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# Inhibitive and Synergistic Properties of Ethanolic Extract of Anogeissus Leiocarpus Leaves on the Corrosion of Aluminium in HCl Solution

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### ABSTRACT

The corrosion inhibition of aluminium in HCl in the presence of ethanol extract of *Anogeissus leiocarpus* at room temperature was studied using the thermometric technique. The effect of addition of halides (KCl, KBr, KI) is also reported. The percentage inhibition efficiency (% I) increased with increase in concentration of ethanol extract of *Anogeissus leiocarpus*. The addition of the halides to the plant extract increased the inhibition efficiency to a maximum of 95.18% with KI at 0.6g/L concentration. The higher the corrodent (HCl) concentration the higher the corrosion rate, while lower inhibition efficiency (and increase in reaction number values) was found to be in the order  $I^- > Br^- > Cl^-$  which clearly indicates that the radii and the electro negativity of halides play a significant role in the adsorption process. It was also noted that only KCl was synergistic to the ethanol extract of *Anogeissus leiocarpus*, while other halides tested were antagonistic. All the data acquired reveal that the ethanolic extract of *Anogeissus leiocarpus* act as an inhibitor in the acid environment due to the phytochemicals: saponin, tannins, flavonoid, anthraquinones, cardiac glycosides, alkaloids and steroid that it contains there in.

Keywords: Anogeissus leiocarpus, Corrosion inhibition, Halides, Phytochemicals, Synergism

#### Introduction

The most commonly used alloy in aircraft manufacturing is Al 7075. Pitting corrosion in the presence of aggressive chloride ions is the most frequently encountered cause of failure of these high-strength aluminium alloys (Bereket and Yurt, 2001). It is generally accepted that pitting proceeds by destruction of the protective oxide by adsorption of chloride ions followed by formation of chloro complexes that subsequently pass into solution (Bereket and Yurt, 2001).

Compounds that retard or stop this process when present in aggressive medium are prospective corrosion inhibitors. There are two types of corrosion inhibitors; inorganic and organic. Protective action of inorganic inhibitors is related with the formation of oxide film or hardly soluble salt on the metal surface. On the other hand protective action of organic inhibitors comes from the adsorption on the oxide films. The most common inorganic inhibitors used for aluminium or aluminium alloys are chromates (Robinson, 1979). But due to high toxicity of chromate there is considerable interest in their replacement (Monrz and Pollock, 1986). Green corrosion inhibitors have the advantage of being inexpensive, nontoxic, and eco-friendly. These advantages have provoked numerous and intensive searches on the use of naturally occurring substances or their

extracts for the inhibition of the corrosion of metals (Eddy et al., 2010). It has been established that the inhibitory actions of plant extracts are due to the presence of some organic compounds such as saponin, tannin, alkaloid, steroids, glycosides, and amino acids (Eddy et al., 2009a,b). Most of these compounds have centers for p-electrons and functional groups (such as -C=C-, -OR, -OH, -COOH, -NR<sub>2</sub>, -NH<sub>2</sub>, and -SR), which provide electrons that facilitate the adsorption of the inhibitor on the metal surface. Also, the presence of hetero atoms such as N, P, O, and S enhances the adsorption (which is the initial mechanism of inhibition) of the inhibitor on the metal surface. Recent researches have also indicated that amino acid contents of the plant extracts have a significant role to play in the corrosion inhibition mechanism of plant extracts (Eddy et al., 2010).

Plant of interest in this research *Anogeissus leiocarpus*, is a widely distributed plant in the sub-Saharan region of Africa. It belongs to the family combretaceae. *Anogeissus leiocarpus* is a branchlets tomentoes, leaves altenate, elliptic to ovale lenceolate, obtuse and mucronate or a cute of apex, 2-8cm long, 1.2-3.5cm broad, at first more densely, silky than calaxy prebensent breneath, receptable above the ovary consisting of narrow tubular lower portion, fruits in suhglobose cone like heads each, fruit broadly winged back by the

persistent tubular portion of the receptacle. Traditionally, in most part of Hausa land, leaves decoction or infusion of the plant is used in the treatment of cough, wound infections and rashes in small children (Sani *et al.*, 2007).

Several researches have been carried out on the inhibition of the corrosion of metals by some plant extracts. Extracts of Gnetum africanum (Eddy et al., 2009b), Raphia hookeri (Abdel-Gaber, 2006; Ebenso et al., 1998; 2004), exudate gum (El-Etre, 2006), bitter leaf (Loto, 2003), gum Arabic (Umeron et al., 2006b), Datura metel (Rejendran et al., 2005), Carica papava (Ebenso and Ekpe, 1996; Abdel Gaber et al., 2006; Okafor and Ebenso, 2007), Occinum viridis (Oguzie, 2006; Eddy et al., 2010), Telfairia occidentalis (Ramesh et al., 2001; Rehan, 2003), Vernonia amygdalina (Odiongenyi, 2009), mango juice (Loto et al., 2003), Rosmmarius officinalis (Kliskic et al., 2000), Azadirachta indica (Ekpe et al., 1994), Lasianthera Africana (Eddy et al., 2009a), Aloe vera (Ebenso et al., 2008; Eddy and Odoemelam, 2009), Musa sapientum (Eddy and Ebenso, 2008), Colocasia esculenta (Eddy, 2009b), Phyllanthus amarus (Okafor et al., 2008; Eddy, 2009a), Piper guineense (Ebenso and Odiongenyi, 2008), Opuntia (El-Etre, 2003), natural honey (El-Etre and Abdullahi, 2000) and tobacco leaves (Davis and Von Fraunhofer, 2003) have been investigated for their corrosion inhibition potentials. However, literature is scanty on the use of ethanol extract of Anogeissus leiocarpus as an inhibitor for the corrosion of aluminium in HCl. Therefore, the objective of the present work is to investigate the inhibitive and synergistic effect of Anogeissus leiocarpus for the localised corrosion of aluminium in HCl solution and to also relate those properties to the phytochemicals it contains there in.

#### **Materials and Methods**

Materials used for the study were aluminium sheets of composition (wt %) Al(98.70), Si(0.48), Cl(0.014), K(0.04), Ca(0.01), Ti(0.005), V(0.016), Mn(0.012), Fe(0.50), Ni(0.013), Cu(0.048), Ga(0.013), In(0.10), Te(0.010), Ba(0.009), Os(0.032), Ir(0.03). Mini pal, a compact energy dispersive X-ray spectrometer designed for the elemental analysis of a wide range of samples was used for the determination of the aluminium composition. The system was controlled by a personal computer running the dedicated Mini Pal analytical software. The pellet of the aluminium sample was loaded into the sample chamber of the spectrometer, a voltage (30 kV max.) and a current (1mA max.) was applied to produce the X-rays to excite the sample for 10 minutes. The spectrum from the sample was analysed to determine the concentration (%) of the elements in the sample.

The sheet was mechanically pressed-cut to form different coupons, each of dimension,  $3 \times 4 \times 0.11$  cm. Each coupon was degreased by washing

with ethanol, dried with acetone and preserved in a desiccator. All reagents (HCl) and chemicals (KCl, KBr and KI) used for the study were of Analar grade and double distilled water was used for their preparation.

## **Extraction of Plant**

Samples of *Anogeissus leiocarpus* leaves were obtained from the Botanical garden, Biological sciences department, Bayero Univeristy, Kano, Northwest of Nigeria. Samples of the leaves of *Anogeissus leiocarpus* were washed, air dried, ground, sieved and soaked in a solution of ethanol for 1 week to percolate and were filtered. The filtrates were further subjected to concentration using a rotar vapour (BUCHI R110, 40°C) to obtain thick syrup which was later allowed to air dry. The dry extract so obtained were used in preparing different concentrations of the plant extract by dissolving 0.2, 0.4 and 0.6 g of the extract each differently in 1 dm<sup>3</sup> of 0.2, 0.4, 0.6 and 0.8M HCl respectively (Eddy *et al.*, 2009a, b).

### **Chemical Analysis**

Phytochemical analysis of ethanol extract of the plant sample was carried out according to the method reported by Eddy *et al.* (2009a, b). For the identification of saponin, frothing and Na<sub>2</sub>CO<sub>3</sub> tests were adopted. For the identification of tannin, bromine water, and ferric chloride tests were used. For the identification of cardiac glycodises, Leberman's and Salkowski's tests were adopted and for the identification of alkaloid, Dragendorf, Hagger and Meyer reagents were used.

## Thermometric method

The reaction vessel is a three-necked round bottom flask and the procedure for determining the corrosion behaviour by this method was described elsewhere by other authors and also reported by Ebenso (2003) and Umoren et al. (2006a; 2007). The flask was well lagged to prevent heat losses. In the thermometric technique, the corrodent (HCl) concentration was varied at 0.2, 0.4, 0.6 and 0.8 M, while halides (KCl, KBr and KI) used have their concentrations to be 0.2, 0.4, 0.6M (for synergism) respectively. The volume of the test solution used was 50cm<sup>3</sup>. The initial temperature in all the experiments was kept at room temperature. The progress of the corrosion reaction was monitored by determining the changes in temperature with time (each minute for the first five minutes, each five minutes for the next 25 minutes and each ten minutes for the last thirty minutes) using a calibrated thermometer (0 -100°C) to the nearest  $\pm$  0.05°C. The data was generated for a period of one hour. Reaction number was calculated as follows:

From the rise in temperature of the system per minute, the reaction number (RN) was calculated using equation (1):

$$RN(^{o}Cmin^{-1}) = \frac{T_m - T_i}{t}$$

where  $T_m$  is the maximum temperature attained by the system,  $T_i$  is the initial temperature and t is the time required to reach the maximum temperature.

$$\% I = \frac{RN_f - RN_i}{RN_f} x \ 100$$

where  $RN_f$  is the reaction number of aqueous acid in the absence of *Anogeissus leiocarpus*, and  $RN_i$  is the reaction number of aqueous acid in the presence of *Anogeissus leiocarpus*.

#### **Results and Discussion**

The results and discussion of this research based on the study of the inhibitive and synergistic property of plant extract and halides on Aluminium in HCl solution is hereby presented. This will be related to the phytochemicals present in the plant extract.

# Effect of Corrodent Concentration Only on the Corrosion of Aluminium Coupon

The effect of reaction temperature variation with time for the corrosion of Aluminium in varying HCl solutions was conducted. 0.2, 0.4 and 0.6M HCl all have their effects closely related, while for 0.8M HCl the rate of corrosion increases abruptly from 30minutes till the end of the reaction. Therefore, an increase in concentration of the corrodent increases the rate of corrosion of Aluminium (Ebenso, 2003; Eddy *et al.*, 2009a, b; 2010).

# Effect of Plant Extract and Corrodent on the Corrosion of Aluminium Coupon

From the above, the inhibition efficiency (%I) of the used inhibitor was computed using equation (2):

.....(2)

The result of the effect of plant extract in different HCl solutions on the corrosion of aluminium coupons was also tested. It was observed that the presence of the plant extracts reduces the reaction temperatures and also the rate of reaction, thereby inhibiting the corrosion of aluminium. It was also observed that the higher the concentration of the plant extract the better the inhibition while the higher the corrodent concentration the higher the rate of corrosion. Similar results have been reported earlier by Ebenso (2003) and Eddy *et al.* (2009a, b).

# Effect of Halide Type and Corrodent Without Plant Extract on Aluminium Corrosion

Figures 1 and 2 presents the corrosion of Aluminium coupons in 0.2 and 0.4 KCl, KBr and KI respectively in varying HCl solutions (that of 0.6M KCl, KBr and KI not shown). It can be observed in all the systems that KI has the least corrosion effect on aluminium in the two corrodent concentrations tested. This could be related to the large ionic size of iodide ion and its low electronegativity when compared to chloride and bromide. Electronegativity decreases from Cl<sup>-</sup> to I<sup>-</sup> (Cl<sup>-</sup> = 3.0, Br<sup>-</sup> = 2.8, I<sup>-</sup> = 2.5), while the atomic radius also increases from Cl<sup>-</sup> to I<sup>-</sup> (Cl<sup>-</sup> = 0.90Å, Br<sup>-</sup> = 1.14 Å, I<sup>-</sup> = 1.35 Å) (Ebenso, 2003).

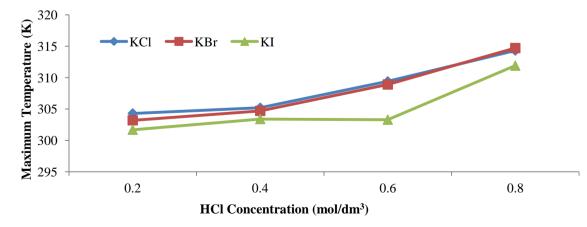


Fig 1: Variation of Temperature with Time for the Corrosion of Aluminium in 0.2M KCl, KBr and KI in Varying HCl Solutions

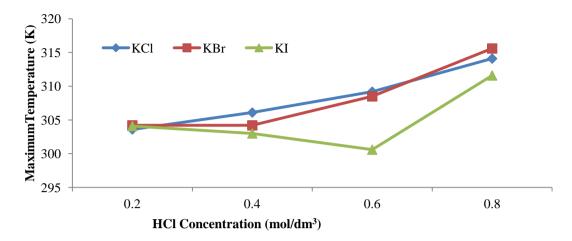


Fig 2: Variation of Temperature with Time for the Corrosion of Aluminium in 0.4M KCl, KBr and KI in Varying HCl Solutions

# Effect of Halide Type with Plant Extract on the Corrosion of Aluminium in HCl Solution

The addition of plant extract (0.2g/L) to the corrosion solution containing HCl and the halides reduced considerably the reaction temperature and thereby reducing the rate of corrosion. Comparing the effectiveness of such a combination, it was observed that KI had the best inhibitive property in combination with the plant extract. This can also be attributed to the reasons earlier stated.

Similar results were obtained when the concentration of the plant extract was raised to

0.4g/L. This is evident in Figures 3, 4 and 5 respectively showing the variation of reaction temperature with time for the corrosion of Aluminium coupon in 0.2, 0.4 and 0.6M KCl, KBr and KI. In all cases, the inhibition decreases at 0.2 and 0.4M HCl while a rapid increase was observed at 0.6 and 0.8M HCl for KCl and KBr. This clearly shows there is competition between chloride, bromide and plant extract on aluminium surface at higher HCl concentrations.

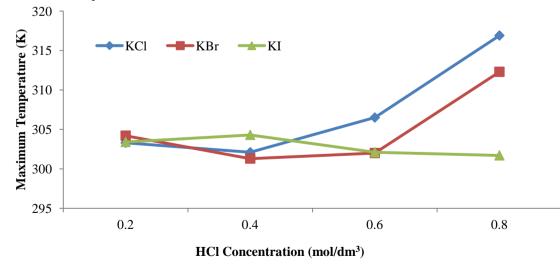


Fig 3: Variation of Temperature with Time for the Corrosion of Aluminium in 0.2M KCl, KBr and KI in 0.4g/L inhibitor in Varying HCl Solutions

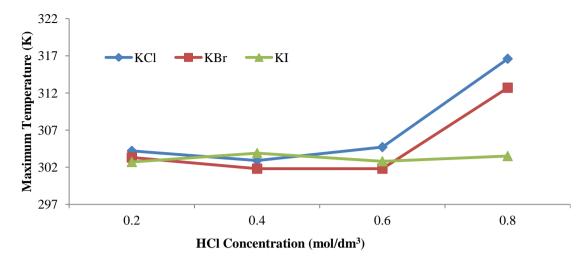


Fig 4: Variation of Temperature with Time for the Corrosion of Aluminium in 0.4M KCl, KBr and KI in 0.4g/L inhibitor in Varying HCl Solutions

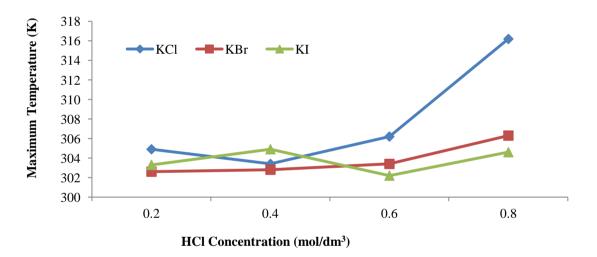


Fig 5: Variation of Temperature with Time for the Corrosion of Aluminium in 0.6M KCl, KBr and KI in 0.4g/L inhibitor in Varying HCl Solutions

The addition of 0.2 and 0.4M KI, KBr and KCl on 0.6g/L plant extract does not have defined characteristics with an undulating increase and decrease in corrosion reaction temperature with time. But such results was not observed when 0.6g/L plant extract was added to a solution containing either 0.6M KCl, KI or KBr. Between 0.2 to 0.6M HCl the reaction temperature was steady, but all increased beyond 0.6M HCl with the highest reaction temperature observed for KCl.

Table 1 shows the phytochemical constituents of the ethanol extract of *Anogeissus leiocarpus*. The constituents analyzed were saponin, tannins, flavonoid, anthraquinones, steroid, cardiac glycosides and alkaloids. The

results indicated that these phytochemicals (with exception of steroids and anthraquinones) were detected in ethanol extract of *Anogeissus leiocarpus*, while the aqueous extract contains saponin, which justified the choice of ethanol extract of the leaves for the study. It is therefore concluded that the inhibitive properties of ethanol extract of *Anogeissus leiocarpus* is due to the presence of saponins, tannins, flavonoid, cardiac glycosides and alkaloids present in the extract of the plant. These phytochemicals are rich in hetero atom functional groups and p-electrons in triple or conjugated double bonds hence they are expected to be good corrosion inhibitors (Eddy *et al.*, 2009a, b).

| toenennear co | inposition of cenan | or extracts of mosen | ssus icolear |
|---------------|---------------------|----------------------|--------------|
|               | Phytochemicals      | Results              |              |
|               | Alkaloid            | +                    |              |
|               | Glycoside           | +                    |              |
|               | Steroid             | -                    |              |
|               | Tannin              | +                    |              |
|               | Anthraquinone       | -                    |              |
|               | Saponin             | +                    |              |
|               | Flavonoid           | +                    |              |
|               |                     |                      |              |

# Table 1: Phytochemical composition of ethanol extracts of Anogeissus leoicarpus leaves.

*Key:* + (*Detected*); - (*Not Detected*)

## **Percentage Inhibition Efficiency**

Tables 2, 3 and 4 shows the inhibition efficiencies for the corrosion of Aluminium in varying HCl, plant extract and halide (KI, KBr and KCl) concentrations. Table 2 presents the calculated values of Inhibition efficiencies (%) for Aluminium corrosion in varying HCl, plant extract and KI concentrations. It can be observed that as the plant extract concentration increases, the inhibition efficiency also increases. An increase in the KI concentration in the test solution results in an increases in the inhibition efficiency of the halide itself. While increases in the HCl concentration decrease the inhibition efficiency. The mixtures of KI and plant extract have higher inhibition efficiency than KI or plant extract only. Similar results were reported by Eddy *et al.* (2009a, b; 2010) and Ebenso (2003).

 Table 2: Calculated values of inhibition efficiencies (%) for Aluminium corrosion in varying HCl, plant extract and KI concentrations

| Corrodent<br>Concentration |         | 0.20M HCl |      |      | 0.40M HCl |      |             | 0.60 | м но | 21          | 0.80M HCl |      |      |
|----------------------------|---------|-----------|------|------|-----------|------|-------------|------|------|-------------|-----------|------|------|
| Halide                     | Extract | KI        | PE   | KI + | KI        | PE   | <b>KI</b> + | KI   | PE   | <b>KI</b> + | KI        | PE   | KI + |
| Conc.                      | Conc.   |           |      | PE   |           |      | PE          |      |      | PE          |           |      | PE   |
|                            | 0.0g/L  | 0.0       | 0.0  | 0.0  | 0.0       | 0.0  | 0.0         | 0.0  | 0.0  | 0.0         | 0.0       | 0.0  | 0.0  |
| <b>0.20M</b>               | 0.2g/L  | 77.3      | 86.7 | 88.6 | 38.9      | 83.3 | 86.7        | 30.7 | 13.2 | 70.0        | 32.5      | 16.9 | 90.4 |
|                            | 0.4g/L  | 68.2      | 86.7 | 92.4 | 33.3      | 88.9 | 89.3        | 88.7 | 86.8 | 91.5        | 13.3      | 38.6 | 83.1 |
|                            | 0.6g/L  | 78.2      | 88.4 | 88.6 | 66.7      | 55.6 | 88.9        | 79.3 | 79.3 | 90.0        | 16.9      | 1.2  | 92.8 |
|                            | 0.0g/L  | 0.0       | 0.0  | 0.0  | 0.0       | 0.0  | 0.0         | 0.0  | 0.0  | 0.0         | 0.0       | 0.0  | 0.0  |
| <b>0.40M</b>               | 0.2g/L  | 77.3      | 86.7 | 88.6 | 38.9      | 83.3 | 46.7        | 30.7 | 13.2 | 90.6        | 32.5      | 16.9 | 96.4 |
|                            | 0.4g/L  | 68.2      | 86.7 | 91.5 | 33.3      | 88.9 | 55.6        | 88.7 | 86.8 | 84.9        | 13.3      | 38.6 | 90.0 |
|                            | 0.6g/L  | 78.2      | 88.4 | 86.7 | 66.7      | 55.6 | 77.8        | 79.3 | 79.3 | 90.0        | 16.9      | 1.2  | 92.8 |
|                            | 0.0g/L  | 0.0       | 0.0  | 0.0  | 0.0       | 0.0  | 0.0         | 0.0  | 0.0  | 0.0         | 0.0       | 0.0  | 0.0  |
| 0.60M                      | 0.2g/L  | 77.3      | 86.7 | 97.7 | 38.9      | 83.3 | 66.7        | 30.7 | 13.2 | 91.0        | 32.5      | 16.9 | 96.4 |
|                            | 0.4g/L  | 68.2      | 86.7 | 93.2 | 33.3      | 88.9 | 44.4        | 88.7 | 86.8 | 91.0        | 13.3      | 38.6 | 90.0 |
|                            | 0.6g/L  | 78.2      | 88.4 | 86.7 | 66.7      | 55.6 | 66.7        | 79.3 | 79.3 | 91.0        | 16.9      | 1.2  | 95.2 |

Key: KI (Potassium Iodide); PE (Plant Extract)

From the results presented in Table 3, similar results to that of the use of KI were obtained with some exceptions. It was observed that the inhibition efficiency of KBr was lower than that of the plant extract which is much lower than

the combination of the two (plant extract and KBr) in 0.20M and 0.40M HCl concentrations, while at higher concentrations of 0.60M and 0.80M HCl and concentrations of both plant extract and halide, lower inhibition values were obtained.

Table 3: Calculated values of Inhibition efficiencies (%) for Aluminium corrosion in<br/>varying HCl, plant extract and KBr concentrations

| Corrodent<br>Concentration |         | 0.20M HCl |      |       | 0.40M HCl |      |       | 0.60M HCl |      |       | 0.80M HCl |           |  |
|----------------------------|---------|-----------|------|-------|-----------|------|-------|-----------|------|-------|-----------|-----------|--|
| Halide                     | Extract | KBr       | PE   | KBr + | KBr       | PE   | KBr + | KBr       | PE   | KBr + | KBr       | PE KBr +  |  |
| Conc.                      | Conc.   |           |      | PE    |           |      | PE    |           |      | PE    |           | PE        |  |
|                            | 0.0g/L  | 0.0       | 0.0  | 0.0   | 0.0       | 0.0  | 0.0   | 0.0       | 0.0  | 0.0   | 0.0       | 0.0 0.0   |  |
| <b>0.20M</b>               | 0.2g/L  | 75.4      | 86.7 | 90.5  | 11.1      | 83.3 | 50.0  | 22.6      | 13.2 | 32.1  | 80.7      | 16.9 42.2 |  |
|                            | 0.4g/L  | 56.4      | 86.7 | 85.8  | 50.0      | 88.9 | 94.4  | 1.9       | 86.8 | 86.8  | 80.7      | 38.6 12.0 |  |
|                            | 0.6g/L  | 50.8      | 92.0 | 92.4  | 38.9      | 55.6 | 33.3  | 11.3      | 79.2 | 83.0  | 14.5      | 1.2 34.9  |  |
|                            | 0.0g/L  | 0.0       | 0.0  | 0.0   | 0.0       | 0.0  | 0.0   | 0.0       | 0.0  | 0.0   | 0.0       | 0.0 0.0   |  |
| <b>0.40M</b>               | 0.2g/L  | 75.4      | 86.7 | 84.9  | 11.1      | 83.3 | 55.6  | 22.6      | 13.2 | 11.3  | 80.7      | 16.9 12.0 |  |
|                            | 0.4g/L  | 56.4      | 86.7 | 93.2  | 50.0      | 88.9 | 76.0  | 1.9       | 86.8 | 77.4  | 80.7      | 38.6 10.8 |  |
|                            | 0.6g/L  | 50.8      | 92.0 | 86.7  | 38.9      | 55.6 | 38.9  | 11.3      | 79.2 | 96.2  | 14.5      | 1.2 90.4  |  |
|                            | 0.0g/L  | 0.0       | 0.0  | 0.0   | 0.0       | 0.0  | 0.0   | 0.0       | 0.0  | 0.0   | 0.0       | 0.0 0.0   |  |
| 0.60M                      | 0.2g/L  | 75.4      | 86.7 | 84.9  | 11.1      | 83.3 | 61.1  | 22.6      | 13.2 | 3.8   | 80.7      | 16.9 50.6 |  |
|                            | 0.4g/L  | 56.4      | 86.7 | 93.2  | 50.0      | 88.9 | 33.3  | 1.9       | 86.8 | 73.6  | 80.7      | 38.6 51.8 |  |
|                            | 0.6g/L  | 50.8      | 92.0 | 83.0  | 38.9      | 55.6 | 61.1  | 11.3      | 79.2 | 96.2  | 14.5      | 1.2 73.5  |  |

Key: KBr (Potassium Bromide); PE (Plant Extract)

Table 4 presents the calculated values of Inhibition efficiencies (%) for Aluminium corrosion in varying HCl, plant extract and KCl concentrations. Here the use of KCl alone and the combination of KCl with plant extract proved very low values of inhibition, suggesting that inhibition of the aluminium corrosion were barely observed. Both KCl alone and its combination with the plant extract cannot be used as an inhibitor at higher HCl concentrations.

| Corrodent<br>Concentration |         | 0.20M HCl |      |       |      | 0.40M HCl |       |      | 60M H | ICI   | 0.80M HCl |      |       |
|----------------------------|---------|-----------|------|-------|------|-----------|-------|------|-------|-------|-----------|------|-------|
| Halide                     | Extract | KCl       | PE   | KCl + | KCl  | PE        | KCl + | KCl  | PE    | KCl + | KCl       | PE   | KCl + |
| Conc.                      | Conc.   |           |      | PE    |      |           | PE    |      |       | PE    |           |      | PE    |
|                            | 0.0g/L  | 0.0       | 0.0  | 0.0   | 0.0  | 0.0       | 0.0   | 0.0  | 0.0   | 0.0   | 0.0       | 0.0  | 0.0   |
| <b>0.20M</b>               | 0.2g/L  | 13.6      | 86.7 | 96.2  | 22.0 | 83.3      | 61.1  | 69.8 | 13.2  | 56.6  | 52.0      | 16.9 | 52.0  |
|                            | 0.4g/L  | 64.0      | 86.7 | 77.3  | 71.0 | 88.9      | 76.4  | 49.1 | 86.8  | 13.2  | 51.0      | 38.6 | 39.0  |
|                            | 0.6g/L  | 83.0      | 92.0 | 92.4  | 94.0 | 55.6      | 38.9  | 15.1 | 79.2  | 88.7  | 61.4      | 1.2  | 75.9  |
|                            | 0.0g/L  | 0.0       | 0.0  | 0.0   | 0.0  | 0.0       | 0.0   | 0.0  | 0.0   | 0.0   | 0.0       | 0.0  | 0.0   |
| <b>0.40M</b>               | 0.2g/L  | 13.6      | 86.7 | 44.0  | 22.0 | 83.3      | 33.3  | 69.8 | 13.2  | 43.0  | 52.0      | 16.9 | 25.0  |
|                            | 0.4g/L  | 64.0      | 86.7 | 31.8  | 11.7 | 88.9      | 66.7  | 49.1 | 86.8  | 32.1  | 51.0      | 38.6 | 69.0  |
|                            | 0.6g/L  | 83.0      | 92.0 | 3.4   | 19.4 | 55.6      | 66.7  | 15.1 | 79.2  | 3.8   | 62.4      | 12.0 | 62.7  |
|                            | 0.0g/L  | 0.0       | 0.0  | 0.0   | 0.0  | 0.0       | 0.0   | 0.0  | 0.0   | 0.0   | 0.0       | 0.0  | 0.0   |
| 0.60M                      | 0.2g/L  | 13.6      | 86.7 | 8.0   | 22.0 | 83.3      | 16.7  | 69.8 | 13.2  | 7.5   | 52.0      | 16.9 | 30.0  |
|                            | 0.4g/L  | 64.0      | 86.7 | 7.2   | 11.7 | 88.9      | 33.3  | 49.1 | 86.8  | 7.6   | 15.1      | 38.6 | 49.0  |
|                            | 0.6g/L  | 83.0      | 92.0 | 6.1   | 19.4 | 55.6      | 66.7  | 15.1 | 79.2  | 5.7   | 10.6      | 1.2  | 56.0  |

Table 4: Calculated values of Inhibition efficiencies (%) for Aluminium corrosion invarying HCl, plant extract and KCl concentrations

Key: KCl (Potassium Choride); PE (Plant Extract)

# Synergism

Synergism is a combined action of a compound greater in total effect than the sum of individual effects. It has become one of the most important factors in inhibition process and serves as a basis for all modern corrosion inhibitor formulation. Synergism of corrosion inhibitors is either due to interaction between components of the inhibitors or due to interaction between the inhibitor and one of the ions present in aqueous solution (Eddy *et al.*, 2009a; Cenoui *et al.*, 2010). Synergistic studies were carried out on the combination of the inhibitor-plant extract (0.2, 04, 0.6M) with KI, KCl, and KBr (0.2, 04, 0.6M) in HCl (0.2, 04, 0.6, 0.8M) respectively. Synergism parameter (S) of the inhibitor due to halide was calculated using Equation (3)

$$S = \frac{1 - I_A - I_B + I_A I_B}{1 - I_{AB}}$$
 (3)

where  $I_A$  and  $I_B$  are inhibition efficiencies of the inhibitor and halide, respectively, and  $I_{AB}$  is the inhibition efficiency of the inhibitor, when it is combined with halide. Values of S calculated are recorded in table 4. S approaches 1 when no interaction between the inhibitor compounds exists. When S<1, the antagonistic interaction prevails, this may be attributed to competitive adsorption. In this study, the values were found to be less than unity (except for KCl and KBr in some cases) indicating that the adsorption of KI and KBr on the surface of aluminium antagonizes the adsorption of the inhibitor and that the performance of ethanol extract of *Anogeissus leoicarpus* as an inhibitor can be enhanced by synergistic combination of KCl and not KI and KBr. It was also observed that the synergism factor was higher at higher plant extract, KCl and HCl concentrations (Cenoui *et al.*, 2010). The values that were found to be less than unity indicate that their adsorption on the surface of Aluminium antagonizes the adsorption of the inhibitor can be enhanced by synergistic combination with KCl.

| Corrodent<br>Concentration |         | 0.2    | OM HC  | I     | 0.40  | )M HC  | ני     | 0.6   | OM HO  |       | 0.80M HCl |       |       |
|----------------------------|---------|--------|--------|-------|-------|--------|--------|-------|--------|-------|-----------|-------|-------|
| Halide                     | Extract | KI     | KCl    | KBr   | KI    | KCl    | KBr    | KI    | KCl    | KBr   | KI        | KCl   | KBr   |
| Conc.                      | Conc.   |        |        |       |       |        |        |       |        |       |           |       |       |
|                            | 0.0g/L  | 1.0    | 1.0    | 1.0   | 1.0   | 1.0    | 1.0    | 1.0   | 1.0    | 1.0   | 1.0       | 1.0   | 1.0   |
| 0.20M                      | 0.2g/L  | -74.6  | 13.2   | -71.0 | -36.4 | -30.8  | -17.0  | -44.3 | -18.1  | -10.8 | -6.7      | 17.9  | 33.8  |
|                            | 0.4g/L  | -63.0  | -70.8  | -56.0 | -49.6 | 104.5  | -46.1  | -83.1 | 351.8  | -0.9  | -6.9      | 66.3  | 247.7 |
|                            | 0.6g/L  | -112.0 | -88.7  | -54.0 | -40.8 | 281.4  | -63.9  | -61.8 | 14.4   | 11.8  | -0.4      | -3.2  | -1.0  |
|                            | 0.0g/L  | 1.0    | 1.0    | 1.0   | 1.0   | 1.0    | 1.0    | 1.0   | 1.0    | 1.0   | 1.0       | 1.0   | 1.0   |
| <b>0.40M</b>               | 0.2g/L  | -74.6  | -27.9  | -76.0 | -68.3 | 59.1   | -15.3  | -48.9 | 22.7   | -32.5 | -6.3      | 35.9  | 111.9 |
|                            | 0.4g/L  | -63.7  | -175.0 | -52.0 | -52.1 | 157.5  | -43.5  | -89.7 | 138.2  | -1.0  | -5.7      | 85.5  | 272.9 |
|                            | 0.6g/L  | -114.0 | -368.0 | -58.0 | -20.3 | 162.4  | -54.6  | -61.8 | 454.0  | 10.1  | -0.4      | -3.8  | -0.4  |
|                            | 0.0g/L  | 1.0    | 1.0    | 1.0   | 1.0   | 1.0    | 1.0    | 1.0   | 1.0    | 1.0   | 1.0       | 1.0   | 1.0   |
| 0.60M                      | 0.2g/L  | -67.6  | -140.0 | -76.0 | -47.5 | 108.0  | -13.8  | -44.3 | 117.7  | 70.4  | -6.3      | 30.3  | 28.3  |
|                            | 0.4g/L  | -62.5  | -872.0 | -52.0 | -65.4 | 319.8- | -133.0 | 59.0  | 655.9  | -1.1  | -5.7      | 120.1 | -63.6 |
|                            | 0.6g/L  | -114.0 | 1149.0 | -60.0 | -54.6 | 162.4  | -34.4  | -61.8 | -189.0 | 10.1  | -0.4      | 4.1   | -0.5  |

Table 5: Synergism parameter (S) for plant extract, halide and plant extract-halide mixture for the corrosion aluminium in HCl solution

# Conclusion

From the results and findings of this study, the following conclusions can be drawn:

- 1. Ethanol extract of *Anogeissus leiocarpus* is a good inhibitor for the corrosion of aluminium in HCl solution.
- 2. The inhibition efficiency of the extract is due to the presence of saponins, tannins, flavonoids, cardiac glycosides, and alkaloids present in the plant extract.
- 3. KI has the highest inhibition efficiency followed by KBr and KCl for reason that iodide has the highest ionic radii and lower electronegativity.
- 4. The higher the plant extract concentration the higher the inhibition efficiency and vice versa.
- 5. During corrosion of aluminium in HCl solution without the plant extracts, the concentration of KCl and KBr increases the rate of corrosion of aluminium, while for KI a reverse case was observed.
- 6. The higher the corrodent (HCl) concentration the higher the rate of aluminium corrosion.
- 7. From the synergistic studies, values that were found to be less than unity indicate that there adsorption on the surface of Aluminium antagonizes the adsorption of the inhibitor and that the performance of ethanol extract of Anogeissus leiocarpus as an inhibitor can only be enhanced by synergistic combination with KCl.

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