IONIC RADII OF HALIDE IONS AND ITS CORROSION INHIBITORY ENHANCEMENT ON SIDA ACUTA.

* L O .C UBANI¹, A. BILAR², F.C NWADIRE¹, C. ODIH¹ AND M.S. EKWERE¹

1. Department of Chemistry, Micheal Okpara University of Agriculture, Umudike, Abia State, Nigeria.
2. Department of Chemistry, Federal University of Technology, Owerri
*Corresponding Author: ubani.okechukwu@mouau.edu.ng

ABSTRACTS

Corrosion Inhibitory efficiencies of Sida acuta leaf extracts in combination with halide ions (F⁻, Cl⁻, Br⁻ and I⁻) as an enhancement on aluminum corrosion in H₂SO₄ was studied at room temperature (25°C) under varying acid concentrations of 0.05M, 0.1M and 0.5M using weight loss method. From the results obtained, Sida acuta acts as a good inhibitor for aluminum corrosion in acidic environment and its inhibitory efficiencies increases with time of exposure. Based on the experimental results, the corrosion rate increases rapidly in the blank with a weight loss accelerating from 0.009g to 0.038g but with the introduction of plant extract, weight loss got reduced from 0.007g to 0.027g as well as having inhibition efficiency of 36% to 12% as the concentration of the acid was increased from 0.05M to 0.5M over the time series of 24 h to 96 h. However, the inhibitory efficiency of Sida acuta in H₂SO₄ medium was further improved when halide ions were introduced. The weight loss of NaI moved from 0.002g to 0.011g and hence had the highest inhibition efficiency among the halide ions from 78% to 50%. NaBr showed a weight loss ranging from from 0.003g to 0.022g as well as having inhibition efficiency of 67% to 42% while NaCl showed a weight loss of 0.005g to 0.023g as well as having inhibition efficiency of 55% to 32% as the acid concentration was increased from 0.005M to 0.5M over the time exposure of 24 h to 96 h. Nevertheless, the weight loss of NaF increases rapidly from 0.020g to 0.050g even more than the blank under the same reaction conditions and hence does not show inhibition efficiency. Therefore, the increase in inhibition efficiency (%I) and surface coverage (θ) in the presence of the halides was found to be in a special sequence. This synergistic effect increased according to the following pattern Cl⁻ < Br⁻ < I⁻ suggesting a possible role by ionic radii in the corrosion inhibitory process which also increases in the order, F/F⁻ (0.072/0.133nm), Cl/Cl⁻ (0.099/0.181nm) < Br/Br⁻ (0.114/0.195nm) < I/I⁻ (0.133/0.216 nm). Fluoride ion does not show any inhibitory enhancement on Sida acuta owing to its least ionic radius.

Keywords: corrosion, halide ions, atomic radii, Sida acuta, synergism.

INTRODUCTION

Industrial revolution that is ever expanding within different parts of the world has several advantages and disadvantages in the quality of environment. Most industries utilize metals or their ores (such as mild steel, aluminum, zinc and copper) in the fabrication of their installations. In most cases, these metals are exposed to aggressive medium/media and are prone to corrosion [1]. Corrosion inhibitor can be divided into two broad categories, those that enhance the formation of a native protective oxide film through an oxidizing effect and those that inhibit corrosion by selecting adsorbing on the metal surface and creating a barrier that
prevents access of the corrosive agent to the surface. The use of plant products as corrosion inhibitors are justified by the phytochemical compounds present therein, with molecular and electronic structures bearing close similarity to those of conventional organic inhibitor molecules[2]. Green corrosion inhibitors are biodegradable and do not contain heavy metals or other toxic compounds. Extensive studies have thus been undertaken to identify synergistic effects with other additives[3].

Synergism is described as a combined action of compounds greater in total effect than the sum of the individual effects. For corrosion inhibitor systems, synergism usually arises either as a consequence of interaction between components of the inhibitor formulation or due to interaction between the inhibitor and one of the ions present in the aqueous solutions. This is normally a non-linear effect in terms of the concentration of the components. Antagonism is the opposite of synergism and occurs when the combined effect of the inhibitors is less than the sum of the effects of the components. Synergism has become one of the most important effects in inhibition process and serves as the basis for most modern corrosion inhibitor formulations. To this end, halide ions have particularly proved capable in improving the corrosion inhibition effectiveness of a wide range of organic substances. It is thought that the halide ions are able to improve adsorption of the organic cations by forming intermediate bridges between the positively charged metal surface and the positive end of the organic inhibitor. Corrosion inhibition synergism thus results from the increased surface coverage arising from the ion-pair interactions between the organic inhibitor and halide ions.

Preliminary phytochemical screening of the ethanolic extracts of Sida acuta have revealed that the extracts is a complex mixture of various phytochemical components like saponins, flavonoids, tannins, alkaloids, organic acid and anthraquinones in the leaves and tannins, alkaloids and anthraquinones only present in the stem extract [4]. Plant extracts are rich source of phytochemicals such as alkaloids, tannins, glycosides, saponins, flavonoids, polyphenols, etc. which are organic and contain heteroatoms in their molecules. These organic constituents are the adsorption species which allow plant extracts to act as metal corrosion inhibitors. It is therefore inferred that the enhancement of the inhibition efficiency of plant extracts brought about by addition of halide ions is due to the ability of halide ions to stabilize the adsorbed films on metal surfaces.

MATERIALS AND METHOD.

Experimental

The leafy parts of Sida acuta were collected and identified at Plant Health Department Micheal Okpara University of Agriculture, Umudike. The leaves samples were washed, air dried at room temperature for 4 weeks, ground using blender to expose the surface area for extraction and then weighed. Then 2.5litres of ethanol was poured into 300g of Sida acuta and was left for 2days for proper extraction. The mixture was filtered using Whatmann No.1 filter paper and the solvent was then allowed to evaporate so as
to obtain the concentrate of *Sida acuta*. A total mass of 1.5g of *Sida acuta* was weighed using electronic weighing balance. 0.05M, 0.1M, 0.5M Concentrations of H$_2$SO$_4$ was prepared from stock solution using serial dilution. The Aluminum coupon was cut into pieces having a dimension of 2cm X 2.5cm with a total surface of 5cm. A small hole was bored near the upper edge of the coupons using a punch electric drilling machine for suspension of the coupons. The coupons were then sand papered until mirror polished surfaces were obtained. The coupons were de-greased with ethanol, washed with de-ionized water, dried in acetone and their initial weights was recorded in grams. The coupons were finally suspended using the fishing lines for the weight loss study.

**Weight loss method**

This involves the immersion of coupons in the media under investigation and retrieving them at specified durations and checking the weight loss in grams. Each coupon was tied and suspended from horizontally placed fishing lines on top of a designated beaker containing 250ml of corrodaent, Plant extracts(0.1g/l) and 3% of NaCl, or NaI, or NaBr or NaF. Each weighed coupons was suspended such that it was totally immersed in the solution without touching either the side of bottom of the containers with the aid of a glass rod and hook. The immersed weighed coupons were left uncovered to react freely with the atmosphere and the duration of immersion was noted. After the expiration of time allowed, the reacted coupons were washed gently and properly in water and ethanol, dried with cotton wool and dipped in acetone to remove every moisture and oxygen. The coupons were retrieved at 24h interval progressively for 96h (4 days). Thereafter, each of the dried coupons was carefully reweighed on the electronic balance to obtain a new weight and the weight loss, corrosion rate and inhibitory efficiencies were carefully deduced according to the following equations

Weight loss = weight before - weight after………1

Corrosion rate (cm/h) = \( \frac{\text{Weight loss}}{\text{Area} \times \text{time}} \)

Surface area (Ω) = \( 1 - \frac{W_1}{W_0} \) \( \text{………3} \)

Inhibition efficiency (%) = \( \left( 1 - \frac{W_1}{W_0} \right) \times 100 \) \( \text{………4} \)

Where \( W_0 \) and \( W_1 \) are the weight losses of the aluminum coupons in the absence and presence of inhibitor and enhancer respectively in H$_2$SO$_4$ at room temperature.

**RESULTS AND DISCUSSION**
The plots show weight loss and inhibitory efficiency-time curves for aluminum dissolution in the presence of blank, plant extract (control) and halide ions enhancers. For the blank, weight loss increases from 0.009g to 0.025g but when Sida acuta extract was introduced (control), the presence of Sida acuta gave a weight loss of 0.007g to 0.022g leading to decrease in corrosion rate from $7.5 \times 10^{-5}$ to $4.583 \times 10^{-5}$ g cm$^{-2}$ h$^{-1}$ over the time exposure of 24 h to 96 h. The maximum percentage inhibitory efficiency for Sida acuta is 36% at 72 h. However, when halide enhancers were introduced, there was slow increase in weight...
loss from 0.05g to 0.015g, 0.03g to 0.012g and 0.002g to 0.010g for NaCl, NaBr and NaI respectively at the same concentration of the extract within the same duration of time from 24h to 96h. with their percentage maximum inhibitory efficiencies as 55%, 64% and 68% at 72 h. However, there was rapid increase in weight loss when NaF was introduced from 0.020g to 0.040g with zero inhibitory efficiency.

Figure 3: Plot of weight loss against time of exposure for aluminum corrosion in 0.1M H₂SO₄ in blank, control and Halide ions

![Graph showing weight loss against time for aluminum corrosion in 0.1M H₂SO₄ with different Halide ions]

Figure 4: Plot of Inhibition efficiency against time of exposure for aluminum corrosion in 0.1M H₂SO₄ in control and Halide ions (Chloride, Bromide and iodide)

When the concentration of the acid was increased from 0.05M to 0.1M, there was a corresponding increase in weight loss from 0.015g to 0.031g for the blank. But with the
introduction of *Sida acuta* extract, the weight loss decreases from 0.012g to 0.025g with inhibitory efficiency of 30%. Consequently, there was a remarkable decrease in weight loss with an increased inhibitory efficiency when the halide ions were introduced ranging from 0.008g to 0.020g, 0.006g to 0.016g and 0.003g to 0.015g with the inhibitory efficiencies of 46%, 50% and 61% for NaCl, NaBr and NaI respectively. Nevertheless, NaF gave a very sharp increase in weight loss from 0.025g to 0.045g, with a zero inhibitory efficiency under the same experimental conditions.

**Figure 5:** Plot of weight loss against time of exposure for aluminum corrosion in 0.5M H₂SO₄ in blank, control and Halide ions

**Figure 6:** Plot of Inhibition efficiency against time of exposure for aluminum corrosion in 0.5M H₂SO₄ in control and Halide ions (Chloride, Bromide and Iodide)
The concentration of the acid was further increased from 0.1M to 0.5M, the blank responded by having a rapid increase in weight loss from 0.020g to 0.038g as expected but with Sida acuta extract, the weight loss drops from 0.014g to 0.027g which leads to decrease in corrosion rate with a maximum inhibitory efficiency at 30%. However, with the introduction of halide ions, the weight loss drops from 0.012g to 0.023g, 0.011g to 0.022g and 0.010g to 0.011g in NaCl, NaBr, and NaI respectively having a corresponding maximum inhibitory efficiency as 43%, 50% and 71% but when NaF was introduced, there was an increase in weight loss from 0.038g to 0.050g with no inhibitory efficiency.

**Discussion**

The weight loss of aluminum in different concentrations of the H$_2$SO$_4$ (0.05M, 0.1M and 0.5M) in the absence of Sida acuta extract (blank), presence of Sida acuta extract and Sida acuta-halide mixtures after every 24h for 96h of immersion was determined at room temperature (25°C). The corrosion rates and percentage inhibitory efficiencies were evaluated. Results shows that corrosion rate of aluminum dissolution in H$_2$SO$_4$ was reduced in the presence of Sida acuta extract compared to the free acid (blank). The inhibitory effect of the Sida acuta could be attributed to the presence of some phytochemical constituents in the extract. Previous studies have shown that Sida acuta contains saponins, flavonoids, tannins, alkaloids, organic acid and anthraquinones [5]. Further reduction in corrosion rate was observed on addition of halide ions to sida acuta extract with the exception of fluoride ion. The reduction in corrosion rate in the presence of the halides was observed to follow the trend: sida acuta extract + NaCl < sida acuta extract + NaBr < sida acuta extract + NaI. From the results obtained, it shows that the surface coverage and inhibition efficiency of Sida acuta was greatly enhanced on addition of halide ions. Similar observations had been reported by some authors [6] and was described to be a synergistic effect. 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.

The degree of surface coverage values was found to increase in the order NaI > NaBr > NaCl. The inhibition efficiencies of the extract increases with the addition of the halide salts with the highest inhibition efficiency obtained when the extracts combined with iodide ions. This has been attributed to the stabilization of adsorbed halide ions by electrostatic interaction with the extract which leads to greater surface coverage and hence greater inhibition efficiency. Halide ions are good ligands because they exhibit low electronegativity (less than 3.5) except fluoride ion [7]. Electronegativity decreases while the atomic radius increases from Cl$-$ < Br$-$ < I$^-$. Hence, Aluminium can form compounds with halide ions, thereby inhibiting the corrosion of Aluminium in the presence of Sida acuta extract. The synergistic effect increased in the order Cl$-$ < Br$-$ < I$^-$ suggesting a possible role by ionic radii in the corrosion inhibitory process.
which also increase in the order, F/F\(^-\) (0.072/0.133nm), Cl/Cl\(^-\) (0.099/0.181nm) < Br/Br\(^-\) (0.114/0.195nm) < I/I\(^-\) (0.133/0.216 nm).

It is pertinent to note here that the ionic radius of an anion is larger than the radius of the atom from which it is formed owing to the fact that there is a repulsive force between the newly added electron(s) and the electrons already present coupled with the fact that the nuclear effective force for the electron cloud is weakened.

CONCLUSION

The synergistic effect increased in the order Cl\(^-\) < Br\(^-\) < I\(^-\) suggesting a significant role by ionic radii in the corrosion inhibitory process embarked upon by *Sida acuta*. Fluoride ion does not show any inhibitory enhancement on *Sida acuta* owing to its least ionic radius.

REFERENCES


