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Thermodynamics of *Azardirachta indica* (Neem) Leaves Ark's as Corrosion Inhibitors for Aluminum in HCl

P. S. Desai*

Department of Chemistry, Arts, Science and Commerce College, Kamrej Char Rasta,Surat -394 185,Gujarat, India.

Abstract : Corrosion inhibition of aluminum in 0.5 M HCl by Azardirachta indica (Neem) leaves arks was investigated by using gravimetric technique at 313K to 333K. The results point out that the extract inhibited the corrosion process in the medium by good quality of adsorption and inhibition efficiency improved with concentration. Inhibition mechanisms were assumed from the temperature dependence of the inhibition efficiency as well as from activation parameters that direct the process. Adsorption of plant extracts on the aluminum surface was found to obey the Langmuir, Freundlich and Termkin's adsorption isotherm. The phenomenon of physical adsorption is proposed from the obtained thermodynamic parameters.
Keywords : Adsorption;Aluminum; Corrosion; Hydrochloric Acid; Azardirachta Indica (Neem).

Introduction

Aluminum alloy is well-known to exhibit passive behavior in aqueous solutions. The corrosion of the metal has been reported to depend on processes associated with the passivating surface oxide film such as metal ion transfer to the metal/oxide interface, metal ion and oxygen ion transfer to the oxide/solution interface, ion migration in the oxide film, and electron transfer from the metal to acceptor species in solution [1]. Any process of deterioration and consequent loss of a metallic material, through an unwanted chemical or electrochemical attack by its environment, starting at its surface is called corrosion[2]. A huge number of organic compounds[3-5]is identified to be applicable as inhibitors of aluminum corrosion, but their efficiency in acidic environments has been rather restrained. These compounds characteristically contain N, O or S hetero atom in a conjugated system. Such inhibitors used in the industry are exceedingly toxic, so they are hazardous to the environment and highly expensive; due to these factors their applications are limited. Due to the toxicity of some corrosion inhibitors[6], there has been increasing search for eco-friendly corrosion inhibitors [7, 8].

Natural products of plant origin containing different organic compounds (e.g., alkaloids, tannins, pigments, organic, and amino acids) are known to inhibit action [9, 10]. Inhibitors in this class are those that are environment friendly, less polluting, cheap, and easily available and are obtained from natural products such as plant extracts [11]. Neem is an evergreen of tropical and sub-tropical distribution, belonging to the Meliaceae family and is very popular for its pesticide properties [12]. Neem leaves are very bitter in taste due essentially to the presence of an array of complex limonoids including azadirachtin in addition to its tannin content. Oguzie[13] studied the adsorption and corrosion inhibitive properties of Azadirachta indica in acid solutions and he explained corrosion process by adsorption of the extract organic matter on the steel surface following Langmuir adsorption isotherm. An earlier studied by Desai [14] reported on the successful application of extracts from Neem leaves as corrosion inhibitors for mild steel in hydrochloric acid solutions and the possible mechanisms of the process. In continuation of entire protection of aluminum in acid media, the present research paper provides information on the inhibitive effect of Azardirachta indica leaves arks on aluminum corrosion in 0.5 M HCl solution. The effect of inhibitive action has also been assessed at varied temperature313 to 333K.

Experimental

Materials

Aluminum alloy specimens having weight percentage composition as follows; Si-0.49%, Fe-0.68%, Cu-0.082%, Mn-0.16%, Mg-0.37% and the remainder being Al-98.02% were used. The specimens were of dimensions 5 cm x 2 cm and thickness 0.12 cm. The alloy specimen were polished mechanically using emery series of silicon carbide abrasive paper of grade nos. 220, 400 and 600, washed thoroughly with distilled water and degreased in absolute ethanol, dried in acetone, weighed and stored in a moisture-free desiccator prior to use.

Stock solutions of the plant extract were prepared by the Neem leaves were dried, grind to powder form and boiling with double distilled water to making extract of different concentrations 0.25, 0.5, 0.75, 1.0 and 1.25 %.

All chemicals and reagents used were of analytical grade and used as source without further purification. The aggressive media was 0.5M HCl solution. Inhibitor Azardirachta indica (Neem) leaves ark's was used in the concentration range 0.25 to 1.25%.

Weight loss experiments

Corrosion loss is most commonly assessed by weight loss method, rectangular specimen having area of 0.2259 dm^2 with small hole of about 5 mm diameter near the upper edge of the specimen for suspension have been used. For the weight loss study of the effect of temperature on corrosion of aluminum in 0.5M HCl, the specimens were immersed in 230 ml of the corrosive solution and weight loss was determined at solution temperature of 313, 323 and 333 K for an immersion period of 2 hours without and with Azardirachta indica leaves ark were used as inhibitors in 0.25 to 1.25% concentration. Thermostatic water bath is controlled automatically to the range of $\pm 0.1^0$C of the desired temperature. Attention is paid to compensate the evaporation loss of corrosive media. Tests were conducted with different concentrations of inhibitor. At the end of the tests, the specimens were removed from the corrosive environment and were cleaned after the test with chromic-phosphate mixture solution. After cleaning the test specimens were washed with distilled water followed by acetone and then dried with air dryer and finally reweighed to determine corrosion rate using CAH 123 electronic weighing balance with the accuracy of ±0.001.Triplicate experiments were performed in each case and the mean values reported.

After removal the corrosion products, calculate the corrosion rate in mpy. From the corrosion rate, inhibition efficiency (η%), energy of activation (E_a), heat of adsorption (Q_{ads}) free energy of adsorption (ΔG^0_{ads}), enthalpy of adsorption (ΔH^0_{ads}) and entropy of adsorption (ΔS^0_{ads}) were calculated by the following equations and data were presented in Table 1 to 3.

Corrosion rate was calculated by the following equation:

$$CR(mpy) = \frac{534W}{DAt} \quad (1)$$

Where, 'W' is the weight loss of Aluminum in grams, 'A' is the surface area of specimen in inches square, 'D' is the density of aluminum and 't' is the time in hours.

The inhibition efficiency (η%) and degree of surface coverage (θ) at each concentration of ark of Azardirachta indica (Neem) leaves were calculated by comparing the corrosion rate in absence (CR_{blank}) and presence of inhibitor (CR_{inh}) using the relationships:

$$\eta\% = \left(\frac{CR_{blank} - CR_{inh}}{CR_{inh}}\right) \times 100 \quad (2) \qquad \theta = \left(\frac{CR_{blank} - CR_{inh}}{CR_{inh}}\right) \quad (3)$$

The values of the free energy of adsorption (ΔG^0_{ads}) were calculated with the following equation.

$$LogC = L\,og\left(\frac{\theta}{1-\theta}\right) - LogB \qquad (4)$$

Where, $LogB = -1.74 - \left(\frac{\Delta G^0_{ads}}{2.303RT}\right)$ and C is the inhibitor concentration.

Energy of activation (E_a) has been calculated from the slopes of log p versus 1/T (p = corrosion rate, T = absolute temperature) and also with the help of Arrhenius equation.

$$L\,og\frac{P_2}{P_1} = \frac{Ea}{2.303R}\left[\left(\frac{1}{T_1}\right) - \left(\frac{1}{T_2}\right)\right] \qquad (5)$$

Where, P_1 and P_2 are the corrosion loss at temperature T_1 and T_2 respectively.

The values of heat of adsorption (Q_{ads}) were calculated by the following equation.

$$Q_{ads} = 2.303R\left[Log\left(\frac{\theta_2}{1-\theta_2}\right) - Log\left(\frac{\theta_1}{1-\theta_1}\right)\right] X \left[\left(\frac{T_1T_2}{T_2-T_1}\right)\right] \qquad (6)$$

The enthalpy of adsorption (ΔH^0_{ads}) and entropy of adsorption (ΔS^0_{ads}) were calculated using the following equation (7) and (8).

$$\Delta H^0 ads = Ea - RT \qquad (7)$$

$$\Delta S^0_{ads} = \frac{\Delta H^0_{ads} - \Delta G^0_{ads}}{T} \qquad (8)$$

Results and Discussion

The results are presented in Tables 1 to 3 and Figs. 1 to 3. To assess their protective value, Azardirachta indica leaves extract was added to solutions of HCl.

The effect of rising temperature on the corrosion rate values is depicted in Table1. The results revealed that on increasing temperature there is an increase of corrosion rate in the absence and presence of Azardirachta indica. The increase in corrosion rate in the absence of extract is higher at all temperatures studied, suggests more aggressiveness of free acid solution. The increase in corrosion rate with increase in temperature may be probably due to decreasing strength of adsorption and roughening of the electrode surface which results from enhanced corrosion[15].

The inhibition efficiency of Azardirachta indica leaves ark's was 84.96, 76.40 and 69.37% with respect to 313,323 and 333K at 1.25% inhibitor concentration for 2 hours immersion period are shown in Table 1. Decreasing tendency of the inhibition efficiency with temperature is due to the reduction in time lag between the processes of the adsorption and desorption occurring on aluminum surface. The decrease of inhibition efficiency with temperature is attributed to desorption of the inhibitor molecules from metal surface at higher temperature.

Table -1 : Effect of temperature on the corrosion rate (mpy), energy of activation (Ea) for the corrosion aluminum in 0.5 M HCl containing various inhibitor concentration for 2 hours.

Inhibitor	I C %	Temperature						Energy of Activation (Ea) kJ.mol-1			
		313K		323K		333K					
		CR mpy	I. E %	CR mpy	I. E %	CR mpy	I. E %	313-323 K	323-333 K	Mean Ea	Ea from Arrhenius Plot
Blank	-	125.6	-	204.9	-	253.8	-	41.14	19.17	30.15	30.60
Azardirachta indica (Neem)	0.25	40.1	68.05	85.0	58.52	129.4	49.02	63.08	37.60	50.34	50.85
	0.50	33.1	73.68	75.5	63.12	111.3	56.16	69.49	34.64	52.07	52.78
	0.75	23.6	81.20	63.7	68.89	98.1	61.35	83.50	38.57	61.03	61.96
	1.00	23.6	81.25	54.3	73.49	83.3	67.17	70.22	38.30	54.26	54.91
	1.25	18.9	84.96	48.3	76.40	77.7	69.37	79.03	42.47	60.75	61.50

The adsorption of these compounds on the aluminum surface reduces the surface area that is available for the attack of the aggressive Cl^- ion from the acid solution. As seen in Figure 1, the corrosion rate decrease with increase in extract concentration due to higher degree of surface coverage, θ as a result of enhanced inhibitor adsorption. Also, Figure 1confirms that the inhibition is due to the adsorption of the active organic compounds which are presents in extract onto aluminum surface. The straight line is obtained when C/θ is plotted against C g/l (Figure 1) with linear correlation coefficient of the fitted data close to unity (R^2=0.996). This indicates that the adsorption of the inhibitor molecules obey Langmuir`s adsorption isotherm [16-17] expressed as Equation (9).

$$\frac{C}{\theta} = C + \frac{1}{K} \qquad (9)$$

Where 'C' is the inhibitor concentration in g/l and 'K' the equilibrium constant for the adsorption/ desorption process of the inhibitor molecules on the metal surface.

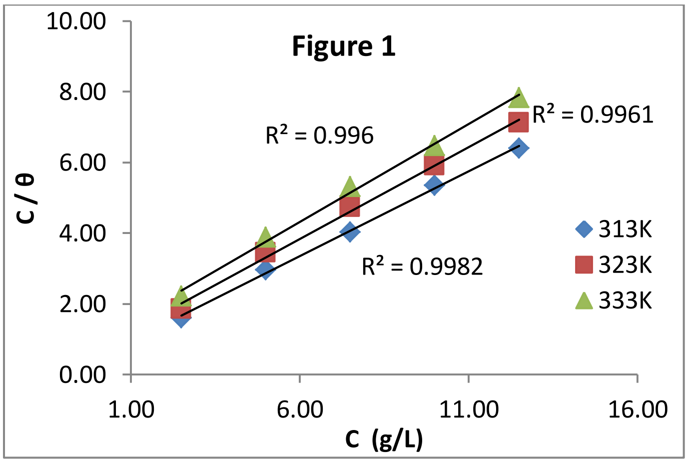

Figure 1: Plot of C/θ versus C (g/L) for Neem leaf extract in 0.5M HCl for 2 h at different temperature.(Langmuir adsorption isotherm)

The relationship between the degree of surface coverage (θ) and inhibitors concentration (C) can be represented by the following Freundlich adsorption isotherm [18]:

$$\text{Log}\theta = \text{nLogC} + \text{LogK} \qquad (10)$$

Where (0 < n < 1) and k is the equilibrium constant for adsorption.Figure 2 shows the plots of Log (θ) versus Log (C) to be linear, with intercept LogK, which suggests that the experimental data fit the Freundlich adsorption isotherm, showing that the adsorption of extract of Neem leaf on the surface of the aluminum obeys Freundlich's adsorption isotherm.

The values of K_{ads} were evaluated from the intercept of the graph and presented in Table 2. K_{ads} is related to the standard free energy of adsorption (ΔG^0_{ads}) by the formula [19,20]:

$$K_{ads} = \frac{1}{55.5} \exp^{-\Delta G^0/RT} \quad (11)$$

Where 55.5 is the molar concentration of water in the solution, R is the universal gas constant white T is the absolute temperature.

Table 2: Some parameters of the linear regression of Freundlich adsorption isotherm for aluminum corrosion in 0.5M HCl solution containing leaf extract.

	313K	323K	333K
R^2	0.966	0.976	0.993
Intercept	-0.223	-0.370	-0.400
K_{ads} ($g^{-1}L$)	5.984×10^{-1}	4.932×10^{-1}	3.981×10^{-1}
ΔG^0_{ads} (kJ mol^{-1})	-9.12	-8.89	-8.57

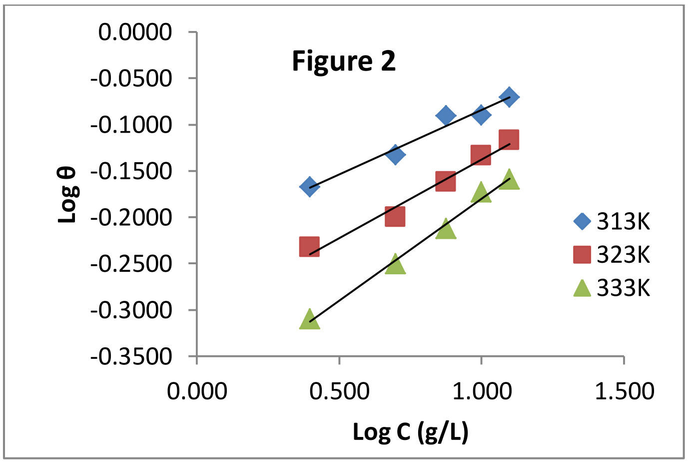

Figure 2: Plot of Log (Θ) versus Log C (g/L) for Neem leaf extract in 0.5M HCl for 2 h at at different temperature. (Freundlich adsorption isotherm)

The thermodynamic parameters for the adsorption of Azardirachta indica (Neem) leaf extract on aluminum surface are shown in Table 2 and 3. The negative values of ΔG^0_{ads} indicate the spontaneity of the adsorption process. Generally, values of ΔG^0_{ads} less negative than -20 kJ mol^{-1} indicate physical adsorption while those more negative than -40 kJ mol^{-1} indicate chemical adsorption [21,22].The values ΔG^0_{ads} obtained in this experiment being less negative than -20 kJ mol^{-1}. Decrease in the inhibition efficiency with increase in temperature indicates a physical adsorption process.

Mean 'E_a' value was calculated by using equation (5) for aluminum in 0.5M HCl is 30.15 kJmol^{-1} while in acid containing inhibitor, the mean E_a values are found to be higher than that of an uninhibited system (Table 1). Higher values of E_a in the presence of the extract which acts as inhibitor is a good indication of strong inhibiting action of the Azardirachta indica extract by increasing the energy barrier for the corrosion process[23]. Higher values of E_a in the presence of Azardirachta indica extract can also be correlated with the increase in thickness of the double layer that enhances the 'E_a' of the corrosion process. The values of 'E_a' calculated from the slope of an Arrhenius plot (Figure 3) and using equation (5) are almost similar which are shown in Table 1.

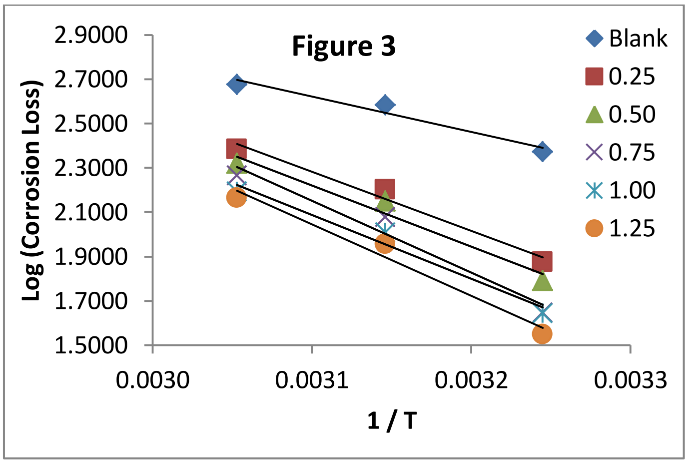

Figure 3: Arrhenius plots for corrosion of aluminum in 0.5 M HCl in absence and presence of Neem.

From Table 3, it is evident that in all cases, the (Qads) values are negative and ranging from -25.94 to -56.19 kJ mol^{-1}. The negative values show that the adsorption, and hence the inhibition efficiency, decreases with a rise in temperature[24].The values of enthalpy of adsorption (ΔH^0ads) found positive, suggesting that the nature of reaction is endothermic. Therefore, this reaction reveals that higher temperature favours the corrosion process. The values of entropy of adsorption (ΔS^0ads) arealso found positive, indicating that the corrosion process is entropically favorable.

Table 3: Effect of temperature on surface coverage area (θ), heat of adsorption (Q_{ads}) and entropy of adsorption ($\Delta S°_{ads}$), Gibbs free energy of adsorption ($\Delta G°_{ads}$) and enthalpy of adsorption ($\Delta H°_{ads}$) of aluminum in 0.5 M HCl environments in presence of inhibitor for 2 hours.

Inhibitor	I. C %	θ	θ	θ	(Q_{ads}) kJmol $^{-1}$		$\Delta H°_{ads}$ kJmol^{-1}	$\Delta S°_{ads}$ kJmol^{-1}	$\Delta G°_{ads}$ kJmol^{-1}
		313 K	323 K	333 K	313-323K	323-333K	Mean	Mean	Mean
Blank	-	-	-	-	-	-	27.51	-	-
Azardirachta indica (Neem)	0.25	0.680	0.585	0.490	-34.63	-34.28	47.70	0.2575	-9.23
	0.50	0.737	0.631	0.562	-41.36	-25.94	49.43	0.2594	-8.05
	0.75	0.812	0.689	0.614	-56.19	-29.76	58.39	0.2873	-7.76
	1.00	0.812	0.735	0.672	-37.51	-27.18	51.62	0.2643	-7.43
	1.25	0.850	0.764	0.694	-46.83	-31.93	58.11	0.2847	-7.29

Plant extracts contain a variety of organic and resinous matter which is responsible for their corrosion inhibiting efficiency. Neem leaves are exceedingly bitter due to the high tannin content as well as the presence of a series of complex triterpene glycosides in their composition [12]. According to Martinez and Stern [26,27], the inhibitive properties of tannins result from reaction of the polyphenolic fraction of the tannin molecule with metal ions, thereby forming a highly cross-linked network of metaltannate moieties, which ensures effective protection of the metal surface. The isoprenoids include diterpenoids (namely sugiol, nimbiol, margasone) and triterpenoids containing protomeliacins, liminoids, azadirone and its derivatives, genudin and its derivatives, vilarin type of compounds and C-secomeliacins such as nimbin, salannin and azadirachtin. All of above compounds contain one five membered heterocyclic ring with oxygen heteroatom and is liable to resist the corrosion process and possible synergistic interactions between the adsorbed species could also contribute to the high inhibition efficiency of the extract. This process is the protection ofthe metal surface from the attack of the aggressive ions of the acid. Neem leaf extracts also contain other organic matter thus the adsorption layer formed on the metal surface involving several organic species.

Conclusion

Azardirachta indica (Neem) leaves extract was found to inhibit the corrosion of aluminum in 0.5M hydrochloric acid solution and inhibition efficiency increases with increasing extract concentration. At the highest concentration of 1.25%, the inhibition efficiency increased clearly to a maximum value of 85%. Decrease in the inhibition efficiency with increase in temperature indicates a physisorption process. The adsorption isotherms obey the all two Langmuir and Freundlich adsorption isotherms.

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