



ORIGINAL ARTICLE

Spondias mombin L. as a green corrosion inhibitor for aluminium in sulphuric acid: Correlation between inhibitive effect and electronic properties of extracts major constituents using density functional theory

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Received 14 August 2010; accepted 9 September 2010

Available online 17 September 2010

KEYWORDS

Weight loss;
Spondias mombin L.;
Aluminium;
Corrosion;
Sulphuric acid;
Density functional theory;
Inhibition

Abstract The inhibition of aluminium in 0.5 M H₂SO₄ by extracts of *Spondias mombin* L. was investigated using the standard gravimetric technique at 30–60 °C. The trend of inhibition efficiency with temperature was used to propose the mechanism of inhibition. It was found that the *S. mombin* L. extract acts as an inhibitor for acid-induced corrosion of aluminium. Inhibition efficiency (%*I*) of the extract increased with an increase in concentration of the *S. mombin* L. extract but decreased with temperature. Furthermore, inhibition efficiency (%*I*) synergistically increased on addition of potassium iodide. Inhibitor adsorption characteristics were approximated by Langmuir adsorption isotherm at all the concentrations and temperatures studied. The mechanism of physical adsorption is proposed from the trend of inhibition efficiency with temperature and from the calculated values of Gibbs free energy, activation energy and heat of adsorption. Quantum chemical calculations were performed using the density functional theory at B3LYP/6-31G (d) level of theory to find out whether a clear link exists between the inhibitive effect of the extract and the electronic properties of its main constituents.

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Peer review under responsibility of King Saud University.
doi:10.1016/j.arabjc.2010.09.002



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1. Introduction

The scientific corrosion literature has descriptions and lists of numerous synthetic chemical compounds that exhibit inhibitive properties for aluminium in acidic solutions, e.g., fluconazole (Obot and Obi-Egbedi, 2008), clotrimazole (Obot et al., 2009; Obot and Obi-Egbedi, 2008), 2,3-diaminonaphthalene (Xiao-Ci et al., 2000), aminopyrimidines (Masoud et al., 2010), tetrazole derivatives (Khaled and Al-Qahtani, 2009) purine (Amin et al., 2009) etc. Of these only few are actually used in practice. This is partly due to the fact that desirable

properties of an inhibitor usually extend beyond those simply related to metal protection. Considerations of cost, biodegradability, toxicity, availability and environmental friendliness are of considerable importance. Consequently, there exists the need to develop a new class of corrosion inhibitors with low toxicity and good efficiency.

The exploration of natural products of plant origin as inexpensive eco-friendly corrosion inhibitors is an essential field of study. In addition to being environmentally friendly and ecologically acceptable, plant products are cheap, readily available and are renewable sources of materials (Oguzie, 2008). The extracts from their leaves, barks, seeds, fruits and roots comprise mixtures of organic compounds containing nitrogen, sulphur, and oxygen atoms and some (Umoren et al., 2008; Umoren and Ebenso, 2008; El-Etre, 2006; Zucchini and Omar, 1985; Oguzie, 2006) have been reported to function as effective inhibitors of metal corrosion in different aggressive environments. Recent literature has shown that plant materials, such as *Opuntia extract* (Oguzie, 2005), *Telferia occidentalis extract* (Oguzie, 2006), *limonene* (Chaieb et al., 2009), *Prosopis cineraria* (Sharma et al., 2008), zallouh root (El-Etre, 2008), olives leaves (El-Etre, 2007), *Datura stramonium* (Raja and Sethuraman, 2007), *Gossipium hirsutum extract* (Abiola et al., 2009) as well as *Phyllanthus amarus extract* (Abiola and Otaigbe, 2009) are effective inhibitors for metal in aggressive solutions. Our research group has recently reported on the corrosion inhibitive effectiveness of metals by *Dacryodes edulis* (Umoren et al., 2008a), *Pachylobus edulis* (Umoren et al., 2008b), *Vigna unguiculata* (Umoren et al., 2008c), *Gum arabic* (Umoren et al., 2006), *Raphia hookeri* (Umoren et al., 2009) and the latest on *Ipomoea invulcrata* (Obot and Obi-Egbedi, 2009).

Despite the high availability and many varieties of plant materials, only relatively few have been thoroughly investigated,

and even at that reports on the detailed mechanisms of the adsorption process are still scarce. The present report continues to focus on the broadening application of plant extracts for metallic corrosion control and reports on the inhibiting effect of extracts of *Spondias mombin* (SM) on aluminium corrosion in acidic solution. *S. mombin* L. is a tree, a species of flowering plant in the family *Anacardiaceae*. It is native to tropical Americans, including the West Indies. The tree has been naturalized in parts of Africa, India and Indonesia. Phytochemical analysis (Njoku and Akumefula, 2007) of the extracts of *S. mombin* L. plant parts shows that it is rich in naturally synthesized biodegradable organic compounds. Ascorbic acid (AA) has been identified as the major chemical constituent of the plant. Riboflavin (RB), Thiamine (TH), and Nicotinic acid (NA) have also been isolated (Njoku and Akumefula, 2007) (Fig. 1). The present study is aimed at (i) To establish the effectiveness of *S. mombin* extract as corrosion inhibitor (ii) To study the effect of temperature on the corrosion process in the absence and presence of extract and (iii) To attempt to correlate the inhibitive effect with the electronic/molecular parameters of the extract's active component using density functional theory.

2. Experimental

2.1. Materials preparation

The sheet of aluminium used for this study has the following chemical composition (wt. %): Al (99.95%), Cu (0.01%), Mg (0.02%), Si (0.02%), Mn (0.002%) and Zn (0.005%) and was obtained from Joebros Limited, Uyo, Nigeria. The sheet was 0.04 cm in thickness and was mechanically press-cut into 4 × 2 cm coupons. These were polished with grade 600 emery

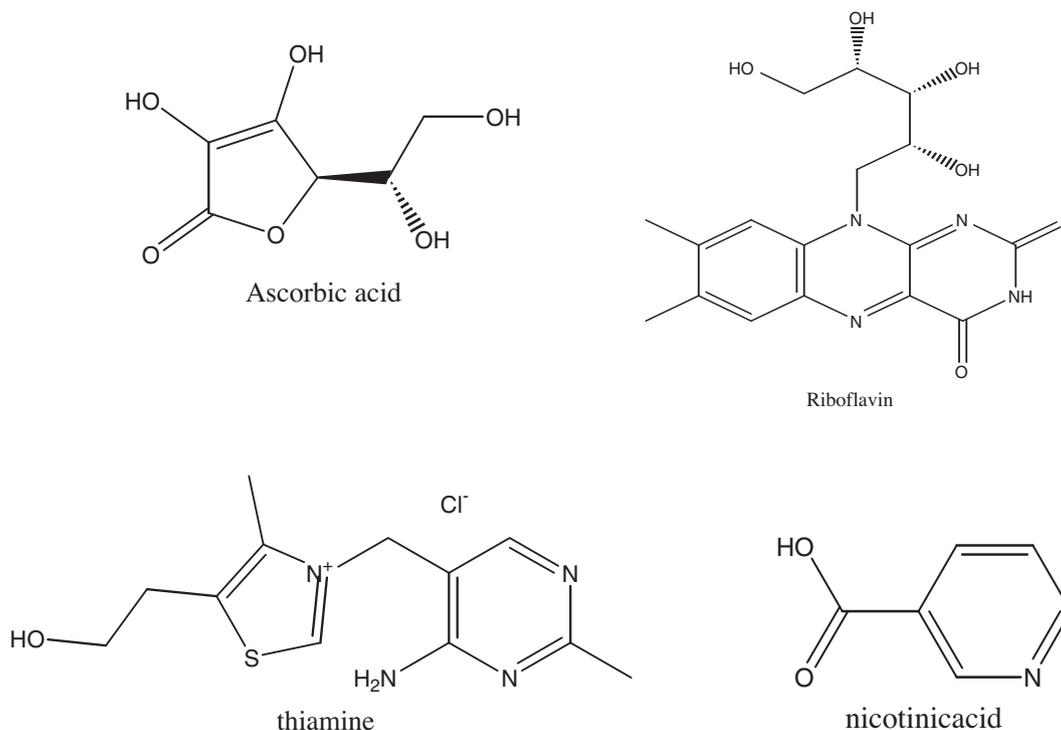


Figure 1 Compounds isolated from *Spondias mombin* L. extracts.

paper, degreased in absolute ethanol, dried in acetone and stored in a moisture-free desiccator prior to use as described previously (Umoren et al., 2006; Obot and Obi-Egbedi, 2009). The 0.5 M H₂SO₄ solution, prepared from BDH grade H₂SO₄ was employed as the corrodent for the study.

Stock solutions of the *S. mombin* L. were prepared as reported by Abiola et al. (2009) and El-Etre (2007). The dried leaves were blended to powder form; 0.5 g of the powdered leaves was refluxed in 100 mL of 0.5 M H₂SO₄ solution for 3 h. The refluxed solution was allowed to stand for 8 h, filtered and stored. The filtrate was diluted with appropriate quantity of 0.5 M H₂SO₄ to obtain inhibitor test solutions of 1%, 4% and 5% v/v concentrations. The effect of iodide ions on inhibition efficiency was studied by combining 5.0 mM KI with different concentrations of the extract to observe any enhancement in inhibitive performance.

2.2. Gravimetric measurements

The gravimetric method (weight loss) is probably the most widely used method of corrosion inhibition assessment (Musa et al., 2010; Khadom et al., 2010; Bouklah et al., 2006; Mercer, 1985). The simplicity and reliability of the measurement offered by the weight loss method is such that the technique forms the baseline method of measurement in many corrosion monitoring programmes (Afidah and Kasim, 2008). Weight loss measurements were conducted under total immersion using 250 mL capacity beakers containing 200 mL test solution at 30–60 °C maintained in a thermostated water bath. The aluminium coupons were weighed and suspended in the beaker with the help of rod and hook. The coupons were retrieved at 4 h interval progressively for 24 h, immersed in concentrated (SG. 1.42) nitric acid at room temperature, rinsed severally in de-ionized water, cleaned, dried in acetone, and re-weighed. 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. Then the tests were repeated at different temperatures. In order to get good reproducibility, experiments were carried out in triplicate. In this present study, the standard deviation values among parallel triplicate experiments were found to be smaller than 5%, indicating good reproducibility. A visual examination was carried out after the weight loss measurements were over. It should be noted that in the absence of inhibitor the uniform corrosion attack was observed, while on the other hand in the presence of extracts, such an attack was not observed: therefore, the surface area was bright and did not present any corrosion form which is an indication that no attack has occurred on the surface area of the aluminium coupon.

The corrosion rate (ρ) in mg cm⁻² h⁻¹ was calculated from the following equation (Umoren et al., 2010):

$$\rho = \frac{\Delta W}{S t} \quad (1)$$

where W is the average weight loss of three aluminium coupons, S the total area of one aluminium specimen, and t is the immersion time (24 h). With the calculated corrosion rate, the inhibition efficiency (% I) was calculated as follows (Umoren et al., 2009):

$$\%I = \left(\frac{\rho_1 - \rho_2}{\rho_1} \right) \times 100 \quad (2)$$

where ρ_1 and ρ_2 are the corrosion rates of the mild steel coupons in the absence and presence of inhibitor, respectively.

2.3. Computational details

B3LYP, a version of the DFT method that uses Becke's three parameter functional (B3) and includes a mixture of HF with DFT exchange terms associated with the gradient corrected correlation functional of Lee, Yang and Parr (LYP) (Lee et al., 1988) was used in this paper to carry out quantum calculations. Then, full geometry optimization together with the vibrational analysis of the optimized structures of the inhibitor was carried out at the (B3LYP/6-31G (d)) level of theory using Spartan'06 V112 program package (Spartan and Wavefunction, 2006) in order to determine whether they correspond to a maximum or to a minimum in the potential energy curve. The theoretical parameters were calculated for the extract major components, namely Ascorbic acid, Riboflavin, Thiamine and Nicotinic acid in aqueous phase. It is well known that the phenomenon of electrochemical corrosion occurs in liquid phase. As a result, it was necessary to include the effect of a solvent (water) in the computational calculations. In the Spartan '06 V112 program, SCRF methods (Self-consistent reaction field) were used to perform calculations in solution. These methods model the solvent as a continuum of uniform dielectric constant and the solute is placed in the cavity within it.

3. Results and discussion

3.1. Weight loss, corrosion rates and inhibition efficiency

The loss in weight of aluminium coupons in 0.5 M H₂SO₄ in the absence and in the presence of different concentrations of *S. mombin* L. extract for 24 h was determined at 30–60 °C. Fig. 2 shows a representative plot of weight loss-time curves for aluminium coupons in the absence and presence of the extract at 30 °C. Similar curves were obtained for the other temperatures (not shown). It is clear that the weight loss of aluminium coupons in the presence of the extract varies

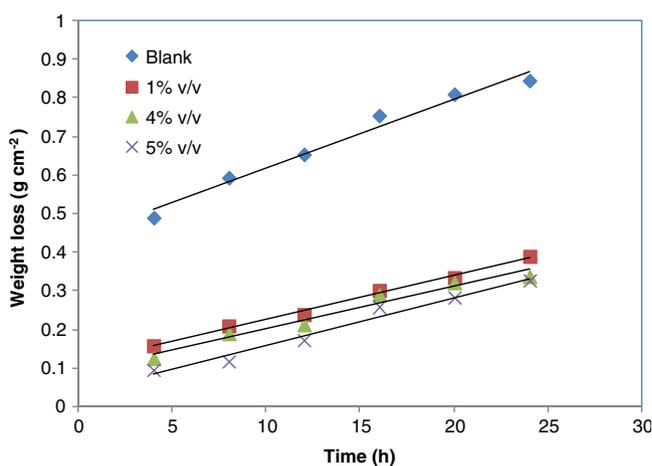


Figure 2 Variation of weight loss against time for aluminium corrosion in 0.5 M H₂SO₄ in the absence and presence of different concentrations of *Spondias mombin* L. extracts at 30 °C.

linearly with time, and much lower than that obtained in the blank solution. The linearity obtained indicates the absence of insoluble film during corrosion, and that the extract components were first adsorbed onto the metal surface and thereafter, impede the corrosion process (El-Mahdy and Mohamed, 1995; Abdallah et al., 2008).

The effects of different concentrations of *S. mombin* L. extract on corrosion rates in 0.5 M H₂SO₄ solution after 24 h of exposure are shown in Fig. 3. The plant extract is seen to reduce the corrosion rate at all studied concentrations indicating inhibition of the corrosion reaction. The effect becomes more pronounced with increasing extract concentration, which suggests that the inhibition process is sensitive to the amount of the additive present. On the other hand, corrosion rate is seen to increase with increase in temperature. Similar observations have been reported (Obot and Obi-Egbedi, 2010).

The effectiveness of the extract in retarding the corrosion of aluminium coupon in 0.5 M H₂SO₄ was obtained by comparing the corrosion rates of the aluminium coupon in the presence of the extract and in the blank acid solution and expressed in terms of the inhibition efficiency (%I). Fig. 4 illustrates the variation of inhibition efficiency with extract concentration in 0.5 M H₂SO₄ at 30–60 °C. The figure clearly shows that inhibition efficiency increases as the concentration of the extract increases reaching a maximum value at the higher concentration (5% v/v) of the extract studied (Table 1). However, inhibition efficiency decreases with increase in temperature. Similar results involving plant extracts used as corrosion inhibitor for aluminium in acid media have been reported in our previous publications (Obot and Obi-Egbedi, 2009a,b). It has been pointed out that the increase in inhibition efficiency with increase in extract concentration is an indication of an increase in the number of components of the extract adsorbed over the aluminium surface blocking the active sites, in which direct acid attacks proceed and protect the metal from corrosion, while the decrease in inhibition efficiency with temperature rise is suggestive of electrostatic interaction (physical adsorption) of the phytoconstituents of the extract on aluminium surface forming a protective layer and shielding the metal from corrosion (Oguzie, 2007).

The corrosion-inhibiting effect of *S. mombin* L. extract can be attributed to phytochemical constituents including alkaloids tannins, saponins, flavonoids, ascorbic acid, riboflavin,

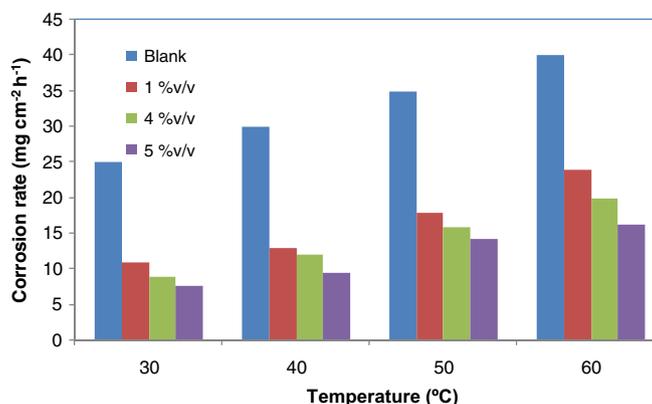


Figure 3 The relationship between corrosion rate and temperature in the absence and presence of different concentrations of *Spondias mombin* L. extracts.

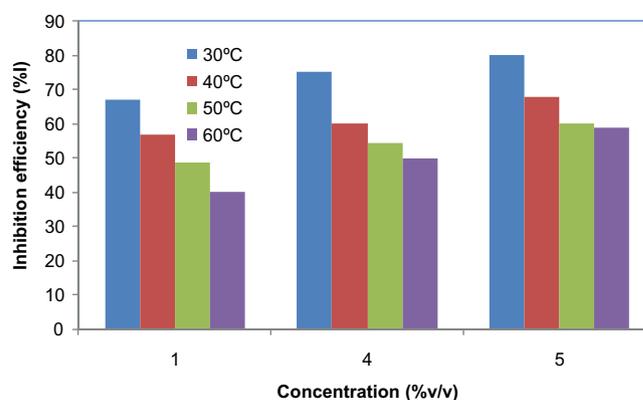
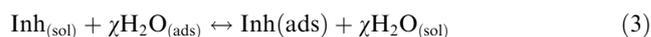


Figure 4 Variation of inhibition efficiency of *Spondias mombin* L. extracts with concentration at different temperatures.

thiamine and nicotinic acid. The different constituents may react with freshly generated Al³⁺ ions on a corroding metal surface forming organometallic [Al–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 extract concentration and temperature.

3.2. Adsorption and thermodynamic considerations

Organic corrosion inhibitors are known to decrease metal dissolution via adsorption on the metal/corrodent interface to form a protective film which separates the metal surface from the corrosive medium. The adsorption route is usually regarded as a substitution process between the organic inhibitor in the aqueous solution [Inh_(sol)] and water molecules adsorbed at the metal surface [H₂O_(ads)] as follows Oguzie et al., 2007; Ameer et al., 2002:



where χ represents the number of water molecules replaced by one molecule of adsorbed inhibitor. The adsorption bond strength is dependent on the composition of the metal and corrodent, extract components, concentration as well as tempera-

Table 1 Calculated values of inhibition efficiency and the degree of surface coverage for aluminium corrosion in 0.5 M H₂SO₄ in the absence and presence of *Spondias mombin* L. extract and extract-iodide mixtures at 30–60 °C.

System/concentration	Inhibition efficiency (%I)				Surface coverage (θ)			
	30 °C	40 °C	50 °C	60 °C	30 °C	40 °C	50 °C	60 °C
Blank	–	–	–	–	–	–	–	–
1% v/v	67.2	56.7	48.6	40.0	0.67	0.57	0.49	0.40
4% v/v	75.4	60.0	54.3	50.0	0.75	0.60	0.54	0.50
5% v/v	80.3	68.0	60.0	58.0	0.80	0.68	0.60	0.58
1% v/v + 5 mM KI	83.6	62.8	60.0	52.5	0.83	0.63	0.60	0.53
4% v/v + 5 mM KI	93.3	71.3	68.6	65.0	0.93	0.71	0.69	0.65
5% v/v + 5 mM KI	95.1	86.0	73.4	70.0	0.95	0.86	0.73	0.70

ture. In depth consideration of some of these variables will normally yield useful information regarding the adsorption mechanism. Although, the complex nature of the corrosion inhibition process is not in doubt, 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).

The increase in the efficiency of inhibition by *S. mombin* L. extract determined by weight loss method with increase in the extract concentration indicates that the extract is adsorbed on the aluminium surface at higher concentration leading to greater surface coverage. The surface coverage was evaluated from the expression: %I = θ × 100; assuming a direct relationship between inhibition efficiency (%I) and surface coverage (θ). Thus, in order to clarify the nature of adsorption, theoretical fitting of the surface coverage values to different isotherms was undertaken and the value of correlation coefficient (R²) was used to determine the best fit isotherm. Langmuir adsorption isotherm was found to be the best fit. Langmuir isotherm is given by the expression (Ekanem et al., 2010):

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \tag{4}$$

where θ is the surface coverage, C is the concentration, and K_{ads} is the equilibrium constant of adsorption process.

The plot of C/θ against C is shown in Fig. 5 for extract alone (a) and extract-iodide mixtures (b), respectively. The slopes of the linear plots were greater than unity and correlation coefficient (R²) at all temperatures being 0.99 (Table 2). Also from Table 2, the K_{ads} values decrease with increasing temperature showing that the molecules of the extracts were physically adsorbed on the aluminium surface. The considerable deviation of the slope from unity observed may be explained on the basis of the interaction among the adsorbed species on the surface of the metal. Given the complex composition of the extract, the different components can be adsorbed on the cathodic and anodic sites of the metal surface, and such adsorbed species may interact by mutual repulsion or attraction. It is therefore, pertinent to say that the adsorption of the extract on the aluminium surface at all the temperatures studied can be more appropriately represented by a modified Langmuir equation suggested by Villamil et al. (1999) taking

into consideration the interactions between adsorbate species as well as changes in heat of adsorption with changing surface coverage as follows:

$$\frac{C}{\theta} = \frac{n}{K_{ads}} + nC \tag{5}$$

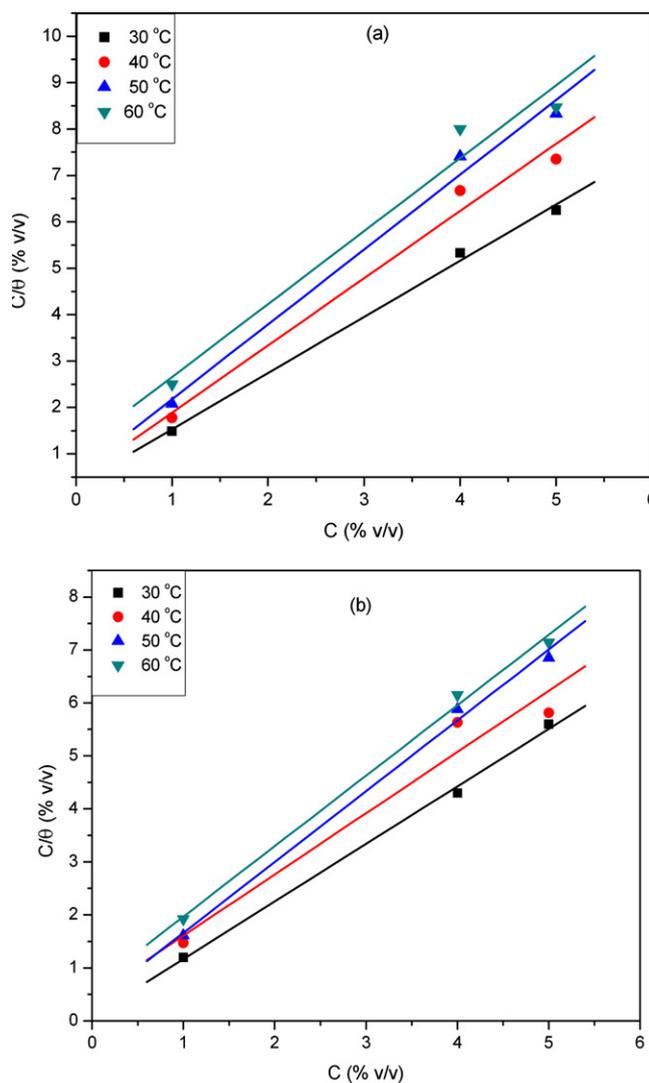


Figure 5 Langmuir adsorption model for (a) extract and (b) extract + KI at 30–60 °C.

Table 2 Some Langmuir and adsorption parameters for aluminium corrosion in 0.5 M H₂SO₄.

Temperature (°C)	R ²	K _{ads}	Slope	ΔG _{ads} ^o (kJ mol ⁻¹)	ΔH _{ads} ^o (kJ mol ⁻¹)	ΔS _{ads} ^o (J mol ⁻¹ K ⁻¹)
30	0.99	3.17	1.21	-13.05	-29.70	-54.90
40	0.99	2.26	1.44	-12.57	-29.70	-54.70
50	0.99	1.76	1.61	-12.30	-29.70	-53.80
60	0.99	0.93	1.57	-10.92	-29.70	-56.40

From the intercepts of the straight lines on the C/θ -axis, one can calculate K_{ads} , which is related to the standard free energy of adsorption, ΔG_{ads}^o by the equation below:

$$K_{ads} = \frac{1}{55.5} \exp\left(\frac{-\Delta G_{ads}^o}{RT}\right) \quad (6)$$

The calculated free energies (ΔG_{ads}^o) are given in Table 2. The negative values of ΔG_{ads}^o indicate spontaneous adsorption of the extract components onto aluminium surface (Ebenso et al., 2008) and strong interaction between extract components and the metal surface (Sibel et al., 2005). Generally, values of ΔG_{ads}^o around -20 kJ mol^{-1} or lower are consistent with the electrostatic interaction between charged organic molecules and the charged metal surface (physisorption); those around -40 kJ mol^{-1} or higher involve charge sharing or transfer from the organic molecules to the metal surface to form a co-ordinate type of bond (chemisorptions) (Obot and Obi-Egbedi, 2010). The values of ΔG_{ads}^o for *S. mombin* L. extract are less than -40 kJ mol^{-1} indicating physical adsorption mechanism.

The dependence of ΔG_{ads}^o on temperature can be explained by two cases as follows (Noor, 2007):

- ΔG_{ads}^o may increase (becomes less negative) with the increase of temperature which indicates the occurrence of exothermic process.
- ΔG_{ads}^o may decrease (becomes more negative) with increasing temperature indicating the occurrence of endothermic process.

Therefore, the increase of ΔG_{ads}^o with temperature reveals that the inhibition of aluminium by *S. mombin* L. extract is an exothermic process. In an exothermic process, adsorption is unfavourable with increasing reaction temperature due to the inhibitor desorption from the aluminium surface (Tang et al., 2003).

Thermodynamically, ΔG_{ads}^o is related to the enthalpy and entropy of the adsorption process, ΔH_{ads}^o and ΔS_{ads}^o , via:

$$\Delta G_{ads}^o = \Delta H_{ads}^o - T\Delta S_{ads}^o \quad (7)$$

The Langmuir adsorption isotherm, however, can be expressed as follows (Abdallah, 2002; Noor and Al Moubaraki, 2008):

$$\log\left(\frac{\theta}{1-\theta}\right) = \log A + \log C - \frac{Q_{ads}}{2.303RT} \quad (8)$$

where A is a constant and Q_{ads} is the heat of adsorption, equal to the enthalpy of adsorption (ΔH_{ads}^o) as a good approximation at constant pressure. If $\log(\theta/(1-\theta))$ is plotted against $1000/T$ at various extract concentrations (Fig. 6), the slopes of the linear part of these curves give $\Delta H_{ads}^o/2.303R$ from which ΔH_{ads}^o values were computed and given in Table 2. Since ΔH_{ads}^o is

negative, the adsorption of inhibitor components onto the aluminium surface is an exothermic process. In an exothermic process, physisorption can be distinguished from chemisorption by considering the absolute value of ΔH_{ads}^o . For physisorption, ΔH_{ads}^o is lower than 40 kJ mol^{-1} , while for chemisorption, ΔH_{ads}^o approaches 100 kJ mol^{-1} (Benabdellah et al., 2007). In the present study, the average value of ΔH_{ads}^o was lower than 40 kJ mol^{-1} implying that physisorption mechanism took place.

The entropy of inhibitor adsorption ΔS_{ads}^o was calculated using Eq. (7), and is presented in Table 2. ΔS_{ads}^o was negative because inhibitor molecules, freely moving in the bulk solution (inhibitor molecules were chaotic), were adsorbed in an orderly

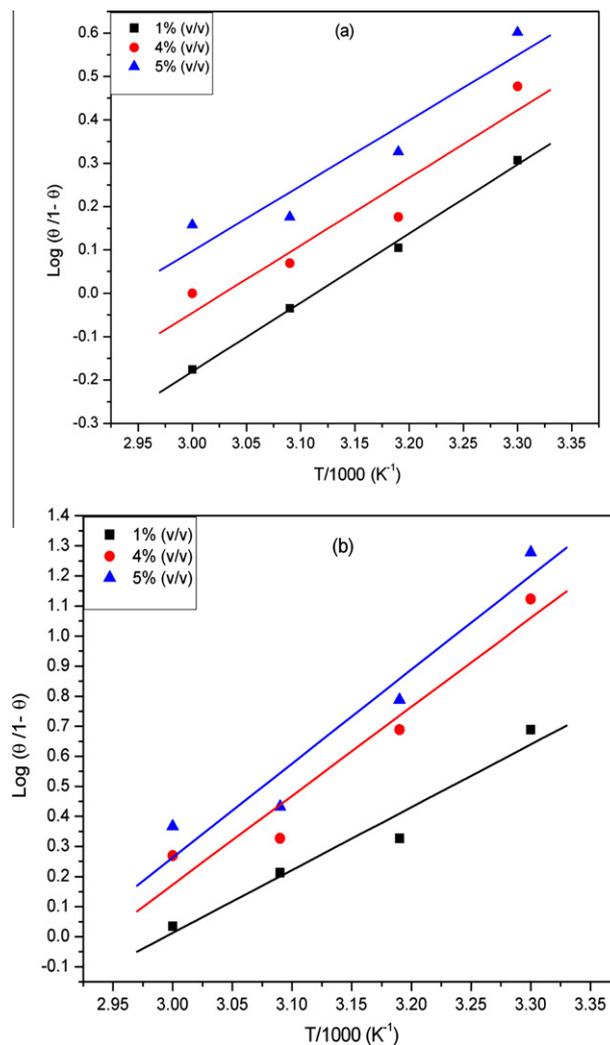


Figure 6 Plot of $\log(\theta/(1-\theta))$ versus $1/T$ for (a) extract and (b) extract + KI.

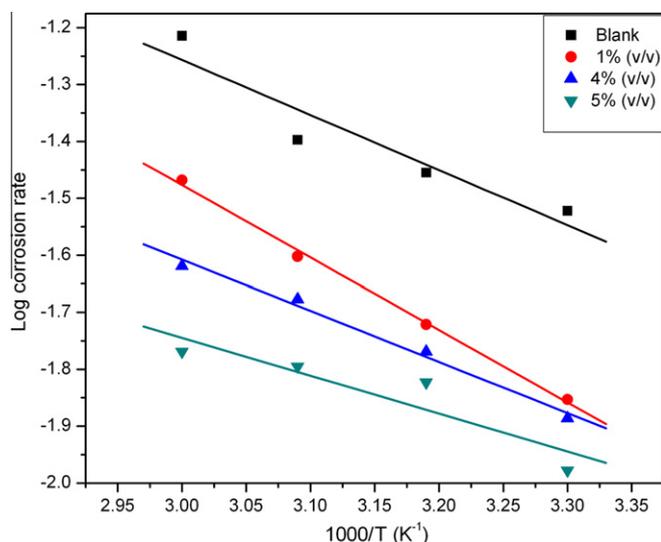


Figure 7 Arrhenius plot for aluminium corrosion in 0.5 M H₂SO₄ in the absence and presence of different concentrations of *Spondias mombin* L. extracts.

fashion onto the aluminium surface resulting in a decrease in entropy (Mu et al., 2005). In addition, as the adsorption was an exothermic process, it should have been accompanied by a decrease in entropy (Thomas and Thomas, 1981).

3.3. Effect of temperature

Temperature is an important parameter in studies on metal dissolution (de Souza and Spinelli, 2009). The corrosion rate in acid solutions, for example, increases exponentially with temperature increase because the hydrogen evolution overpotential decreases (Popova et al., 2003). To assess the effect of temperature on corrosion and corrosion inhibitive process, weight loss experiments were performed at 10 °C intervals in the temperature range of 30–60 °C in uninhibited acid (0.5 M H₂SO₄) and in inhibited solutions containing different concentrations of *S. mombin* L. extract. The relationship between the corrosion rate (ρ) of aluminium in acidic media and temperature (T) is often expressed by the Arrhenius equation:

$$\log \rho = \log A - \frac{E_a}{2.303RT} \quad (9)$$

where ρ is the corrosion rate E_a is the apparent activation energy, R is the molar gas constant (8.314 J K⁻¹ mol⁻¹), T is the absolute temperature, and A is the frequency factor. The plot of $\log \rho$ against $1/T$ for aluminium corrosion in 0.5 M H₂SO₄ in the absence and presence of different concentrations of *S. mombin* L. extract is presented in Fig. 7. The calculated energy of activation is given in Table 3. The relationships between the temperature dependence of % I of an inhibitor and the E_a can be classified into three groups according to temperature effects (Priya et al., 2008).

1. % I decreases with increase in temperature, E_a (inhibited solution) > E_a (uninhibited solution).
2. % I increases with increase in temperature, E_a (inhibited solution) < E_a (uninhibited solution).
3. % I does not change with temperature, E_a (inhibited solution) = E_a (uninhibited solution).

Table 3 Energy of Activation for aluminium corrosion in the absence and presence of different concentrations of *Spondias mombin* L. extract in 0.5 M H₂SO₄.

System/concentrations	Activation energy E_a (kJ mol ⁻¹)
Blank	18.54
1% v/v	24.34
4% v/v	32.17
5% v/v	37.76

It is clear from Table 3 that case (i) is applicable in this work, i.e. E_a in the inhibited solution is higher than that obtained for the free acid solution indicating that the corrosion reaction of aluminium is inhibited by *S. mombin* L. extract (Ebenso, 2003), hence supports the phenomenon of physical adsorption (Umoren and Obot, 2008). Higher values of E_a in the presence of inhibitor can be correlated with increasing thickness of the double layer which enhances the E_a of the corrosion process (Singh et al., 2008). It is also an indication of a strong inhibitive action of *S. mombin* L. extract by increasing energy barrier for the corrosion process, emphasizing the electrostatic character of the inhibitor's adsorption on the aluminium surface (physisorption) Obot and Obi-Egbedi, 2008. According to Damaskin (Damaskin, 1971), the value of activation energy lesser than 80 kJ mol⁻¹ and even smaller than 5 kJ mol⁻¹ represents physical adsorption. This assertion supports the experimental results obtained in the present work.

3.4. Effect of iodide ion addition

Halides have been reported to inhibit the corrosion of some metals in strong acids, and this effect depends on the ionic size and charge, the electrostatic field set up by the negative charge of the anion on adsorption sites and the nature and concentration of the halide ion (Umoren et al., 2009). It has also been reported (Umoren et al., 2006) that the inhibitive effect increases in the order Cl⁻ < Br⁻ < I⁻, which seems to

indicate that the radii of halide ions may have an important role to play. For example, the iodide ion (radius: 135 pm) is more predisposed to adsorption than is the bromide ion (radius: 114 pm) or the chloride ion (radius: 90 pm).

In the acid extracts used in this study, the majority of the organic constituents should exist as protonated species and

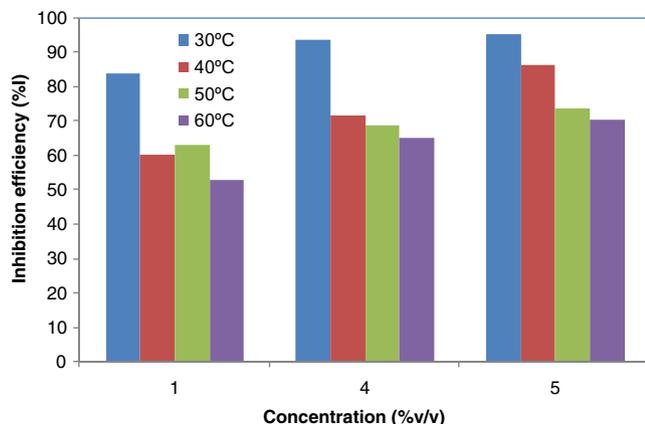


Figure 8 Variation of inhibition efficiency with concentrations of *Spondias mombin* L. extract in the presence of 5 mM KI.

others in the molecular form. The protonated species can be adsorbed onto cathodic sites on the corroding metal surface and reduce H_2 gas evolution, whereas the molecular species could be chemisorbed at active anodic sites and restrict the anodic dissolution reaction. If protonated species contribute significantly to the inhibiting effect of the extract, a synergistic increase in inhibition efficiency should be observed in the presence of halide additives. On the other hand, if molecular species in the extract are more active, the halide additives will have negligible effect (Oguzie et al., 2010). Table 1 and Fig. 8 clearly show that iodide ions remarkably enhanced the inhibition efficiency of the extract in 0.5 M H_2SO_4 , thus confirming an important role of the protonated species, which is enhanced in the presence of the iodide ions thereby resulting in improved surface coverage and inhibition efficiency. This result also corroborates the physisorption mechanism proposed for the adsorption process of *S. mombin* L. extract which is in agreement with the values of ΔG_{ads}^o , ΔH_{ads}^o and E_a obtained.

3.5. Quantum chemical calculations

In the last few decades, theoretical investigations based on quantum chemical calculations have been proposed as a powerful tool for predicting a number of molecular parameters directly related to the corrosion-inhibiting property of any

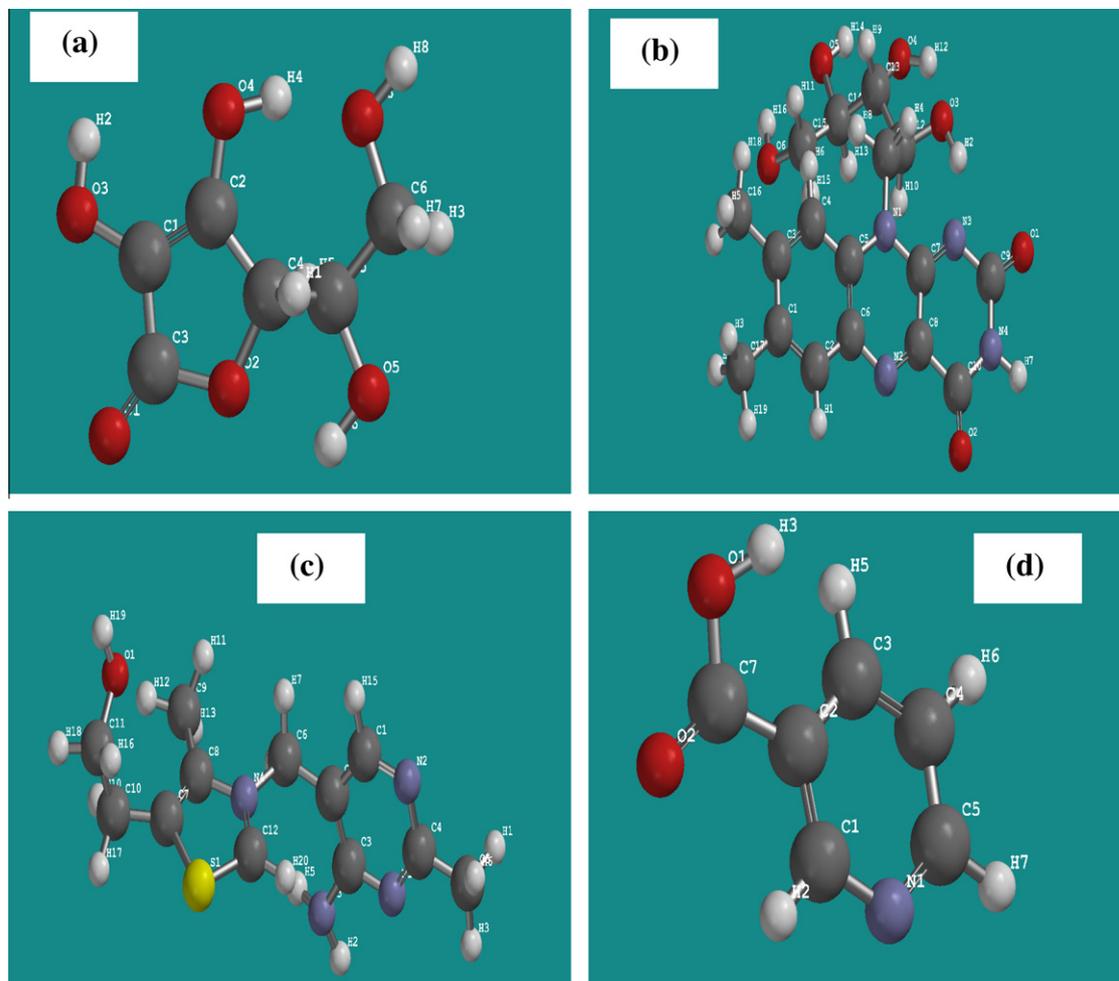
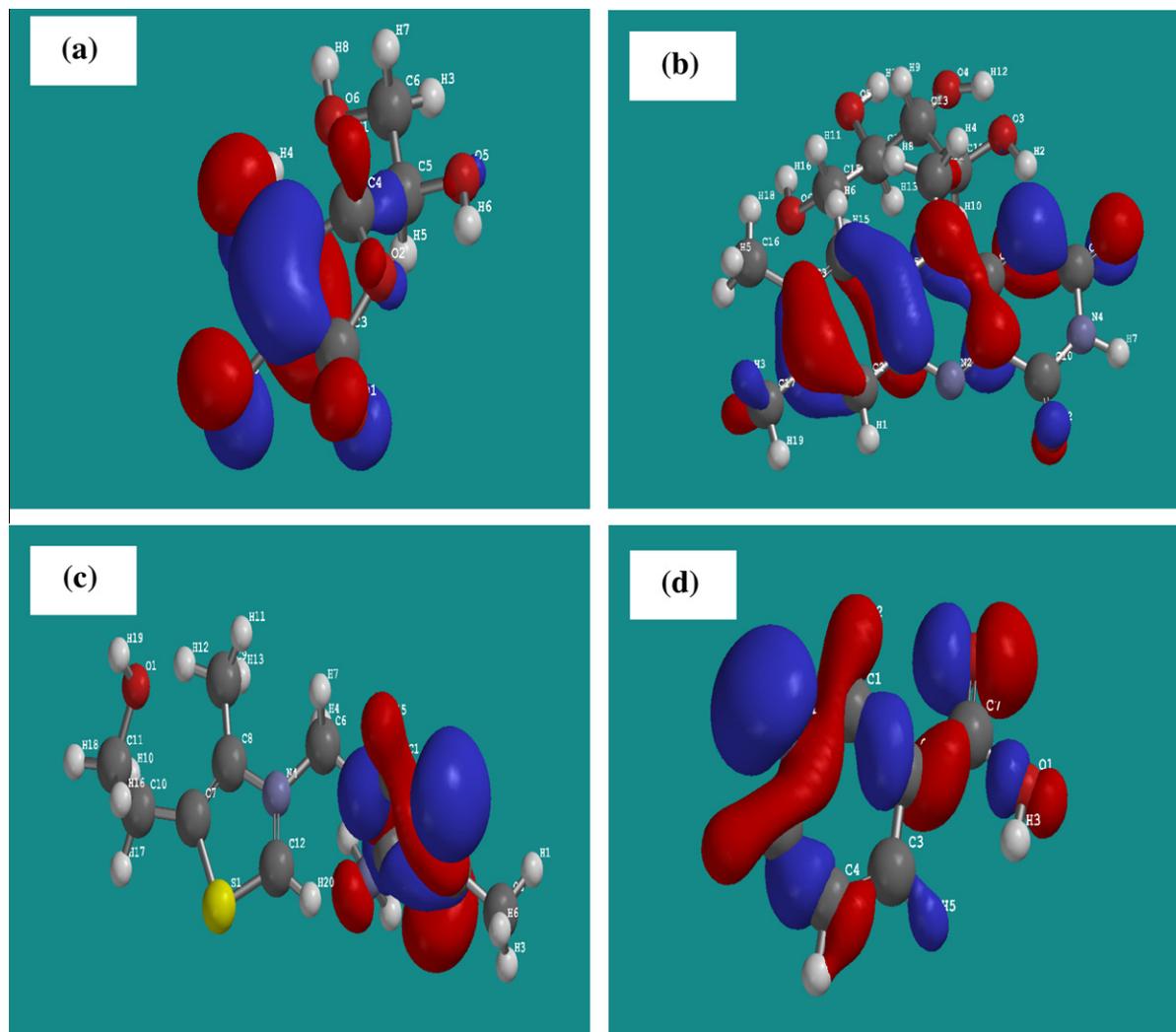


Figure 9 Optimized molecular structures of (a) AA (b) RB (c) TH and (d) NA (ball and stick models).

Table 4 Calculated quantum-chemical properties for the most stable conformations of RB, TH, AA, and NA.

Properties	RB	TH	AA	NA
Total energy (au)	-1330.27	-1159.80	-684.78	-436.86
E_{HOMO} (eV)	-6.68	-9.61	-6.03	-7.33
E_{LUMO} (eV)	-3.19	-5.58	-0.60	-1.79
$E_{\text{LUMO}}-E_{\text{HOMO}}$ (eV)	3.49	4.03	5.43	5.54
μ_{Total} (debye)	6.69	6.40	7.42	5.10
Molecular area (\AA^2)	361.77	289.75	172.79	139.61
Molecular volume (\AA^3)	347.77	263.90	148.92	120.63
Molecular weight (amu)	376.37	265.36	176.12	123.11

**Figure 10** The highest occupied molecular orbital (HOMO) density of (a) AA (b) RB (c) TH (d) NA.

chemical compound (Khaled, 2003; Bouayed et al., 1999; Jamaizadeh et al., 2008; Kutej et al., 1995). Among several theoretical methods available, the density functional theory (DFT) is one of the most important theoretical models used in explaining the science of solids and chemistry. A number of chemical concepts have been correlated within the framework of DFT (Parr and Yang, 1995). The most fundamental parameter in DFT is the electron density $\rho(r)$ upon which all

the chemical quantities are expressed (Parr and Yang, 1989). Recently, the density functional theory (DFT) has been used to analyze the characteristics of the inhibitor/surface mechanism and to describe the structural nature of the inhibitor on the corrosion process (Lashkari and Arshadi, 2004; Sein et al., 2001; Blajier and Hubin, 2004). Furthermore, DFT is considered a very useful technique to probe the inhibitor/surface interaction as well as to analyze the experimental data.

Frontier orbital theory is useful in predicting adsorption centers of the inhibitor molecules responsible for the interaction with surface metal atom (Fang and Li, 2002). Moreover, the gap between the LUMO and HOMO energy levels of the molecules was another important factor that should be considered. It has been reported that excellent corrosion inhibitors are usually those organic compounds that not only offer electrons to unoccupied orbital of the metal, but also accept free electrons from the metal (Zhao et al., 2005). It is well established in the literature that the higher the HOMO energy of the inhibitor, the greater the trend of offering electrons to unoccupied orbital of the metal, and the higher the corrosion inhibition efficiency. In addition, the lower the LUMO energy, the easier the acceptance of electrons from metal surface, as the LUMO–HOMO energy gap decreased and the efficiency of inhibitor improved. The dipole is the first derivative of the energy with respect to an applied electric field and is a measure of the asymmetry in the molecular charge distribution. A low value of the dipole moment favors accumulation of inhibitor molecules on the metal surface and is also an indication of the hydrophobic character of the molecule. Values of μ ranging from 3 to 5 have been reported in the literature (Cruz

et al., 2003; Roque et al., 2008). Figs. 9–12 show the optimized geometry, the HOMO density distribution, the LUMO density distribution and the Mulliken charge population analysis plots for Ascorbic Acid (AA), Riboflavin (RB), Thiamine (TH), and Nicotinic acid (NA) which constitute the main constituent of *S. mombin* L. extract in aqueous phase obtained with DFT at B3LYP/6-31G (d) level of theory.

The regions of highest electron density (HOMO) are the sites at which electrophiles attack and represent the active centers, with the utmost ability to bond to the metal surface, whereas the LUMO orbital can accept the electrons in the orbital of the metal using antibonding orbitals to form feedback bonds (Martinez and Stajlar, 2003). We observed that the HOMO orbital of AA is mainly around the lactone nucleus. The HOMO of RB is around the tricyclic nucleus, while the HOMO of TH is on the pyrimidine nucleus of the molecule. Finally, the HOMO of NA is located on the entire nicotinic acid (NA) moiety. The electron density (Mulliken charge centers) is saturated all over each molecule; hence we should expect flat-lying adsorption orientations.

Table 4 provides some quantum-chemical parameters related to the molecular electronic structure of the most stable

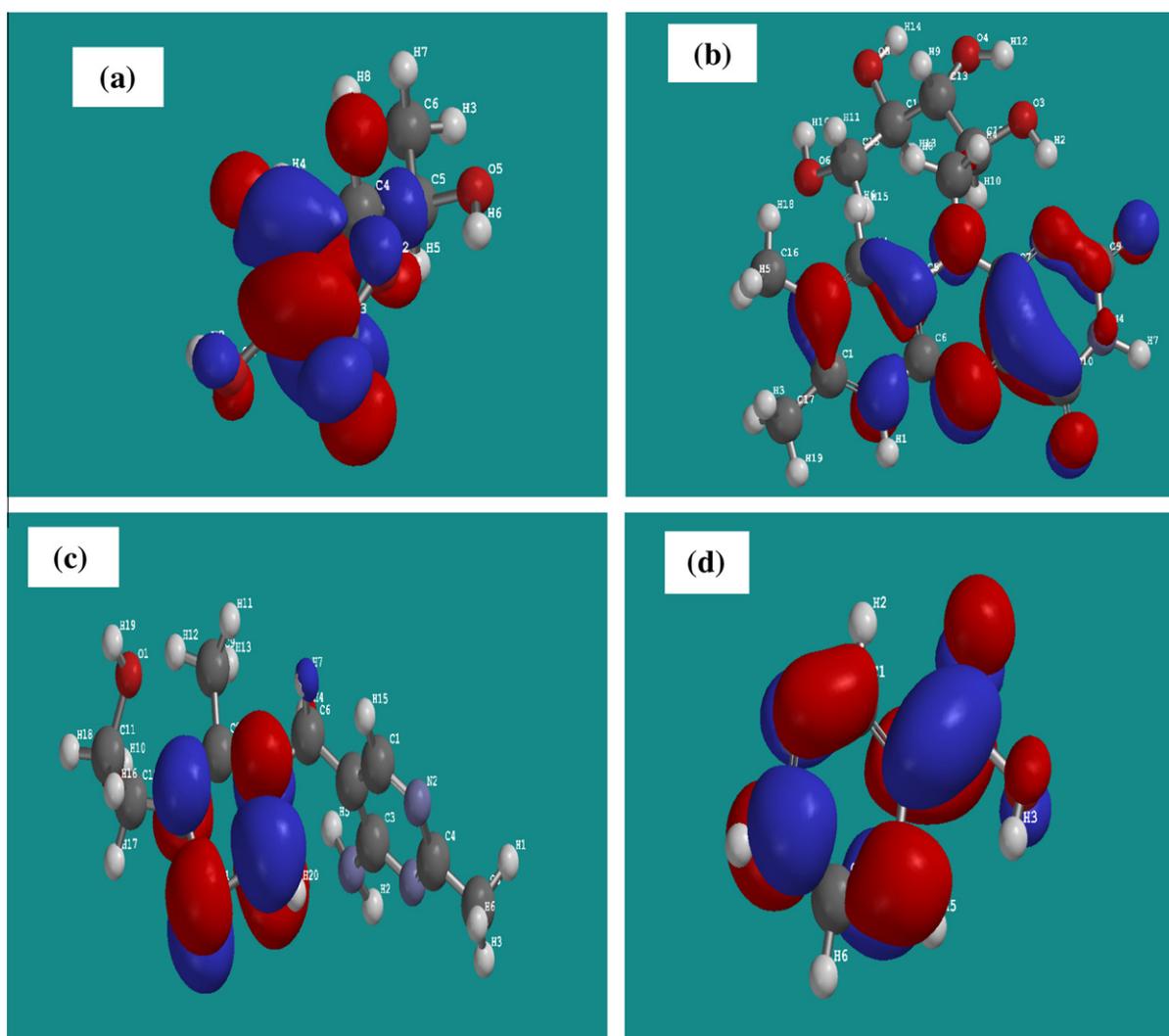


Figure 11 The lowest unoccupied molecular orbital (LUMO) density of (a) AA (b) RB (c) TH (d) NA.

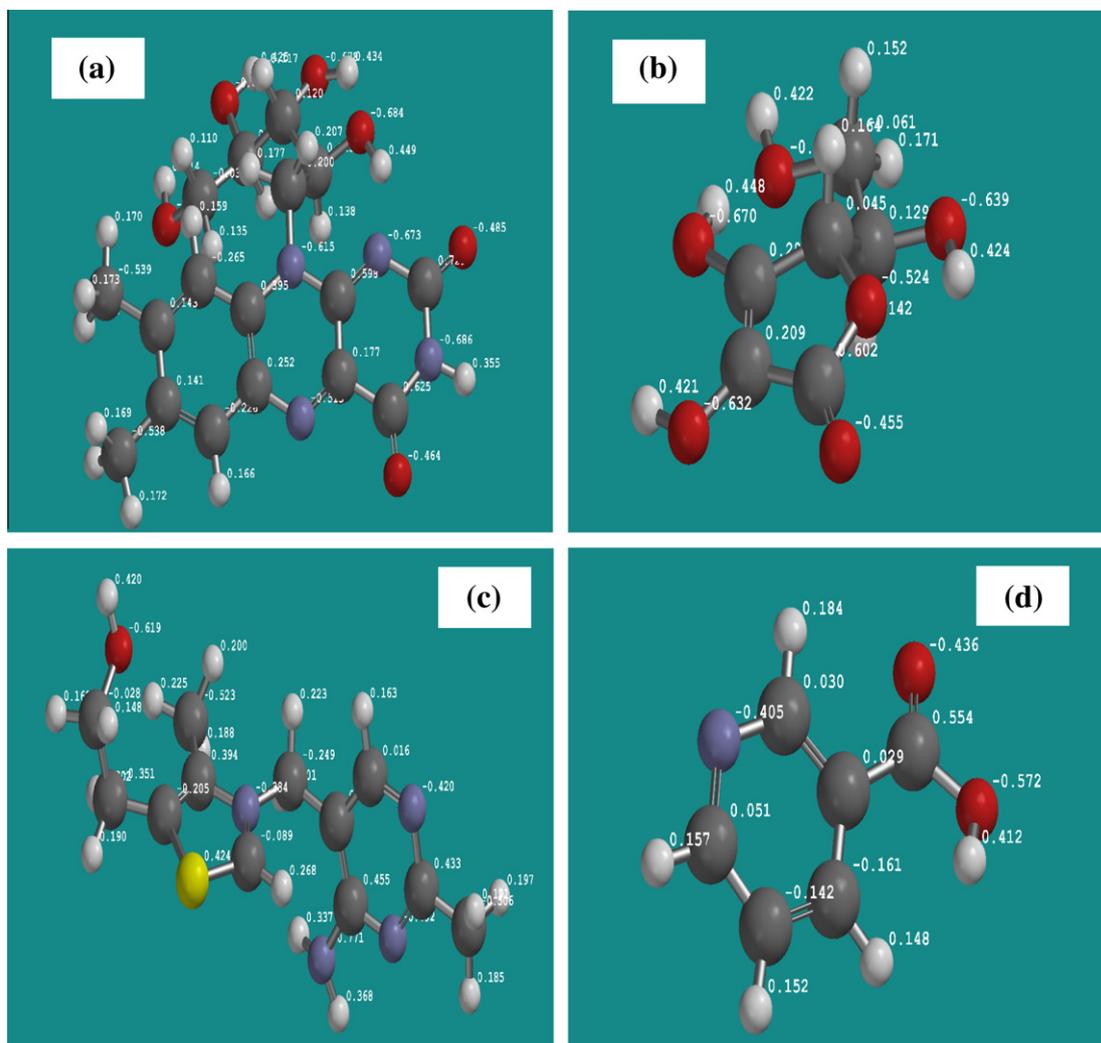


Figure 12 The Mulliken Population analysis (a) AA (b) RB (c) TH (d) NA.

conformation of the molecules. From Table 4, the obtained values do not show any well-defined and clear cut correlations, and none was actually expected, since the molecules differ considerably in their chemical structures and we do not yet know their individual inhibition efficiencies. Nonetheless, certain features point towards the individual corrosion-inhibiting efficacies of the molecules. For instance, the calculations indicate that RB has the more negative total energy, showing its high stability over the other molecules. AA has the highest HOMO energy (-6.03 eV) and highest dipole moment (7.42 D), indicating a strong tendency of the molecule to donate electrons to appropriate acceptor molecules of low empty molecular orbital energy of the metal and increasing adsorption between AA and metal surface. TH has the lowest LUMO energy showing that the molecule would readily accept electrons from the antibonding orbital of metal. Moreover, RB has the lowest ΔE value, which corresponds to higher stability of the [Al-TH] complex as well as high values of molecular area, molecular volume and molecular weight, which describes the reactivity of the inhibitor towards the metal surface (Delley, 1990).

It is clear from our theoretical studies that the corrosion-inhibiting properties of the different extract constituents do not follow any well-defined or regular trend and any one of

them could exert a dominant effect under specific conditions and concentrations. In other words, as the extract concentration is varied, certain features could become enhanced or suppressed leading to inhibition of aluminium corrosion. Similar observations have been documented on the study of *Dacryoidis edulis* extracts (Oguzie et al., 2010).

4. Conclusions

1. *S. mombin* L. extract was found to be an inhibitor for aluminium corrosion in H_2SO_4 .
2. Inhibition efficiency (%I) of the extract increased with an increase in concentration of *S. mombin* L. extract and with decrease in temperature. On the other hand, inhibition efficiency (%I) synergistically increased on addition of potassium iodide salt.
3. The adsorption of the *S. mombin* L. extract alone and in combination with the potassium iodide can be approximated by the Langmuir adsorption isotherm.
4. Activation energies were higher in the presence of *S. mombin* L. extract showing physisorption. This trend in the mechanism of inhibition was further corroborated by

the values of heat of adsorption obtained. Moreover, the adsorption process is spontaneous, exothermic and accompanied with a decrease in entropy of the system from thermodynamic point of view.

5. DFT-based quantum-chemical computations of parameters associated with the electronic structures of specific components of the extract confirmed their inhibiting potentials.
6. This present study provides new information on the inhibiting characteristics of *S. mombin* L. extract under specified conditions. The environmentally friendly inhibitor could find possible applications in metal surface anodizing and surface coating in industries.

Acknowledgements

The authors wish to acknowledge the Department of Chemistry, University of Uyo, Nigeria, for providing the facilities for the work. Professor E.E. Ebenso is also appreciated for helpful suggestions and comments.

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