# Corrosion inhibition and adsorption behaviour for aluminuim by extract of *Aningeria robusta* in HCl solution: Synergistic effect of iodide ions

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## Abstract

The corrosion inhibitive effects of *Aningeria robusta* extract for aluminium in 2 M HCl solution and the influence of potassium iodide additives on the inhibition efficiency was assessed using hydrogen evolution method at 30 and 60 °C. Inhibition efficiency was determined by comparing the corrosion rates in the absence and presence of additives. The trend of inhibition efficiency with temperature was used to propose the mechanism of inhibition. It was found that the *Aningeria robusta* 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 *Aningeria robusta* extract and with increase in temperature. On the other hand, inhibition efficiency (%I) synergistically increased on addition of potassium iodide but decreased with increase in temperature. Inhibitor adsorption characteristics were approximated by Langmuir adsorption isotherm at all the concentrations and temperatures studied. The mechanism of chemical adsorption is proposed for the *Aningeria robusta* extract and physical adsorption for the extract-iodide mixture from the trend of inhibition efficiency with temperature and from the calculated values of activation energy and heat of adsorption.

**Keywords**: Hydrogen evolution; *Aningeria robusta* extract; aluminium; corrosion; hydrochloric acid; synergism

## 1. Introduction

The corrosion of metallic materials in acidic solution causes considerable costs. In order to reduce the corrosion of metals, several techniques have been applied. The use of inhibitors during acid pickling procedure is one of the most practical methods for protection against corrosion in acidic media. Most of the effective and efficient organic inhibitors are those compounds containing hetero-atoms such as oxygen, nitrogen, sulphur, and phosphorus which allowed adsorption on the metal surface [1, 2]. To be effective, an inhibitor must also displace water from the metal surface, interact with anodic or cathodic reaction sites to retard the oxidation and reduction corrosion reaction, and prevent transportation of water and corrosion-active species on the surface. Inhibitors, which reduce corrosion on metallic materials, can be divided into three kinds: (i) inorganic inhibitors, (ii) organic inhibitors and (iii) mixed material inhibitors [3]. However, in the application of these inhibitors for corrosion control, factors such as cost, toxicity, availability and environmental friendliness are very important. Thus, recently researchers are focussing on natural product as corrosion inhibitor.

Naturally occurring substances as inhibitors of acid cleaning process has continued to receive attention as replacement for synthetic organic inhibitors [4-11]. The greatly expanded interest on naturally occurring substances is attributed to the fact that they are cheap, readily available, ecologically friendly, and posses no threat to the environment. In addition, they are biodegradable and renewable source of materials. Recent literature has shown that plant materials such as *Azadirachta indica* [12], *Occimum viridis* [13], *Strychnos nux-vomica* [14], *Prosopis cineraria* [15], *Hibiscus sabdariffa* extract [16], olives leaves [17], *Datura stramonium* [18], *Aloe vera extract* [19] as well as *Phyllantus amarus extracts* [20] are effective inhibitors for metal in aggressive solutions. Our research group has recently reported on the corrosion inhibitive effectiveness of metals by *Dacroydes edulis* [21], *Pachylobus edulis* [22], *Vigna unguiculata* [23], *Gum arabic* [24], *Raphia hookeri* [25] and the latest on *Ipomoea invulcrata* [26]. Raja [27] review in detail on the natural products as corrosion inhibitor.

The upgrading of inhibition efficiency of organic compounds in the presence of some anions, particularly halide ions, have been reported by us and other authors and was ascribed to a synergistic effect [3,28,29]. 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 thus results from increased surface coverage arising from ion-pair interactions between the organic cations and the anions.

The present work was designed as a contribution to the growing interest on environmentally beningn corrosion inhibitors to study (i) corrosion inhibition of aluminium in 2 M hydrochloric acid solutions by extracts of *Aningeria robusta* using hydrogen evolution (gasometric) method at 30 and 60 °C; (ii) to evaluate the activation energy, heat of adsorption process as well as determining the best adsorption isotherm for the adsorption of the extracts of *Aningeria robusta* onto the aluminium surface and (iii) the effect of iodide ions on the inhibition efficiency of the *Aningeria robusta* extracts.

## 2. Experimental

### *2.1. Material 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 commercially 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 different grades (# 800, 1000 and 1200) emery paper, degreased in absolute ethanol, dried in acetone and stored in a moisture-free desiccators prior to use as described previously [30, 31]. The 2 M HCl solution, prepared from BDH grade HCl was employed as the corrodent for the study.

Stock solutions of the leaves extracts of *Aningeria robusta* were prepared as reported by Abiola et al. [32]. The dried leaves were blended to powder form; 0.5 g of powder of leaves was refluxed in 100 ml of 2 M HCl 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 2 M HCl to obtain inhibitor test solutions of 10–50 %v/v concentrations. The halide salt, potassium iodide (KI, BDH) used was in the concentration range of 3 – 5 mM. However, 5 mM KI was used for the synergistic studies.

### *2.2 Hydrogen evolution measurements*

The following mechanisms can be proposed for hydrogen evolution reaction (HER) on electrodes in acidic media [33]:

1. A primary discharge step (Volmer reaction)

$$M + H_3O^+ + e \leftrightarrow MH_{ad} + H_2O \tag{1}$$

2. An electrochemical-desorption step (Heyrowsky reaction)

$$MH_{ad} + H_3O^+ + e \rightarrow M + H_2 + H_2O \tag{2}$$

3. A recombination step (Tafel reaction)

$$MH_{ad} + MH_{ad} \rightarrow 2M + H_2 \tag{3}$$

For hydrogen evolution reaction, the cathodic reaction may have three different steps: First, water molecule or hydronium ion is discharged on elecctrode surface to produce hydrogen atom in acidic solution and an adsorbed hydrogen atom, $MH_{ads}$, is generated (Volmer reaction). Second, one electron is transferred to a hydronium ion and the hydrogen evolution reaction occurs on metal surface (Heyrowsky reaction) or a pure chemical reaction takes place subsequently (Tafel reaction) [34].

In spite of three states for the formulation of the mechanism, no one of the three reactions formulated occurs as a single step but combines with another; i.e. Volmer reaction (slow) with the following Heyrowsky (faster) or Tafel (faster) reaction must be. If Volmer reaction is fast, Tafel and/or heyrowsky reaction must be slow. The step of a slow reaction follows a fast step. So, the presence of *Aningeria robusta* extract may hinder the formation of $MH_{ads}$ and supress reaction (1) or hinder the electron transfer to $H_3O^+$ ion and supress reaction (2).

Thus in monitoring the rate of hydrogen evolution from the Al coupons in the aqueous acidic medium, gasometric assembly was employed. This technique, apart from its experimental rapidity, ensures a more sensitive monitoring in situ of any perturbation by the inhibitor vis-a-vis gas evolution on the metal-corrodent interphase. Several authors have reported on comparable agreement between gasometric technique and other techniques of corrosion monitoring. These include polarization measurement [35], weight loss [36], and thermometric technique [37]. The gasometric assembly is essentially an apparatus that measures the volume of gas evolved from a corrosion reaction system. It consists of essentially a two-necked round-bottom flask that serves as the reaction medium containing the corrodent and the metal coupons. Other parts are a seperating funnel, a burrete fitted with taps, and an outer glass jacket that serves as a water condenser. The gasometric assembly is shown in Figure 1.

In monitoring corrosion studies using this technique, 100 mL of the corrodent (2 M HCl) was introduced into the two-necked flask and the initial volume of air in the burette was noted. Thereafter, an aluminium coupon weighed approximately 2 g was dropped into the corrodent and the flask was quickly closed. The volume of hydrogen gas evolved from the corrosion reaction was monitored by volume changes in the level of paraffin oil in the graduated burette at fixed time intervals [37]. In another experiment, a set of fresh coupons was immersed in the flask containing the corrodent and different concentrations of *Aningeria robusta* extracts, potassium iodide, and extract in combination with the fixed amount of potassium iodide (5 mM). The study was conducted at 30 and 60 $^{o}$C maintained using a thermostated water bath. Each experiment was repeated three times to ensure reproducibility, and the average values are reported.

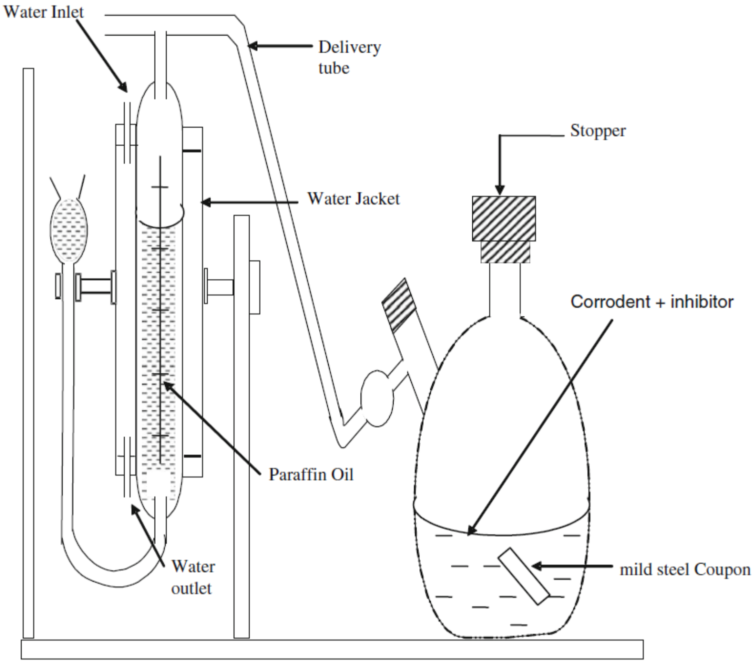

**Fig. 1.** Gasometric assembly for measurement of hydrogen gas evolved

## 3. Results and discussion

### *3.1 Hydrogen evolution and corrosion rates*

Corrosion of Al in aqueous solution has been reported [38] to depend on the concentration of anions in solution. A general mechanism for the dissolution of Al metal would be similar to that reported by Oguzie et al. [39]:

$$\text{Al (s)} + H_2O \leftrightarrow AlOH_{ads} + H^+ + e \tag{4}$$

$$AlOH_{ads} + 5H_2O + H^+ \leftrightarrow Al^{3+}.6H_2O + 2e \tag{5}$$

$$Al^{3+} + H_2O \leftrightarrow [AlOH]^{2+} + H^+ \tag{6}$$

$$[AlOH]^{2+} + X^- \leftrightarrow [AlOHX]^+ \tag{7}$$

The controlling step in the metal dissolution is the complexation reaction between the hydrated cation and the anion present Eq. (7). In the presence of chloride ions the reaction will correspond to:

$$[AlOH]^{2+} + Cl^{-} \rightarrow [AlOHCl]^{+} \tag{8}$$

The soluble complex ion formed increases the metal dissolution rate which depends on the chloride concentration.

The free corrosion of aluminium in 2 M HCl was characterized by rapid effervescence resulting from hydrogen gas evolution and corrosion rates in the absence and presence of *Aningeria robusta* extracts was calculated using hydrogen evolution measurements. Fig. 2(a) shows the volume of hydrogen evolved during the corrosion reaction of aluminium in 2 M HCl containing different concentrations of *Aningeria robusta* extracts measured as a function of reaction time at 30 $^{o}$C. The plots in Fig. 2(a) illustrate the decreased deflection of hydrogen gas evolution rate on introduction of *Aningeria robusta* extracts into the corrodent, indicating that *Aningeria robusta* extracts actually affords corrosion inhibition of aluminium in the acidic environments when compared to the blank. Similar trend was observed at 60 $^{o}$C. Further reduction in the volume of $H_2$ was also observed on the addition of the iodide ions at 30 $^{o}$C (Fig. 2(b)). Similar trend was observed at 60 $^{o}$C, but with higher values. The rates of $H_2$ gas evolution were observed to decrease with increasing *Aningeria robusta* extracts concentration, suggesting that the inhibiting action was concentration dependent. The volume of $H_2$ evolved at 60 $^{o}$C was higher than at 30 $^{o}$C.

The calculated values of hydrogen evolution rates (which can be correlated to corrosion rate) and inhibition efficiency for aluminium corrosion in 2 M HCl in the absence and presence of the additives at different temperatures are given in Table 1. The hydrogen evolution rates and inhibition efficiency were computed from Equations (9) and (10) respectively as follows:

$$CR_H = \frac{V_t - V_i}{t_t - t_i} \tag{9}$$

where $V_t$ and $V_i$ are the volumes of hydrogen evolved at time $t_t$ and $t_i$, respectively.

$$\%I = \left( \frac{CR_{blank} - CR_{inh}}{CR_{blank}} \right) x100 \tag{10}$$

where $CR_{blank}$ and $CR_{inh}$ are the hydrogen evolution rates in the absence and presence of the inhibitor and inhibitor-iodide mixtures respectively.

Results in Table 1 show that corrosion rates were reduced in the presence of *Aningeria robusta* extracts and extracts-iodide mixtures compared to the blank acid solution. Inspection of the table further reveals that corrosion rate of aluminium in the presence of the extracts decreases with increase in concentration, indicating that the protection ability of *Aningeria robusta* extracts was concentration dependent. Also, corrosion rate is seen to increase with temperature rise both in the absence and in the presence of the additives. Addition of potassium iodide to the extracts causes further reduction in the corrosion rate at all the temperatures studied with the most pronounced reduction recorded for addition of 5 mM potassium iodide. From Table 1, it is observed that inhibition efficiency increases with increase in the concentration of *Aningeria robusta* extracts and with temperature. Increase in inhibition efficiency with increase in temperature is suggestive of chemical adsorption of *Aningeria robusta* extracts components onto the aluminium surface. On the other hand, inhibition efficiency decreases with increase in temperature in the presence of extract-iodide mixtures suggesting physical adsorption mechanism.

Plant products are organic in nature, containing constituents such as tannins, organic and amino acids, alkaloids, and pigments that are known to exhibit inhibiting action [40]. Perusal of literature reveal that no phytochemical study has yet been carried out on the plant but preliminary phytochemical investigation in our laboratory showed that *Aningeria robusta* extracts contains tannins, saponins, flavonoids and cardiac glycoside. It is therefore, pertinent to say that the adsorption of these compounds onto aluminium surface is responsible for corrosion inhibition effect. One of the main criticisms of the use of plant extract as corrosion inhibitors is the inability to pinpoint the major active component that is responsible for the inhibiting action owing to the complex chemical composition of the crude extract. However, further investigation and the use of surface analytical techniques will enable the characterization of the active materials in the adsorbed layer, and assist in identifying the most active ingredients in the extract of *Aningeria robusta* extracts which is currently being pursued in our laboratory. The adsorption of these compounds on the metal surface reduces the surface area available for corrosion.

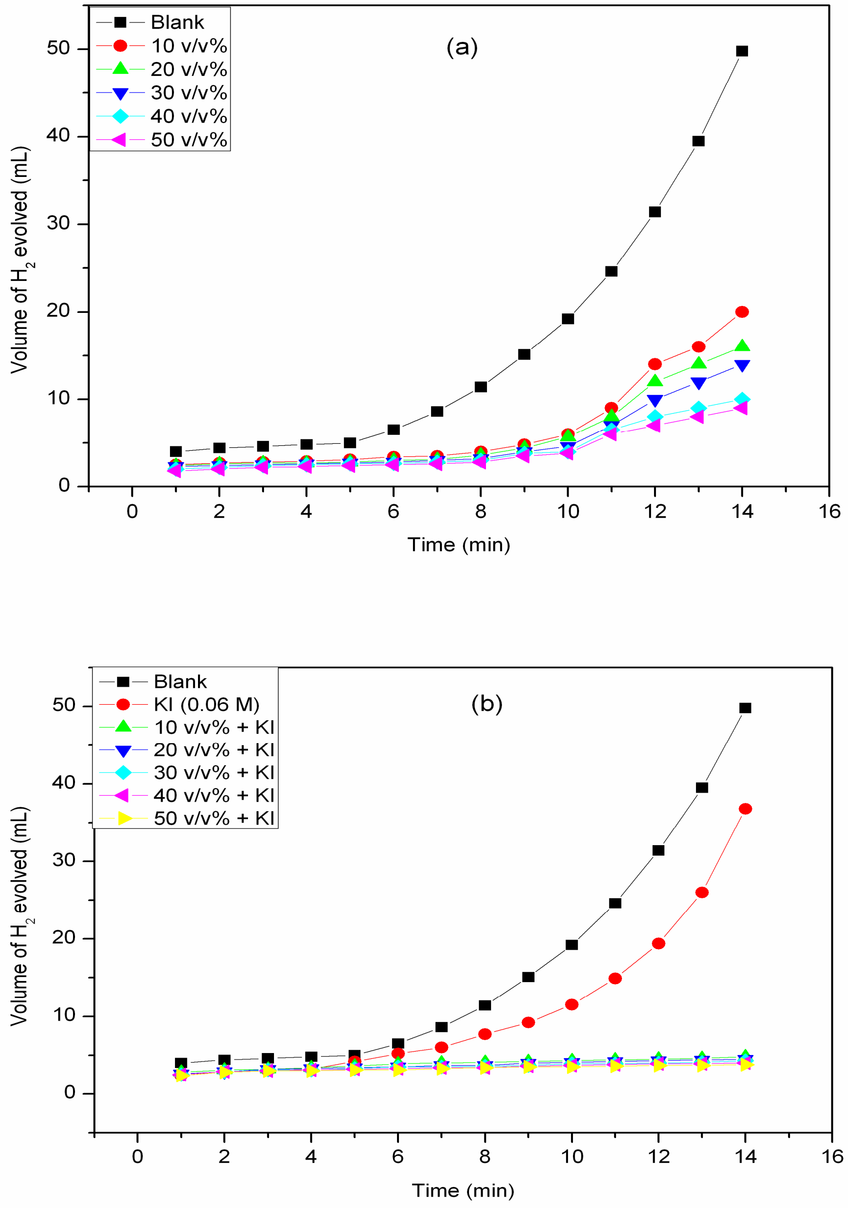

Fig. 2. Variation of volume of $H_2$ evolved with time for aluminium corrosion in 2 M HCl in the presence of (a) extract alone and (b) extract + KI at 30 $^{o}$C

Table 1. Calculated values of hydrogen evolution rate and inhibition efficiency for aluminium in 2 M HCl in the absence and presence of *Aningeria robusta* extract, 5 mM KI and extract-iodide mixtures at 30 and 60 °C from hydrogen evolution measurements.

| System/concentration | Hydrogen evolution rate (mL min$^{-1}$) | | Inhibition efficiency (%I) | |
|---|---|---|---|---|
| | 30 °C | 60 °C | 30 °C | 60 °C |
| Blank | 3.1 | 10.8 | - | - |
| 5 mM KI | 2.4 | 6.1 | 23 | 44 |
| 10 %v/v | 2.6 | 8.8 | 16 | 19 |
| 20 %v/v | 2.5 | 7.0 | 19 | 35 |
| 30 % v/v | 2.4 | 6.6 | 23 | 39 |
| 40 %v/v | 2.2 | 6.1 | 29 | 44 |
| 50 %v/v | 1.8 | 5.6 | 65 | 48 |
| 10 %v/v + KI | 1.1 | 5.0 | 65 | 54 |
| 20 %v/v + KI | 0.8 | 4.9 | 74 | 55 |
| 30 %v/v +KI | 0.7 | 4.5 | 77 | 58 |
| 40 %v/v +KI | 0.6 | 3.9 | 81 | 64 |
| 50 %v/v + KI | 0.3 | 3.0 | 90 | 72 |

### *3.2 Adsorption considerations*

The effectiveness of organic compounds as corrosion inhibitors can be ascribed to the adsorption of molecules of the inhibitors through their polar functions on the metal surface. Some authors [41, 42] have pointed out that adsorption on corroding surfaces never reaches the real equilibrium and tends to an adsorption steady state. However, when the corrosion rate is sufficiently small, the adsorption steady has a tendency to become quasi-equilibruim state. Therefore, it is reasonable to consider the quasi-equilibrium adsorption in a thermodynamic manner using the appropraite equilibrium isotherms. Adsorption isotherms provide information about the interaction among adsorbed molecules themselves as well as their interactions with the metal surface. Surface coverage values were evaluated from the hydrogen evolution measurements assuming direct relationship between inhibition efficiency and surface coverage as follows: $\%I = \theta \times 100$. The surface coverage values were fitted to different adsorption isotherm models and best results judged by the correlation coefficient ($R^2$) was obtained with Langmuir adsorption isotherm. Langmuir isotherm is given by the expression:

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \tag{11}$$

where $\theta$ is the surface coverage, C is the concentration, $K_{ads}$ is the equilibrium constant of adsorption process.

The plot of $C/\theta$ against C is shown in Fig. 3. Linear plots were obtained with very good correlation coefficient which seems to suggest that adsorption of the extract alone and on addition of iodide ions follow Langmuir adsorption isotherm. The Langmuir adsorption parameters in the presence of extracts and extract-iodide mixture is presentable in Table 2.

From the table, it is clearly seen that $K_{ads}$ values are in the order extract-iodide mixture > extract alone. Large values of $K_{ads}$ imply more efficient adsorption hence better inhibition efficiency [9].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 [26]. Given the complex composition of the extract, the different component 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 this temperature can be more appropraitely represented by a modified Langmuir equation suggested by Villamil et al. [43] taking into consideration the interactions between adsorbate species as well as changes in heat of adsorption with changing surface coverage as follows:

$$\frac{C}{\theta} = \frac{n}{K_{ads}} + nC \tag{12}$$

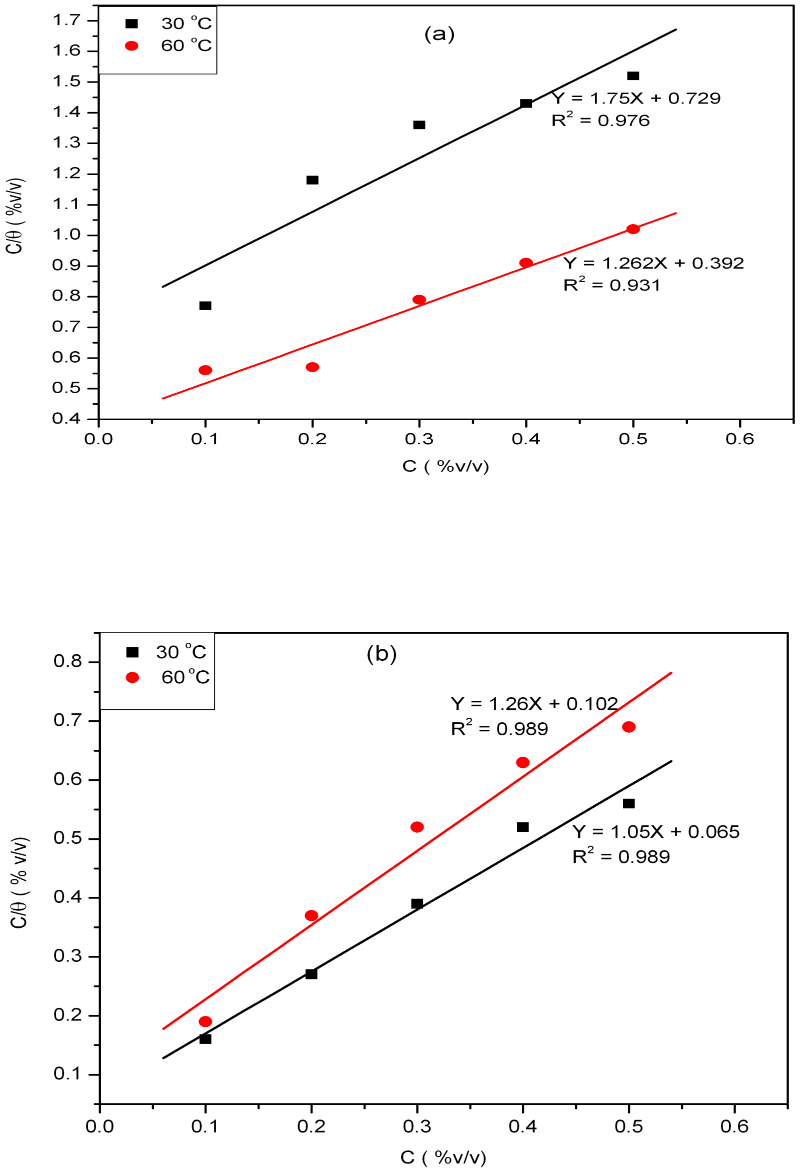

Fig. 3. Langmuir isotherm plot for (a) extract alone and (b) extract + KI at 30 and 60 $^{o}$C

Table 2. Some parameters from Langmuir isotherm model for aluminium in 2 M HCl.

| System/Concentration | Temperature ($^{o}$C) | $K_{ads}$ | ($R^2$) | Slope |
|---|---|---|---|---|
| *Aningeria robusta* Extract | 30 | 1.4 | 0.931 | 1.75 |
| | 60 | 2.6 | 0.976 | 1.26 |
| *Aningeria robusta* Extract + KI | 30 | 15.4 | 0.989 | 1.05 |
| | 60 | 9.8 | 0.982 | 1.26 |

Table 3. Calculated values of activation energy ($E_a$) and heat of adsorption ($Q_{ads}$) for Al dissolution in 2M HCl in the absence and presence of *Aningeria robusta* extract and extract + KI mixtures at 30- 60 $^oC$

| System/concentration | $E_a$($kJmol^{-1}$) | $Q_{ads}$ ($kJ\ mol^{-1}$) |
|---|---|---|
| Blank (2 M HCl) | 35.2 | – |
| 10% v/v | 33.3 | 10.7 |
| 20% v/v | 28.2 | 27.0 |
| 30% v/v | 28.6 | 21.7 |
| 40% v/v | 28.1 | 19.6 |
| 50% v/v | 31.4 | 19.1 |
| 10% v/v + KI | 42.2 | –12.7 |
| 20% v/v + KI | 50.7 | –24.7 |
| 30% v/v + KI | 50.8 | –23.2 |
| 40% v/v + KI | 47.2 | –17.7 |
| 50% v/v + KI | 62.5 | –32.1 |

### *3.3 Effect of Temperature*

When the electrochemical corrosion reaction involves a cathodic process of hydrogen depolarization, the corrosion rate increases exponentially with rise in temperature, according to Arrhenius-type dependence. Thus, the influence of temperature on the corrosion behaviour of Al in 2M HCl in the absence and presence of *Aningeria robusta extract* of varying concentrations and extract-iodide mixtures were investigated by hydrogen evolution method at 30 and 60°C. In examining the effect of temperature on the corrosion inhibition process, the apparent activation energies ($E_a$) were calculated from the Arrhenius equation [33]:

$$\log\frac{\rho_2}{\rho_1} = \frac{E_a}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{13}$$

where $\rho_2$ and $\rho_1$ are the corrosion rates at temperature $T_1$ and $T_2$ respectively, and R the molar gas constant. An estimate of heat of adsorption was obtained from the trend of surface coverage with temperature as follows [44]:

$$Q_{ads} = 2.303R\left[\log\left(\frac{\theta_2}{1-\theta_2}\right) - \log\left(\frac{\theta_1}{1-\theta_1}\right)\right]x\left(\frac{T_{1X}T_2}{T_2 - T_1}\right)kJmol^{-1} \tag{14}$$

where $\theta_1$ and $\theta_2$ are the degrees of surface coverage at temperatures $T_1$ and $T_2$, The calculated values for both parameters are given in Table 3.

Increased activation energy ($E_a$) in inhibited solutions compared to the blank suggests that the inhibitor is physically adsorbed on the corroding metal surface while either unchanged or lower $E_a$ in the presence of inhibitor suggest chemisorptions [45]. It is seen from Table 3 that $E_a$ values were lower in the presence of *Aningeria robusta extract* compared to that in their absence hence leading to reduction in the corrosion rates. On the other hand the reverse is the case in the presence of extract-iodide mixture. It has been suggested that adsorption of an organic inhibitor can affect the corrosion rate by either decreasing the available reaction area (geometric blocking effect) or by modifying the activation energy of the anodic or cathodic reactions occurring in the inhibitor-free surface in the course of the inhibited corrosion process [46]. The $E_a$ values support the earlier proposed chemisorption mechanism for *Aningeria robusta extract* and physisorption mechanism for extract-iodide mixtures respectively. Hence, corrosion inhibition is assumed to occur primarily through chemical adsorption on the aluminium surface in the presence of

*Aningeria robusta extract*, giving rise to the activation of these surfaces to hydrogen atom recombination. Similar results have been reported in earlier publications [45, 47].

The positive $Q_{ads}$ values indicate that the degree of surface coverage increased with rise in temperature, supporting the earlier proposed chemisorption mechanism for *Aningeria robusta extract* and the negative $Q_{ads}$ values indicates that the degree of surface coverage decreases with rise in temperature in the presence of extract-iodide mixtures supporting physisorption mechanism [24].

### 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 [48]. It has also been reported [40] 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: 135pm) is more predisposed to adsorption than is the bromide ion (radius: 114pm) or the chloride ion (radius: 90pm).

From Table 1, it is seen that the inhibition efficiency of *Aningeria robusta* extract alone attains a maximum value of 48% (50% v/v) at 60 $^oC$. The addition of 5 mM KI to the *Aningeria robusta* extract solution enhances the value of inhibition efficiency significantly up to 90% (50% v/v) at 30 $^oC$. This synergistic effect is found to increase with increase in the concentration of *Aningeria robusta* extract. The synergistic inhibitive effect brought about by the concentrations of *Aningeria robusta* extract and iodide ions on the corrosion of Al in 2 M HCl can be explained as follows. The strong chemisorptions of iodide ions on the metal surface is responsible for the synergistic effect of iodide ion, in combination with *Aningeria robusta* extract components in their cationic forms [49]. The extract components are then adsorbed by coulombic attraction on the metal surface where iodide ions are already adsorbed by chemisorptions. Stabilization of adsorbed iodide ions with extract components in cationic forms lead to greater surface coverage and thereby greater inhibition [40].

The synergistic parameters were calculated using the relationship initially given by Aramaki and Hackerman and reported elsewhere [50]:

$$S_1 = \frac{1 - I_{1+2}}{1 - I'_{1+2}} \tag{15}$$

where $I_{1+2}= (I_1 + I_2)$; $I_1$ = inhibition efficiency of the iodide; $I_2$ = inhibition efficiency of *Aningeria robusta* extract; $I`_{1+2}$ = measured inhibition efficiency for the *Aningeria robusta* extract in combination with iodide ions. $S_1$ approaches 1 when no interaction between the inhibitor compounds exists, while $S_1 > 1$ points to a synergistic effect. In the case $S_1 < 1$, the antagonistic interaction prevails, which may be attributed to competitive adsorption. Values of $S_1$ for different concentrations of *Aningeria robusta* extract in combination with iodide ion are given in Table 4. $S_1$ values given in Table 4 are more than unity, thereby suggesting that the enhanced inhibition efficiency caused by the addition of iodide ions to *Aningeria robusta* extract is only due to synergistic effect. Thus it can be suggested that iodide ion ($I^-$) is initially adsorbed on the metal surface, *Aningeria robusta* extract components in the form of cation are then adsorbed by the coulombic attraction on the metal surface, where the iodide ions are already chemisorbed and thus suppresses the self-corrosion rate by the stabilization of the adsorbed anion and by the increase in surface coverage. Furthermore, the *Aningeria robusta* extract organic cation itself is weakly adsorbed on aluminium, since the metal surface is positively charged in HCl solution [51]. However, adsorption of iodide ion caused a decrease in the positive charge of Al due to formation of Al-anion surface bond, which produces a negative pole, facilitating the adsorption of the organic cation from *Aningeria robusta* extract.

Table 4. Synergistic parameters ($S_1$)

| Concentrations of *Aningeria robusta* extract | Synergism parameter ($S_1$) |
|---|---|
| 10 %v/v | 1.16 |
| 20 %v/v | 1.43 |
| 30 %v/v | 1.43 |
| 40 %v/v | 1.37 |
| 50 %v/v | 1.35 |

## 4. Conclusion

1. *Aningeria robusta* extract was found to be an inhibitor for aluminium corrosion in HCl.
2. Inhibition efficiency (%I) of the extract increased with an increase in concentration of *Aningeria robusta* extract and with increase in temperature. On the other hand, inhibition efficiency (%I) synergistically increased on addition of potassium iodide but decreased with increase in temperature.
3. The adsorption of the *Aningeria robusta* extract alone and in combination with the potassium iodide can be approximated by the Langmuir adsorption isotherm.
4. Activation energies were lower in the presence of the *Aningeria robusta* extract suggesting a chemisorption mechanism while activation energies were higher in the presence of extract-iodide mixture showing physisorption. This trend in the mechanism of inhibition was futher corroborated by the values of heat of adsorption obtained..
5. This present study provides new information on the inhibiting characteristics of *Aningeria robusta* extract under specified conditions. The environmentally friendly inhibitor could find possible applications in metal surface anodizing and surface coating in industries.

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