Int. J. Chem. Sci.: 10(3), 2012, 1365-1373
ISSN 0972-768X
www.sadgurupublications.com

GREEN INHIBITOR FOR ALUMINIUM AND MILD STEEL IN ACIDIC MEDIA : A CASE STUDY OF EXUDATES OF *EUCALYPTUS CITRIODORA*

M. A. EZEOKONKWO*, P. O. UKOHA and N. J. N. NNAJI

Department of Pure and Industrial Chemistry, University of Nigeria, Nsukka Enugu State, NIGERIA

ABSTRACT

Investigation of exudates of *Eucalyptus citriodora* as corrosion inhibitor of aluminium and mild steel was carried out using the weight loss technique. In various concentrations of hydrochloric acid solutions, the presence of exudates of *Eucalyptus citriodora* inhibited aluminium and mild steel corrosions. Phenomenon of physical adsorption is proposed for the inhibitions and the processes followed the Temkin adsorption isotherm. Free energies of adsorption indicate spontaneous adsorption. The equilibrium constants of the adsorption processes predict better corrosion inhibition of aluminium than mild steel. Lateral interaction from Temkin plots; suggest repulsive lateral interactions between inhibitor species.

Key words: Aluminium, Mild steel, Weight loss, Acid corrosion, Acid inhibition.

INTRODUCTION

The use of natural occurring substances known as 'green inhibitors' for the control of corrosion, has continued to attract interest. This could be due to the environmental requirements that are currently imposed on the development of cleaner inhibitors[1,2]. In addition, these natural inhibitors are cheap, readily available and possess no threat to the environment[3]. Several works have been reported in the literature on the use of some local plant materials as good corrosion inhibitors. The inhibition efficiencies of some of these plant materials have been attributed to the presence of tannins, saponins, and other phytochemical[4-10]. There are also reports on the use of tannins as eco-friendly corrosion inhibitors[11,12]. Earlier studies have shown that the good inhibition efficiency of some plant materials is due to the adsorption of molecules of phytochemical present in the plant on the metal surface and thus reduces the rate of corrosion process[1,4,11].

*Author for correspondence; E-mail: mercy.ezeokonkwo@unn.edu.com; mercyamara4ever@yahoo.co.uk; puis.ukoha@unn.edu.com; joemeks4u@yahoo.com; Ph.: +234 (0) 8035486024

Measurement of mass loss is one of the widely used methods of inhibition assessment. Studies have shown that vegetable tannins are good inhibitors in acidic media of various metals and alloys and the inhibition mechanisms are dependent on the concentrations of the aggressive environment[1].

The present work reports the corrosion inhibitory action of tannins from the exudates of *Eucalyptus citriodora* for aluminium and mild steel in various concentrations of HCl at 30^{o}C. *Eucalyptus citriodora* is one of the two species of eucalyptus that exudates in the tropics. The other species is *Eucalyptus microtecha*[13]. Earlier studies have shown that *Eucalyptus citriodora* exudates contain 33.7% tannins and 22.7% non-tannins[14]. Other authors have observed that the extract from ethanol gave a higher yield of about 70% tannins compared to 60% yield from water extract[15]. These observations show that the plant materials have high quantity of tannins and that greater quantity of the tannins are extracted in non-aqueous polar solvents than in water since some of the resinous polymeric compounds which are insoluble in water are soluble in ethanol[16]. This makes the exudates of *Eucalyptus citriodora* a viable source of tannin for corrosion inhibition. In view of the fact that large quantities of eucalyptus citriodora exudates are wasted every year in Nigeria[17], there is need to effectively explore these tannins in order to put them in good use in the metallurgy industry.

EXPERIMENTAL

Materials and methods

Aluminium and mild steel (0.03 mm in thickness) used for this study were mechanically press cut into 4 cm x 2 cm and used without further polishing. However, they were degreased in absolute ethanol, dried in acetone and stored in a moisture free desiccator before use. *Eucalyptus citriodora* exudates were obtained from the plantation of Layin Zomo, Zaria, Nigeria and the tannins were extracted as previously reported in the literature[16]. The concentration of the inhibitor (*Eucalyptus citriodora* tannin) prepared and used in this study was 1.0 g per 200 mL hydrochloric acid but solutions of hydrochloric acid were of various concentrations. The hydrochloric acid was of analytical grade and the concentrations range from 0.1 M – 0.5 M. Doubly distilled water was used for the preparation of the solutions.

Weight loss measurements

Weight loss measurements were carried out according to the procedure previously reported in the literature[18]. The concentrations of the corrodent were kept at 0.1 M to 0.5 M and the volume of the test solution was 200 mL. All tests were carried out at 30^{o}C. The difference in weight between the initial weight at a giving time and the final weight of the metals was recorded as the weight loss in every case. The corrosion rate was calculated from the weight loss of the metal coupons using the formula:

$$\text{Corrosion rate } (C_{corr}) = \frac{M_1 - M_2}{At} \quad \ldots(1)$$

where M_1 and M_2 are the masses of the specimen before and after corrosion respectively, A is the total area of the specimen and t is the corrosion time.

The inhibiting efficiencies (%I) of inhibitors were calculated using :

$$\% \text{ I} = (1 - \frac{W_0}{W_1}) \text{ x } 100 \quad \ldots(2)$$

where W_O and W_1 are the corrosion rates for aluminium in the presence and absence of inhibitor respectively in HCl solution at the same temperature. The degree of surface coverage (θ) is given by the equation:

$$\theta = 1 - \frac{W_0}{W_1} \quad \ldots(3)$$

RESULTS AND DISCUSSION

Inhibition efficiency

The values of inhibition efficiency obtained from weight loss measurements for inhibitor concentration in various concentrations of hydrochloric acid solutions at 30^{o}C are as shown in Table 1.

Table 1: Variation of inhibition efficiency with corrodent concentrations at 300^{o}C

Corrodent concentration	Inhibition efficiency (% I)	
	Aluminium	Mild steel
0.1 M	63.510	21.259
0.2 M	44.480	29.293
0.3 M	0.000	19.772
0.4 M	23.140	40.799
0.5 M	26.580	23.143

Inhibition efficiency values tabulated in Table 1 reveal that tannins of *Eucalyptus citriodora* inhibit aluminium and mild steel corrosions in various hydrochloric acid solutions. Obtained inhibition efficiency values by applying Equation 3 were possible due to assumptions that tannins of *Eucalyptus citriodora* adsorbed on both aluminum and mild steel surfaces. This adsorption is believed to be through non-bonding election pairs of oxygen atoms and the π-election of the aromatic rings of the tannins of *Eucalyptus citriodora*. This is because these are electron rich centres, which expectedly should release elections instead of the aluminum or mild, steel and thus reduce corrosion.

Adsorption and thermodynamics studies

Understanding the adsorption mechanism/pattern of tannins of *Eucalyptus citriodora* on either aluminium or mild steel, adsorption isotherm describing the adsorption processes was determined of the common absorption isotherms, the Temkin absorption isotherm seems to give the best fit for our absorption data. This absorption isotherm can be put in linear form from Equation 4 as follows[19]:

$$K_{ads}C = \exp(f\theta) \qquad \ldots(4)$$

$$\mathrm{Ln}C = f\theta - \mathrm{Ln}K_{ads} \qquad \ldots(5)$$

where K_{ads} is the equilibrium constant of the adsorption process, C is the concentration of hydrochloric acid solutions containing 1 g of inhibitor and f is the factor of energetic homogeneity[20].

To the best of our knowledge, Equation 5 for the first time, was first used else where[21]. Table 2 shows obtained adsorption parameters.

Table 2: Adsorption parameters from Temkin isotherm for aluminium and mild steel coupons in 0.1 M – 0.5 M HCl solutions containing 1 g inhibitor

	K_{ads}	F	A	ΔG_{ads}(KJ/mol)
Aluminium	12.415	0.391	-0.196	-16.464
Mild steel	0.800	0.0151	-0.008	-9.556

Free energy of adsorption (ΔG_{ads}) values were determined using Equation 6[22] and shown in Table 2.

$$K_{ads} = {}^{1}/_{55.5} \exp\left({}^{\Delta G ads}/_{55.5}\right) \qquad \ldots(6)$$

The results showed that the absorption capacity/equilibrium constant value, of aluminium is higher than that of mild steel. Free energy of absorption values obtained shows that inhibitor absorption on aluminium was more negative than on mild steel. These indicate better absorption on aluminium than on mild steel.

The factor of energetic in homogeneity (f) is related to the lateral interaction factor (a) thus[22]:

$$f = -2a \qquad \ldots(7)$$

Negative values of lateral interaction factor were obtained, indicative of repulsive lateral interactions between the adsorbed inhibitor species[23.] Due to these repulsive lateral interactions between adsorbed inhibitor species, the corrodent molecules penetrated through and were able to corrode both metals.

Free energy of absorption values are not up to - 40 KJ/mol, hence, physisorption of inhibitor molecules occurred on the metals[20,22].

Inhibitor constituents and inhibition mechanism

In aerated acidic solutions, aluminium and iron corrode and become positively charged. On a part, these positively charged metal ions form complexes, which also adsorb on the metal surfaces. On another part, the tannins of *Eucalyptus citriodora*, loose the required electrons and stay in the solutions as protonated species. By so doing, aluminium and iron are protected from electrochemical processes that would lead to their being corroded. Our explanations are consistent with other reports[20,22,24].

The charges on the metal surfaces in aerated acidic solutions are +3 (aluminium) and +2 (mild steel). There is therefore stronger adsorption between Al^{3+} surface sites and tannins of *Eucalyptus citriodora*, hence, better adsorption than between Fe^{2+} surface sites and tannins of *Eucalyptus citriodora*.

Kinetic studies

Earlier work has shown that corrosion inhibition of metals using organic inhibitors derivable from agricultural by-products, is a first order adsorption process which obeys the following expression[25].

$$\text{Log } W_f = Kt + C \qquad \ldots(8)$$

where W_f is the final weight of metal coupon after treatment, K is the rate constant, t is the time and C is the intercept on y-axis. The values of the rate constant obtained from the plots of log W_f versus time, were substituted into -

$$t_{1/2} = \frac{0.693}{K} \qquad \ldots(9)$$

where $t_{1/2}$ is the half-life for first order reaction processes. The values of half-life are shown in Table 3.

Table 3: Half-lives of metals in the presence and absence of inhibitor

System	Half-life ($t_{1/2}$) (Days)	Half-life ($t_{\frac{1}{2}}$) (Days)
	Aluminium	**Mild steel**
0.1 M	330.070 (495.105)	2310.491 (2310.491)
0.2 M	165.035 (216.608)	2310.49 (230.491)
0.3 M	169.060 (533.190)	2310.491 (6931.472)
0.4 M	135.911 (169.060)	1732.868 (2310.491)
0.5 M	96.270 (198.042)	770.164 (1732.868)

Half-life values in parenthesis are for various concentrations of HCl solutions containing 1 g inhibitor and those not enclosed are for various concentrations of HCl blanks.

For aluminium, the various concentrations of HCl solutions containing 1 g inhibitor all have higher half-lives than for blanks. For mild steel, this was observed for 0.3 M, 0.4 M and 0.5 M HCl solutions containing inhibitor. For Fe-metal our results reveal that at higher HCl concentrations, iron was corroded more hence, more tannin-Fe complexes formed and as such better adsorption and corrosion inhibition. Consequently, at lower HCl concentrations, fewer tannin-Fe complexes were formed and as such, poor adsorption and corrosion inhibition of inhibitor. Calculated corrosion inhibition efficiencies shown in Table 1, show that in 0.1 M and 0.2 M HCl solutions, inhibition efficiencies of 21.3 and 29.3 were low as against a higher value of 40.8 at 0.4 M HCl solution.

We assumed that the kinetics of metal corrosion in aerated acidic solutions obey the following equation[23] :

$$\text{Log } C_{corr} = \text{Log } K + B\log C \qquad \ldots(10)$$

where C_{corr} is the concentration of HCl solution in the presence and absence of inhibitor, K is the rate constant and B is the reaction constant which represents the measure for the inhibitor effectiveness. The following kinetic parameters were obtained.

Table 4: Rate constants (K) for metals in various concentrations of HCl solutions

	Aluminium	Mild steel
Blank	0.00585	0.0181
HCl + inhibitor	0.00226	0.0141

Table 4 reveals lower reaction constants for aluminium and mild steel in HCl solutions (in the presence of inhibitor). These suggest that the presence of tannins of *Eucalyptus citriodora*, reduce aluminium and mild steel corrosion in aerated acidic solutions. Our results are in agreement with other report[23].

CONCLUSIONS

The following major conclusions can be drawn from the present study:

(i) Tannins of *Eucalyptus citriodora* inhibit aluminium and mild steel corrosions in acidic media;

(ii) Tannins of *Eucalyptus citriodora* inhibit aluminium corrosion than mild steel corrosion in acidic media;

(iii) Free energy of adsorption values are negative and suggest spontaneous adsorption of inhibitor species on aluminium and mild steel;

(iv) Values of free energy of adsorption (ΔG_{ads}) are indicative that: physisorption was the adsorption mechanism involved in the corrosion inhibitions of aluminium and mild steel in acidic media;

(v) Temkin adsorption isotherm fitted best-obtained adsorption data for tannins of *Eucalyptus citriodora* on aluminium and mild steel in acidic solutions. Repulsive lateral interactions between adsorbed inhibitor species existed.

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Accepted : 08.07.2012