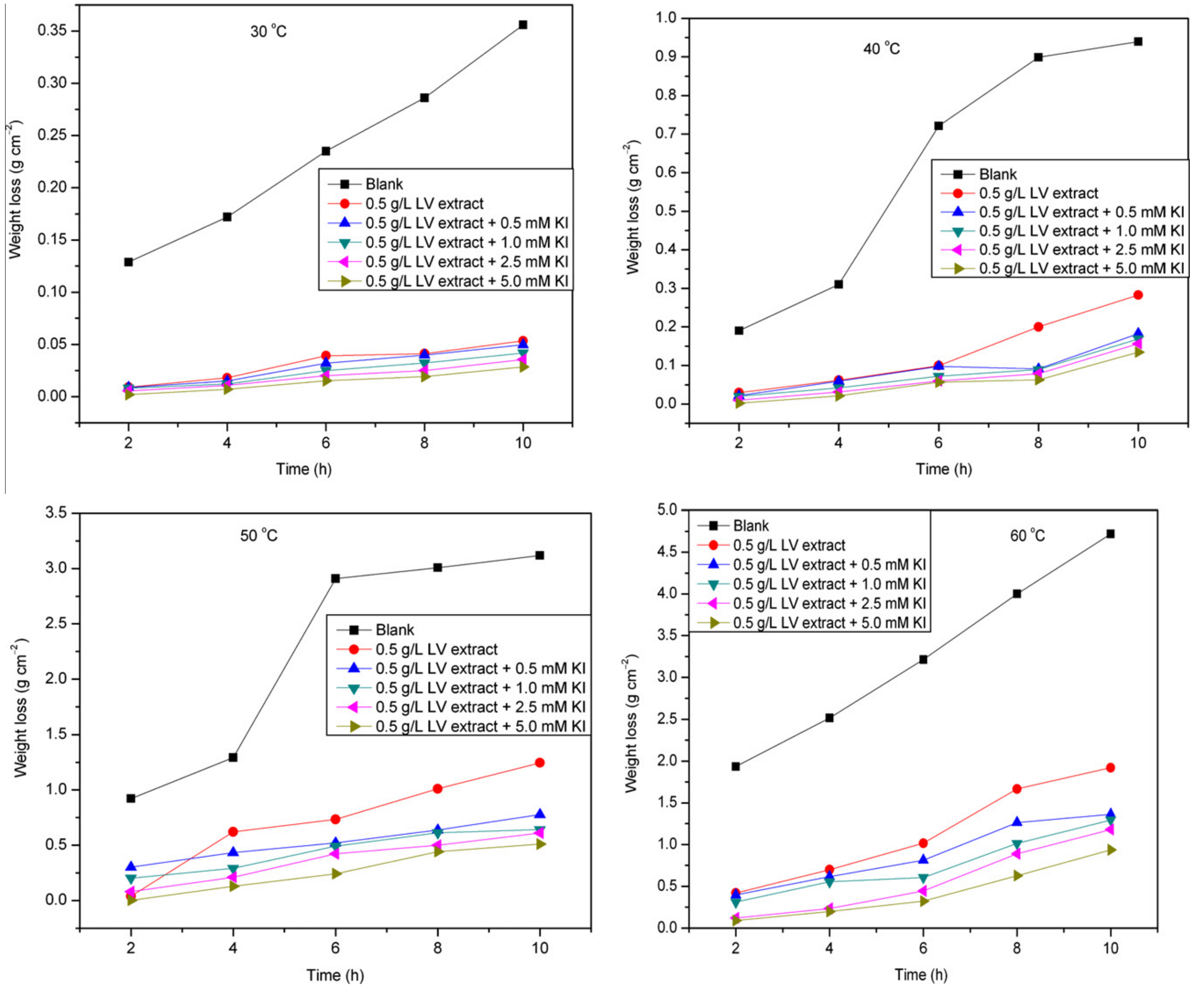

Figure 1 Plot of weight loss against time for mild steel in 1 M H_2SO_4 without and with *S. acuta* leaves extracts and in combination with different concentrations of KI at 30, 40, 50 and 60 °C.

in inhibition efficiency with increase in temperature indicates that the components of the plant extracts were physically adsorbed on the mild steel surface. It is noted that the inhibition efficiency of the leaves extract at all experimental temperatures was higher than that of the stem extract both in the presence of the extracts alone and on the addition of iodide ions. This seems to suggest that the leaves extract is a better corrosion inhibitor than the stem extract and may be attributed to higher concentration of the phytochemical constituents of the leaves extract compared to that of the stem extract.

3.2. Hydrogen evolution measurements

By immersion of mild steel alloy in aqueous solutions, the sources of hydrogen are water decomposition and reaction of water with the metal (Lunarska and Chernyayeva, 2006). Evolved hydrogen may recombine and leave the surface as a gas or may enter the metal causing the hydrogen-induced degradation of the metal. In order to reduce the susceptibility to hydrogen uptake, the modification of solution by the addition of inhibitors or the modification of the metal surface may be applied. The requirement for effective inhibition of hydrogen uptake is to inhibit the hydrogen evolution, to promote the hydrogen gas recombination and to inhibit the hydrogen entry. Since hydrogen evolves in corrosion processes, the inhibition of corrosion should have inhibited also the hydrogen evolution. On the other hand, the inhibition of hydrogen evolution does not necessarily mean a decrease in the hydrogen charging of the metal. The presence of corrosion inhibitors may substantially affect the hydrogen ingress processes. Therefore, the mutual influence of inhibitors on the corrosion and on the hydrogen evolution should be studied.

The corrosion rates of mild steel in the absence and presence of leaves and stem extracts of *S. acuta* and the extracts–KI combination were assessed by monitoring the volume of hydrogen gas evolved at fixed time intervals. Fig. 3 shows representative plots of the volume of the hydrogen gas evolved as a function of reaction time at 30, 40, 50 and 60 °C for mild steel in 1 M H_2SO_4 without and with 0.5 g/L LV extract and this concentration of the extract in combination with different

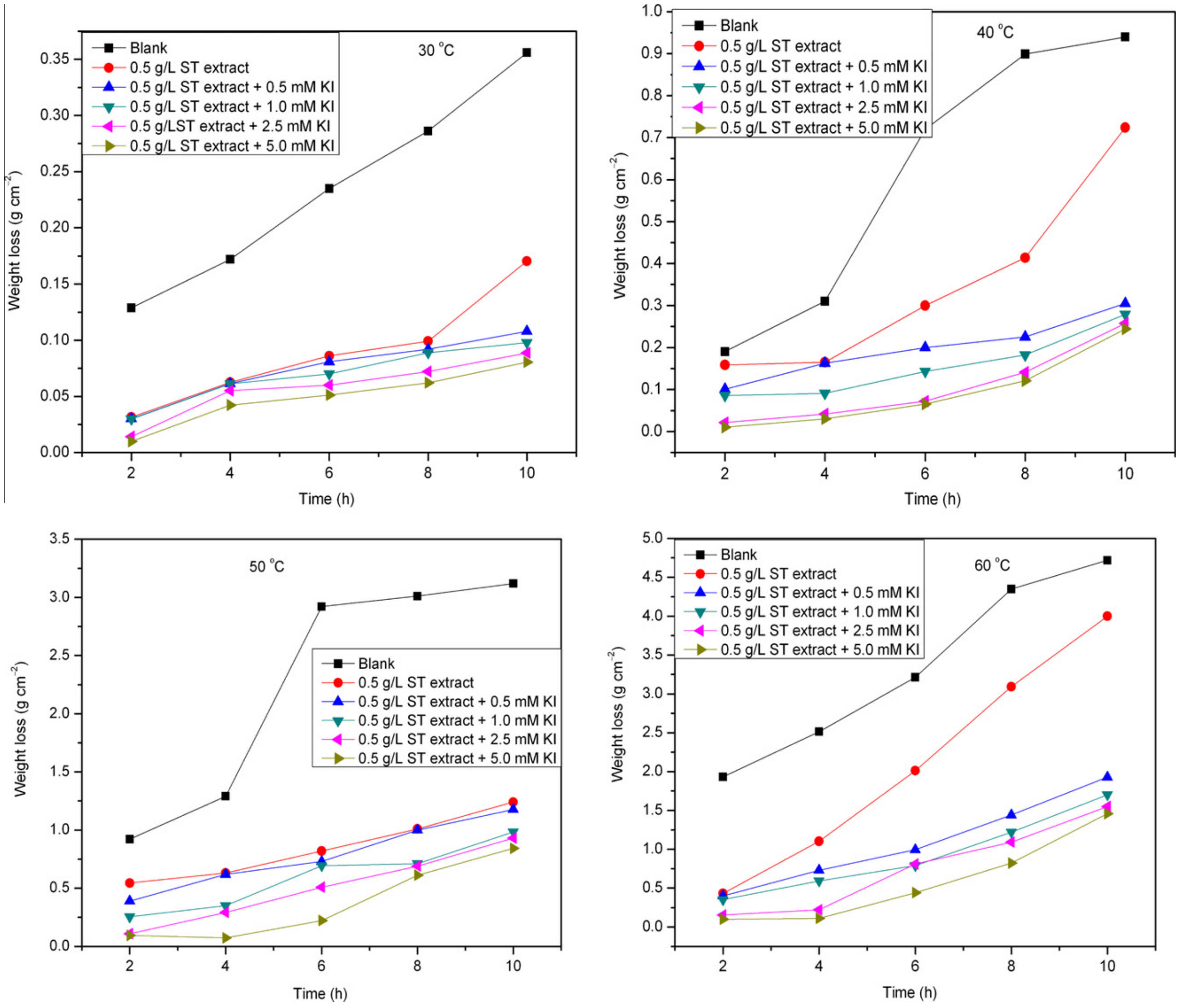

Figure 2 Plot of weight loss against time for mild steel in 1 M H_2SO_4 without and with *S. acuta* stem extracts and in combination with different concentrations of KI at 30, 40, 50 and 60 °C.

Table 1 Calculated values of corrosion rate and inhibition efficiency for mild steel in 1 M H_2SO_4 in the absence and presence of leaves and stem extract of *S. acuta* and extracts–KI mixtures 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	1.780	4.700	15.600	23.600				
LV extract (0.5 g/L)	0.267	1.414	6.224	9.603	85.00	69.92	60.10	59.31
LV extract + 5.0 mM KI	0.143	0.674	2.549	4.687	91.97	85.66	83.66	80.14
LV extract + 2.5 mM KI	0.178	0.783	3.051	5.900	90.00	83.34	80.44	75.00
LV extract + 1.0 mM KI	0.209	0.846	3.207	6.478	88.26	82.00	79.44	72.55
LV extract + 0.5 mM KI	0.249	0.914	3.884	6.818	86.01	80.55	75.10	71.11
ST extract (0.5 g/L)	0.852	3.290	12.324	20.000	52.14	30.00	21.00	15.26
ST extract + 5.0 mM KI	0.402	1.222	4.214	7.290	77.42	74.00	72.99	69.11
ST extract + 2.5 mM KI	0.443	1.289	4.674	7.762	75.11	72.58	70.04	67.11
ST extract + 1.0 mM KI	0.489	1.395	4.923	8.519	72.53	70.32	68.44	63.90
ST extract + 0.5 mM KI	0.540	1.525	5.887	9.650	69.66	67.56	62.26	59.11

concentrations of KI. Similar plots for the uninhibited and inhibited solutions containing the stem (ST) and ST–KI mixtures are depicted in Fig. 4. It is observed from the figures that the volume of hydrogen gas evolved varies linearly with time

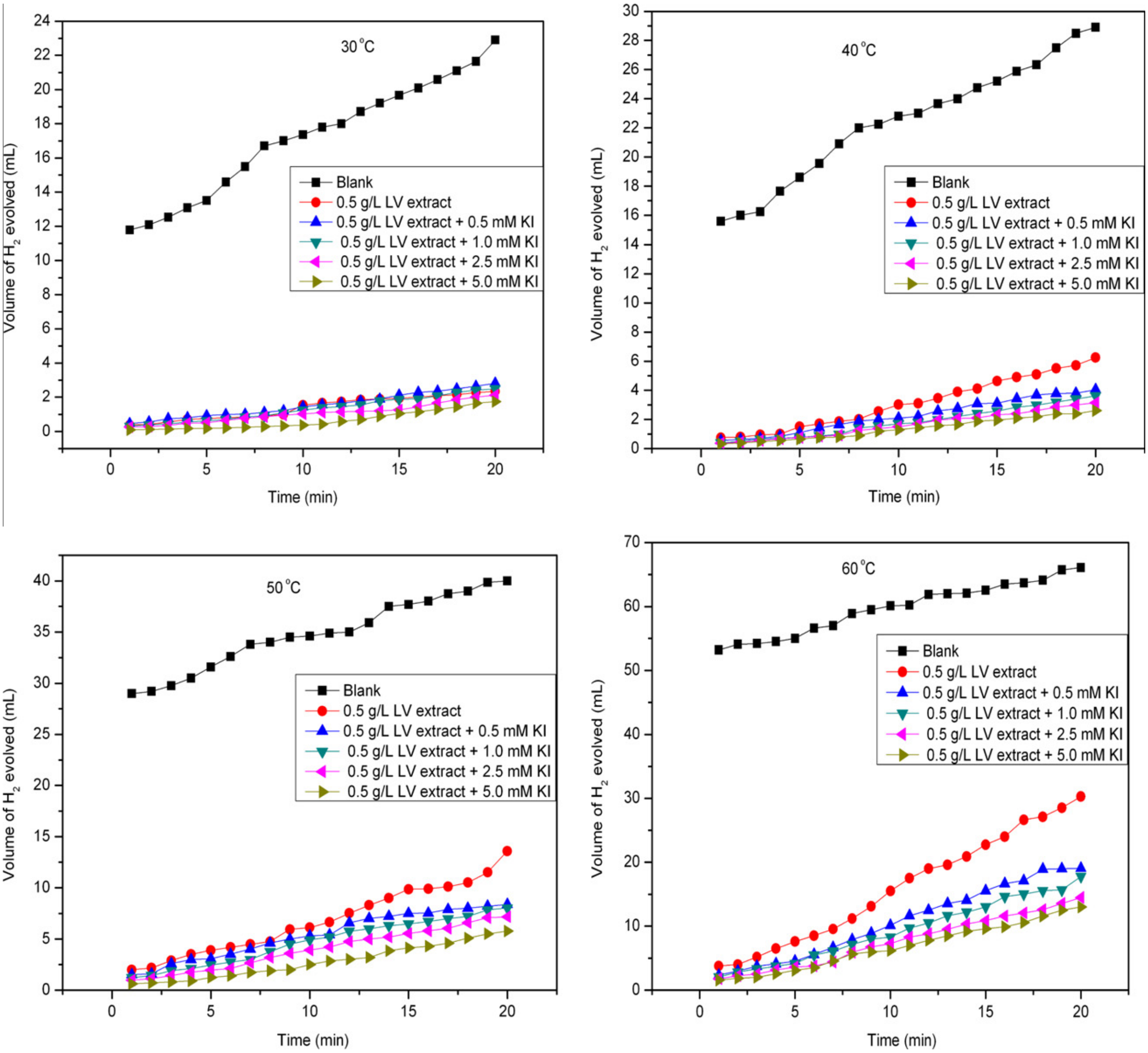

Figure 3 Plot of volume of H_2 evolved against time for mild steel in 1 M H_2SO_4 without and with *S. acuta* leaves extracts and in combination with different concentrations of KI at 30, 40, 50 and 60 °C.

and was less in the presence of *S. acuta* extracts compared to the blank solution. Further reduction in the volume of hydrogen gas evolved is noticed on the introduction of iodide ions to inhibited solutions containing the extracts of the plant parts. Also the volume of H_2 evolved increases with the temperature rise.

Table 2 presents the computed values of the hydrogen evolution rate and the inhibition efficiency of the various additives. Results in the table reveal that the rates of hydrogen evolution were reduced on the introduction of the *S. acuta* plant parts extract to the uninhibited solution. The increase of the rate of hydrogen evolution in the uninhibited solution can be rationalized on the basis that sulphuric acid reacts with iron and forms metal sulphates that are soluble in aqueous media (El-Meligi and Ismail, 2009). There are two reactions occurring, namely the anodic reaction and cathodic reaction. The following equations represent iron reaction in acidic solutions (El-Meligi and Ismail, 2009):

Anodic reaction (oxidation reaction):

$$Fe \rightarrow Fe^{2+} + 2e \tag{5}$$

Cathodic (reduction reaction or hydrogen evolution reaction):

$$2H^{+} + 2e \rightarrow H_2 \uparrow \tag{6}$$

The decrease in the hydrogen evolution rate observed for the extract–KI combination for both plant parts indicates enhancement of inhibitory action of *S. acuta* in the presence of the iodide ions. The highest values for the hydrogen evolution rate were obtained at 60 °C for all the systems investigated and the stem extract had the highest values in comparison to the leaves extract even with the iodide ion additive. This suggests that the components of the plant parts extract are adsorbed onto the metal surface and block the electrochemical reaction efficiently by decreasing the available surface area.

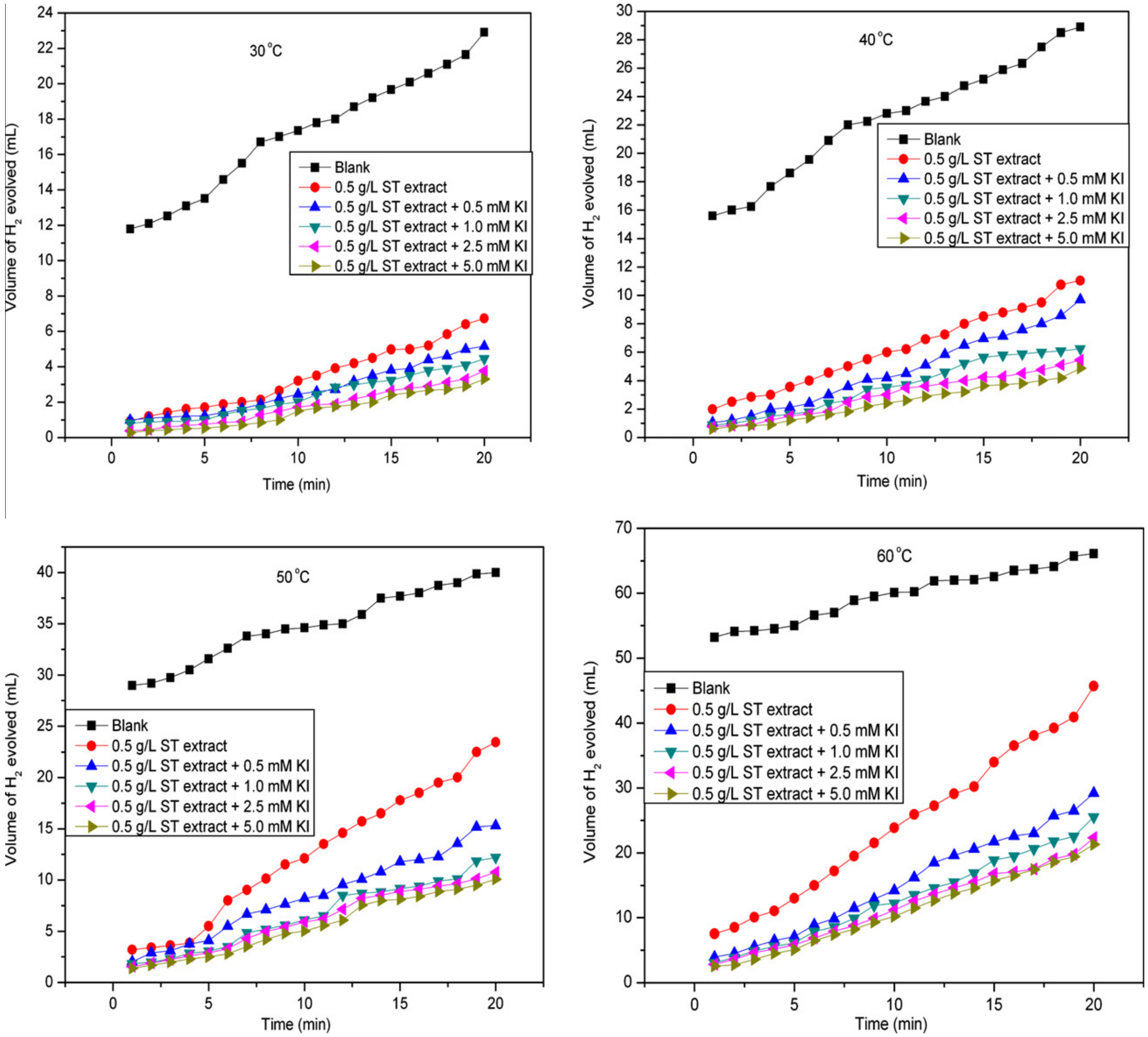

Figure 4 Plot of volume of H_2 evolved against time for mild steel in 1 M H_2SO_4 without and with *S. acuta* stem extracts and in combination with different concentrations of KI at 30, 40, 50 and 60 °C.

Table 2 Calculated values of hydrogen evolution rate and inhibition efficiency for mild steel in 1 M H_2SO_4 in the absence and presence of leaves and stem extract of *S. acuta* and extracts–KI mixtures at 30–60 °C from hydrogen evolution measurements.

Systems/concentration	Hydrogen evolution rate (mL min^{-1})				Inhibition efficiency (η%)			
	30 °C	40 °C	50 °C	60 °C	30 °C	40 °C	50 °C	60 °C
Blank	0.590	0.780	1.450	2.660				
LV extract (0.5 g/L)	0.117	0.312	0.680	1.513	80.17	60.00	53.10	43.12
LV extract + 5.0 mM KI	0.087	0.130	0.289	0.649	85.25	83.33	80.07	75.60
LV extract + 2.5 mM KI	0.106	0.157	0.359	0.725	82.03	79.87	75.24	66.62
LV extract + 1.0 mM KI	0.125	0.181	0.401	0.888	78.81	76.79	72.34	66.62
LV extract + 0.5 mM KI	0.141	0.202	0.419	0.953	76.10	74.10	71.00	64.17
ST extract (0.5 g/L)	0.337	0.552	1.172	2.284	42.88	29.23	19.17	14.14
ST extract + 5.0 mM KI	0.165	0.243	0.504	1.064	72.03	68.85	65.24	60.00
ST extract + 2.5 mM KI	0.189	0.273	0.538	1.116	67.97	65.00	57.86	51.99
ST extract + 1.0 mM KI	0.223	0.312	0.611	1.277	62.20	60.00	57.86	51.99
ST extract + 0.5 mM KI	0.258	0.485	0.766	1.460	56.27	52.82	47.17	45.11

The values of inhibition efficiency are also listed in Table 2 and can be seen to follow the trend reported for weight loss measurements. It synergistically increased on addition of iodide ion to both the leaves and stem *S. acuta* extracts but decreased with increasing temperature. The inhibition efficiency of the two independent methods used in this study is different. The values for the hydrogen evolution method are lower than those of the weight loss technique. This may be attributed to the difference in immersion time needed for the inhibiting species to get adsorbed and form a protective film on the mild steel thereby insulating the metal from the attack of the aggressive anions present in the solution. In addition, it has been argued that corrosion rate values from gasometric method represent instantaneous values while those from the gravimetric method represent average values (Umoren and Ekanem, 2010).

3.3. Synergism between S. acuta extracts and iodide ions

Results obtained in the present study clearly show that the inhibition efficiency of the *S. acuta* leaves and stem extracts was greatly enhanced on the addition of iodide ions and could be ascribed to a synergistic effect. The anodic dissolution of steel in aqueous solution is known to be significantly facilitated by hydroxyl ions that form intermediate catalytic complexes on the metal surface (Bockris et al., 1961). Halide ions, at some concentrations, may replace hydroxyl ions adsorbed on the surface of the metal, thus leading to a reduction in the catalytic effect of the hydroxyl ions as follows (Bala, 1984; Chin and Nobe, 1972):

$$\mathrm{Fe} + \mathrm{H_2O} + \mathrm{X^-} \Longleftrightarrow (\mathrm{FeXOH})_{\mathrm{ads}} + \mathrm{H^+} + \mathrm{e^-} \quad (7)$$

$$(\mathrm{FeOH})^-_{\mathrm{ads}} \xrightarrow{\mathrm{rds}} (\mathrm{FeXOH})^+ + \mathrm{e^-} \quad (8)$$

$$(\mathrm{FeXOH}) + \mathrm{H^+} \rightarrow \mathrm{Fe^{2+}} + \mathrm{X^-} + \mathrm{H_2O} \quad (9)$$

where X represents the halide ions. The effect is more pronounced with I^- and is initiated by the specific adsorption of the anion onto the metal surface. The greater influence of the iodide ion is often attributed to its large ionic radius, high hydrophobicity, and low electronegativity, compared to the other halide ions (Jeyaprabha et al., 2006; Oguzie et al., 2007). It is generally accepted that the presence of halide ions in acidic media synergistically increases the inhibition efficiency of some organic compounds. It is thought that the anions are able to improve adsorption of the organic cations in solution by forming intermediate bridges between the metal surface and the positive end of the organic inhibitor. Corrosion inhibition synergism then results from increased surface coverage arising from ion-pair interactions between the organic cations and the anions.

Two approaches were adopted to characterize the synergistic inhibitive effect of iodide ions addition to both the leaves and stem extracts of *S. acuta*. In one approach, the concentration of the extracts was kept constant and the concentration of iodide ions varied while the reverse was adopted in the second approach. Fig. 5 shows the plot of inhibition efficiency (η%) as a function of concentration for (a) leaves and (b) stem of *S. acuta* extract in the presence of fixed KI concentration (5 mM). Similarly, Fig. 6 shows the plot of η% vs. KI concentration added to a fixed extracts' concentration (0.5 g/L) for (a) leaves and (b) stem extracts at different temperatures. Fig. 6 clearly reveals the existence of synergism phenomenon between iodide ions and the *S. acuta* parts extract considering that η% was increased on addition of the iodide ions to the extracts in comparison to the extract alone.

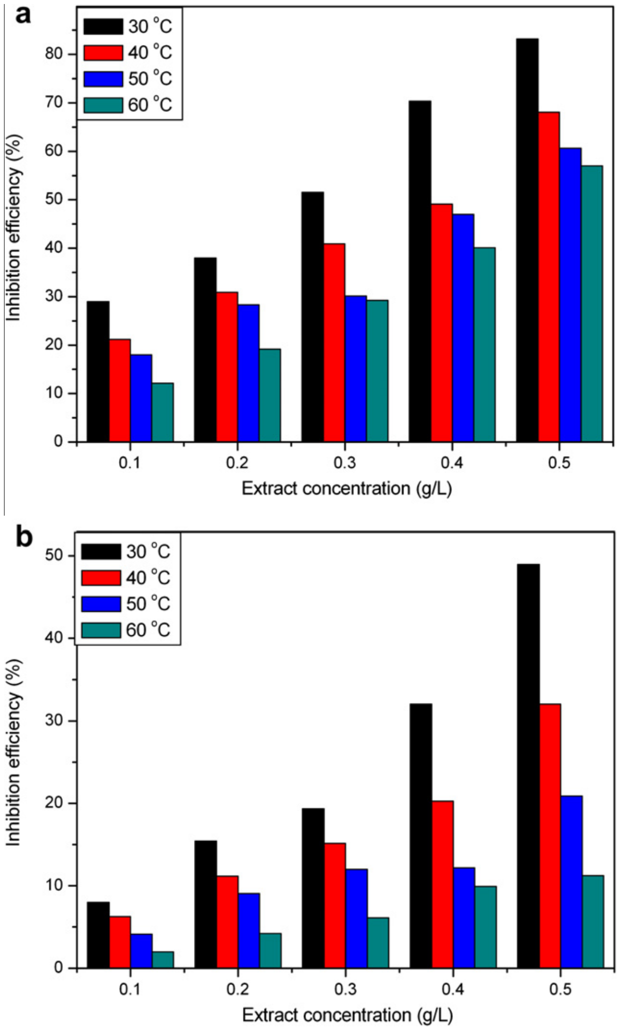

Figure 5 Plot of inhibition efficiency against extract concentration in combination with fixed 5 mM KI for mild steel in 1 M H_2SO_4 at different temperatures for (a) LV and (b) ST extracts.

To further confirm whether synergism is taking place, one has to determine the synergism parameter (s), as initially proposed by Murakawa et al. (1967) for describing the combined inhibition behavior of amines and halide ions. Generally, for the interaction of inhibitors A and B this synergism parameter (S_1) is defined as follows:

$$S_1 = \frac{1 - \eta_A - \eta_B + \eta_A \eta_B}{1 - \eta_{AB}} \quad (10)$$

where η_A and η_B are the inhibition efficiencies observed with compound A and B, respectively, acting alone, and η_{AB} is the experimentally observed inhibition efficiency for the combination of A and B. The expression actually compares the theoretically expected corrosion rate (numerator), based on the known rates when either A or B is present and on the condition that they do not interact, with the experimentally observed rate in the presence of the inhibitor mixture (denominator).

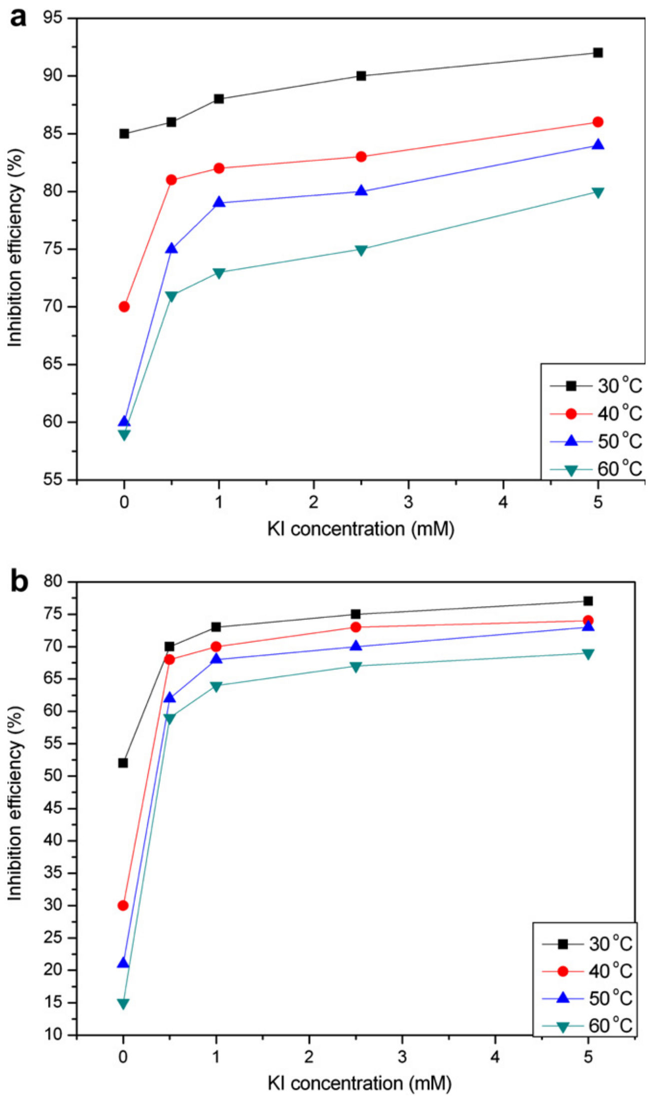

Figure 6 Plot of inhibition efficiency against KI concentration in combination with fixed 0.5 g/L extract concentration for mild steel in 1 M H_2SO_4 at different temperatures for (a) LV and (b) ST extracts.

Consequently, in the case where inhibitors A and B have no effect on each other and adsorb at the metal/solution interface independently, $S_1 = 1$ (Li et al., 2009). Alternatively, synergistic effects manifest themselves if $S_1 > 1$ and antagonistic effects if $S_1 < 1$. This parameter was evaluated from the inhibition efficiency values obtained from weight loss and hydrogen evolution measurements. The calculated values of S_1 for the different concentrations of iodide ion from the two techniques employed in the study are listed in Table 3. These values are greater than unity which suggest that the enhanced inhibition efficiency caused by the addition of iodide ions to the extracts is only due to synergistic effect.

3.4. Adsorption considerations

For the plant extract to inhibit the corrosion of mild steel, there must have to be an adsorption of the components of the plant part extracts on the metal surface leading to greater surface coverage as the first step of the inhibition mechanism.

Table 3 Synergism parameter (S_1) for different concentrations KI from weight loss measurements and hydrogen evolution 30 °C.

Plant part	KI concentration (mM)	Synergism parameter (S_1)	
		Weight loss	Hydrogen evolution
Leaves (LV)	5.0	1.89	1.88
	2.5	1.45	1.49
	1.0	1.19	1.28
	0.5	1.11	1.21
Stem (ST)	5.0	1.82	1.71
	2.5	1.30	1.24
	1.0	0.99	1.01
	0.5	0.89	0.98

The values of the degree of surface coverage (θ) defined as the fraction of the mild steel surface that was covered by the inhibitor are quite useful for the determination of inhibitor adsorption characteristic. Assuming direct relationship between surface coverage and inhibition efficiency, the surface coverage

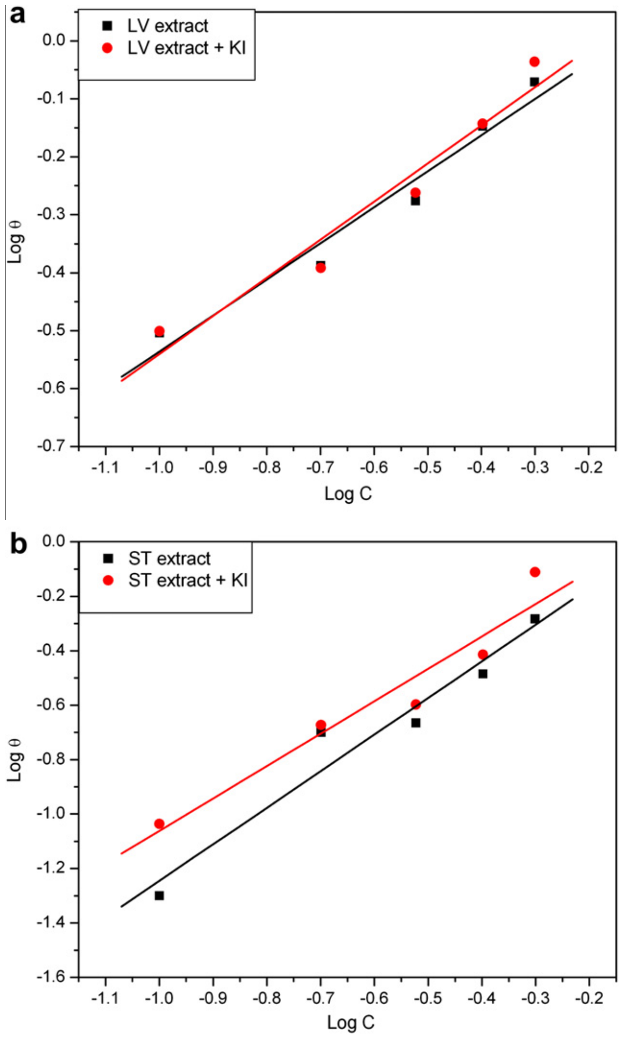

Figure 7 Freundlich adsorption isotherm plot for mild steel in 1 M H_2SO_4 with *S. acuta* extracts alone and in combination with KI for (a) leaves and (b) stem at 30 °C.

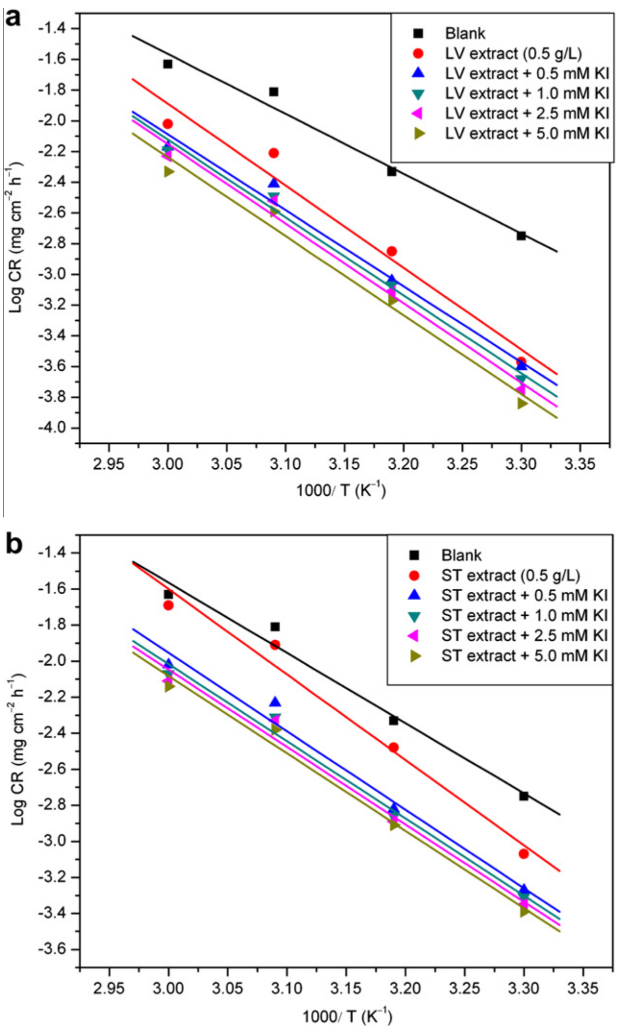

Figure 8 Arrhenius plot for mild steel in 1 M H_2SO_4 without and with *S. acuta* extracts and in combination with different concentration of KI for (a) leaves and (b) stem.

can be evaluated from the expression: $\eta\% = \theta \times 100$. Attempts were made to fit θ values obtained from the weight loss measurements to various isotherms and correlation coefficient (R^2) values were used to determine the best-fit isotherm. By far, the best result was obtained for Freundlich isotherm that has a general form (Kliskic et al., 2000):

$$\theta = K_{\text{ads}} C^n \tag{11}$$

or

$$\log\theta = \log K_{\text{ads}} + n\log C \tag{12}$$

where $0 < n < 1$; θ is the surface coverage, C is the inhibitor concentration and K is equilibrium constant of adsorption process and is related to free energy of adsorption by the equation (Noor, 2009):

$$\log K_{\text{ads}} = -\log C_{H_2O} - \frac{\Delta G^{\circ}_{\text{ads}}}{2.303RT} \tag{13}$$

where C_{H_2O} is the concentration of water expressed in g L^{-1} (the same as that of inhibitor concentration), R is the molar gas constant (kJ mol^{-1} K^{-1}) and T is the absolute temperature (K).

The logarithm of surface coverage (θ) plotted against logarithm of concentration (C) is shown in Fig.7 for (a) leaves and (b) stem extracts alone and in combination with iodide ions at 30 °C. Linear plots were obtained indicating that the experimental results fit the Freundlich isotherm. The calculated values of K_{ads} and $\Delta G^{\circ}_{\text{ads}}$ were found to be 7.335 g L^{-1} and −15.138 kJ mol^{-1}, respectively, for leaves extract alone and 1.311 g L^{-1} and −10.799 kJ mol^{-1} for leaves extract in combination with 5 mM KI. Values of 1.256 g L^{-1} and −10.691 kJ mol^{-1} as well as 1.347 and −10.868 kJ mol^{-1} were obtained for stem extract and stem extract–KI mixtures, correspondingly. It is seen that the values of the $\Delta G^{\circ}_{\text{ads}}$ in all the cases are negative. The negative values of $\Delta G^{\circ}_{\text{ads}}$ indicate the spontaneous adsorption of the additives on the mild steel surface and stability of the adsorption layer on the metal. Literature survey reveals that negative values of $\Delta G^{\circ}_{\text{ads}}$ around 20 kJ mol^{-1} or lower are consistent with the electrostatic interaction between charged molecules and the charged metal (physisorption) while those around 40 kJ mol^{-1} or higher involve charge sharing or transfer from organic molecules to metal surface to form co-ordinate type of bond (chemisorption) (Oguzie et al., 2010; Obot et al., 2009). Results obtained indicate that the values of $\Delta G^{\circ}_{\text{ads}}$ for all the systems indicate spontaneous adsorption of the additives onto the mild steel surface via physisorption mechanism.

Table 4 Activation parameters for mild steel corrosion in 1 M H_2SO_4 in the absence and presence of leaves and stem of *S. acuta* extracts and extracts–KI mixtures.

Systems/concentration	E_a (kJ mol^{-1})	Q_{ads} (kJ mol^{-1})	ΔH^* (kJ mol^{-1})	ΔS^* (J mol^{-1} K^{-1})
Blank	74.60	–	71.92	−60.01
LV extract (0.5 g/L)	102.09	−38.14	99.59	−16.76
LV extract + 5.0 mM KI	94.63	−27.45	92.54	−8.14
LV extract + 2.5 mM KI	97.09	−28.89	94.59	−2.71
LV extract + 1.0 mM KI	99.08	−27.80	96.06	−1.09
LV extract + 0.5 mM KI	99.39	−25.76	96.52	−0.91
ST extract (0.5 g/L)	90.71	−48.68	87.65	−13.66
ST extract + 5.0 mM KI	83.39	−11.29	81.27	−39.29
ST extract + 2.5 mM KI	81.99	−10.70	79.32	−46.47
ST extract + 1.0 mM KI	82.25	−10.24	80.33	−44.00
ST extract + 0.5 mM KI	82.25	−13.34	80.54	−43.97

3.5. Effect of temperature

Temperature can modify the interaction between the mild steel electrode and the acidic medium in the absence and the presence of inhibitors. To assess the influence of temperature on corrosion and corrosion inhibition processes, the weight loss measurements were carried out at 30–60 °C temperature range. The results obtained indicated that corrosion rates increase with rise of temperature both in uninhibited and inhibited solutions. More so, inhibition efficiency for the extracts alone and in combination with iodide ions decreases with increase in temperature. The dependence of corrosion rate on the temperature can be regarded as an Arrhenius-type process, the rate of which is given by:

$$\log \mathrm{CR} = \log A - \left(\frac{E_\mathrm{a}}{2.303RT}\right) \tag{14}$$

where CR is the corrosion rate, E_a is the apparent activation energy, R is the molar gas constant, T is the absolute temperature and A is the frequency factor.

The Arrhenius plot is shown in Fig. 8 for mild steel in free acid solution and inhibited solution containing (a) leaves extract and leaves extract–KI mixtures and (b) stem extract and stem extract–KI mixtures. Linear plots were obtained from the slope ($-E_\mathrm{a}/2.303R$), activation energy (E_a) values are deduced and listed in Table 4. The temperature dependence of the inhibiting effect and the comparison of the values of the apparent activation energy of the corrosion process in the absence and presence of inhibitors can provide further evidence (Szauer and Brandt, 1981; Ivanov, 1986) concerning the mechanism of the inhibiting action. The decrease of the inhibitor efficiency with temperature rise, which refers to a higher value of E_a, when compared to that in an acid with no inhibitor, is interpreted as an indication for an electrostatic character of the inhibitor's adsorption. The lower value of E_a in an inhibited solution when compared to that of an uninhibited one shows that strong chemisorption bond between the inhibitor and the metal is highly probable (Zerga et al., 2010). Activation energy, E_a values in the table are higher for inhibited solution (for the different systems) than the uninhibited one, indicating a strong inhibitive action of the additives by increasing energy barrier for the corrosion process, emphasizing the electrostatic character of the inhibitor's adsorption on the mild steel surface (physisorption).

Experimental corrosion rate values obtained from weight loss measurements for mild steel in 1 M H_2SO_4 in the absence and presence of *S. acuta* (leaves and stem) extracts and *S. acuta* extracts–iodide ion combination were used to further gain insight on the change of enthalpy (ΔH^*) and the entropy (ΔS^*) of activation complex in the transition state using transition state equation (Noor and Al-Moubaraki, 2008)

$$\log\left(\frac{\mathrm{CR}}{T}\right) = \left[\left(\log\left(\frac{R}{Nh}\right)\right) + \left(\frac{\Delta S^*}{2.303R}\right)\right] - \frac{\Delta H^*}{2.303RT} \tag{15}$$

where CR is the corrosion rate, h is the plank's constant, N is the Avogadro's number, R is the universal gas constant and T is the absolute temperature. Fig. 9 shows the plot of log (CR/T) vs. $1/T$ for mild steel corrosion in 1 M H_2SO_4 for the different systems studied. Straight lines were obtained with slope of ($-\Delta H/2.303R$) and intercept of [log(R/Nh) + ($\Delta S/2.303R$)] from which the values of ΔH^* and ΔS^*, respectively, were calculated and listed in Table 4. The positive values of ΔH both in the absence and presence additives reflect the endothermic nature of the steel dissolution process and it indicates that the dissolution of steel is difficult (Guan et al., 2004). Large and negative values of ΔS^* in the uninhibited and inhibited systems imply that the activation complex in the rate determining steps represents association rather than dissociation step, meaning that a decrease in disordering takes place on going from reactants to the activated complex. Similar observations have been reported in the literature for mild steel dissolution in the absence and presence of inhibitors in H_2SO_4 solution (Zerga et al., 2010; Noor and Al-Moubaraki, 2008).

Further insight into the adsorption mechanism is offered by considering the thermodynamic functions for the mild steel dissolution in 1 M H_2SO_4 in the presence of *S. acuta* leaves and stem extracts and extracts–KI mixtures. In this regard, heat of adsorption (Q_ads) was evaluated from the variation of surface coverage with reciprocal of temperature from the kinetic/ thermodynamic model (Solmaz et al., 2008; Avic, 2008)

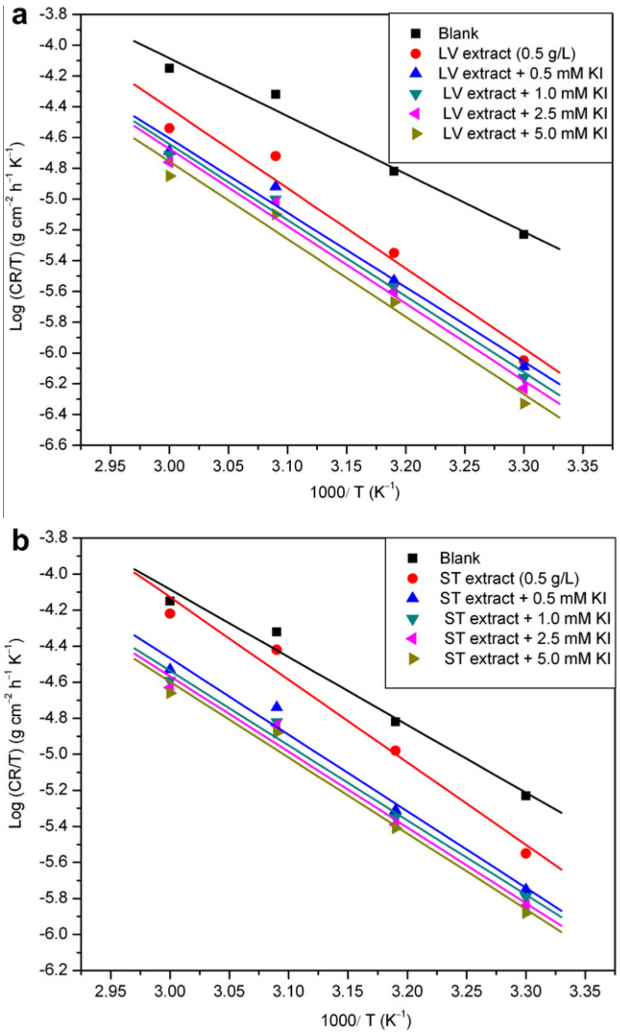

Figure 9 Transition state plot for mild steel in 1 M H_2SO_4 without and with *S. acuta* extracts and in combination with different concentrations of KI for (a) leaves and (b) stem.

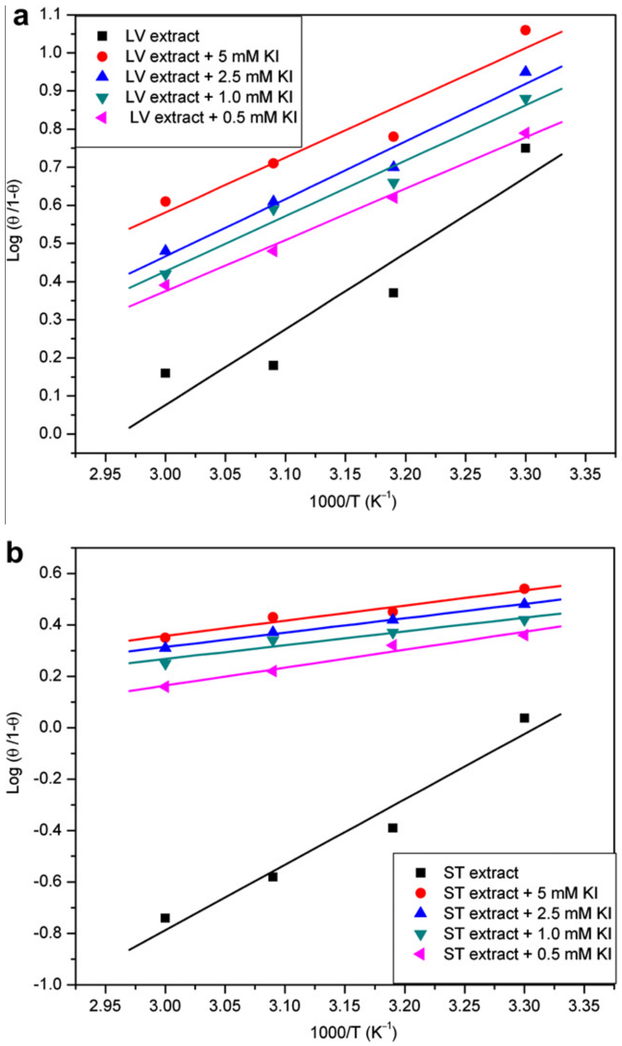

Figure 10 Plot of log $(\theta/1-\theta)$ vs. $1/T$ for mild steel in 1 M H_2SO_4 containing *S. acuta* extracts and in combination with different concentrations of KI for (a) leaves and (b) stem.

$$\log\left(\frac{\theta}{1-\theta}\right) = \log A + \log C - \left(\frac{Q_{\mathrm{ads}}}{2.303RT}\right) \tag{16}$$

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. The plot of log $(\theta/1-\theta)$ as a function of $1/T$ for the different additives is shown in Fig. 10. The values of the heat of adsorption were estimated from the slope of the linear plots and are listed in Table 4. In all cases, the values of Q_{ads} are negative indicating that the inhibitor adsorption and hence inhibition efficiency decreases with rise in temperature. The negative values of heat of adsorption obtained also support the physical adsorption mechanism proposed.

4. Conclusions

Leaves and stem extracts of *S. acuta* is found to inhibit the corrosion of mild steel in 1 M H_2SO_4 solution. The inhibition efficiency increased on the addition of iodide ions due to synergistic effect but decreased with the rise in temperature. The leaves were found to be a better inhibitor than the stem both in the absence and presence of iodide ions and could be attributed to high concentration phytochemicals in it. The adsorption characteristics of *S. acuta* extracts were approximated by Freundlich adsorption isotherm model. The synergism parameter (S_1) evaluated for different concentrations of KI was found to be greater than unity showing that the enhanced inhibition efficiency of both leaves and stem extracts of *S. acuta* on the addition of iodide ions was due to synergistic effect. The phenomenon of physical adsorption is proposed from a decrease in inhibition efficiency with an increase in temperature. The inhibition mechanism was further corroborated by the values of thermodynamic and kinetic parameters obtained from the experimental data.

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