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Solanum torvum as a green inhibitor for aluminium corrosion in alkaline medium and its adsorption characteristics

S. Lakshmi,S. Geetha and G. Saranya
Department of Chemistry, Sri Sarada College for Women, Salem – 16, Tamilnadu.

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ABSTRACT

The inhibitive effect of the extract of Solanum torvum leaves on the corrosion of aluminium in 1M NaOH solution was studied using at weight loss method at 30 - 60°C. The extract acts as an excellent corrosion inhibitor with 91% efficiency at the highest concentration in the alkaline environment and the inhibition efficiency increased with increasing concentration of the extract. The adsorption of the inhibitor on aluminium surface decreases with rise in temperature, suggesting physical adsorption of the organic matter on the metal surface. These results were supported by kinetic and thermodynamic parameters for corrosion and adsorption processes calculated from the experimental data at the various temperatures studied.

Introduction

Aluminium and its alloys find extensive application in many engineering and scientific technologies and the study of their corrosion behaviour in different aggressive environments has continued to have considerable attraction. One of the most important application of aluminium and its alloys is found in aluminium / air battery system. The battery performance is determined by the electrochemical and corrosion properties of aluminium anodes [1,2]. aluminium - alkaline solution systems are found in nuclear water reactors during a loss of coolant accident [LOCA]. The chemical environment generated by the injection of coolant into the emergency - core – cooling system has a pH around 10 [3]. The release of aluminium into solution via corrosion may result in precipitate, which may lead to a system failure. The corrosion rate of aluminium in alkaline solution is a function of the operating conditions such as, the temperature, the pH, the solution properties, etc.,

The inhibition of the corrosion of aluminium and its alloys in alkaline solution is well known and a number of inhibitors have already been described and investigated. Several authors conducted a lot of work to find effective inhibitors for aluminium corrosion in allkaline media. Organic additives, especially those containing nitrogen, oxygen or sulphur in the conjugated system [4-6] and inorganic compounds has continued to generate considerable attention [7-10]. In our earlier work we have reported the use of thiourea and sulphanilic acid as corrosion inhibitors [11]. But some of these inhibitors are toxic, expensive and non-biodegradable. The safety and environmental issues of corrosion inhibitors used in industries has always been a global concern. These inhibitors cause temporary or permanent damage to organ system viz, kidney, liver or disturb a biochemical process and enzyme system at some site in the body [12].

In recent years, according to the art of green chemistry, attention has been focused on corrosion inhibiting properties of plant extracts because these are environmentally friendly, inexpensive, readily available and renewable sources of materials. The use of natural products as corrosion inhibitors have been widely reported by several authors [13-18]. The use of botanical products in corrosion inhibitor development involves the identification and testing of plant extracts in corrosion environment. Investigations into the use of natural substances as corrosion inhibitors have been conducted in acidic medium and there seem to be scanty reports on corrosion inhibition of metals in alkaline environment using natural substances.

As a contribution to the current interest on ecofriendly, green, corrosion inhibitors the present study investigates the inhibiting effect of leaf extracts of Solanum torvum belonging to solanaceae family for aluminium corrosion in sodium hydroxide.

Figure1. Plant of Solanum torvum

Solanum torvum is a prickly, tomentose, erect shrub, 1.5-3 m high, leaves having no prickles, white bell-shaped flowers and lobed fruits seated on the calyx belonging to the family Solanaceae. It is a common plant found throughout the Indian subcontinent. Leaves have been reported to contain the steroidal gluco-alkaloid, solasonine. In addition, they contain steroidal sapogenins, neochlorogenin, neosolaspigein and solaspigenine. They have also been found to contain triacontanol, tetratriacontanic acid, z-tritriacontanone, sitosterol, stigmasterol and campesterol. Different parts of the plants are used as sedative, diuretic and digestive. They are also used in the treatment of coughs and colds. Leaves are used as haemostatic. Extract of the fruits and leaves are said to be useful in case of liver and spleen enlargement and in the treatment of cough.

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In the present work, the corrosion inhibition of aluminium in 1M NaOH using Solanum torvum extract at 30-60°C using weight loss technique has been investigated. The kinetic and thermodynamic parameters for adsorption were also calculated and discussed.

Experimental part

Materials preparation

Commercial aluminium specimens of dimension 3 x 3 x 0.2cm, containing 95% pure aluminium were used without further polishing. The specimens were degreased in absolute ethanol, dried in acetone, and stored in moisture - free desiccators prior to use. The NaOH used was analytical grade, and 1M NaOH was employed as the corrodent for this study.

Preparation of extract

Stock solution of the plant extract was prepared by refluxing 5g of the dried powder leaves of the plant for 1h in 500ml 1M NaOH solution. The refluxed solution was left overnight before filtering. The filtrate was diluted with the appropriate quantity of 1M NaOH to obtain inhibitor test solutions in concentrations of 5, 10, 15, 20 and 25 % v/v [18, 20 & 21].

Weight loss determination

The procedure for weight loss determination was similar to that described elsewhere [22 - 25]. The specimens were weighed and their initial weight recorded before immersion in 100ml, of 1M NaOH solution (in open beakers) without and with different concentrations (5-25 % v/v) of the extract at 30 - 60°C for a total period of 2 hour immersion.

After 2hr the specimens were taken out, scrubbed with a bristle brush under running water, dried and reweighed. The experimental readings were recorded to the nearest 0.0001g on a Mettler digital analytical balance. Duplicate experiments were set up for each of the concentration.

Results and discussion

Corrosion rates and inhibition efficiency

The material loss as corrosion rate (mm/year) of the aluminium specimens as a function of the extract concentration in 1M NaOH solution monitored at 30°C is summarized in Table1.

Table 1 shows that the corrosion rates decreased with the increase in the concentration of the extract in NaOH solutions. This result showed that solanum torvum extract acts as corrosion inhibitor for aluminium in NaOH solution at the studied concentration, signifying the inhibition of aluminium corrosion in NaOH solution.

The values of percentage inhibition efficiency (% I) and surface coverage (θ) were determined from the corrosion rate using the following equations [26].

$$\%I = \frac{r_a - r_p}{r_a} \times 100 \qquad (1)$$

$$\theta = \%\ I/100 \qquad (2)$$

$$\text{Corrosion rate (mm/year)} = \frac{87.6\text{W}}{\text{DAt}} \qquad (3)$$

where r_a is the corrosion rate in the absence of inhibitor, r_p is the corrosion rate in the presence of the inhibitor, W is the weight loss of aluminium (mg), D, the density of the specimen (g cm^{-3}), A the area of specimen (cm^2), and t the immersion time (h).

Figure 2. Plot of corrosion rate against extract concentration for aluminium in 1M NaOH at 30-60°C

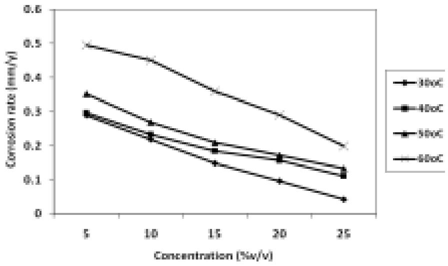

Figure 3. Plot of inhibition efficiency (% I) against extract concentration for aluminium in 1M NaOH at 30-60°C

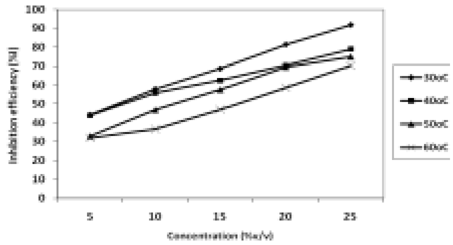

Table 1 shows that the inhibition efficiencies increase with increase in extract concentration and reach a maximum value of 91% with 25 % v/v extract. This indicates the adsorption of phytochemical constituents of the extract such as glycoside, saponin, alkaloids and sterols onto aluminium surface.

The adsorption of these compounds on the aluminium surface reduces the surface area available for the attack of the aggressive OH^- ions from the alkaline solution for corrosion. The degree of protection increases with increase in extract concentration due to a higher degree of surface coverage resulting from enhanced inhibitor adsorption. Similar view has been expressed on the inhibition of aluminium by plant extract in alkaline solution [20, 27, 28].

Effect of temperature

Temperature study was carried out to get more information about the effectiveness of Solanum torvum and the nature of adsorption and thereafter to evaluate the activation process. Weight loss measurements are determined in the range of temperature 30 - 60°C, with and without inhibitor at different concentrations during 2h immersion period. From the data given in Table 1 it is clearly understood that the increase in temperature leads to an increase in the corrosion rate with or without inhibitor.

Figure 3 showed that inhibition efficiency (% I) decreased with increasing temperature as a result of the higher dissolution of aluminium at higher temperature. This may be attributed to the fact that a higher temperature could quench the inhibitor performance to a large extent and this suggests physical adsorption mechanism of Solanum torvum on aluminium surface [29].

The values of the activation energy, E_a given in Table 2 were calculated with the help of the Arrhenius equation.

$$\log \frac{\rho_2}{\rho_1} = \frac{E_a}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \qquad (4)$$

where ρ_1 and ρ_2 are the corrosion rates at temperatures T_1 and T_2, respectively. Higher E_a values in the presence of the inhibitor compound compared to that in the blank solution indicates that the inhibitor will be effective at ordinary temperature but the efficiency will be considerably diminished at higher temperatures [30, 31].

Kinetic and thermodynamic studies

Basic information about the interaction between the inhibitor molecule and metal surface can be provided by adsorption isotherm. The degree of surface coverage values for various concentrations of Solanum torvum extract from the weight loss measurements obtained (θ = % I/100), assuming a direct relationship between surface coverage and inhibition efficiency has been adopted to determine the adsorption characteristics of Solanum torvum in 1M NaOH solution.

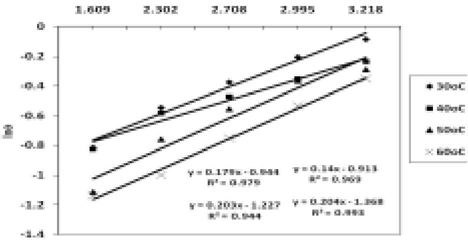

Figure 4. Freundlich adsorption isotherm for aluminium corrosion in IM NaOH at 30-60°C

The absorbed changes in θ are shown (Figure-4) as a function of concentration of extracts in 1M NaOH at 30-60°C. The linear plots obtained with unit correlation coefficients ($R^2 >$ 0.86) suggested that the experiential data fits the Freundlich adsorption isotherm which is given by [18] ;

$$\theta = KC^n \qquad (5)$$

where θ <n <1, or

$$\ln\theta = \ln K + n\ln C \qquad (6)$$

C is the concentration of Solanum torvum extracts and K is the adsorption equilibrium constant from which free energy of adsorption ΔG^0_{ads} is calculated using the equation

$$K = \frac{1}{55.5}\exp\left[\frac{-\Delta G^0{}_{ads}}{RT}\right] \qquad (7)$$

ΔG^0_{ads} at 30°C for the alkali solutions containing 5-25% v/v of extract, were found to be – 6.97, –7.39, –7.77, –8.24 and –9.57 KJ mol^{-1} respectively [32].

The negative values of ΔG^0_{ads} obtained indicate the spontaneous adsorption of the inhibitor and are usually characteristic of strong interaction with the metal surface. It was found that the ΔG^0_{ads} values are less than –40KJ/mole indicating that Solanum torvum is physically adsorbed on the metal surface [33-35].

Adsorption equilibrium constant increased with increase in the concentration of Solanum torvum. The maximum efficiency of 91% was observed in the case of 25% v/v extract concentration. The lower concentration of the inhibitor causes multilayer film which collapse and expose the metal to the corrodent and hence higher concentration of inhibitor is required for maximum adsorption in a single layer. The same fact was suggested in other reports [36-37].

Conclusions

1. Solanum torvum shows significant inhibitive effect on aluminium corrosion in alkaline environment.
2. Inhibition efficiency increases with the increase of extract concentration and upto 91% inhibition efficiency was obtained for 25% v/v.
3. The inhibition efficiency of Solanum torvum extract is temperature dependent and its addition leads to a relative increase of apparent activation energy.
4. Adsorption of inhibitor species on aluminium surface in 1M NaOH suggest physisorption mechanism and it is clear cut by following the trend of inhibitor adsorption with solution temperature.
5. The adsorption of the extracts onto aluminium surface was found to obey Freundlich adsorption isotherm from the fit of the experimental data at all the concentrations and temperatures studied.

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Table 1. Corrosion rate (mm / year) and inhibition efficiency (% I) of Solanum torvum extract during aluminium corrosion in 1M NaOH at different temperatures.

System /	Corrosion rate (mm/year)				Inhibition efficiency (% I)			
Concentrations	30^0C	40^0C	50^0C	60^0C	30^0C	40^0C	50^0C	60^0C
1M NaOH	0.5196	0.5289	0.5395	0.7219	-	-	-	-
5% v/v	0.2896	0.2966	0.3518	0.4962	44.27	43.92	32.87	31.98
10% v/v	0.2185	0.2334	0.2689	0.4516	57.95	55.87	46.83	36.77
15% v/v	0.1486	0.1842	0.2085	0.3590	68.66	62.38	57.50	47.16
20% v/v	0.0968	0.1571	0.1714	0.2903	81.37	70.30	69.37	58.59
25% v/v	0.0427	0.1119	0.1332	0.1982	91.78	78.84	74.86	70.30

Table 2. Activation energy (E_a) of aluminium dissolution in 1M NaOH in the absence and presence of different concentrations of Solanum torvum extract.

System	E_a (KJ mol^{-1})
1M NaOH	9.85
1M NaOH 5%	15.69
1M NaOH 10%	20.98
1M NaOH 15%	25.58
1M NaOH 20%	31.27
1M NaOH 25%	35.31

Table 3. Degree of surface coverage (θ) of Solanum torvum extract for aluminium corrosion in 1M NaOH.

Extract concentration	Surface Coverage (θ)			
(% v/v)	30^0C	40^0C	50^0C	60^0C
5	0.4427	0.4392	0.3287	0.3198
10	0.5795	0.5587	0.4683	0.3677
15	0.6866	0.6238	0.5750	0.4716
20	0.8137	0.7030	0.6937	0.5859
25	0.9178	0.7884	0.7486	0.7030