Corrosion Inhibitive Effect and Adsorption Behaviour of *Hibiscus Sabdariffa* Extract on Mild Steel in Acidic Media

Emeka E. Oguzie[*]

Electrochemistry and Materials Science Research Laboratory, Department of Chemistry, Federal University of Technology, PMB 1526, Owerri, Nigeria

Abstract

The inhibiting action of the calyx extract of *Hibiscus sabdariffa* on mild steel corrosion in 2 M HCl and 1 M H_2SO_4 solutions was assessed using a gasometric technique. The results demonstrate that *Hibiscus sabdariffa* extract suppressed the corrosion reaction in both acid media and inhibition efficiency increased with extract concentration with slightly higher values obtained in 1 M H_2SO_4. Synergistic effects increased the efficiency of the extract in the presence of halide additives. Adsorption characteristics of the extract were approximated by the Langmuir isotherm. The inhibition mechanisms, estimated from the temperature dependence of inhibition efficiency as well from kinetic and activation parameters show that the extract functioned via mixed-inhibition mechanism. It is suggested that molecular as well as protonated organic species in the extract contribute to the observed inhibiting action.

Keywords: corrosion inhibition, plant extracts, inhibition efficiency, Langmuir isotherm, chemisorption.

Introduction

Iron and its alloys find extensive applications in industry, where they are used in a variety of service environments. Excessive corrosion attack is known to occur on metals deployed in service in aggressive environments. A significant method to protect such metals is the introduction of corrosion inhibitors that hinder the corrosion reaction and thus reduce the corrosion rate. Inorganic substances such as phosphates, chromates, dichromates, silicates, borates, tungstates, molybdates and arsenates have been found effective as inhibitors of metal corrosion. These inhibitors have also found useful application in the formulation of primers and

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[*] Corresponding author. E-mail address: oguziemeka@yahoo.com

anti-corrosive coatings, but a major disadvantage is their toxicity and as such their use has come under severe criticism. Among the alternative corrosion inhibitors, organic substances containing polar functions with nitrogen, sulphur, and/or oxygen in the conjugated system have been reported to exhibit good inhibiting properties [1-4]. The inhibitive characteristics of such compounds derive from the adsorption ability of their molecules, with the polar group acting as the reaction centre for the adsorption process. The resulting adsorbed film acts as a barrier that separates the metal from the corrodent and efficiency of inhibition depends on the mechanical, structural and chemical characteristics of the adsorption layers formed under particular conditions.

Recent awareness of the corrosion inhibiting abilities of tannins, alkaloids, organic and amino acids as well as organic dyes [3-8] has resulted in sustained interest on the corrosion inhibiting properties of natural products of plant origin. Such investigation is of much importance because in addition to being environmentally friendly and ecologically acceptable, plant products are inexpensive, readily available and renewable sources of materials. Although a number of insightful papers have been devoted to corrosion inhibition by plant extracts [9-12], reports on the detailed mechanisms of the adsorption process are still scarce. Such has been the current research focus in our laboratory [13]. The present paper reports on the corrosion inhibition and adsorption behaviour of extracts from the calyces of *Hibiscus sabdariffa* on mild steel corrosion in sulphuric and hydrochloric acid solutions using the gasometric technique. The influence of temperature as well as the synergistic effect of halide ions on adsorption and inhibition efficiency has also been studied. Kinetic and activation parameters that govern corrosion and inhibition processes have been evaluated. The plant popularly known as roselle belongs to the *Malvaceae* family. Its fleshy red calyces are used in various foods and medicines [14].

Experimental
Materials preparation
Tests were performed on mild steel sheets with weight percentage composition as follows: C – 0.05, Mn – 0.6, P – 0.36, Si – 0.03 and the balance Fe. Each sheet, which was 0.14 cm in thickness was mechanically pressed – cut into coupons of dimensions 3×1.5 cm. These were used as source without further polishing, but were however degreased in absolute ethanol, dried in acetone and stored in a moisture-free desiccator prior to use.

All chemicals and reagents used were BDH grade. The blank corrodents were respectively 1 M H_2SO_4 and 2 M HCl solutions. Stock solutions of the plant extract were prepared by boiling weighed amounts of the dried and ground calyces of *Hibiscus sabdariffa* for 3 hours in 1 M H_2SO_4 and 2 M HCl solutions, respectively. The resulting reddish solutions were cooled then filtered and stored. From the respective stock solutions, inhibitor test solutions were prepared in the concentration range 10 – 50 %. The effect of halide additives was studied by combining 5.0 mM of the halide salts KCl, KBr and KI respectively with solutions of the 10 % extract.

Gasometric experiments
The apparatus and procedure for gasometric determination of corrosion rates have been extensively described elsewhere [15]. Briefly, a two-necked flask was connected via a delivery tube to a burette which was in turn connected to a reservoir of paraffin oil. 250 mL of the test solution were then introduced into the flask and the initial volume of air in the burette recorded. Thereafter, two mild steel test coupons were dropped into the test solution and the reaction vessel immediately closed. The volume of hydrogen gas evolved by the corrosion reaction was estimated from the volume change in the level of the paraffin oil in the burette. The progress of the corrosion reaction was monitored by careful volumetric measurement of the evolved hydrogen gas at fixed time intervals. Experiments were conducted at 30 and 60 ^{o}C.

Results
Hydrogen evolution and corrosion rates
The corrosion rates of the mild steel coupons in absence and presence of *Hibiscus sabdariffa* extract were assessed from hydrogen evolution measurements. Typical hydrogen evolution data for uninhibited as well as inhibited steel samples are shown in Figs. 1 and 2 for 1 M H_2SO_4 and 2 M HCl, respectively. The rate of mild steel dissolution (slope of the linear part of the curve) was found to decrease with increasing concentration of the extract. This implies that the extract retarded the dissolution of mild steel in the acidic environments, the degree of inhibition depending on the concentration of the extract present.

Inhibition efficiency
The inhibition efficiency (I %) of the extract was calculated from the equation:

$$I\% = \left(1 - \frac{\rho_{inh}}{\rho_{blank}}\right) \text{x } 100 \qquad (1)$$

where ρ_{inh} and ρ_{blank} correspond to the corrosion rates in the presence and absence of inhibitor, respectively, as determined from the H_2 evolution curves. Table 1 shows that *Hibiscus sabdariffa* extract exhibited reasonable inhibition efficiency in both 1 M H_2SO_4 and 2 M HCl in the studied concentration range, which effect increased with increasing inhibitor concentration.
Fig. 3 shows that halide additives, namely KCl, KBr and KI, generally improved the inhibition efficiency of the extract at the temperatures studied. Such enhancement in the efficiency of organic inhibitors in the presence of halide salts has been previously observed and was ascribed to the synergistic effect [16-18].
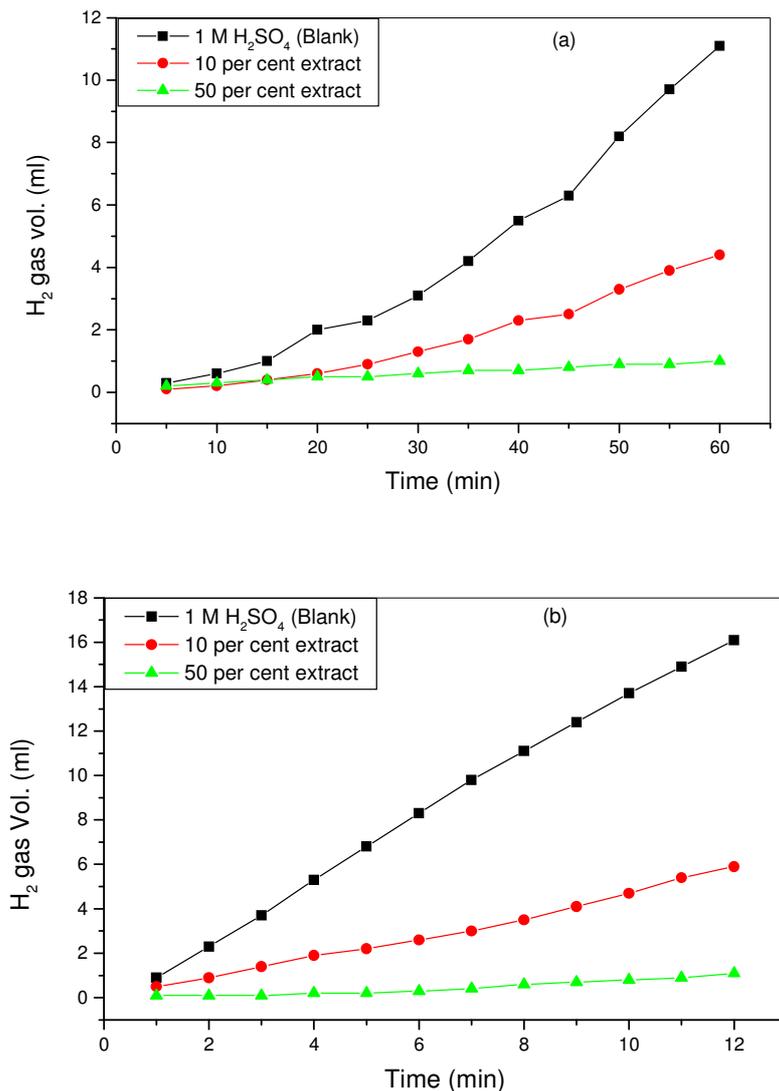
Figure 1. Hydrogen evolution during mild steel corrosion in 1 M H$_2$SO$_4$ at 30 and 60 ^{o}C in absence and presence of *Hibiscus sabdariffa* extract.

Table 1. Inhibition efficiency (I %) of *Hibiscus sabdariffa* extract on mild steel corrosion in 1 M H$_2$SO$_4$ and 2 M HCl at different temperatures.

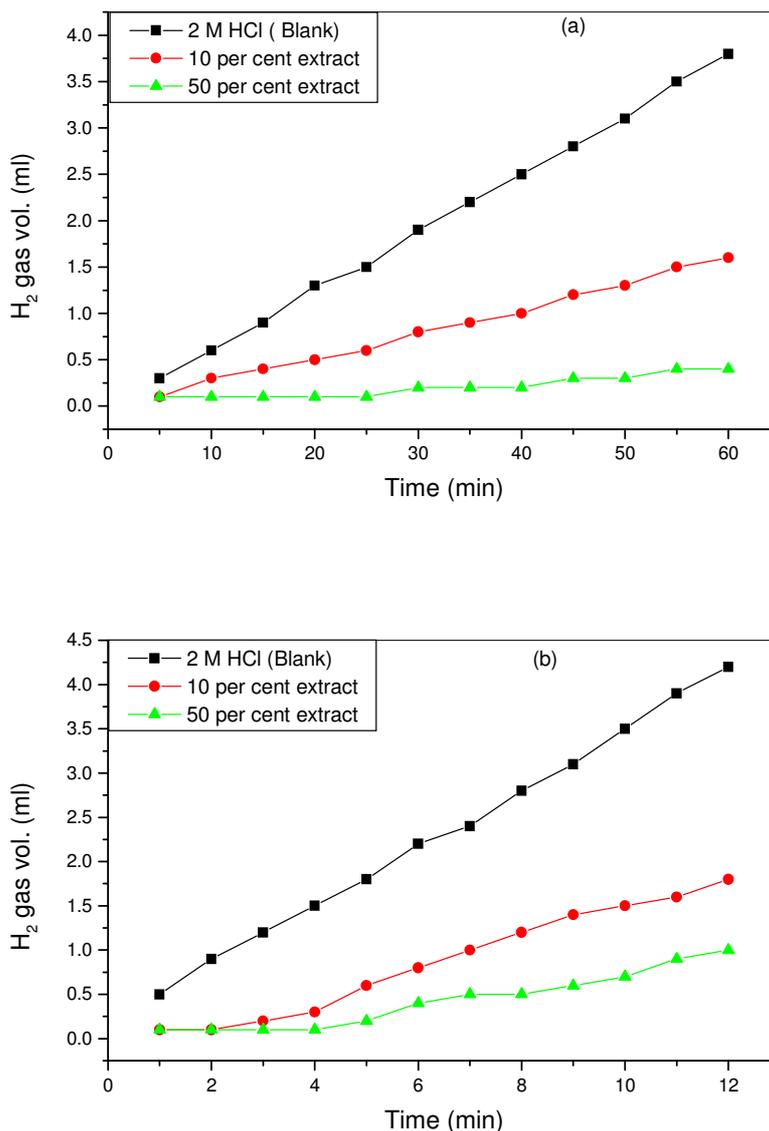| Extract conc. (%)	1 M H$_2$SO$_4$		2 M HCl	
	30 ºC	60 ºC	30 ºC	60 ºC
10	59.4	65.5	57.7	48.6
20	67.8	74.5	62.5	57.0
30	76.8	82.6	73.1	62.4
40	84.9	87.8	83.5	66.2
50	93.0	93.3	90.4	73.9

Figure 2. Hydrogen evolution during mild steel corrosion in 2 M HCl at 30 and 60 $^{\circ}$C in absence and presence of *Hibiscus sabdariffa* extract.

Discussion

The spontaneous corrosion of mild steel in acidic solutions can be represented by the anodic dissolution reaction

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

accompanied by the corresponding cathodic reaction

$$2H^+ + 2e \rightarrow H_2 \tag{3}$$

Accordingly, the progress of the corrosion reaction can be accurately followed by measuring the volume of H_2 gas evolved from the corrosion reaction. The

gasometric technique has been shown to provide a rapid and sensitive means of monitoring in situ the effect of an inhibitor on the rates of gas evolution at the metal-corrodent interphase [20-24]. Results obtained from this technique have been satisfactorily corroborated by other methods such as gravimetric and thermometric [10,25], potentiostatic polarization [11] and impedance spectroscopy [21].

The decreased deflection of H_2 gas evolution rate on introduction of *Hibiscus sabdariffa* extract into the corrodents as shown in Figs. 1 and 2 indicates that the extracts actually afford corrosion inhibition of mild steel in the acidic environments. Fig. 4 shows the adsorption curves of the extracts on to mild steel from 1 M H_2SO_4 and 2 M HCl, illustrating the relationship between surface coverage and concentration [1]. Adsorption of the extract is further substantiated by the fit of the experimental data to the Langmuir adsorption isotherms (Fig. 5).
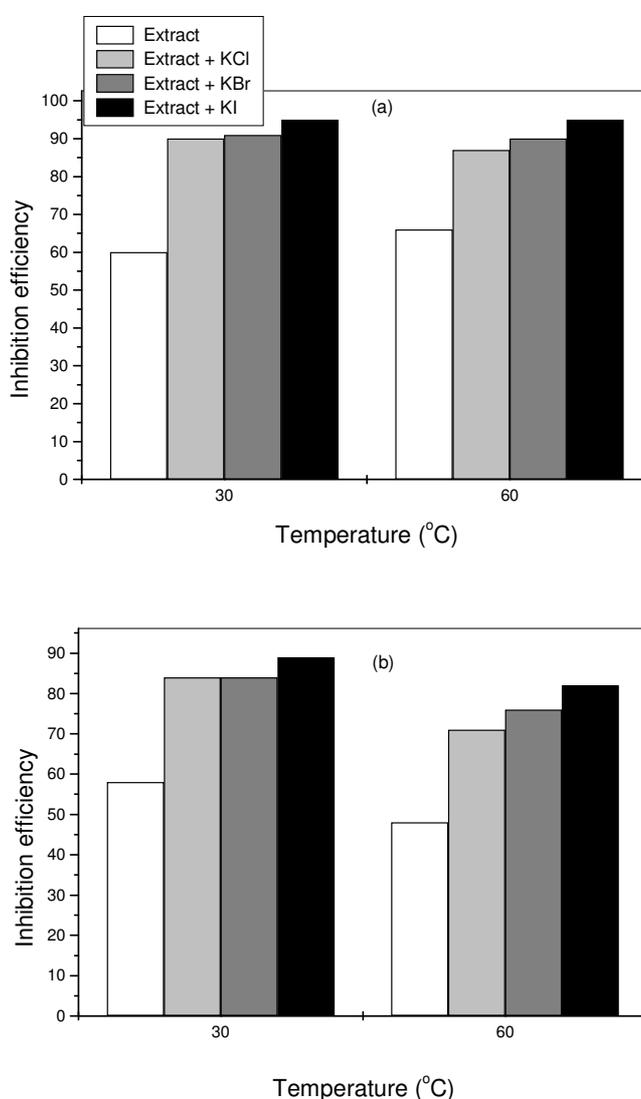

Figure 3. Influence of halide additives (0.5 mM) on the inhibition efficiency of 10 % *Hibiscus sabdariffa* at different temperatures.

In discussing corrosion inhibition by surface-active organic compounds various factors are taken into consideration including the number and types of adsorbing groups and their electron structure. The calyx extract under investigation contains different organic substances with proven corrosion inhibiting capabilities such as ascorbic acid, amino acids, flavonoids, pigments and β-carotene [14]. This makes it difficult to assign the observed inhibiting effect to a particular constituent. The net adsorption of the organic matter on the corroding steel surface creates a barrier that isolates the metal from the corrodent. Inhibition efficiency increases with an increase in the metal surface fraction occupied by the organic matter.
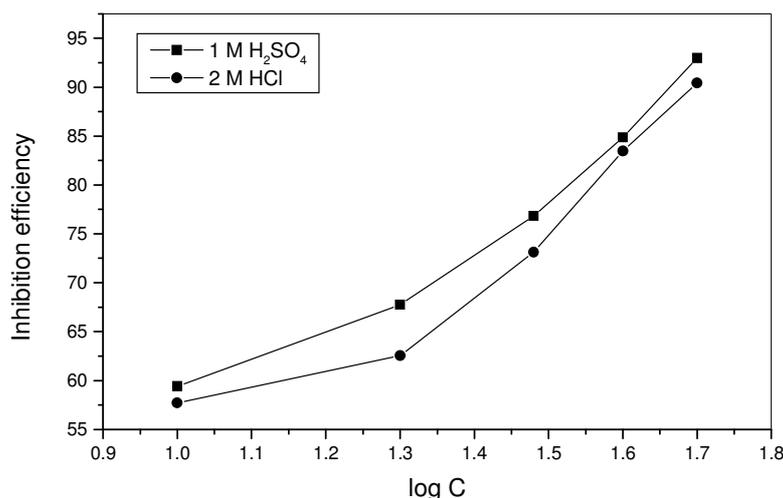

Figure 4. Plots of inhibition efficiency versus the logarithmic concentration of *Hibiscus sabdariffa* extract in 1 M H_2SO_4 and 2 M HCl.

Organic inhibitors are known to affect the kinetics of metal corrosion by cutting back the rate of either or both the anodic and cathodic reactions. A given inhibitor functions by means of a specific mechanism, depending on the type and composition of metal and corrodent, inhibitor structure and concentration as well as temperature. Initial deduction of the adsorption mechanism of *Hibiscus sabdariffa* extract involved the assessment of the effects of varying system temperature between 30 and 60 ^{o}C on corrosion and inhibition processes. The variation of inhibition efficiency with temperature is given in Table 1. The apparent activation energies (E_a) for the corrosion process in absence and presence of inhibitor were evaluated from a modified form of the Arrhenius equation:

$$\log \frac{\rho_2}{\rho_1} = \frac{E_a}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{4}$$

where ρ_1 and ρ_2 are the corrosion rates at temperatures T_1 and T_2, respectively. An estimate of the heats of adsorption (θ) was obtained from the trend of surface coverage with temperature as follows [26]:

$$Q_{ads} = 2.303 \, R \left[\log \left(\frac{\theta_2}{1-\theta_2} \right) - \log \left(\frac{\theta_1}{1-\theta_1} \right) \right] \times \frac{T_1 T_2}{T_2 - T_1} \tag{5}$$

θ_1 and θ_2 are the degrees of surface coverage at temperature T_1 and T_2, and R is the gas constant. θ is related to inhibition efficiency (I %) as follows:
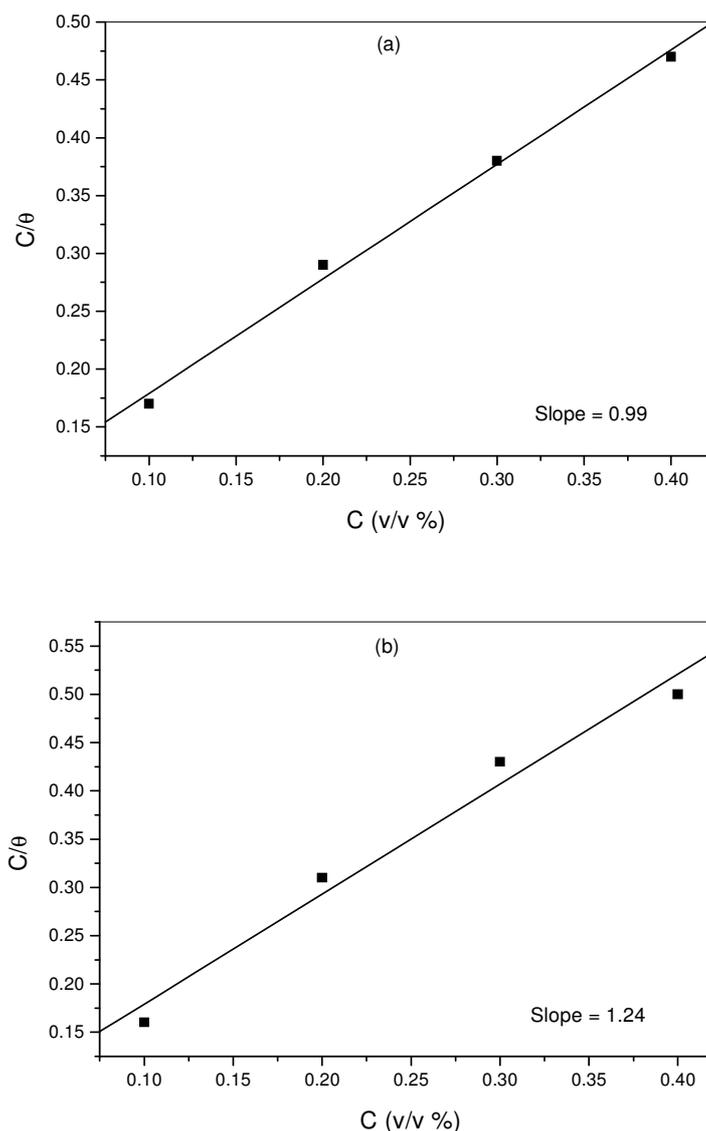
$$\theta = \frac{I \%}{100} \tag{6}$$

Figure 5. Langmuir adsorption isotherm for *Hibiscus sabdariffa* extract on mild steel in (a) 1 M H_2SO_4 and (b) 2 M HCl.

The calculated values of E_a and Q_{ads} are given in Table 2. The results in Tables 1 and 2 show that inhibition efficiency increased with rise in temperature in 1 M H_2SO_4 and E_a in the presence of the extract was lower than that in the uninhibited

acid. The positive Q_{ads} values also signify that the degree of surface coverage increased with rise in temperature. Such behaviour is often interpreted as being indicative of chemical adsorption of organic matter on the steel surface [27]. A different behaviour is however observed in 2 M HCl, where the decrease in inhibition efficiency with rise in temperature, including higher E_a in the presence of the extract, as well as negative Q_{ads} values, suggest physical or coulombic type of adsorption.

Table 2. Calculated values of activation energy (E_a) and heat of adsorption (Q_{ads}) for mild steel corrosion in 1 M H_2SO_4 and 2 M HCl with *Hibiscus sabdariffa* extract as inhibitor.

System	E_a (kJ mol^{-1})	Q_{ads} (kJ mol^{-1})
1 M H_2SO_4 (blank)	54.7	–
H_2SO_4 + 10 % extract	50.2	8.4
H_2SO_4 + 50 % extract	53.4	1.4
2 M HCl (blank)	46.3	–
HCl + 10 % extract	51.7	- 10.1
HCl + 50 % extract	74.3	- 32.2

The complex compositions of plant extracts make such classification somewhat insufficient for describing their inhibition mechanisms. For instance in the aqueous acid extracts of *Hibiscus sabdariffa* under study, the inhibiting organic constituents may exist as either protonated or molecular species, depending on the nature of the chemical changes occurring to the inhibitor as well as changes to the electrolyte. Protonated species adsorb on cathodic sites on the metal and inhibit the hydrogen evolution reaction, whereas molecular species decrease the anodic dissolution of the metal [27-29]. Considering the positive surface charge on a corroding steel specimen in acidic solution [19,27], protonated species are normally poorly adsorbed. Improved adsorption should however be obtained in hydrochloric acid solutions due to the tendency of chloride ions to be strongly adsorbed on the metal surface and hence facilitate physical adsorption of cation-type inhibitors. For that reason, a comparison of the inhibition efficiency of the extract in 2 M HCl and 1 M H_2SO_4 should give an insight into the mode of adsorption of the inhibiting species (whether ionic or molecular), particularly since both solutions have identical anion concentration. Higher efficiency in 2 M HCl implies predominant adsorption of protonated species, which adsorb electrostatically. Alternatively, if the species responsible for the inhibitive effect adsorb as molecules, the inhibiting effect in both acid solutions should be comparable.

A further consideration involves assessment of the effect of halide additives on inhibition efficiency. It is generally accepted that halide ions facilitate adsorption of organic inhibitors during mild steel corrosion in acidic media 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 in

solution and the specifically adsorbed halide ions on the metal surface [7,8]. Hence, if protonated species play a part in corrosion inhibition, a synergistic increase in efficiency should be observed in the presence of the halide additives, as shown in Fig. 3.

The observed inhibiting effect of *Hibiscus sabdariffa* extract can be attributed to the involvement of both protonated and molecular species in the adsorption process. The similarity in inhibition efficiency values in both corrodents and even the slightly higher value in 1 M H_2SO_4 implies that chemisorption of molecular species play a leading role, which is in agreement with the observed variation of I % with temperature in this medium. Physisorption of protonated species becomes an important factor in 2 M HCl, accounting for the reduction in I % with temperature increase. Inhibition efficiency in both corrodents increased on introduction of the halides as a result of improved physisorption of protonated species.

The Langmuir isotherm given by [30]:

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \tag{7}$$

is shown in Fig. 5 for the extract adsorption from 1 M H_2SO_4 (Fig. 5a; R^2 = 0.997) and 2 M HCl (Fig. 5b; R^2 = 0.988). C is the adsorbate concentration and K_{ads} is the equilibrium constant for the adsorption process. Though linear plots were obtained, the deviations of the slope from unity as well as the y-axis intercept imply that the isotherm may not be strictly applicable. This is indicative of some divergence from pure monolayer adsorption and can be attributed to interactions between adsorbate species on the metal surface as well as changes in the adsorption heat with increasing surface coverage [31,32], factors which were not taken into consideration in derivation of the isotherm. It is however obvious that adsorption from 1 M H_2SO_4 displayed a closer fit to the Langmuir isotherm, which is in agreement with the experimental results. The adsorption data generally will be more appropriately described by a modified equation taking the above factors into consideration. Such a modified Langmuir isotherm has been proposed by Villamil et al. as follows [33]:

$$\frac{C}{\theta} = \frac{n}{K_{ads}} + nC \tag{8}$$

Conclusions

Extracts from the calyces of *Hibiscus sabdariffa* suppressed mild steel corrosion in 1 M H_2SO_4 and 2 M HCl at the temperatures studied. Inhibition efficiency increased with an increase in extract concentration and synergistically increased in the presence of halide ions. Analyses of the experimental results suggest that both protonated and neutral organic species in the extract contribute to the observed inhibitive behaviour, the predominant effect in 1 M H_2SO_4 being chemisorption of molecular species, while the physical adsorption of protonated

species predominates in 2 M HCl. Halide ions improved physisorption of protonated species in both corrodents.

References
1. M.A. Ameer, E. Khamis, G. Al-Senani, *Ads. Sci. Tech.* 18 (2000) 177.
2. A. Popova, M. Christov, T. Deligeorgiev, *Corrosion* 59 (2003) 756.
3. E.E. Oguzie, G.N. Onuoha, A.I. Onuchukwu, *Mater. Chem. Phys.* 89 (2004) 305.
4. M.A. Quraishi, H.K. Sharma, *J. Appl. Electrochem.* 35 (2005) 33.
5. A.A. El-Hosary, R.M. Saleh, *Progress in the Understanding and Prevention of Corrosion*, Institute of Materials, London, 2 (1993) 911.
6. S. Martinez, I. Stern, *J. Appl. Electrochem.* 31 (2001) 973.
7. E.E. Oguzie, *Mater. Chem. Phys.* 87 (2004) 212.
8. E.E. Oguzie, G.N. Onuoha, A.I. Onuchukwu, *Anti-Corros. Meth. Mater.* 52(2005) 293.
9. F. Zucchi, I.H. Omar, *Surf. Tech.* 24 (1985) 391.
10. A.Y. El-Etre, *Corros. Sci.* 45 (2003) 2485.
11. M. Abdallah, *Portugaliae Electrochim. Acta* 22 (2004) 161.
12. M. Kliskic, J. Radosevic, S. Gudic, V. Katalinik, *J. Appl. Electrochem.* 30 (2000) 823.
13. E.E. Oguzie, *Pigment & Resin Tech.* 34 (6) (2005) 321.
14. Y. Li, K.L. Chin, F. Malekian, M. Berhane, J. Gager, *Circular Ufnr,* No. 604 (2005) 1.
15. A.I. Onuchukwu, A.I. Baba, *Mater. Chem. Phys.* 18 (1987) 381.
16. G. Mu, X. Li, *J. Colloid Interface Sci.* 289 (2005) 184.
17. D.Q. Zhang, L.X. Gao, G.D. Zhou, *J. Appl. Electrochem.* 33, (2003) 361.
18. E.E. Oguzie, Y. Li, F.H. Wang, *J. Colloid Interface Sci.* 310 (2007) 90.
19. E.E. Oguzie, Y. Li, F.H. Wang, *Electrochim. Acta* 52 (2007) 6988.
20. A.I. Onuchukwu, *Mater. Chem. Phys.* 20 (1988) 323.
21. A. Aytac, U. Ozmen, M. Kabasakaloglu, *Mater. Chem. Phys. 89* (2005)176.
22. E.E. Ebenso, E.E. Oguzie, *Mater. Lett.* 59 (2005) 2163.
23. E.E. Oguzie, *Mater. Chem. Phys.* 99 (2006) 441.
24. E.E. Oguzie, *Corros. Sci.* 49 (2007) 1527.
25. M.N. Moussa, A.S. Fouda, A.I. Taha, A. Elnenaa, *Bull. Korea Chem. Soc.* 9 (1998) 192.
26. H.M. Bhajiwala, R.T. Vashi, *Bull. Electrochem.* 17 (2001) 441.
27. A. Popova, E. Sokolova, S. Raicheva, M. Christov, *Corros Sci.* 45 (2003) 33.
28. N. Hackerman, E.L. Cook, *J. Electrochem. Soc.* 97 (1950) 2.
29. E. Ahlberg, M. Friel, *Electrochim. Acta* 34 (1989) 190.
30. M. Lebrini, F. Bentiss, H. Vezin, M. Lagrenee, *Corros. Sci.* 48 (2006) 1279.

31. C. Chakrabarty, M.M. Singh, P.N.S. Yadav, C.V. Agarwal, *Trans. SAEST.* 18 (1983) 15.

32. E.E. Oguzie, B.N. Okolue, E.E. Ebenso, G.N. Onuoha, A.I. Onuchukwu, *Mater. Chem. Phys.* 87 (2004) 394.

33. R.F.V. Villamil, P. Corio, J.C. Rubin, S.M.L. Agostinho, *J. Electroanal. Chem.* 472 (1999) 112.