Eurasian ChemTech Journal 9 (2007) 91-96

Non-Toxic Plant Extract as Corrosion Inhibitor for Chill Cast Al-Zn-Mg Alloy in Caustic Soda Solution

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Abstract

The corrosion inhibition of Hibiscus Teterifa on the corrosion of chill cast Al-Zn-Mg alloy in 0.5 Molar solution of NaOH was studied using weight loss method. The alloy of composition 4.5% Zn, 2% Mg and balance Al was chill cast at the Foundry Shop of the National Metallurgical Development Centre, Jos, Nigeria. After casting, the alloy was cut and machined to corrosion coupons and immersed into 0.5 M solution of NaOH containing varying concentrations of the inhibitor (5-20% v/v) at temperatures of 30, 50 and 70°C respectively. It was found that the adsorption of Hibiscus Teterifa could prevent this alloy from weight loss and the adsorption accorded with the Langmuir adsorption isotherm. Thermodynamic parameters such as adsorption heat and adsorption free energy were obtained from experimental data. The kinetic data activation energy at different concentrations of the inhibitor was calculated. The most suitable range of inhibitor concentration was discussed. The inhibitive action was satisfactorily explained by using both thermodynamic and kinetic models. The mechanism of inhibition is by physical adsorption and the adsorbed molecules of the inhibitor lies on the surface of the alloy blocking the active corrosion sites on the alloy hence, lowering the corrosion rate.

Introduction

Corrosion inhibitors are widely used in industry to prevent or reduce corrosion rate of metals in alkaline, acidic media and industrial processes such as acid pickling and cleaning of refinery equipment, oil well acidizing and acid descaling [1]. The action of inhibitors is always associated with changes in the state of the surface being protected due to adsorption or formation of poorly soluble compounds with metal cations. Such compounds decrease the area of active metal surface and/or increase the corrosion energy [2].

The first and primary step in the action of these inhibitors in acid solutions is generally agreed to be adsorption unto the metal/alloy surfaces, which are usually oxide- free in the solutions. The adsorption of the inhibitors unto the metal/alloy surfaces retards the cathodic or anodic electrochemical processes that accompany corrosion of the metal/alloy [2,3]. The adsorption may be due to electrostatic attractive forces between ionic charges or dipoles on the adsorbed species and or the electric charges on the metal/alloy at the metal/alloy/solution interface [2,4,5].

Studies have shown that the efficiency of inhibition (expressed as the relative reduction in corrosion rate) is related to the amount of adsorbed inhibitor on the metal surface [6]. The inhibitor after absorption may form a surface film that acts as a physical barrier restricting the diffusion of ions/molecules to or from the metal/alloy surface and may prevent the metal atoms from participating in either the anodic or cathodic reactions of corrosion [7,8]. This simple blocking effect decreases the number of surface metal atoms that are available for corrosion reactions hence lowering the rates of corrosion, and therefore the rate of corrosion is inversely proportional to the amount of inhibitor adsorbed [2,3,9].

Already some researches have been carried on the possibility of using some plant extracts as corrosion inhibitors. Aku *et al.* [9] and Ebenso *et al.* [5] have used extracts from Carica Papaya (papaw), Azadiachta Indica (Meem) and Autorpio Turkiale Sap as in-

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Printed in Kazakhstan

hibitors in acid pickling of mild steel. Chetouani *et al.* [8] studied the corrosion inhibition of iron in HCl acid using jojoba oil. Libin *et al.* [4] used neutral red as corrosion inhibition of cold rolled steel in HCl acid, they concluded that the inhibition action of these plant are influence by the organic compounds in the plant, that the organic compounds act by adsorption on the metal surface.

The use of naturally occurring plant extracts as inhibitors is particularly interesting and economical because they are cheap, non-toxic, ecological friendly and poses littler or no threat to the environment [2,3].

Hibiscus Teterifa commonly called Zobo drink is non-toxic plant grown in abundance in the Northern part of Nigeria, It is commonly used as juice drink during celebrations. Therefore, this research is aimed at looking at the possibility of using this non-toxic plant as a corrosion inhibitor of Al-Zn-Mg alloy in 0.5 Molar caustic solution, since it has being reported by Idenyi *et al.* [10] and Fontana [1] that aluminium based alloys have low corrosion resistance in alkaline media.

Experimental Procedures

Materials and Methods

Materials

The aluminium alloy used in this research was chill cast at the Foundry shop of the National Metallurgical Development centre, Jos, Nigeria. Its composition is 4.5% Zn, 2% Mg and balance Al. The plant extract (Zobo) which served as the inhibitor was obtained by taking 5 kg of the dried flower of the plant (Hibiscus Teterifa) and extracted with ethanol (10 l) in a Soxhlet Extractor. From this stock solution, solutions of different concentrations volume by volume were prepared.

Methods

Determination of the Chemical Composition of Plant Extracts (Inhibitor)

The chemical composition of the plant extract was determined at the Scientific Services Laboratory of the National Metallurgical Development Centre, Jos, Nigeria.

Corrosion Testing

After casting the alloy was cut and machined to corrosion coupons of dimensions 1.5×1.5×1.5 cm. Seventy-five coupons were produced, twenty-five each for the different temperatures (30°C, 50°C and 70°C). The coupons were polished and degreased in absolute ethanol, dried, weighed and stored in a dessicator. Three sets of 0.5 M NaOH solutions containing the inhibitor of concentrations of 5, 10, 15, and 20% v/v were prepared and the coupons immersed in these solutions each at 30°C, 50°C and 70°C. The weight loss of each coupon after 45 minutes was taken over a period of 225 minutes. Then the rate of corrosion, inhibition efficiency, degree of surface coverage, free energy, activation energy and heat of adsorption were determined.

Determination of Corrosion Rate and Inhibition Efficiency (%)

The weight loss were determined by finding the difference between the initial weight of the coupon and the new weight after 45 minutes from the relationships [1,8].

$$W = W_0 - W_F \tag{1}$$

where W – weight loss after 45 minutes, W_0 – initial weight, W_F – final weight after 45 minutes.

And the standard expression for measurement of corrosion rate in Mills per Year (*MPY*) was used which is given as follows [1,12]:

$$MPY = 534W/DAT \tag{2}$$

where MPY – mils per year, W – weight loss in mg, D – density of the materials in g/cm^3, T – time of exposure in hours, A – area in in^2.

The inhibition efficiency was computed using the relationship [2,4,8]:

$$\text{Inhibitor Efficiency} = \frac{W_0 - W}{W_0} \times 100\% \tag{3}$$

where W and W_0 are the corrosion rates with and without inhibitor respectively.

Thermodynamic and Kinetic Models

The activation energy E_a of the corrosion reaction was calculated using Arrhenius equation given by [3,7,11]:

$$\log\frac{R_1}{R_2} = \frac{E_a}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{4}$$

where R_1 and R_2 are the corrosion rates at any given two different temperatures.

Also the Arrhenius plot of the corrosion reaction (Fig. 8) was produced and the free energy of adsorption at different temperatures were determined by equation 5 [4,8]:

$$\Delta G_{ads} = RT\ln(55.5K) \tag{5}$$

where $K = \frac{O}{C(I-O)}$, O – is the degree of surface coverage, C – is the concentration of inhibitor (v/v).

Also the heat of adsorption ΔH_{ads} of the inhibitor was calculated using equation [3,9]:

$$\Delta H_{ads} = 2.303R\left\{\log\left(\frac{O_2}{1-O_2}\right) - \log\left(\frac{O_1}{1-O_1}\right)\right\} \times \frac{T_2T_1}{T_2-T_1}\ \text{[kJ/mol]} \tag{6}$$

where O_2 and O_1 are degree of surface coverage at any two temperatures.

Results and Discussion

Results

Table 1 gives the chemical composition of the metallic cations of the plant extract and the resulted of the organic compounds reveal that this plant extract contain Nitrogenous compound in range of 0.05-1.0%, mostly as free amino acids-asparagines, alanime, betaine, citric acid (35-40%), others malic, benzoic, formic acid occur in trace amount.

Table 1

Chemical composition (metallic cations) of the plant extracts Hibiscus Teterifa (inhibitor)

Element, mg/l	Ca	Mg	Cu	Zn
Percentage	77.3562	15.6085	0.3060	1.2833
Element, mg/l	Mn	Cr	Co	Cd
Percentage	3.3731	0.3889	ND	ND

Figures 1-3 show the variation of the corrosion rates with time of exposure for the three different values of temperature. Figures 4-6 are the variations of inhibition efficiency with time for different temperatures, while Figs. 7-11 shows the variation of surface coverage, activation energy, heat of adsorption and free energy with inhibitor concentration for the different temperatures.

Discussion

Visual Observation of the Coupons

Visual observation of the two categories of coupons (without inhibitor and with inhibitor) after 225 minutes of exposure revealed changes in colour of the coupons from bright shiny surfaces to dull ones. Micro cracks and pits were observed on the coupons which are indication of corrosion attack by the alkaline media. However, the change in colour was more intense with the solutions without inhibitor so was the presence of macro-cracks which was more pronounced in those solutions without inhibitor.

Corrosion Rate and Inhibition Efficiency

From the result of the chemical analysis of the plant extract, it can be seen that the plant extract contains metallic cations of calcium (77%) followed by magnesium (15%), manganese and zinc. The copper and chromium are present in minor quantities while cobalt and cadmium were not detected, the present of organic compounds was also detected.

From the results obtained on the corrosion rate against exposure time for the three different temperatures plotted in Figs. 1-3, it is clear that that corrosion rate generally increase with increase in temperature and decrease with increase in inhibitor concentration. The decrease in corrosion rate with increase inhibitor concentration stopped at 15% inhibitor concentration beyond this level the corrosion rate increases with increase in inhibitor concentration this means that increasing the inhibitor concentration beyond 15% the protective bond of the inhibitor was broken down and the corrosion rate increases [2,3].

The increase in corrosion rate with increase in temperature can be explained to be as result of the increases in the rate of chemical reaction occurring during corrosion and it is a well known fact that increase in temperature brings about increase in rate of chemical reaction hence the rate of corrosion in this case [1,12]. This general decreased in corrosion rate with the increase in inhibitor concentration is attributed to the adsorption of molecule of the inhibitors on the alloy surface, since these inhibitor contain metallic elements (Ca, Mg, Cr and Mn) and organic compounds, these acts as physical barrier to restrict the diffusion of ions to and from of the alloy and

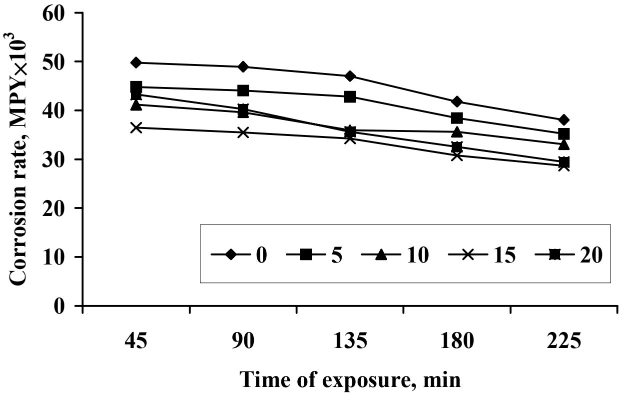

Fig. 1. Variation of corrosion rate with time of exposure at 30°C.

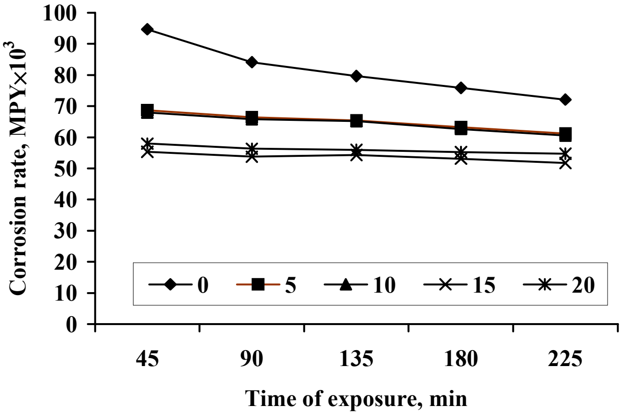

Fig. 2. Variation of corrosion rate with time of exposure at 50°C.

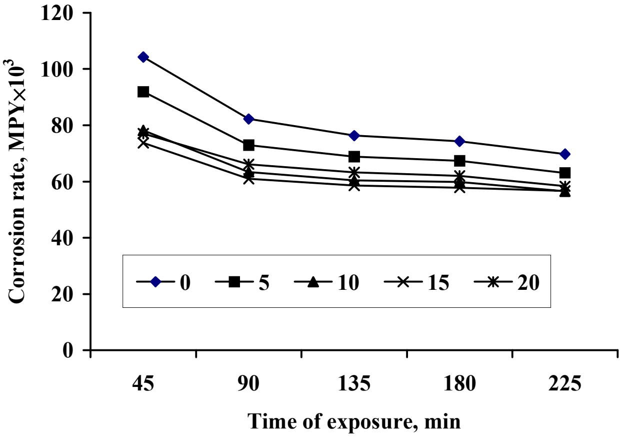

Fig. 3. Variation of corrosion rate with time of exposure at 70°C

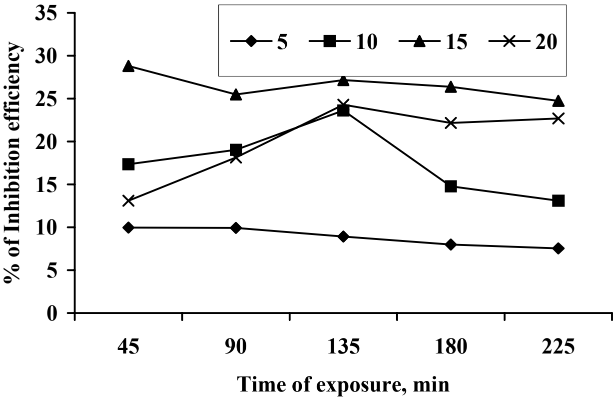

Fig. 4. Variation of percentage of Inhibition efficiency with time of exposure at 30°C.

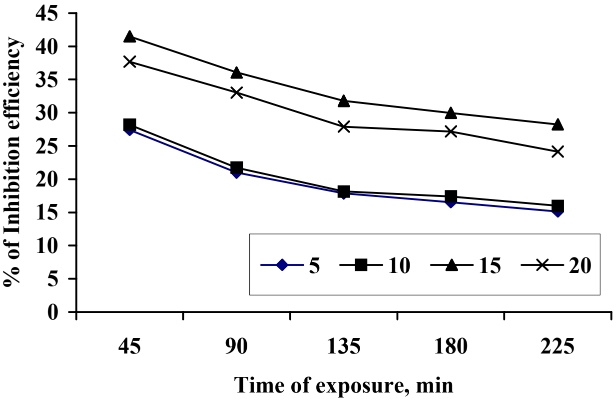

Fig. 5. Variation of percentage of Inhibition efficiency with time of exposure at 50°C.

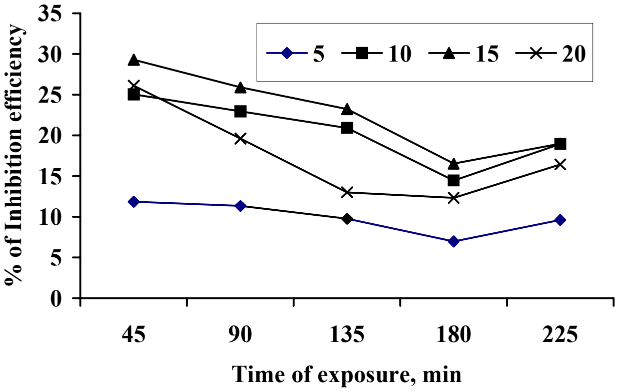

Fig. 6. Variation of percentage of Inhibition efficiency with time of exposure at 70°C.

then prevent the alloy atoms (ions) from participating in further anodic or cathodic reactions, hence resulting in decrease in the corrosion rate [2,3,5,11]. The compounds in the plant extract especially the nitrogen containing organic compounds can adsorb on the metal surface and block the actives sites on the surface, thereby reducing the corrosion rate in the medium, which means the organic compounds are the major ions responsible for the decreased in corrosion [2,3,4,8,10].

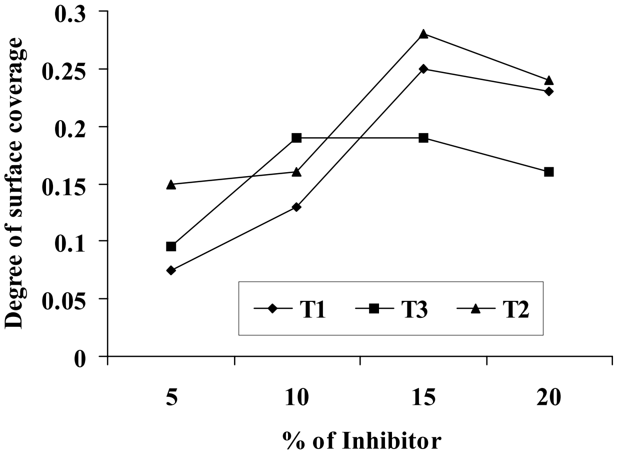

Fig. 7. Variation of degree of surface coverage with percentage of inhibitor.

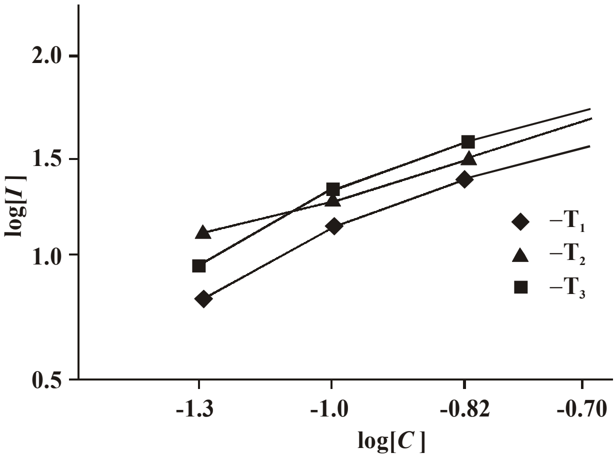

Fig. 8. Variation of log inhibition efficiency with log inhibitor concentration at different temperatures.

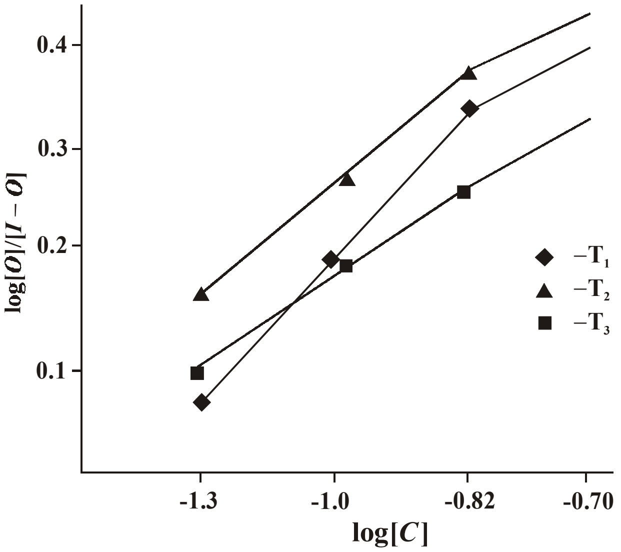

Fig. 9. Variation of $\log([O]/[1-O]$ with log inhibitor concentration at different temperatures.

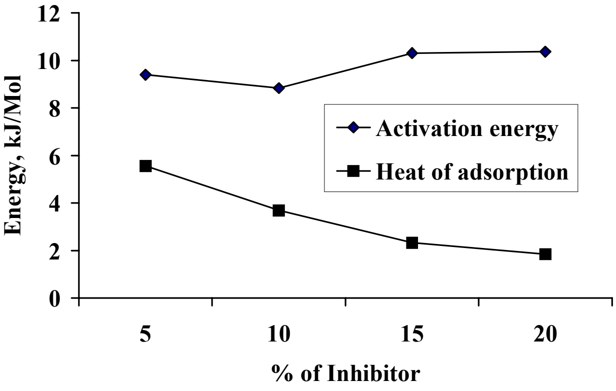

Fig. 10. Variation of heat of adsorption and activation energy with percentage of inhibitor.

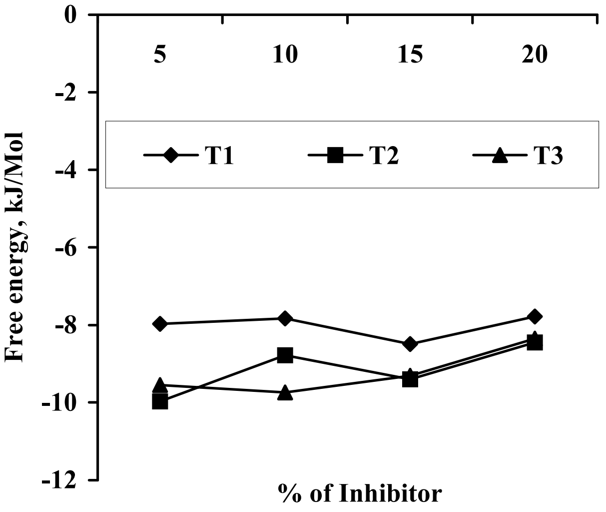

Fig. 11. Variation of free energy with percentage of inhibitor.

The general decrease in the rate of corrosion with exposure time at all the temperatures considered and inhibitor concentrations is probably due to the deposition of corrosion products as the corrosion progresses which tends to shield the corroding surface from further corrosion attack, there by depressing the rate of corrosion [1,12].

From the plots of % inhibition efficiency against exposure time (Figs. 4-6) it can be seen that 15% inhibitor concentration has the highest protection efficiency, for all the temperatures considered and that the protection efficiency decreased with time of exposure. However, the highest inhibition efficiency of 44.5% was obtained at 50°C followed 30% at 30°C and 29% at 70°C respectively (Figs. 4-6) showing that the inhibitor act best at 50°C. The plot of the degree of surface coverage against inhibitor concentration (Fig. 7) revealed that 15% inhibitor concentration has the highest protection efficiency since the highest degree of surface coverage by the inhibitor occurred at 15% v/v inhibitor concentration, which is in agreement with the earlier studied of [4,8,9].

It can be seen in Figure 10 that the activation energy increases with increase in the concentration of the inhibitor and decrease in temperature thus indicating that the inhibitor is more effective at lower temperature [4]. Also since the values obtained are lower than 10 kJ/mol it means that the mechanism of the corrosion reaction is by physical adsorption of the inhibitor unto the alloy surface [1,3]. While the negative sign of free energy of adsorption (see Fig. 11), also suggest a strong interaction of the inhibitor molecules on the alloy surface, and indicate spontaneous adsorption of the inhibitor on the alloy surface [4,9].

Since the values obtained for heat of adsorption (Fig.10) are all less than 10 kJ/mol then physical adsorption phenomenon can be proposed because the nature of adsorption depends on the values of ΔH_{ads}, if $\Delta H_{ads} < 10$ kJ/mol the adsorption is probably physical adsorption and if $\Delta H_{ads} > 10$ kJ/mol the adsorption is chemical [4,5].

The straight line graphs shown in Figures 8 and 9 indicate that adsorption of the inhibitor on the metal surface follow the Langmuir adsorption, suggesting monolayer physical adsorption at lower concentrations of the inhibitor, at higher concentrations multilayer adsorption takes place. this behaviour is with agreement with the weight loss and gives added support that the organic compounds containing nitrogen atoms are effective as inhibitor in this medium [4,8,13].

Conclusions

Hibiscus Teterifa inhibits the corrosion of this alloy in 0.5 M NaOH solution subject to a maximum level of 15% inhibitor concentration.

The mechanism of interaction between the inhibitor and the alloy is by physical adsorption. The adsorbed inhibitor molecules are attached at the alloy surface thereby blocking active corrosion sites hence lowering the corrosion rate.

The adsorption of Hibiscus Teterifa on the alloy surface in 0.5 M NaOH obeyed the Langmuir adsorption isotherm.

This inhibitor is recommended to be used at 15% concentration in 0.5 M NaOH and for a short period of time only.

Acknowledgment

The authors acknowledge with thanks the management of the National Metallurgical Development Centre, Jos and Ahmadu Bello University Zaria, Nigeria for allowing us used their equipments.

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Received 13 February 2007.