Effect of Temperature on Corrosion Inhibition Efficiency of *Withania Somnifera* (Ashwagandha) on Aluminium in HCl Solution

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Abstract

Weight loss and thermometric methods have been used to study the corrosion inhibition efficiency of leaves extract of *Withania somnifera* on aluminium in HCl solution at two temperatures i.e. 308 K and 313 K. Both methods show good agreement with each other. Inhibition efficiency of *Withania somnifera* has been found more at 303 K than at 318 K. Efficiency of the inhibitor increases with increasing concentration of inhibitor as well as with that of HCl. Study reveals that inhibitor works excellently at its concentration of 0.8% for 2N HCl where its inhibition efficiency is maximum i.e.99.28%

Keywords : Corrosion inhibition efficiency, corrosion rate, reaction number, *Withania somnifera*, alkaloid, surface coverage.

Introduction

Aluminium and its alloys are very important in many industrial as well as household applications due to their corrosion passivity in neutral media and atmospheric conditions due to formation of passive oxide layer on them. Although it is very reactive in emf series but becomes passive on exposure to water and atmosphere but it dissolves in hydrochloric acid liberating H_2 gas.

$$2Al + 6\ HCl + 12\ H_2O \longrightarrow 2\ [Al\ (H_2O)_6\ ]Cl_3 + 3H_2$$
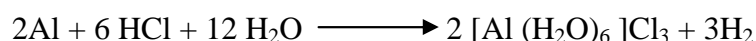
Compounds containing N, S and O have been found as good inhibitors due to high basicity and electron density and thus assist corrosion inhibition [1]. O, N and S are the active center for the process of adsorption on the metal surface. The size, orientation, shape and electric charges of the molecule also play a part in the effectiveness of inhibition.

In addition to the heterogenous organic compounds synthesized in laboratory some naturally occurring substances like *Ficus virens*[2], *Delonix regia*[3], *Ocimum basilicum*[4], *Caparis deciduas*[5], *Sansevieria trifascinata*[6], *Phylanthus amarus*[7], *Prosopis julifforar*[8], *Argemone maxicana*[9] have been evaluated as effective corrosion inhibitors.

The naturally occurring plant products are eco-friendly, compatible, nonpolluting, less toxic, easily available, biodegradable and economic to be used as corrosion inhibitors. These inhibitors have many N,O and S containing alkaloids which are get adsorbed on metal surface which essentially block the discharge of H^+ and dissolution of metal ions. Extract of different parts of plant like seeds, leaves, stem, bark can be used as inhibitor to reduce the corrosion rate of metal like aluminium in acidic media. In the present investigation the inhibition efficiencies of *Withania somnifera* have been studied in different concentrations of HCl solution at two temperature i.e. 303 K (30^0 C) and 318K (45^0 C).

Withania somnifera is a very common plant in India and other regions having almost same climatic conditions. Alkaloids and steroidal lactones are the main constituents of Ashwagandha. Plant contains many alkaloids like anaferin, anahygrine, betasisterol, chlorogenic acid, cystein, cuscohygrine, pesudotropine, scopoletin, somniferiene tropanol, withanine, withananine etc. Withaferin A and withanolides A-Y

are the main steroidal lactones. The withanolides are a group of naturally occurring C-28 steroidal lactones built on an intact or rearranged ergostane framework in which C-22 and C-26 are appropriately oxidized to form a six membered lactone ring.
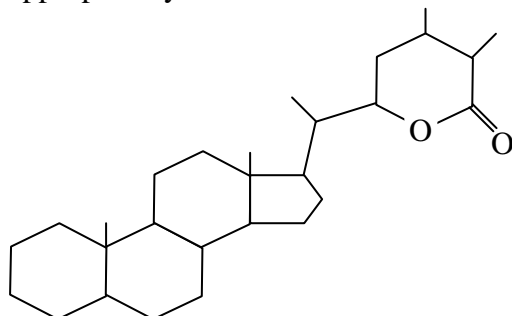
Structure of Withanolides

Experimental

Commercially available aluminium was used for specimen preparation. The specimens were prepared by cutting the aluminium sheet into square shaped pieces having dimension $2.0 \times 2.0 \times 0.3$ cm containing a small hole of about 2mm diameter near the upper edge. Specimens were polished to mirror finish by using emery paper. Solutions of HCl were prepared by using double distilled water. All chemicals used were of AR grade. Extract of leaves of *Withania somnifera* was obtained by refluxing the dried leaves in soxhlet in ethanol. Solutions of different concentrations of extract were prepared in ethanol.

Each specimen was suspended by a V-shaped glass hook made of capillary and plunge into a beaker containing 50mL of the test solution (HCl) at 303K and at 318K. After the sufficient exposure, test specimens were washed with running water and dried by hot air dryer. Duplicate experiments were performed in each case and mean value of weight loss was determined. The percentage inhibition efficiency was calculated as[10].

$$\eta\% = \frac{100(\Delta W_u - \Delta W_i)}{\Delta W_u}$$

Where ΔW_u and ΔW_i are the weight loss of the specimen in uninhibited and in inhibited solution respectively. Degree of surface coverage (θ) was calculated as [11].

$$\theta = \frac{(\Delta W_u - \Delta W_i)}{\Delta W_u}$$

Inhibition efficiency was also determined by thermometric method. In this method specimen was suspended into test solution in a thermal insulated chamber and initial temperature was noted. As soon as the reaction started temperature increased slowly at first then rapidly and achieved a maximum value before falling. The maximum temperature was noted. All observations were repeated also at higher temperature i.e.318K. Percentage inhibition efficiencies were calculated as[12].

$$\eta\% = \frac{100(RN_f - RN_i)}{RN_f}$$

Where RN_f and RN_i are the reaction number in the free (uninhabited) solution and in presence of inhibitor. RN is defined as –

$$RN = \frac{(T_m - T_i)}{t}$$

Where T_m and T_i are maximum and initial temperature respectively and t is the time in minutes required to attain maximum temperature. The corrosion rate (CR) in mm/yr can be obtained by the following equation [13].

$$Corrosion\ Rate\ (mm/yr) = \frac{\Delta W \times 87.6}{A \times T \times D}$$

Where, ΔW is weight loss in mg, A is area of specimen in cm^2, T is time of exposure in hours, D is density of metal in gm/cm^3.

Results And Discussion

Weight loss data and corresponding values of inhibition efficiency and corrosion rate are given in Table-1. It is obvious from the table 1 that inhibition efficiency increases with increasing acid strength and it also increases with increasing concentration of inhibitor. The maximum efficiency (i.e.99.28%) has been observed in 2N HCl at highest inhibitor concentration (i.e.0.8%) at 303K. The corrosion rate has been found maximum in blank solution which decreases with increasing concentration of inhibitor. Observations of inhibition efficiency corresponding to same concentrations of acid and

inhibitor at 318K show that efficiency of the inhibitor is less at 318K than that at 303K although the trends are same at 318K.Maximum efficiency at 318K is 98.53% for the same concentration of inhibitor (i.e. 0.8%) for 2N HCl. Variation of inhibition efficiency with concentration of inhibitor for 2N HCl are shown in fig 1.

The degree of surface coverage of metal (θ) covered by the adsorption of inhibitor to block the active sites on the surface at various concentrations of inhibitor for different HCl concentrations are shown in Table-2. It is clear from the table that degree of surface coverage increases with increasing concentration of inhibitor at both temperatures i.e.303K and 318K, however at 318K the coverage is less than that at 303K.

Thermometric data in the form of reaction number at various concentrations of inhibitor for 1N, 2N, 3N and 4N HCl are shown in Table-3. Table shows that reaction number decreases with increasing concentration of inhibitor although values of RN are lower at 318K than at 303K for the same concentration of inhibitor. Since no significant temperature changes were observed at lower concentration of HCl so higher concentration of acids have been taken for thermometric study. Maximum efficiency (i.e. 99%) has been shown by 0.8% inhibitor in 4N HCl at 303K whereas the maximum efficiency at 318K is 81% for the same acid solution at same concentration of inhibitor. Here also inhibitor shows more efficiency at lower temperature. Variation of RN with concentration of inhibitor for 2N HCl are shown in fig.2. The possible reason for lower efficiency of inhibitor at higher temperature may be due to the reason that at higher temperature the adsorbed molecule of inhibitor start to desorbed from the metallic surface.

Hoar and Holiday gave the Langmuir adsorption isotherm [14]

$$\text{Log } \theta/(1-\theta) = \log A + \log C - Q/2.3 \, RT$$

Where

θ = Surface coverage

A = Temperature dependent constant

C = Bulk concentration of inhibitor (m/l)

Q = Heat liberated in reaction

According to which a straight line should be obtained if a graph is plotted between log ($\theta/1-\theta$) versus logC with gradient equal to one. In our investigation the graph is linear

but gradient is not equal to unity. This deviation from unit behaviour can be explained on the basis of interaction of the adsorbed molecules on the metal surface.

According to langmuir the adsorbed layer is unimolecular i.e. there is no interaction between adsorbed molecules themselves and between adsorbate and adsorbent molecules. Only then the gradient is unity but in actual practice there is an interaction between adsorbed molecules themselves and between adsorbate and adsorbent molecules that is why the gradient is not unity. Variation of log ($\theta/ 1-\theta$) with concentration of inhibitor for 2N HCl are shown in fig.3.

Conclusion

The studies on *Withania somnifera* as corrosion inhibitor for aluminium in HCl have shown that this widely available plant is a very good corrosion inhibitor for aluminium. Studies have shown that both weight loss and thermometric metods show similar trends for different concentrations of acid as well as those of inhibitor. Further it can be concluded from the studies that *Withania somnifera* is a better corrosion inhibitor at 303K than at 318K.

Acknowledgment

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Table 1

Inhibition efficiency (η%) for aluminium in HCl with leave extract of

Withania somnifera at 303K and 318K

Area of specimen: 8.0cm^2

Conc. of inhibitor	0.5N HCl (173 hrs.)			1N HCl (225 hrs.)			2N HCl (25 min)		
	ΔW	η%	C.R.	ΔW	η%	C.R.	ΔW	η%	C.R.
At 303K									
uninhibited	0.207		0.7148	0.117		31.06	0.1279		40.680
0.1	0.163	21.27	0.5629	0.043	63.24	11.41	0.007	97.49	10.053
0.2	0.157	24.15	0.5421	0.015	87.17	3.98	0.005	98.2	7.185
0.4	0.154	25.6	0.5321	0.003	97.43	0.796	0.004	98.56	5.744
0.8	0.152	26.57	0.5249	0.002	98.29	0.531	0.002	99.28	2.872
At 318K									
uninhibited	0.324		1.118	0.364		96.65	0.273		652.51
0.1	0.271	16.35	0.9358	0.136	62.63	17.525	0.008	97.06	19.121
0.2	0.257	20.67	0.8875	0.085	76.64	11.68	0.006	97.8	14.341
0.4	0.254	21.6	0.8771	0.039	89.28	0.355	0.005	98.16	11.95
0.8	0.251	22.53	0.8668	0.037	89.83	9.824	0.004	98.53	9.56

Table 2

Surface coverage and log (θ/ 1-θ) for aluminium in HCl with leave extract of

Withania somnifera at 303K and 313K

Conc. Of inhibitor	0.5N HCl(173 hrs.)			1N HCl(225 hrs.)			2N HCl(25min..)		
	η%	θ	log (θ/ 1-θ)	η%	θ	log (θ/ 1-θ)	η%	θ	log (θ/ 1-θ)
At 303K									
uninhibited									
0.1	21.27	0.2127	-0.5684	63.24	0.6324	0.2356	97.49	0.9749	1.5893
0.2	24.15	0.2415	-0.4970	87.17	0.8717	0.8321	98.20	0.9820	1.7368
0.4	25.60	0.2560	-0.4633	97.43	0.9743	1.5788	98.56	0.9856	1.8353
0.8	26.57	0.2657	-0.4415	98.29	0.9829	1.7595	99.28	0.9928	2.1395
At 318K									
uninhibited									
0.1	16.35	0.1635	-0.7089	62.63	0.6263	0.6544	97.06	0.9706	1.5187
0.2	20.67	0.2067	-0.5841	76.64	0.7664	0.8567	97.80	0.9780	1.6479
0.4	21.60	0.2160	-0.5599	89.28	0.8928	0.9206	98.16	0.9816	1.7271
0.8	22.53	0.2253	-0.5364	89.83	0.8983	0.9461	98.53	0.9853	1.8263

Table 3:

Thermometric data for aluminium in 1.0N, 2.0N, 3.0N and 4.0N HCl in presence of leave extract of *Withania somnifera* at 303K and 318K

Conc of inhibitor	1N HCl (135 min.)		2N HCl (25 min.)		3N HCl (7 min.)		4N HCl (3 min.)	
	RN (K min^{-1})	n%	RN (K min^{-1})	n%	RN (K min^{-1})	n%	RN (K min^{-1})	n%
At 303K								
Free solution	0.0185		7.5000		1.5000		1.3333	
0.1	0.0133	31.57	3.8000	49.33	0.6250	58.33	0.2000	84.99
0.2	0.0118	36.84	2.8000	62.66	0.2500	83.33	0.0666	95.00
0.4	0.0111	42.11	2.0000	73.33	0.1250	91.66	0.0333	97.50
0.8	0.0080	57.89	1.5000	80.00	0.1000	93.33	0.0133	99.00
At 318K								
Free solution	0.019		5.1201		0.120		0.100	
0.1	0.015	21.05	3.0511	40.40	0.061	50.00	0.036	66.00
0.2	0.013	31.57	2.5421	50.35	0.047	60.83	0.028	72.00
0.4	0.012	35.13	1.8200	64.45	0.033	72.50	0.021	75.00
0.8	0.011	42.11	1.2301	75.97	0.026	73.33	0.018	81.00

Fig: 1
Variation of Inhibition Efficiency With Concentration of Inhibitor
For 2NHCl At 303K And 318K

Fig: 2
Variation of Reaction Number With Concentration of Inhibitor
For 2NHCl At 303K And 318K

Fig: 3
Langmuir Adsorption Isotherm
For 2NHCl At 303K And 318K