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Inhibition effects of some plant extracts on the acid corrosion of aluminium alloy

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Corrosion inhibition of aluminium alloy (AA3003) in 0.5 M HCl by extracts of selected plants was investigated using gravimetric technique at 30 and 60°C. The studied plant materials include extracts of *Euphorbia hirta and Dialum guineense*. The results indicate that all the extracts inhibited the corrosion process in the medium by virtue of adsorption and inhibition efficiency improved with concentration. Inhibition mechanisms were deduced from the temperature dependence of the inhibition efficiency as well as from activation parameters that govern the process. Adsorption of both plant extracts on the aluminium alloy was found to obey the Langmuir adsorption isotherm. The phenomenon of physical adsorption is proposed from the obtained thermodynamic parameters.

Key words: Corrosion inhibition, aluminium alloy, acid solution, adsorption.

INTRODUCTION

Acid solution are often used in industry for cleaning, descaling and pickling of metallic structures, processes which are normally accompanied by considerable dissolution of the metal. A useful method to protect metals and alloys deployed in service in aggressive environments against corrosion is addition of organic or inorganic species to the solution in contact with the surface in order to inhibit the corrosion reaction and hence reduce the corrosion rate. A number of organic compounds (Ameer et al., 2000; Kissi et al., 2006; Oguzie et al., 2004; Oguzie, 2005; Tang, 2006; Ebenso, 2003; Zhang, 2003; Harek and Larabi, 2004) are known to be applicable as corrosion inhibitors for aluminium alloy in acidic environments. Such compounds typically contain nitrogen, oxygen or sulphur in a conjugated system and function via adsorption of the molecules on the metal surface, creating a barrier to corrodent attack. The adsorption bond strength is dependent on the composition of the metal and corrodent, inhibitor structure and concentration as well as temperature (Kissi et al., 2006). Despite the broad spectrum of organic compounds, the choice of appropriate inhibitor for a particular application is restricted by several factors. These include increased environmen-
tal awareness and the need to promote environmentally friendly processes. Another factor is the vast variety of possible corrosion systems coupled with the specificity of action of most acid inhibitors which often necessitates the use of combinations of additives to provide the multiple services required for effective corrosion inhibition (Oguzie, 2008). 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 low-cost, readily available and renewable sources of materials. The extracts from their leaves, barks, seeds, fruits and roots comprise of mixtures of organic compounds containing nitrogen, sulphur and oxygen atoms and some have been reported to function as effective inhibitors of metal and alloy corrosion in different aggressive environments Zucchi and Omar.,1985; Gunasekaran and Chauhan, 2004; El-Etre, 2003, 2005; Abdallah., 2004; Li et al., 2005). Gunasekaran and Chauhan (2004) assessed the influence of extracts from *Zenthoxylum alatum* leaf extracts on the corrosion of mild steel in phosphoric acid. Li et al. (2005) investigated the inhibitive effect of beberine, extracted from *Coptis chinensis* on mild steel corrosion in 1 M sulphuric acid (Li et al., 2005). Extensive studies of corrosion inhibition efficiencies on

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plant extracts of *Occimum viridis*, *Telferia occidentalis*, *Azadirachta indica* and *Hibiscus sabdariffa* were carried out by Oguzie (2008). The corrosion inhibition efficacy of these extracts is normally ascribed to the presence, in their composition, of complex organic species such as tannins, alkaloids, essential oils, flavonoids and nitrogen bases.

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. The inhibiting effect of *Euphorbia hirta and Dialum guineense* plant extracts on aluminium alloy (AA3003) in 0.5 M HCl was investigated. This study has dual purposes, first to establish the effectiveness of the plant extracts as corrosion inhibitors and secondly to attempt deduction of the inhibition mechanisms through adsorption isotherms. This work is done at high concentration limit to determine optimum concentration and compare for the two extracts. The equation for corrosion rate is given by $CR = K\Delta W / \rho At$ while the inhibition efficiency is given as $I\% = \left(1 - \rho_{inh}/\rho_{blank}\right)\times 100$.

EXPERIMENTAL PROCEDURE

Materials

Aluminium alloy specimens having weight percentage composition as follows; Si-0.362%, Fe-0.549%, Cu-0.077%, Mn-1.219%, Ti-0.026%, Pb-0.063%, Zn-0.004% and the remainder being Al were used. The specimens were of dimensions 2 cm x 2 cm and thickness 1.32 mm. The alloy specimen were polished mechanically using SiC emery papers of grade nos. 220, 400 and 600, washed thoroughly with distilled water and degreased with ethanol and acetone, air dried before being immersed in the acid solution. The blank corrodent was 0.5 M HCl solution. Stock solutions of the plant extract were prepared by boiling weighed amounts of the dried and ground plant material for 3 h in the 0.5 M HCl. The solutions were cooled and then filtered and stored. From the respective stock solutions, inhibitor test solutions were prepared in the concentration range of 0.1 - 0.3 g/L using excess acid as solvent at room temperature and 60°C using water bath.

Weight loss experiments

The cleaned and dried specimens were weighed before immersion in the respective test solutions of 0.5 M HCl using JA 1003A electronic weighing balance with the accuracy of ±0.005. Tests were conducted with different concentrations of inhibitor. At the end of the tests, the specimens were carefully washed in absolute ethanol having used nitric acid to quench further corrosion from taking place, and then reweighed. Triplicate experiments were performed in each case and the mean values reported.

RESULTS AND DISCUSSION

Weight losses and corrosion rates

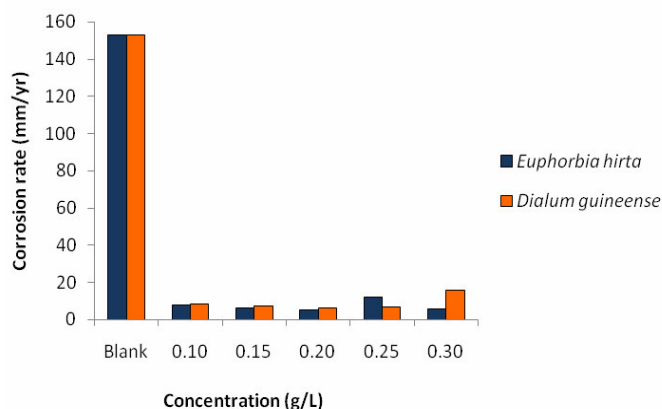The weight loss of the aluminium alloy in 0.5 M HCl with

Figure 1. Corrosion rates of aluminium alloy AA3003 in various concentrations of *Euphorbia hirta* and *Dialum guieense* extracts.

and without the various concentrations of plant extracts is determined after 5h of immersion at 30°C. The corrosion rate values were evaluated as shown in Figure 1 and values of the inhibition efficiencies were obtained as shown in Figure 2. Corrosion rate values of aluminium alloy decrease when the inhibitor concentration increases. The inhibition efficiency increases with increasing inhibitor concentration, reaching optimum value (96%) at 0.2 g/L concentration of both extracts.

Inhibition efficiency and adsorption considerations

The characterization of the corrosion rate of aluminium alloy in the different inhibitor/corrodent solutions was carried out by an assessment of the inhibition efficiency (1%) using Equation 1:

$$I\% = \left(1 - \frac{\rho_{inh}}{\rho_{blank}}\right)\times 100 \qquad 1$$

Where; ρ_{inh} and ρ_{blank} correspond to the corrosion rates in the presence and absence of inhibitor respectively. Figures. 2 shows bar chart of inhibition efficiency to concentration of inhibitor for *E. hirta and D. guineense*, with optimum value of inhibition efficiency of about 96% at 0.2 g/L concentrations of *E. hirta* and *D. guineense* plants extract.

In accounting for the observed protective effect, it should be noted that the extracts comprise mixture of organic and resinous matter (Table 1) some of which have good corrosion inhibiting abilities. The complex chemical compositions make it rather difficult to assign the inhibiting action to a particular constituent or group of constituents. Nevertheless, the net adsorption of the extract organic matter on the metal surface creates a barrier to charge and mass transfer, thus protecting the alloy surface from corrodent attack. The degree of protection varies for different extracts, with notable sensitivity to the inhibitor concentration. Nevertheless, maximum inhi-

Table 1. Major constituents of the studied plants.

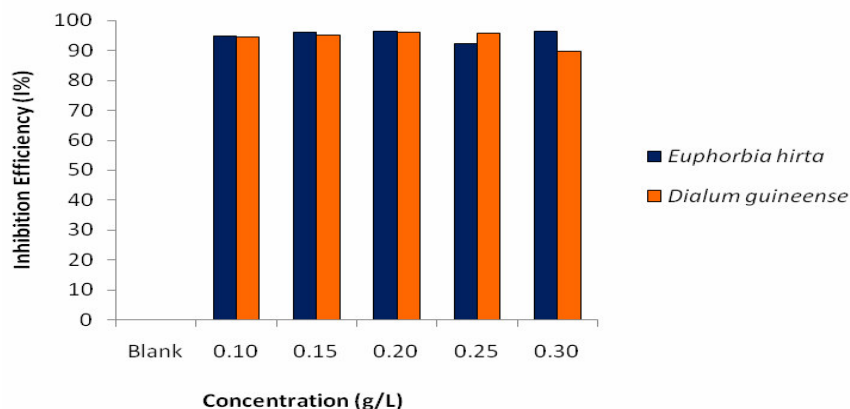| Plant	Major constituents
Euphorbia hirta	Triterpenoids, alkaloids, tannins, glycosides, sterols, essential oil, flavones, phenols.
Dialum guineense	Saponins, tannins, alkaloids, flavonoids, essential oil.

(Okwu et al., 2003 i Wikipedia).

Figure 2. Inhibition efficiencies of various concentrations *Euphorbia hirta* and *Dialum guieense* extracts on aluminium alloy AA3003.

bition efficiency of 96% was observed at concentration of 0.2 g/L for both extracts of *E. hirta* and *D. guineense*. From Table 1, we observed some similarities in the phytochemical components of the extracts, particularly tannins, alkaloids, and essential oil. The inhibitive properties of tannins has been attributed to the reaction of the polyphenolic fraction of the tannins moieties, which ensures effective protection of the metal surfaces. The triterpeniod and other constituents also posses functional groups which are capable of chelating with aluminium ions and thus facilitate strong coordination on the alloy surface (Oguzie, 2008). Having ascertained the effectiveness of these plant materials in the present study, subsequent studies to enable precise interpretation of the nature and composition of the absorbed inhibitor layer will be achieved from in depth studies of the corrosion morphology and characterization of the active materials in the absorbed layer is envisaged.

Langmuir adsorption isotherms

Further elucidation of adsorption mechanism from the experimental data requires estimation of the adsorption modes of the inhibiting species (whether molecular or ionic). The predominant adsorption mode will be dependent on factors such as the extract composition, chemical changes to the extract and the nature of the surface charge on metal. A negative surface charge will favour the adsorption of cations whereas anion adsorption is favoured by a positive surface charge. The ability of Cl⁻ ions in hydrochloric acid to be strongly adsorbed on the metal surface and hence facilitate physical adsorption of inhibitor cations is an important consideration. The plot of the ratio of concentration to surface coverage (C/θ) against concentration (C) displayed a straight line for tested inhibitor (Figures 3 and 4). Table 2 shows the correlation coefficient of the Langmuir adsorption isotherm. The linear plot with high correlation coefficient (0.998) and slope of about unity (0.966) clearly reveals that the surface adsorption process of *E. hirta* and *D. guineense* on the aluminium alloy surface obey the Langmuir adsorption isotherm. Therefore, one can infer that physisorption occurred.

Effect of temperature

Two main types of interaction often describe adsorption of organic inhibitors on a corroding system viz: chemical adsorption and physical adsorption. It has been suggested (Oguzie, 2008; Ahlberg and Friel, 1989) that physisorbed molecules are attached to the metal at the cathodes and essentially retard metal dissolution by stifling the cathodic reaction whereas chemisorbed molecules protect anodic areas and reduce the inherent reactivity of the metal at the sites where they are attached.

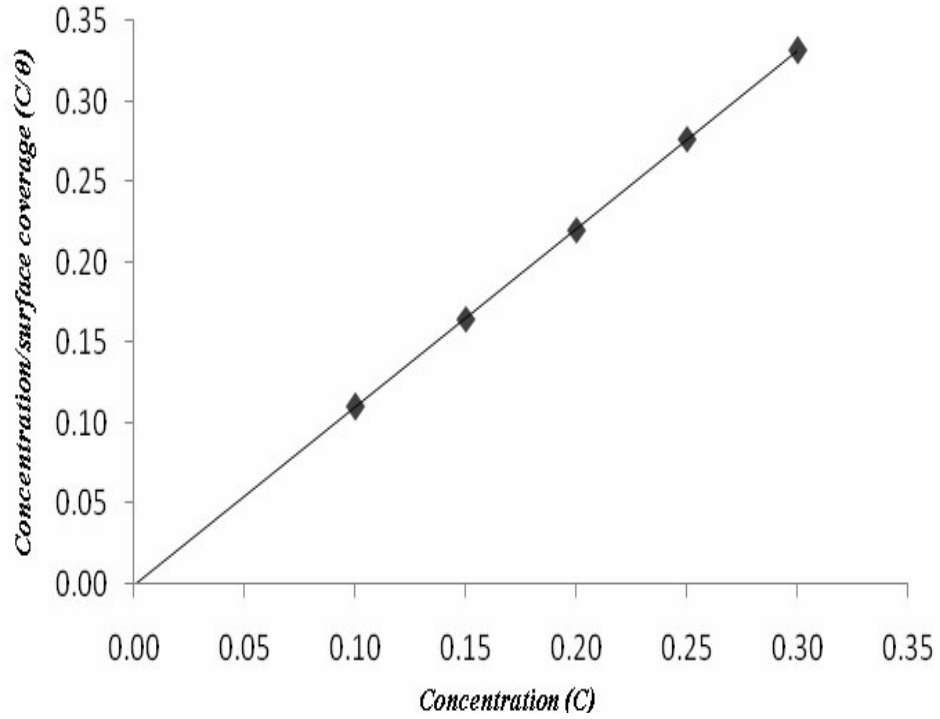The apparent activation energies (Ea) for the corrosion process in absence and presence of inhibitor were eva-

Figure 3. Lamgmuir isotherm for *Euphorbia hirta* adsorption on AA3003 aluminium alloy in 0.5M HCL.
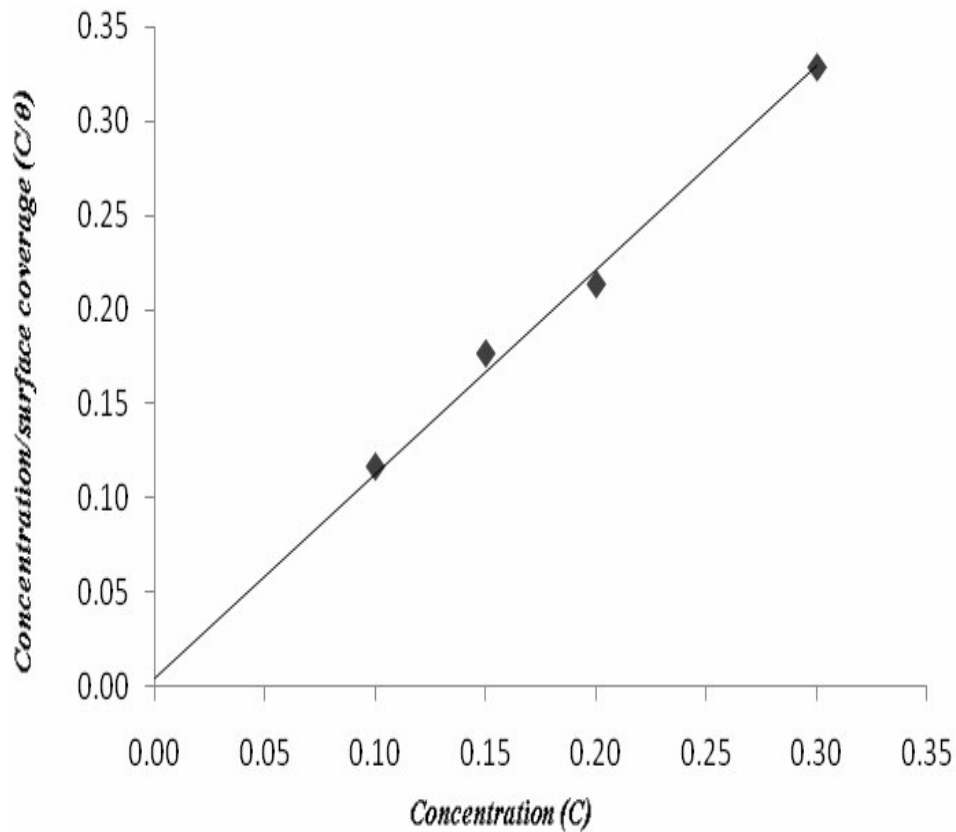

Figure 4. Lamgmuir isotherm for *Dialum guineense* adsorption on AA3003 aluminium alloy in 0.5M HCL.

Table 2. Values of Langmuir Parameters for AA3003 Aluminium Alloy in 0.5M HCl.

Plant extract	Intercept	Slope	K	R^2
EH	0.00	1.11	-750.00	0.999
DG	0.00	1.08	210.53	0.997

Table 3. Calculated values of corrosion rate and inhibition efficiency (1%), activation energy (E_a) and heat of adsorption (Q_{ads}) of *Euphorbia hirta* extract on AA3003 aluminium alloy in 0.5M HCl at different temperatures

Extract concentration	Corrosion rate (mm/yr)		Inhibition efficiency (I%)		E_a(kJmol^{-1})	Q_{ads}(kJmol^{-1})
	30°	60°	30°	60°		
0.10	6.3	10.3	87.8	80.1	45.30	-4.83
0.15	6.1	8.5	88.2	83.6	18.43	-3.18
0.20	7.0	9.2	86.4	82.2	9.15	-2.65
0.25	7.4	8.8	85.8	83.0	37.83	-1.77
0.30	7.7	9.1	85.1	82.4	35.05	-1.65

Table 4. Calculated values of corrosion rate and inhibition efficiency (I%), activation energy (E_a) and heat of adsorption (Q_{ads}) of *Dialum guineense* extract on AA3003 aluminium alloy in 0.5M HCl at different temperatures.

Extract concentration	Corrosion rate (mm/yr)		Inhibition efficiency (I%)		E_a(kJmol^{-1})	Q_{ads}(kJmol^{-1})
	30°	60°	30°	60°		
0.10	6.4	10.7	87.7	79.4	44.24	-5.11
0.15	6.8	9.7	86.9	81.2	4.41	-3.57
0.20	7.2	8.9	86.0	82.7	12.92	-2.08
0.25	8.0	8.8	84.5	82.9	11.06	-0.98
0.30	2.4	5.5	95.3	89.3	37.69	-7.38

luated from Arrhenius equation.

$$\log \frac{\rho_2}{\rho_1} = \frac{E_a}{2.303\,R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \qquad 2$$

Whereas estimates of the heats of adsorption (Q_{ads}) were obtained from the trend of surface coverage with temperature as follows (Ekpe et al., 1999);

$$Q_{ads} = 2.303\,R\left[\log\left(\frac{\theta_2}{1-\theta_2}\right) - \log\left(\frac{\theta_1}{1-\theta_1}\right)\right] \times \frac{T_1 T_2}{T_2 - T_1} \qquad 3$$

ρ_1 and ρ_2 are the corrosion rates in temperatures T_1 and T_2, respectively while θ_1 and θ_2 are the degrees of surface coverage at temperature T_1 and T_2 and R is the gas constant.

$$K = \frac{1}{55.5}\exp\left(\frac{-\Delta G^o_{ads}}{RT}\right) \qquad 4$$

The standard free energy of adsorption, ΔG°_{ads}, which can characterize the interaction of adsorption molecules and metal surface, was calculated by equation (4). The negative values of ΔG°_{ads} ensure the spontaneity of adsorption process and stability of the adsorbed layer on the aluminium surface. Generally, the values of ΔG°_{ads} around -20kJ/mol or lower are consistent with physicsorption, while those around -40kJ/mol or higher involve chemisorptions (Umoren et al., 2006; Ebenso et al. 2009, Obot et al., 2009). The values of free energy, ΔG°_{ads}, are -26.80 and -23.35 kJmol^{-1} for *E. hirta* and *D. guineense* respectively which is consistent with literature survey and therefore authenticates physical adsorption. This implies that the plant extracts adheres on the surface of the corroding system and so gives a very strong inhibitor.

The calculated values of E_a and Q_{ads} are given in Tables 3 and 4. Analysis of the temperature dependence of inhibition efficiency as well as comparison of corrosion activation energies in the presence of inhibitor gives some insight into the possible mechanism of inhibitor adsorption. A decrease in inhibition efficiency with rise in temperature, with analogous increase in corrosion activetion energy in the presence of inhibitor compared to its absence, is frequently interpreted as being suggestive of

formation of an adsorption film of physical (electrostatic) nature. The effect, corresponding to an increase in inhibition efficiency with rise in temperature and lower activation energy in the presence of inhibitor, suggests a chemisorption mechanism (Oguzie et al., 2004; Ebenso, 2003; Popova, 2003). From the foregoing, the trend for the extracts of *E. hirta and D. guineense* suggests a predominant effect physisorption of inhibiting species in 0.5 M HCl.

Conclusion

The extracts from the leaves of *E. hirta and D. guineense* were found to be effective green inhibitors of aluminium alloy (AA3003) in 0.5 M HCl. The corrosion process was inhibited by adsorption of the extract organic matter on the aluminium alloy surface according to the Langmuir isotherm. However, *E. hirta* plant extract exhibited better inhibition efficiency than the *D. guineense* plant extract. The phenomenon of physical adsorption is proposed from the obtained thermodynamic parameters.

ACKNOWLEDGEMENT

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