



Inhibition and Adsorption impact of Leave Extracts of *Cnidoscopus Aconitifolius* on Corrosion of Aluminium Sheet in 1 M Hcl Medium

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KEYWORDS: Activation energy, Gibb's Free Energy, Langmuir adsorption, *Cnidoscopus aconitifolius*, Aluminium sheet.

ABSTRACT: Corrosion inhibition in the presence of alkaloid and non alkaloid extracts of *Cnidoscopus aconitifolius* in 1M HCl was studied using the weight loss and hydrogen evolution techniques at 303, 313 and 333 K. The results obtained revealed that the inhibition efficiency decreased with increase in temperature. Inhibition occurred through adsorption of the alkaloid and non alkaloid extracts molecules on the metal surface. The apparent activation energies, enthalpies and entropies of the dissolution process and the free energies and enthalpies for the adsorption process were determined and discussed. The fundamental thermodynamic functions were used to evaluate important inhibitive properties of *Cnidoscopus aconitifolius*. © JASEM

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Introduction: Corrosion of Aluminium sheet is one of the most common forms of corrosion in acidic medium. The practical importance of such corrosion is in acid pickling of iron, chemical cleaning of scales of boilers, oil and petrochemical industries. Hydrochloric acids and Aluminium sheet are most commonly used in the industries. So this leads to researchers studying the effect of corrosion inhibitors on Aluminium sheet in hydrochloric acid environment (Sudhish et al, 2011). The inhibition of Aluminium in acid solutions by different type of organic compounds has been extensively studied. Among them very few are environmentally acceptable such as natural products i.e. extracts of various parts of plants, pharmaceutically active compounds i.e. antibiotics, antibacterial etc. (Sudhish et al, 2011).

Cnidoscopus aconitifolius, commonly known as Chaya or Tree Spinach, is a large, fast growing leafy perennial shrub that is believed to have originated in the Yucatán Peninsula of Mexico (Grubben & Denton, 2004). The leaves are very high in protein, calcium, iron, carotene, and vitamins A, B and C. The leaves also contain hydrocyanic glycosides, which could cause health problems if the leaves were eaten raw. The leaves are very high in protein, calcium, iron, carotene, and vitamins A, B and C. The leaves also contain hydrocyanic glycosides, which could cause health problems if the leaves were

eaten raw (Grubben and Denton, 2004). In this work, we report the kinetic, activation and adsorption parameters. In addition, the adsorption isotherm for the different temperature range (303, 313 and 333K) was also obtained to show the adsorption model of the inhibitor.

MATERIALS AND METHODS

In order to study the temperature effects on the performance of the alkaloid and non alkaloid extracts of *Cnidoscopus aconitifolius* leaves against aluminium sheet in hydrochloric acid solution without and with different concentrations of the inhibitor at 303, 313 and 333 K, the weight loss method is probably most widely used method of inhibition assessment (Ugi and Abeng, 2013). Aluminium sheet sample was taken as the same size and composition as reported earlier (Ugi et al, 2013). The sheets were mechanically press-cut into 4.00 x 0.08 x 5.00cm and 4cm x 0.008cm x 2.0cm samples. The former meant for weight loss analysis while the later for the hydrogen evolution analysis These were polished with different grades of emery paper, degreased in absolute ethanol, dried in acetone and stored in a moisture free desiccator prior to use (Uwah et al, 2013) and all weighing was done with ADAM PGW – 253e digital analytical balance. The corrosion rates (C_R) of the Aluminium was calculated graphically using the Microsoft Excel spray sheet where a graph of the weight loss per surface area

(mg/cm²) was plotted against time of exposure (hrs) and the corrosion rate values obtained from the slope of the graph that was obtained from the Trendline option of the spray sheet Okafor et al, 2012; Uwah et al, 2013 and Ugi and Uwah, 2012). The surface coverage (θ) and Inhibition efficiency (E%) were determined using the following equations;

$$\theta = \frac{W_o - W_i}{W_o} \quad E\% = \frac{W_o - W_i}{W_o} \times 100$$

where w_o and w_i are the weight loss values in presence and absence of inhibitor, respectively (Loto, 2011 and Nnana et al., 2010).

RESULTS AND DISCUSSION

Weight loss data and analysis: The percentage inhibition efficiency of AECAL and NAECAL extracts has been evaluated by weight loss method at 30°C (Table 1, Figs. 1 and 2). It was observed to increase with increase in concentration of the inhibitor and this behavior indicates that the adsorbed inhibitor molecules formed a barrier film on the aluminium surface (Santhini and Jeyaraj, 2012; Dada et al., 2012 and Ugi and Abeng, 2013) and it decreases with increase in temperature. According to Saratha and Meenakshi, (2010), decrease in inhibition efficiency with increase in temperature indicates physisorption of inhibitor on the corroding

metal surface. It is also attributed to increase in the solubility of the protective films and of any reaction products precipitated on the surface of the metal (Santhini and Jeyaraj, 2012).

Adsorption Isotherm: According to Langmuir adsorption isotherm, θ is related to equilibrium adsorption constant

(K_{ads}) and C by the equation: $\frac{C}{\theta} = \frac{1}{K_{ads}} + C$

Fig. 3 shows the straight lines of C/θ vs. C at different temperatures. The parameters obtained from C/θ vs. C plots were listed in Table 2. These results show that all the linear correlation coefficients (R²) are almost equal to 1 and the slopes are close to 1, which confirmed that the adsorption of the plant extract on aluminium surface good obeyed Langmuir adsorption isotherm Hui et al., (2013) and Pradeep & Mohana, (2013). Table 2 revealed that K_{ads} decreased with increasing temperature, which indicated that the plant extract is easily and strongly adsorbed onto the aluminium sheet surface at lower temperature, however, the adsorbed extract appears to desorb from aluminium sheet surface at higher temperature (Fig 4).

Table 1: Inhibition efficiency of different concentrations of AECAL and NAECAL extracts for corrosion of aluminium in 1M HCl solution evaluated by weight loss technique

Systems	AECAL			NAECAL		
	C _R (mg/cm ² /min)	Surface Coverage (Θ)	η (%)	C _R (mg/cm ² /min)	Surface Coverage (Θ)	η (%)
Blank (1M HCl)	0.472	-	-	0.472	-	-
0.1 g/L	0.207	0.562	56.2	0.441	0.066	6.6
0.5 g/L	0.155	0.671	67.1	0.377	0.201	20.1
0.7 g/L	0.133	0.718	71.8	0.373	0.210	21.0
1.0 g/L	0.131	0.722	72.2	0.357	0.244	24.4
2.0 g/L	0.099	0.791	79.1	0.297	0.371	37.1

Table 2: Adsorption parameters for aluminium in 1 M HCl solutions containing AECAL and NAECAL

Temp. (K)	AECAL				NAECAL			
	Equil. Const. k (g/L)	Corr. Coef. (R2)	Slope	ΔG* ads (KJ/mol)	Equil. Const. k (g/L)	Corr. Coef. (R2)	Slope	ΔG* ads (KJ/mol)
303	23.981	0.9993	1.061	-444.22	9.569	0.9976	1.336	-315.78
313	9.066	0.9959	1.123	-318.40	5.711	0.9956	1.401	-251.65
333	3.050	0.9514	1.184	-171.33	4.953	0.9867	1.477	-245.85

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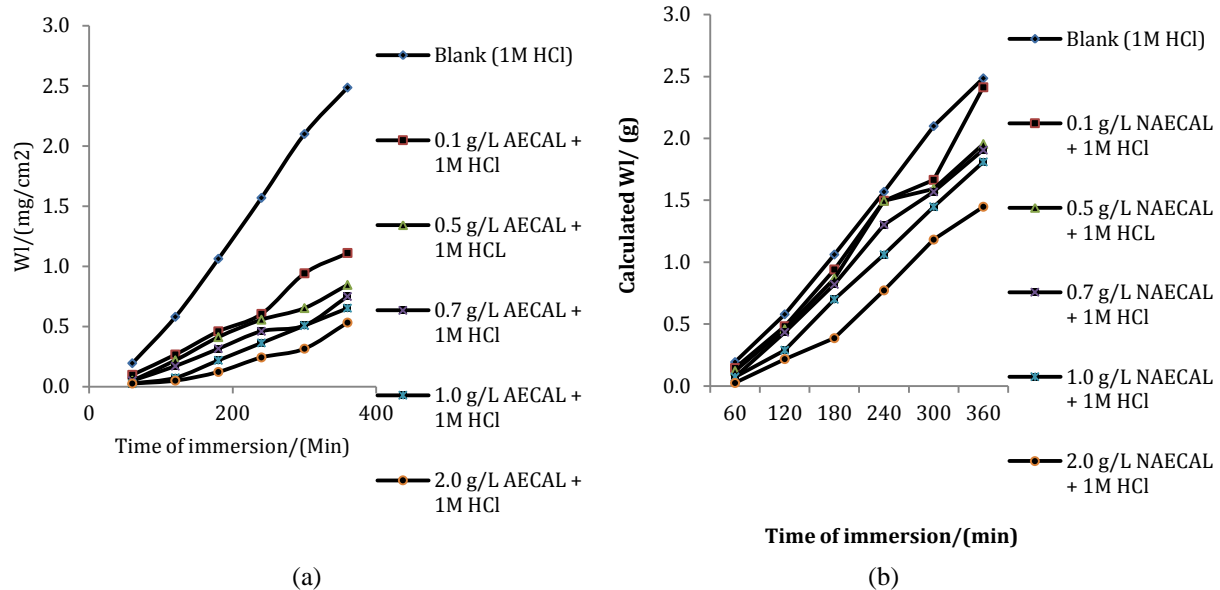


Fig. 1: Variation of weight loss with immersion time for aluminium samples in 1 M HCl solution containing (a) AECAL and (b) NAECAL

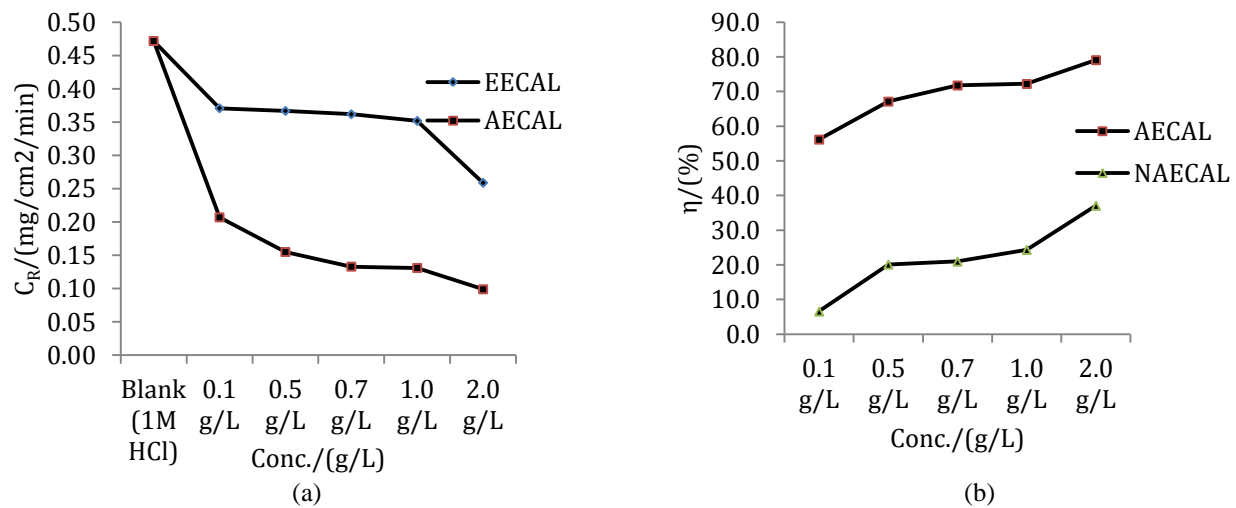


Fig. 2: Variation of (a) C_R and (b) IE(%) with AECAL and NAECAL extract concentrations for Aluminium samples in 1 M HCl solution

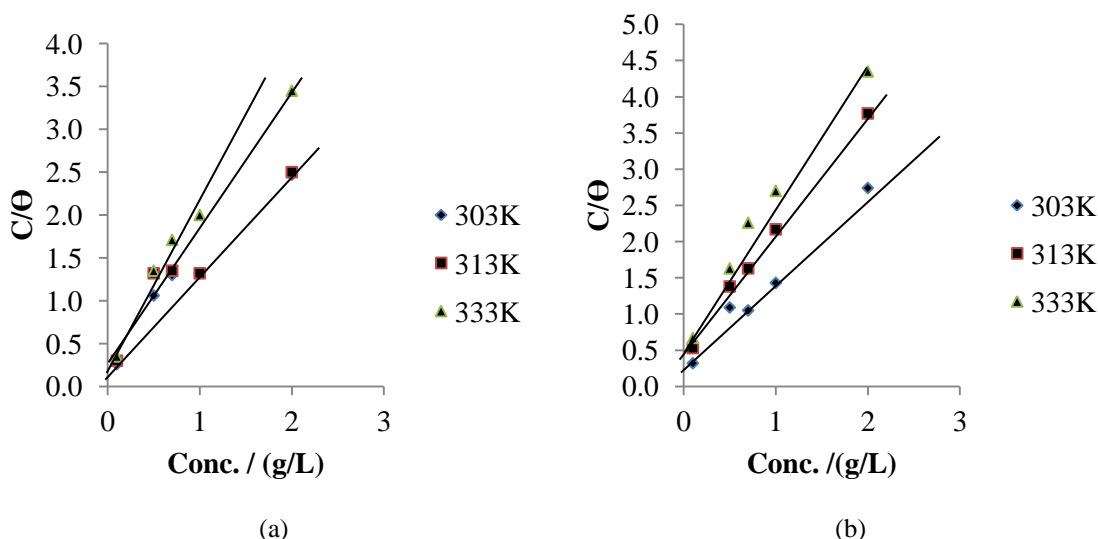


Fig. 3 Langmuir adsorption plots for Al in 1 M HCl at different temperatures in presence of different concentrations of (a) AECAL and (b) NAECAL

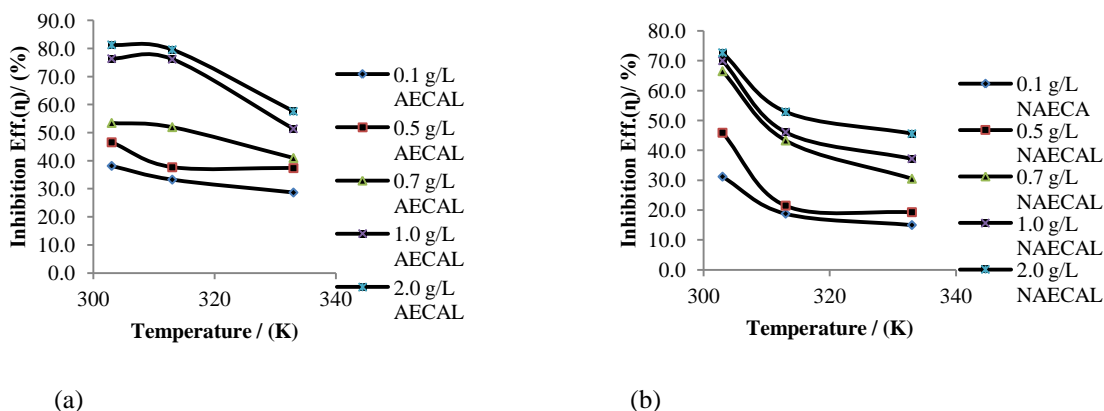


Fig. 4: Variation in inhibition efficiency against Temp. (K) of (a) AECAL and (b) NAECAL on aluminium sheet in 1 M HCl

Thermodynamic consideration: The standard adsorption free energy (ΔG_{ads}°) was obtained according to Hui *et al.*, (2013), Patel *et al.*, (2013); Pradeep & Mohana, (2013): $\Delta G_{ads}^{\circ} = -RT \ln(55.5K_{ads})$ where R is the gas constant ($R= 8.314 \text{ J K}^{-1}$), T is the absolute temperature, K_{ads} is the equilibrium constant, respectively. The thermodynamic parameter, ΔG_{ads}° obtained from equilibrium constant derived from Langmuir isotherm plots is listed in Table 2. The large negative values of ΔG_{ads}° reveal that the adsorption process took place spontaneously and the adsorbed layer on the surface of aluminium is highly stable and the process is a physical adsorption process (Hui *et al.*, 2013). It is worth noting that $-\Delta H_{ads}^{\circ}/2.303R$ is the slope of the straight line from plot of $\log(\ln C_R/T)$ vs. $1/T$ and the intercept $\log(R/h) + \Delta S/2.303R$, from

which the values of ΔH and ΔS were calculated and given in Table 4 according to the transition state equation (Abeng *et al.*, 2013):

$$R_c = \frac{KT}{h} \exp\left(\frac{\Delta S^*_i}{R}\right) \exp\left(\frac{-\Delta H^*_i}{RT}\right)$$

where R is the gas constant ($R= 8.314 \text{ J K}^{-1}$), T is the absolute temperature, h is the plank constant, respectively. The straight line $\ln C_R/T$ vs. $1/T$ is shown in Fig. 5a and b. Inspection of these data reveals that the positive signs of enthalpy (ΔH) reflect the endothermic nature of dissolution process. In this work, from the average ΔH^* values calculated, the absolute values of enthalpy are low approaching those of typical physisorption. The shift towards negative value of entropy (ΔS) imply that the

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activation complex in the rate determining state represents association rather than dissociation, meaning that the disordering decreases on going from reactants to the activation complex (Uwah *et al.*, 2013; Ugi & Uwah, 2012). Negative values of ΔS^* indicates that entropy decreases upon achieving the transition state, which often indicates associative mechanism according to Hui *et al.*, (2013) and Pradeep & Mohana, (2013).

The activation energy at different concentration of the inhibitor in 1 M HCl was calculated by plotting

$\log C_R$ vs. $1/T$ (Fig. 5 c and d and Table 3). E_a values for the inhibited systems were higher than those for the uninhibited system indicating that all the inhibitors inhibited the aluminium dissolution. Low I.E were observed at elevated temperatures and this suggests a physical adsorption in the first stage (Guster and Singh, 2004; Keiser *et al.*, 2002; Camille *et al.*, 2003). This can also be attributed to an appreciable decrease in the adsorption of the inhibitor on the mild steel surface with increase in temperature.

Table 3: Thermodynamic result for AECAL and NAECAL extracts for corrosion of aluminium in 1M HCl solution

System	NAECAL			AECAL		
	E_a (KJ/mol)	ΔH^* ads (KJ/mol)	ΔS^* ads (KJ/mol)	E_a (KJ/mol)	ΔH^* ads (KJ/mol)	ΔS^* ads (KJ/mol)
Blank	10.6	9.6	-19.1	10.6	9.6	-19.1
0.1 g/L	11.5	11.7	-21.1	11.2	9.6	-19.0
0.5 g/L	12.3	12.4	-21.9	11.3	10.0	-19.4
0.7 g/L	13.5	12.5	-21.9	11.6	12.4	-21.9
1.0 g/L	13.6	12.5	-21.9	13.6	12.5	-21.9
2.0 g/L	14.1	14.6	-24.0	14.0	13.3	-22.8

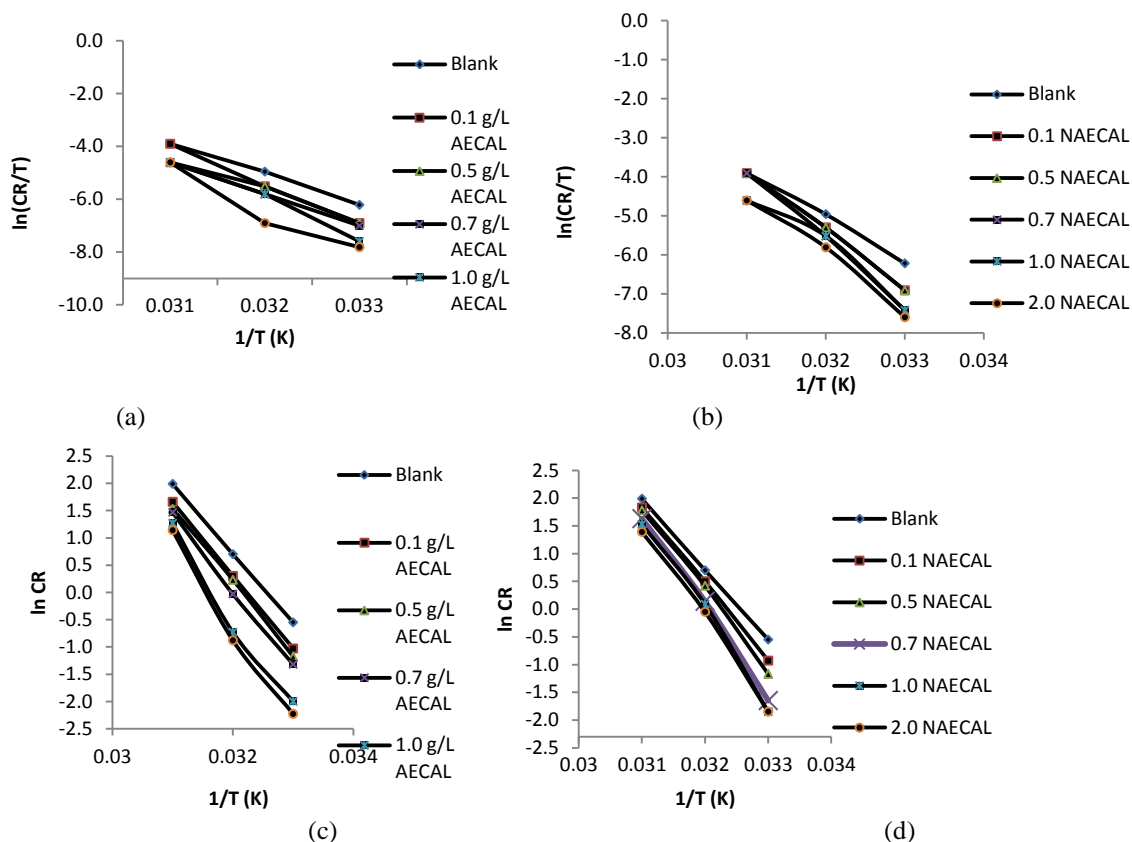


Fig. 5: (a and b) Eyring transition state and (c and d) Arrhenius plots for AECAL and NAECAL extracts for corrosion of aluminium in 1M HCl solution.

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Conclusion: Alkaloid and Non alkaloid extracts of *Cnidioscolus aconitifolius* leaves are good inhibitor for aluminium in 1 M HCl medium. IE% increases with increasing leave extract concentration but with AECAL (79.1%) showing better inhibition than NAECAL (37.1%), Because the leaves of *Cnidioscolus aconitifolius* plant introduced in this experiment are not frequently consumed by both man and animals, the evaluation as stated above of such leaves will find an average friendly alternative and commercial use in the protection of aluminium sheets from the corrosion by the mineral acids like HCl. Both extracts obeyed Langmuir adsorption isotherm as observed from the regression values obtained which are near the value of 1 and the adsorption process followed a mechanism of physical adsorption.

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