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Synergistic and Antagonistic Effects of Anions and *Ipomoea invulcrata* as Green Corrosion Inhibitor for Aluminium Dissolution in Acidic Medium

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The extract of *Ipomoea invulcrata* (IP) has been studied as a possible source of green inhibitor for corrosion of aluminium in 1 M HCl at 30-60 °C using the conventional weight loss technique. The studies reveal that at constant acid concentration, the plant extract acts as an effective inhibitor for aluminium corrosion in acidic medium. Inhibition efficiency increases with concentration but decreases with increase in temperature and immersion time. The enhancement of inhibition efficiency of IP with the addition of KI and KSCN has also been studied. The apparent activation energy and the thermodynamic parameters governing the corrosion process have also been calculated. The adsorption of IP was in accord with the Langmuir adsorption isotherm at all the temperature studied. The mechanism of physical adsorption is proposed for the inhibitory action of IP and is satisfactorily explained by both kinetic and thermodynamic parameters.

Keywords: Ipomoea involcrata, aluminium, corrosion inhibition, adsorption isotherm, thermodynamics.

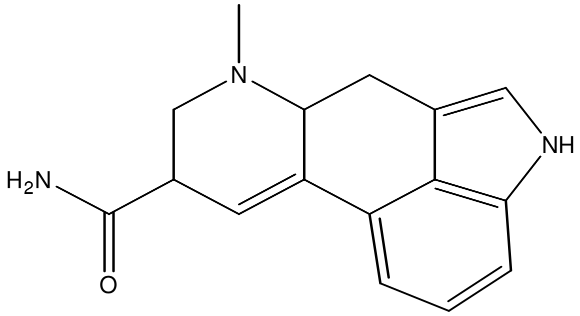
1. INTRODUCTION

The corrosion inhibition of metals in acidic environment can be achieved by the addition of inhibitors to the system that prevent corrosion from taking place on the metal surface. Inhibitors are chemicals that often work by adsorbing themselves on the metallic surface, protecting the metal surface by forming a film [1].

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 [2], clotrimazole [3], 2,3-diaminonaphthalene [4], pyridine and its derivatives [5], tetrazole derivatives [5] and purine [7] 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 renewable sources of materials [8]. The extracts from their leaves, barks, seeds, fruits and roots comprise of mixtures of organic compounds containing nitrogen, sulphur, and oxygen atoms and some [9-13] have been reported to function as effective inhibitor of metal corrosion in different aggressive environments. Recent literatures have shown a growing trend in the use of natural products of plant origin otherwise known as ‘green’ inhibitors for corrosion inhibition of metals, e.g. limonene [14] *Prosopis cineraria* [15], zallouh root [16], olives leaves [17], *Datura stramonium* [18] and *Sansevieria trifasciata* [19]. For a detailed review of natural products as corrosion inhibitors see [20]. Among plant materials tested in our laboratory to date include *Dacroydes edulis* [21], *Pachylobus edulis* [22], *Vigna unguiculata* [23], *Gum arabic* [24] and *Raphia hookeri* [25]. Despite the great availability and varieties of plant materials only relatively few have been thoroughly investigated. The present report continues to focus on the broadening application of plant extracts for metallic corrosion control.

Ipomoea involcrata (IP) (Family: *Convolulaceae*) is a common ornamental vine with heart shaped and bright white pink or purple flowers that has a long history of use in central to southern Mexico. The plant has been shown to contain mainly d-lysergic acid amide (LSA) (Fig.1) and small amounts of other alkaloids namely: chanoclavine, elymoclavine, and ergometrine and d-isolysergic acid amide [26].



7-Methyl-4,6,6a,7,8,9-hexahydro-indolo[4,3-fg]quinoline-9-carboxamide

Figure 1. The chemical structure and name of d-lysergic acid amide.

However, it has never been tested as corrosion inhibitor for aluminium in acidic medium. Thus in the present communication, we report the inhibition of aluminium corrosion using the leave extracts of *Ipomoea involcrata* by weight loss method at 30-60 °C. The effect of anions addition namely KI and KSCN on the inhibition efficiency of IP is also reported.

2. EXPERIMENTAL

The aluminium sheets of the type AA 1060 and purity 98.8% were obtained from Sky Aluminium Ltd, Uyo, Nigeria and of the same composition as those reported previously [22-26]. The test coupons were prepared, degreased and cleaned as previously described [22-26]. All chemicals used were of Analar grade. The procedure for the preparation of the IP extracts is similar to that reported recently by us [26]. *Ipomoea involcrata* were collected from Itak, Akwa Ibom State, Nigeria. They were dried in an N53C-Genlab Laboratory oven at 50 °C, and ground to powder form. Ten gram of the powder was digested in 1 L of 1 M HCl solution. The resultant solution was kept for 24 h, filtered and stored. From the stock solution, the leaves extract test solutions were prepared at concentrations range of 10, 30 and 50% v/v. However, for synergistic studies the concentrations of KI and KSCN prepared and used was 0.005 M.

The apparatus and procedure for weight loss determination of corrosion rates have been widely reported [2, 3]. Experiments were conducted in the test solutions for 4 h progressively for 24 h at 30 - 60 °C in aerated solutions. In each experiment, the cleaned aluminium coupon was weighed and suspended with the aid of glass rod and hook in a beaker containing 100 ml acid solution. The coupon was then taken out of the test solution, washed in 70% nitric acid for 2 minutes to remove the corrosion products using bristle brush, rinsed with distilled water, dried and re-weighed. The weight loss was taken as the difference between the weight at a given time and the initial weight of the test coupon determined using LP 120 digital balance with sensitivity of ±1 mg. The tests were performed in duplicate to guarantee the reliability of the results and the mean value of the weight loss is reported. The reproducibility of the experiment was higher than 95%. Weight loss allowed calculation of the mean corrosion rate in mg cm^{-2} h^{-1}.

The corrosion rate of mild steel was determined using the relation

$$W = \frac{\Delta m}{St} \tag{1}$$

where Δm is the mass loss, S the area and t is the immersion period. The percentage inhibition efficiency (E (%)) was calculated using the relationship

$$E(\%) = \left(\frac{W_{corr} - W_{corr(inh)}}{W_{corr}} \right) x100 \tag{2}$$

where W_{corr} and $W_{corr(inh)}$ are the corrosion rates of Al in the absence and presence of *Ipomoea involcrata* respectively.

3. RESULTS AND DISCUSSION

3.1. Effect of concentrations of IP extract on the weight loss of Al

The weight loss method of monitoring corrosion rate is useful because of its simple application and reliability. Although there are many experimental techniques which can be used to evaluate the inhibition efficiency of IP, weight loss is probably the most widely and frequently used method [2, 5, 9, 10, 14, 16, 22-25].

Thus, the weight loss plot of Al with the addition of IP extracts in 1 M HCl at various temperatures is shown in Fig. 2.

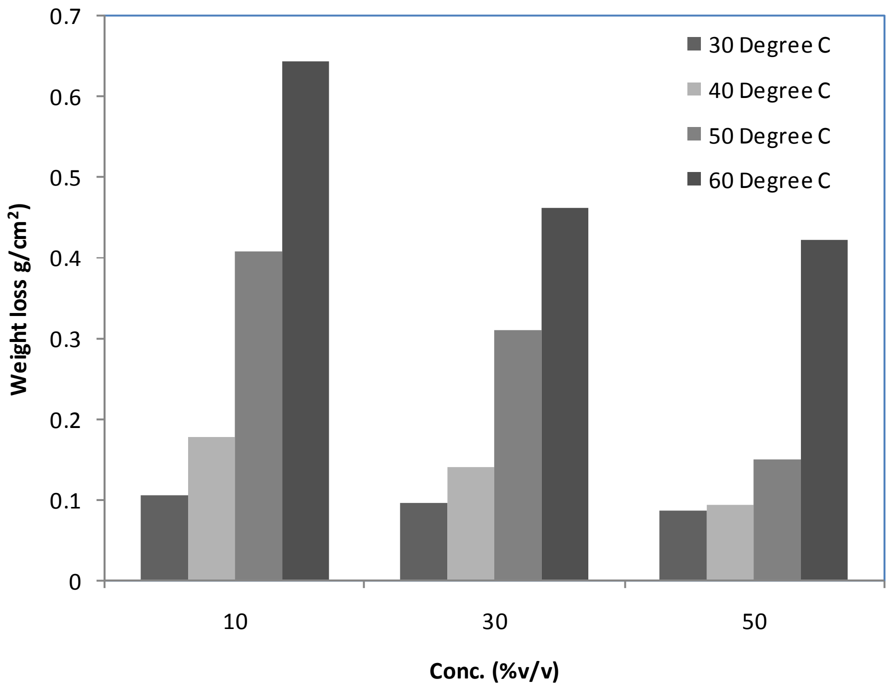


Figure 2. Relationship between weight loss of Al and concentration of IP extracts in 1 M HCl.

It is clear from the plot that the weight loss values of Al in 1 M HCl solution containing IP extracts decreases as the concentration of the inhibitor increases. i.e. the corrosion inhibition is strengthens with the IP extracts concentration. This trend results from the increase adsorption of organic compounds present in the IP extracts onto the Al surface. As a result, the Al surface is effectively separated from the acid medium [3, 27].

3.2. Effect of IP extracts concentration and temperature on inhibition efficiency

The plot of inhibition efficiency against extract concentration of IP in 1 M HCl at 30 - 60 ^{o}C obtained from weight loss measurements is shown in Fig.3.

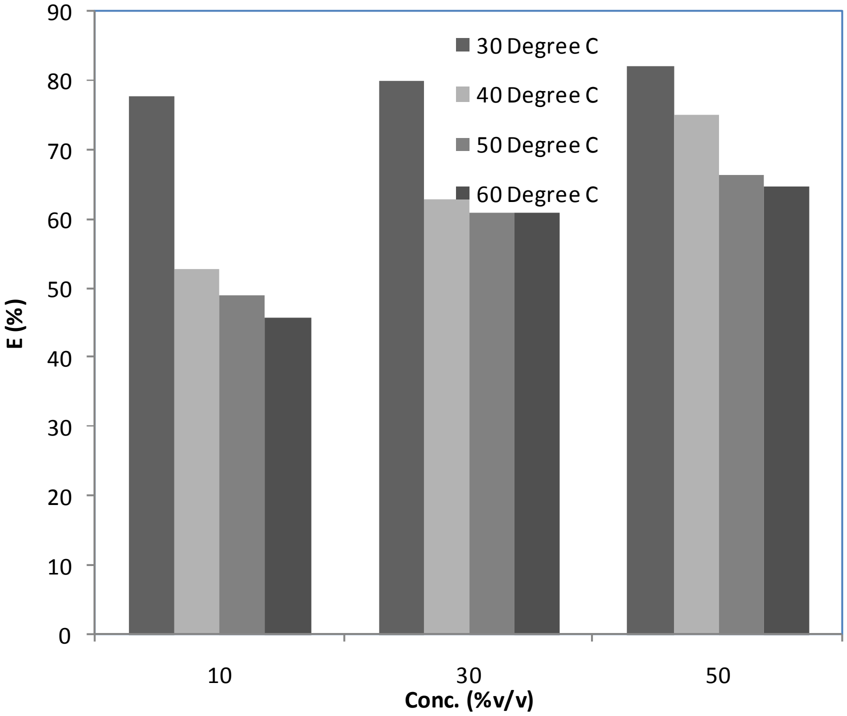


Figure 3. Relationship between inhibition efficiency E(%) and concentration of IP extracts in I M HCl.

The figure shows that inhibition efficiency increases with increase in concentration of IP extract. The maximum inhibition efficiency was 82.1% at 30 ^{o}C with inhibitor concentration of 50% v/v. This clearly shows that the inhibition of Al corrosion in 1 M HCl by extracts of IP is concentration dependent.

Also from Fig.3, inhibition efficiencies were found to decrease with increase in experimental temperature. This is an indication that at higher temperatures there might be a desorption of IP extracts from the Al surface. According to Obot and Obi-Egbedi [2, 4] and corroborated by Umoren et al. [21, 22], increase in inhibition efficiency with increase in temperature is an indication that the adsorption of IP extracts on Al surface is physical in nature

3.3. Effect of immersion time on inhibition efficiency

Fig. 4 shows the effect of changing immersion time (4 - 24 h) at 30 ^{o}C on the inhibition efficiency of IP extracts at different concentrations. It can be seen from the figure that inhibition efficiency is 82.1% when the immersion time is only 4 h, which indicates that the adsorption rate of IP extracts adsorb on the Al surface is relatively high.

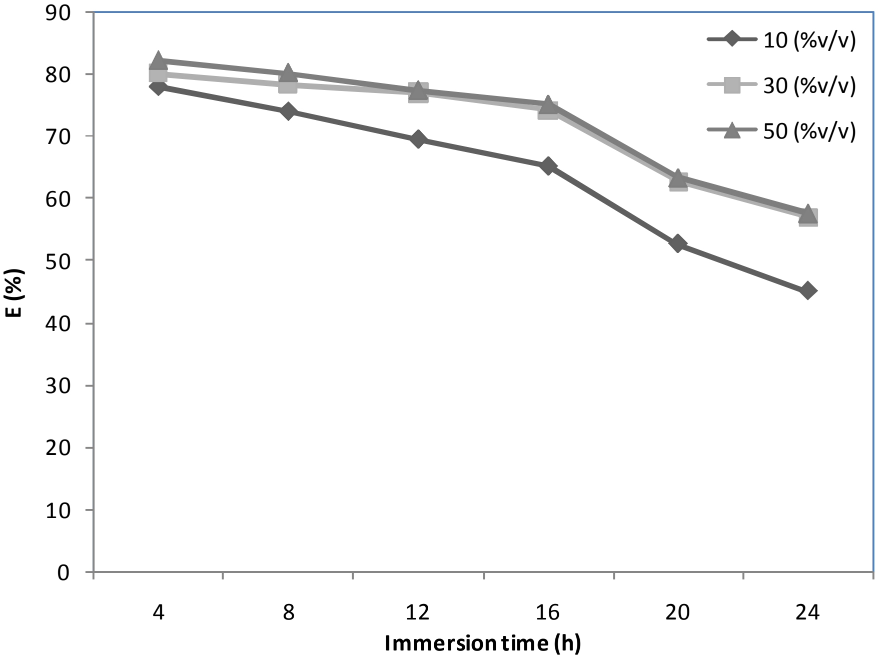


Figure 4. Effect of change in immersion time on E (%) of IP extracts for Al corrosion in 1M HCl.

Fig. 4 also shows that there is a general decrease in inhibition efficiency after 4 h. This may be due to the desorption of the adsorbed protective film at higher immersion time.

3.4. Kinetic parameters

A kinetic model is an important tool in explaining the mechanism of corrosion inhibition for the inhibitor. Corrosion rate for the dissolution of Al in 1 M HCl in the absence and presence of different concentrations of IP extracts (Table 1) was found to increase with increase in temperature It has been reported by a number of authors [9, 25] that for the acid corrosion of aluminium, the natural logarithm of corrosion rate (mg cm^{-2} h^{-1}) is a linear function with 1/T (following the Arrhenius equation) [2]:

$$\log W = \frac{-E_a}{2.303RT} + \log A \tag{3}$$

Where W 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.

Table 1. Calculated values of corrosion rate and inhibition efficiency for Al corrosion in 1M HCl containing IP extracts at different temperatures from weight loss method.

Systems/Concentration (%v/v)	Corrosion rate (mg cm^{-2} h^{-1})				Inhibition Efficiency *E(%)*			
	30 °C	40 °C	50 °C	60 °C	30 °C	40 °C	50 °C	60 °C
Blank	5.94	18.7	39.9	59.70				
50	1.06	4.60	7.45	21.00	82.1	75.1	66.5	64.8
30	1.19	6.95	15.5	23.35	79.9	62.9	61.1	60.9
10	1.31	8.85	20.35	32.35	77.9	52.8	49.0	45.8
IP extracts + KSCN								
50	1.06	5.90	14.40	22.10	82.1	68.5	63.9	62.9
30	1.09	7.35	15.75	24.50	81.7	60.8	60.5	58.9
10	1.17	9.25	19.9 9	39.40	80.1	50.7	59.8	34.0
IP extracts + KI								
50	0.65	3.10	9.45	19.50	89.1	83.5	76.3	67.3
30	0.83	4.30	13.85	21.70	85.1	77.6	65.3	63.7
10	1.04	7.15	18.15	28.50	82.5	61.2	64.5	52.3

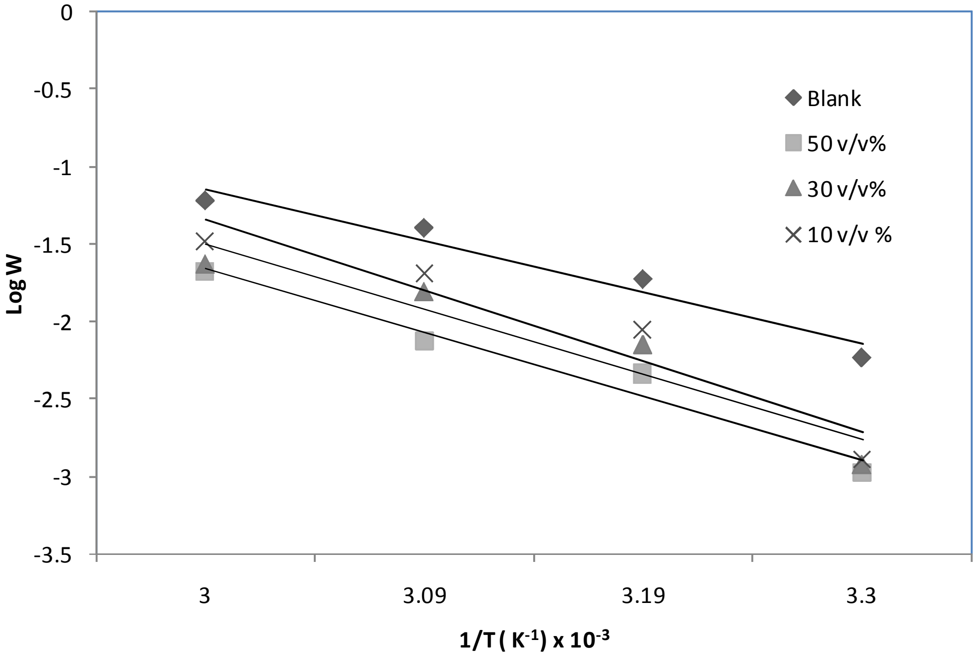


Figure 5. Arrhenius plot of Al corrosion in 1 M HCl in the absent and present of different concentration of IP extracts.

Fig. 5 shows the Arrhenius plot for the blank and different concentrations of IP. The activation energy and pre-exponential factor can be calculated according to the slope and intercept of the regression, respectively. All the kinetic parameters were calculated and listed in Table 2.

Table 2. Activation Energy, E_a (kJ/mol) for Al corrosion in the absence and in the presence of IP extracts 1M HCl

Concentration (%v/v)	E_a (kJ/mol)
Blank	6.34
50	7.85
30	8.08
10	8.67

According to Umoren et al. [28], the activation energies in the presence of inhibitors may be higher, equal to or lower than those in the absence of the inhibitor. In the present study, it could be seen that with increasing concentration of IP extracts the apparent activation energy increased. The increase of the activation energies in the presence of inhibitors is attributed to an appreciable decrease in the adsorption process of the inhibitor on the Al surface with increase of temperature and corresponding increase in the reaction rate because of the greater area of the metal that is exposed to acid [29]. Similar views are held by other authors [2, 3, 22, 23].

3.5. Adsorption isotherms

The experimental data obtained in this study were subjected to analysis in order to determine the type of adsorption isotherm they fit into which gives a clue on the mechanism of inhibition. Two types of adsorption are known namely physical adsorption (physisorption) and chemical adsorption (chemisorption). Physical adsorption results from electrostatic interaction between the charged centres of inhibitor and charged metal surface [30].

Adsorption isotherms are very important in understanding the mechanism of inhibition of corrosion reaction of metals and alloys. The most frequently used adsorption isotherms are Frumkin, Temkin, Freundlich, Flory Huggins, Bockris – Swinkel, El- Awady and Langmuir isotherm. All these isotherms can be represented as follows:

$$f(\theta, x)\exp(-2a\theta) = K_{ads}C \qquad (4)$$

where $f(\theta, x)$ is the configuration factor which depends upon the physical model and the assumptions underlying the derivation of the isotherm. θ is the degree of surface coverage, C is the inhibitor concentration in the electrolyte, x is the size ratio, a is the molecular interaction parameter and K_{ads} is the equilibrium constant of the adsorption process.

If it is assumed that corrosion occurs only in the free sites such that the covered sites have zero corrosion rates, the degree of surface coverage θ for different concentration of IP extracts at different temperatures were evaluated by weight loss method by using the following equation *(* $\theta = E(\%)/100$*).* It can be seen that the values of surface coverage increases with increasing inhibitor concentration

(Table 1) as a result of more inhibitor molecules adsorption on the Al surface. Now assuming that the adsorption of IP extracts belonged to monolayer adsorption and ignoring the lateral interaction between the inhibitor molecules, then the Langmuir adsorption isotherm was applied to investigate the adsorption mechanism by the following equation [31].

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \qquad (5)$$

By plotting values of C/θ versus C, straight line graphs were obtained (Fig. 6) which proves that Langmuir adsorption isotherm is obeyed for each temperature over the range of concentrations studied.

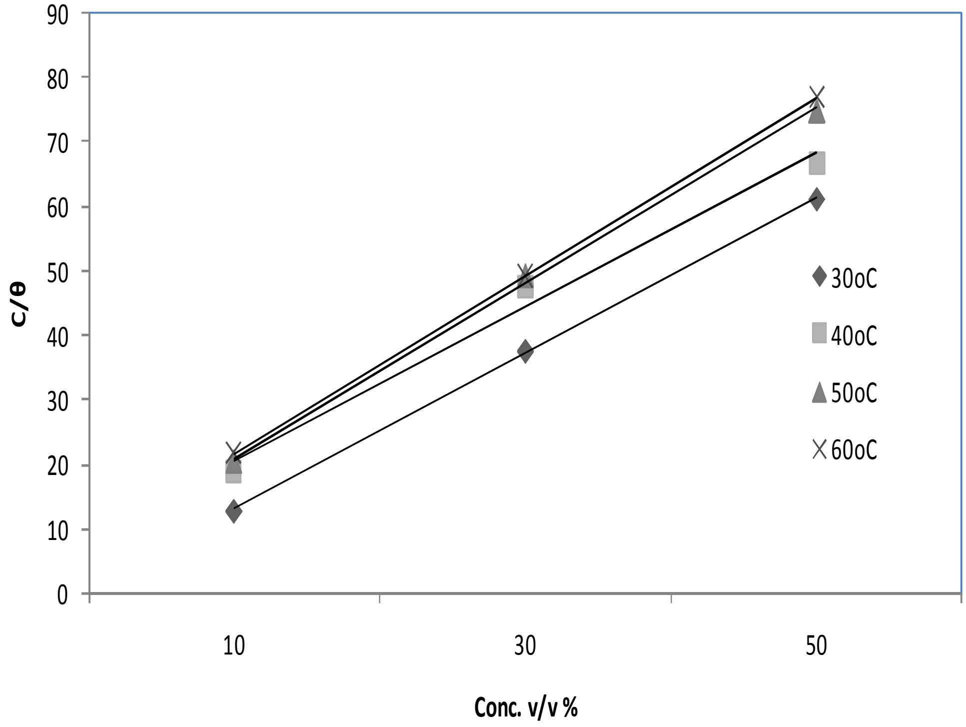


Figure 6. Langmuir Isotherm plot for Al corrosion at different temperatures.

The degree of linearity of Langmuir adsorption isotherm as measured by values of R^2 is nearly equal to 1 (Table 3) which indicates that the assumption and the deduction were correct. In other words, the adsorption of IP extracts on Al surface in 1 M HCl solution is well described by the Langmuir adsorption isotherm [32]. The considerable deviation of the slopes from unity shows that the isotherm cannot be strictly applied. This deviation is attributable to interaction between adsorbate species on the metal surface [26]. A modified Langmuir adsorption isotherm [33] could be applied to this phenomenon, which is given by the corrected equation:

$$\frac{C}{\theta} = \frac{n}{K_{ads}} + nC \qquad (6)$$

The adsorption equilibrium constant K_{ads} decreases with increase in experimental temperature (Table 3), indicating that the interactions between the adsorbed molecules and the metal surface are weakens and consequently, the adsorbed molecules could become easily removable. Such data explains the decrease in the inhibition efficiency with increasing temperature.

Table 3. Calculated thermodynamic parameters from Langmuir adsorption isotherm

Temperature (^oC)	$K_{ads}(M^{-1})$	ΔG^o_{ads} (kJ / mol)	Slope	R^2
30	0.29	-4.05	2.40	0.999
40	0.23	-7.28	2.30	0.986
50	0.19	-5.89	2.71	0.998
60	0.10	-6.19	2.75	1.000

The standard free energy of adsorption ΔG^o_{ads} was calculated using the following equation [34]:

$$K_{ads} = \frac{1}{55.5} \exp\left(\frac{-\Delta G^o_{ads}}{RT} \right) \qquad (7)$$

where R is the molar gas constant, T is the absolute temperature and 55.5 is the concentration of water in solution expressed in molar.

The result is presented in Table 3. The negative values of ΔG^o_{ads} suggests that the adsorption of IP extract onto Al surface is spontaneous. The positive values of adsorption equilibrium constant K_{ads} imply a better adsorption, which leads to an increase in the inhibition efficiency [33]. Furthermore, the values of ΔG^o_{ads} obtained indicate that adsorption of IP extracts occur via physical adsorption mechanism. Generally, values of $\Delta G^o_{ads} \leq$ -20 kJ mol^{-1} (as obtained in this study) are consistent with electrostatic interaction between the charged metals and charged molecules which signifies physical adsorption while values more negative than -40 kJ mol^{-1} signify chemical adsorption [3, 4].

3.6. Mechanism of inhibition action by IP extracts

A general mechanism for the dissolution of Al metal in the presence of aqueous hydrochloric acid solution has earlier been reported [34] as follows:

$$Al_{(s)} + H_2O \leftrightarrow AlOH_{ads} + H^+ + e \qquad (8)$$

$$AlOH_{ads} + 5H_2O + H^+ \leftrightarrow Al^{3+} . 6H_2O + 2e \qquad (9)$$

$$Al^{3+} + H_2O \leftrightarrow [AlOH]^{2+} + H^+ \qquad (10)$$

$$[AlOH]^{2+} + X^- \leftrightarrow [AlOHX]^+ \qquad (11)$$

The controlling step in the metal dissolution is the complexation reaction between the hydrated cation and the anion present Eq. (10). In the presence of chloride ions the reaction will correspond to:

$$[AlOH]^{2+} + Cl^- \rightarrow [AlOHCl]^+ \qquad (12)$$

The soluble complex ion formed increases the metal dissolution rate which depends on the chloride concentration. However, this dissolution can be reduced with the introduction of inhibitor into the aggressive solution.

It is a widely held assumption that the adsorption of an inhibitor at the metal solution interface is the first step in the mechanism of action of inhibitor in aggressive media. Four types of adsorption may take place involving organic molecules at the metal surface interface: (1) electrostatic attraction between the charged molecules and the charged metal; (2) interaction of uncharged electron pairs in the molecule with the metal; (3) interaction of π-electrons with the metal; and (4) a combination of all the above [18].

The data obtained from the temperature dependence of inhibition process suggest a physical adsorption mechanism. To further characterize the mechanism of inhibitor adsorption, it is necessary to establish the adsorption modes of the inhibiting species. The predominant adsorption mode depends upon factors such as the extract composition, types of anion, as well as chemical changes to the extract. As noted earlier, IP extracts contain mainly d-lysergic acid amide (LSA) (Fig.1). This compound contains N and O in their structure including π-electrons which are required for corrosion inhibiting effects. Moreover, it is likely that chanoclavine, elymoclavine, ergometrine, d-isolysergic acid amide and other ingredients of the plant extracts synergistically increase the strength of the layer formed by the d-lysergic acid amide (LSA). Thus, the formation of a strong physisorbed layer between the metal surface and the phytoconstituents of the plant extract could be the cause of the inhibitive effect.

Moreover, since the main component of the plant extract is basic in nature (Fig. 1), protonation occurs easily in HCl medium. The protonated species can get adsorbed onto the cathodic sites of the Al surface and reduce H_2 gas evolution. IP can inhibit the dissolution of Al by adsorption at the metal surface possibly in two different ways: First, the protonated inhibitor electrostatically adsorbed onto the anion-covered surface, through its cationic form; secondly, the inhibitor may compete with Cl^- ions for sites at the water-covered anodic surface. In doing so, the protonated inhibitor loses its associated protons when entering the double and chemisorbed by donating electrons to the metal. But since physisorption plays the major role from the values of kinetic/thermodynamic parameters calculated, cooperative adsorption of the 'green' inhibitor through its cationic form electrostatically onto the anion (Cl^-) covered surface of the Al metal appears predominant. Similar results have been documented elsewhere [18].

3.7. Effect of KI and KSCN addition

Synergistic inhibition is an effective means used to improve the inhibition efficiency of an inhibitor in order to decrease the amount of usage and to diversify the application of inhibitor. Thus, it is necessary for corrosion scientists to discover, explore and use synergism in the complicated corrosive media. Actually, many investigations concerning synergistic inhibition have been carried out [35-37].

Accordingly, the corrosion behaviour of Al in 1M HCl in 0.005 M KI and KSCN in the presence of IP extracts of different concentrations was studied. The obtained weight-loss time values are summarize in Table 1. From the results it is observed that inhibition efficiency E (%) of IP extracts increases significantly with the addition of KI due to synergistic effect [9, 38]. However, slight increase in E (%) was observed with addition of SCN^- to IP extract at 30 °C and antagonistic behaviour at 40 – 60 °C. The antagonistic effects of addition of anions to naturally occurring materials including plant extracts used as corrosion inhibitor in acidic media has been reported in the literature. Oguzie [13] reported antagonistic effect with Cl^- on addition to 10% extract of *Occimum viridis* in 2 M HCl for mild steel. Eddy *et al.* [39] observed that addition of Br^- and I^- ions to *Lasianthera africana* antagonized inhibition of mild steel in 0.1 M H_2SO_4. Also Umoren *et al.* [40] reported antagonistic behaviour between carboxymethyl cellulose and Cl^- ions for corrosion inhibition of mild steel in acidic environment. Although synergistic effect of SCN^- has been observed in earlier report [41], the seeming negative effect of SCN^- with IP extract for Al as observed in this study it is not entirely clear; though the formation of soluble adsorption intermediates which exhibit fast dissolution rates especially at higher temperatures can not be ruled out.

The strong chemisorptions of I^- on the metal surface as reported by Fouda et al. [42] and corroborated by others [37, 38] are responsible for the synergistic effect of iodide ions in combination with cation of the inhibitor. The cation is then adsorbed by coulombic attraction on the Al surface where I^- ion is already adsorbed by chemisorptions. Stabilization of adsorbed iodide ion leads to a greater surface coverage and therefore greater inhibition efficiency. However, the greater influence of I^- over SCN^- at 30 °C may be attributed to its large ionic radius, high hydrophobicity and low electronegativity [35].

4. CONCLUSIONS

1. *Ipomoea invulcrata* extracts (IP) was found to be an efficient 'green' inhibitor for Al in 1M HCl.
2. Inhibition efficiency increased with increase in IP concentration, but decreased with increase in temperature and immersion time.

3. The corrosion process is inhibited by adsorption of the IP extracts onto the Al surface following the Langmuir adsorption isotherm.
4. The values of the free energy of adsorption calculated indicate strong, spontaneous and physical adsorption of the extracts on the Al surface.
5. The presence of the IP extracts increases the activation energy of the corrosion process.
6. The addition of iodide (I^-) ions exerts synergistic effect while thiocynate (SCN^-) antagonizes the inhibition efficiency of the IP extracts at higher temperatures.

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