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Corrosion inhibition of aluminium in acidic and alkaline media by *Sansevieria trifasciata* extract

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Abstract

The inhibitive action of leaf extracts of *Sansevieria trifasciata* on aluminium corrosion in 2 M HCl and 2 M KOH solutions was studied using the gasometric technique. The results indicate that the extract functioned as a good inhibitor in both environments and inhibition efficiency increased with concentration. Synergistic effects increased the inhibition efficiency in the presence of halide additives. Temperature studies revealed a decrease in efficiency with rise in temperature and corrosion activation energies increased in the presence of the extract. A mechanism of physical adsorption is proposed for the inhibition behaviour. The adsorption characteristics of the inhibitor were approximated by Freundlich isotherm.

Keywords: A. Aluminium; C. Acid corrosion; C. Alkaline corrosion

1. Introduction

The study of the corrosion behaviour of aluminium in different aggressive environments has continued to attract considerable attention because of the many important applications of the metal. Aluminium relies on the formation of a compact, adherent passive oxide film for its corrosion immunity in various environments. This surface film is amphoteric and dissolves substantially when the metal is exposed to high concentrations of acids

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or bases [1]. Bared metal surface sites become exposed to the corrodent after the breakdown of the oxide film, leading to a sequence of electrochemical reactions as the metal dissolves. Corrosion is accompanied by many conjugate cathodic processes in which hydrogen gas evolution is often predominant in strong acid or alkaline solutions [2]. Apart from the deleterious effects of hydrogen uptake by a corroding metal, the H_2 gas evolution agitates the interface, dispersing the corrosion product thereby preventing self-inhibition.

Hydrochloric acid solutions are normally used for pickling of aluminium and for its chemical and electrochemical etching, processes that normally lead to substantial loss of the metal to corrosion. An important application in which aluminium is deployed in service in a strong alkaline environment is the aluminium/air battery system. This is an environmentally friendly system because the reaction product, aluminium hydroxide is benign and recyclable. Despite the fact that the energy density of this system is excellent, it is not greatly used in practice due to severe hydrogen evolution problems resulting from corrosion of the aluminium electrode. Control of the H_2 gas evolution must necessarily be achieved without compromising the eco-friendly nature of the system.

In efforts to mitigate aluminium corrosion, the main strategy is to effectively isolate the metal from corrosive agents. This can be achieved by the use of corrosion inhibitors. Inorganic substances such as phosphates, chromates, dichromate and arsenates have been found effective as inhibitors of metal corrosion, but a major disadvantage is their toxicity and as such their use has come under severe criticism. Among the alternative corrosion inhibitors, organic substances containing polar functions with nitrogen, oxygen and/or sulphur atoms in a conjugated system have been reported to exhibit good inhibiting properties [3–9]. Corrosion inhibition occurs via adsorption of their molecules on the corroding metal surface and efficiency of inhibition depends on the mechanical, structural and chemical characteristics of the adsorption layers formed under particular conditions.

Some investigations have in recent time been made into the corrosion inhibiting properties of natural products of plant origin, which have been found to generally exhibit good inhibition efficiencies [10–14]. This area of research is of much importance because in addition to being inexpensive, readily available and renewable sources of materials, plant products are environmentally friendly and ecologically acceptable. Plant products are organic in nature and some of the constituents including tannins, organic and amino acids, alkaloids and pigments are known to exhibit inhibiting action.

As a contribution to the current interest on environmentally friendly, green, corrosion inhibitors, the present study investigates the inhibiting effect of leaf extracts of *Sansevieria trifasciata* on aluminium corrosion in strong acidic and alkaline solutions using the gasometric technique. The plant, which is popularly called snake plant or bowstring hemp, belongs to the family of *Agavaceae* and is known to grow in Africa, Asia and Florida [15]. The effect of temperature as well as the synergistic effect of halide additives namely KCl, KBr and KI on the inhibition efficiency has also been studied. Kinetic and activation parameters that govern metal corrosion have been evaluated.

2. Experimental methods

Aluminium sheets of the type AA 1060 and purity 98.8% were used in this study. The test coupons were prepared, degreased and cleaned as previously described [16,17].

All chemicals and reagents used were of analytical grade. The blank corrodents were, respectively, 2 M HCl and 2 M KOH solutions. Stock solutions of the plant extract were prepared by boiling weighed amounts of the dried and ground leaves of *S. trifasciata* for 3 h in the 2 M HCl and 2 M KOH, respectively. The solutions were cooled and then filtered and stored. From the respective stock solutions, inhibitor test solutions were prepared in the concentration range 10–50 v/v%. The effect of halide additives was studied by introducing 5.0 mM of the halide salts KCl, KBr and KI.

The apparatus and procedure for gasometric determination of corrosion rates have been described elsewhere [18]. The progress of the corrosion reaction was monitored by careful volumetric measurement of the evolved hydrogen gas at fixed time intervals. Experiments were conducted at 30 and 60 °C.

3. Results and discussion

3.1. Hydrogen evolution and corrosion rates

The free corrosion of aluminium in both 2 M HCl and 2 M KOH was characterized by rapid effervescence resulting from hydrogen gas evolution and corrosion rates in the absence and presence of inhibitor was studied using hydrogen evolution measurements. The relative rapidity and effectiveness of the gasometric technique, as well as its suitability for monitoring in situ, any perturbation by an inhibitor with respect to gas evolution in metal/corrodent systems have been established in earlier reports [4,18–20]. Figs. 1 and 2

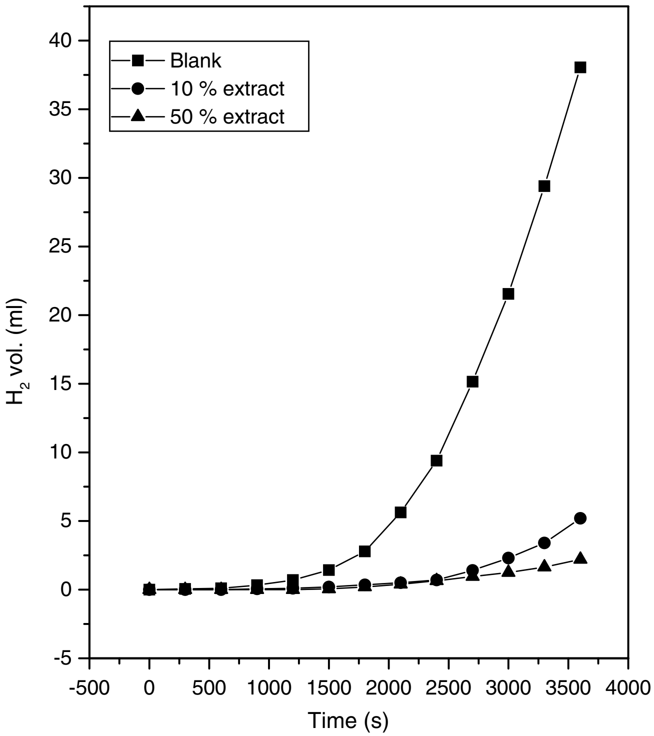

Fig. 1. Hydrogen evolution during aluminium corrosion in 2 M HCl at 30 °C in absence and presence of *Sansevieria trifasciata* extract.

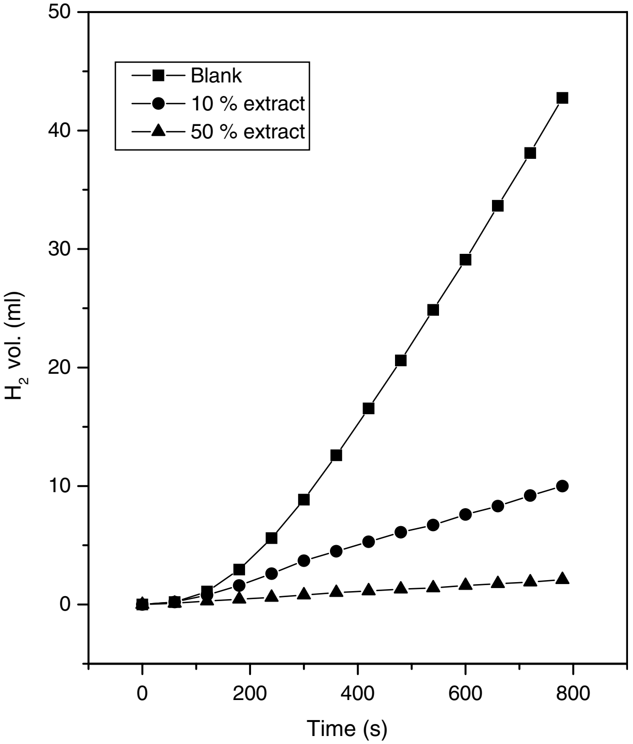

Fig. 2. Hydrogen evolution during aluminium corrosion in 2 M KOH at 30 °C in absence and presence of *Sansevieria trifasciata* extract.

depict plots of the evolved H_2 volume as a function of time for aluminium corrosion in 2 M HCl and 2 M KOH, respectively, in absence and presence of inhibitor (*S. trifasciata* extract) at 30 °C. Figs. 3 and 4 show similar plots at 60 °C.

Inspection of the plots reveals that hydrogen gas evolution commences only after an incubation period, which corresponds to the time interval needed by the corrodent to break down the pre-immersion oxide film on the aluminium surface [4,12]. This time interval is considerably shorter in the alkaline medium. After the incubation period, the volume of evolved H_2 gas varies linearly with reaction time. The plots also illustrate the decreased deflection of H_2 gas evolution rate on introduction of the extract into the corrodent, indicating that the leaf extract of *S. trifasciata* actually affords corrosion inhibition of aluminium in the acidic and basic environments. The rates of H_2 gas evolution were observed to decrease with increasing extract concentration, suggesting that the inhibiting action was concentration dependent.

The corrosion rates of the aluminium coupons were assessed from the slopes of the linear portions of the hydrogen evolution plots and the corresponding values for the different test solutions are given in Table 1. The results show that corrosion rates decreased in the presence of the extracts and increased with rise in temperature for all systems. Also, aluminium is observed to exhibit higher corrosion susceptibility in 2 M KOH possibly accounting for the short incubation periods observed in the H_2 evolution plots.

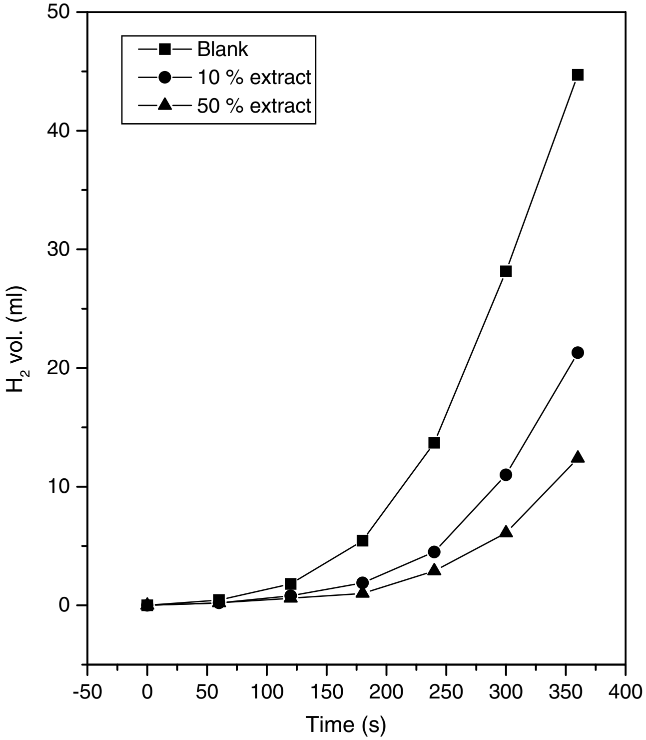

Fig. 3. Hydrogen evolution during aluminium corrosion in 2 M HCl at 60 °C in absence and presence of *Sansevieria trifasciata* extract.

3.2. Inhibition efficiency and adsorption considerations

The protective action of organic substances during metal corrosion is based on the adsorption ability of their molecules, where the resulting adsorption film isolates the metal surface from the corrosive medium. Consequently, in inhibited solutions, the corrosion rate is indicative of the number of free corrosion sites remaining after some sites have been effectively blocked by inhibitor adsorption. If it is assumed that corrosion occurs only at the free sites such that the covered sites have negligible corrosion rates, the degree of surface coverage (θ) and hence the inhibition efficiency ($I\%$) can be calculated as follows:

$$\theta = 1 - \frac{R_{\text{inh}}}{R_{\text{free}}} \tag{1}$$

$$I\% = \left(1 - \frac{R_{\text{inh}}}{R_{\text{free}}}\right) \times 100 \tag{2}$$

where R_{inh} and R_{free} correspond to the corrosion rates in the presence and absence of inhibitor, respectively, as determined from the H_2 evolution curves.

The surface coverage and inhibition efficiency data of *S. trifasciata* extract at different temperatures are given in Table 2. The results suggest that the extract exhibited good inhibition efficiency during aluminium corrosion in both corrodents. Owing to the complex

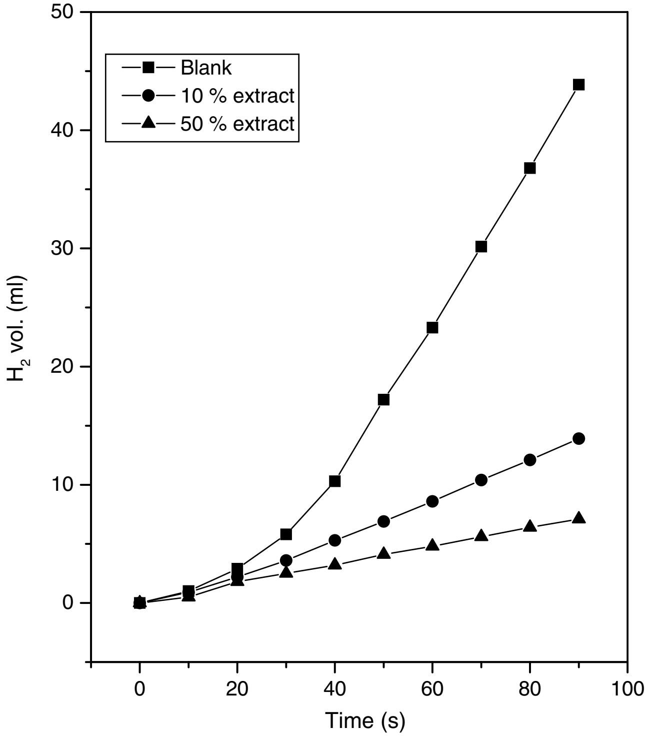

Fig. 4. Hydrogen evolution during aluminium corrosion in 2 M KOH at 60 °C in absence and presence of *Sansevieria trifasciata* extract.

Table 1
Corrosion rates of aluminium in 2 M HCl and 2 M KOH in absence and presence of *Sansevieria trifasciata* extract

System	Corrosion rate (H_2 gas vol. ml s^{-1}) × 10^{-2}	
	30 °C	60 °C
2 M HCl	1.76	18.10
2 M HCl + 10% extract	0.22	8.35
2 M HCl + 50% extract	0.01	4.78
2 M KOH	6.74	60.40
2 M KOH + 10% extract	1.36	16.83
2 M KOH + 50% extract	0.27	7.68

chemical composition of the extract, it is quite difficult to assign the inhibitive effect to a particular constituent. Initial approximate analysis of the extract identified the presence of alkaloids, tannins, phlobatannins, saponins and flavonoids [21]. The extract has been reported to contain 1β,2β-dihydroxy-pregna-5,16-dien-20-one glycosides [22], prain-β-sitisterol and some spirostan sapogenins [23] and a phosphofructokinase with molecular weight 115,000 [24]. In addition, the hemicelluloses obtained from the leaf fibres contain several oligosaccarides [25]. The adsorption of these compounds on the aluminium surface reduces the surface area available for corrosion. The degree of protection increases with an

Table 2
Degree of surface coverage (θ) and inhibition efficiency ($I\%$) of *Sansevieria trifasciata* extract during aluminium corrosion in 2 M HCl and 2 M KOH at different temperatures

Extract conc. (v/v%)	2 M HCl		2 M KOH	
	30 °C	60 °C	30 °C	60 °C
10	87.3 (0.87)	53.9 (0.54)	76.8 (0.77)	72.1 (0.72)
20	88.9 (0.89)	56.7 (0.57)	82.1 (0.82)	76.8 (0.77)
30	91.2 (0.91)	62.5 (0.62)	86.5 (0.86)	82.6 (0.83)
40	93.2 (0.93)	68.9 (0.69)	92.8 (0.92)	88.9 (0.89)
50	94.3 (0.94)	73.6 (0.74)	95.3 (0.95)	92.1 (0.92)

increase in extract concentration due to higher degree of surface coverage resulting from enhanced inhibitor adsorption. Further investigation using surface analytical techniques will enable the characterization of the active materials in the adsorbed layer and identification of the most active ingredients. The influence of the extract on the performance of the aluminium-air battery system could be another useful area of study.

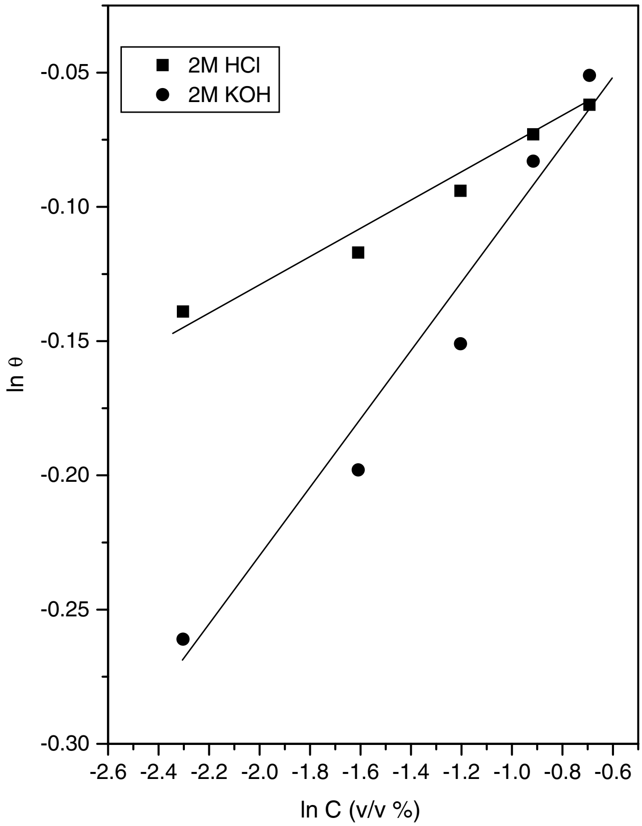

Fig. 5. Adsorption isotherm for *Sansevieria trifasciata* extract on aluminium in 2 M HCl and 2 M KOH at 30 °C.

The observed changes in θ are shown in Fig. 5 as a function of extract concentration in both corrodents at 30 °C. The linear plots obtained suggest that the experimental data fit the Freundlich adsorption isotherm which is given by [14]

$$\theta = KC^n \tag{3}$$

where $0 < n < 1$, or

$$\ln\theta = \ln K + n\ln C \tag{4}$$

C is the extract concentration and K the equilibrium constant for adsorption which is evaluated from the intercepts of the plots and is related to the standard free energy of adsorption, $\Delta G^0_{\mathrm{ads}}$ by

$$K = \frac{1}{55.5}\exp\left(\frac{-\Delta G^0_{\mathrm{ads}}}{RT}\right) \tag{5}$$

The calculated values of K and $\Delta G^0_{\mathrm{ads}}$ were found to be 0.969 and $-10.04\ \mathrm{kJ\ mol^{-1}}$ in 2 M HCl at 30 °C and 0.816 and -10.55 at 60 °C. Values of 1.028 and $-10.19\ \mathrm{kJ\ mol^{-1}}$ as well as 1.016 and $-11.16\ \mathrm{kJ\ mol^{-1}}$ were obtained in 2 M KOH at 30 and 60 °C correspondingly. These values indicate physical adsorption of organic matter on the aluminium surface.

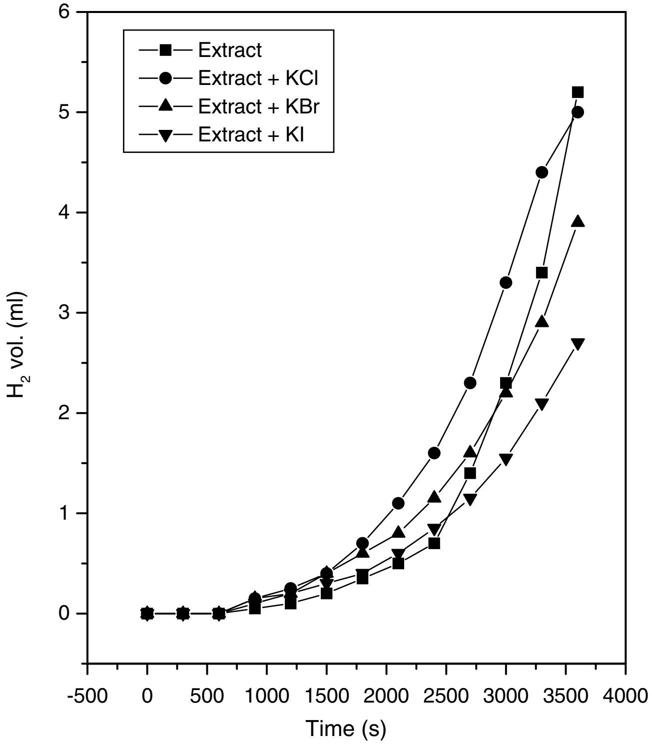

Fig. 6. Influence of halide additives on the inhibitive effect of *Sansevieria trifasciata* extract during aluminium corrosion in 2 M HCl at 30 °C.

3.3. Effect of halide additives

The increase in inhibition efficiency of organic compounds in the presence of some anions, particularly halide ions, has been reported by some authors and was ascribed to a synergistic effect [3,26,27]. It is thought that the anions are able to improve adsorption of the organic cations in solution by forming intermediate bridges between the metal surface and the positive end of the organic inhibitor. Corrosion inhibition synergism thus results from increased surface coverage arising from ion-pair interactions between the organic cations and the anions.

Trials to enhance the performance of 10% *S. trifasciata* extract by adding small amounts of halide salts (0.5 mM) were undertaken in this study. Figs. 6–9 illustrate the trend of inhibitor/halide interactions at different temperatures. The synergistic interactions at lower temperature, particularly in 2 M HCl, only manifest themselves at longer time intervals, below which the interactions are essentially antagonistic. Hydrogen evolution rates appear initially faster at short exposure times for extract/halide solutions compared to extract alone, possibly suggesting that the efficiency of the insoluble adsorption intermediate formed between the extract and corrosion products at lower temperature depends on the environmental capacity to dilute it. At higher temperature however, the adsorption intermediate becomes soluble and inhibitor/halide interactions may become more important in the adsorption, further reducing the rate of H_2 gas evolution.

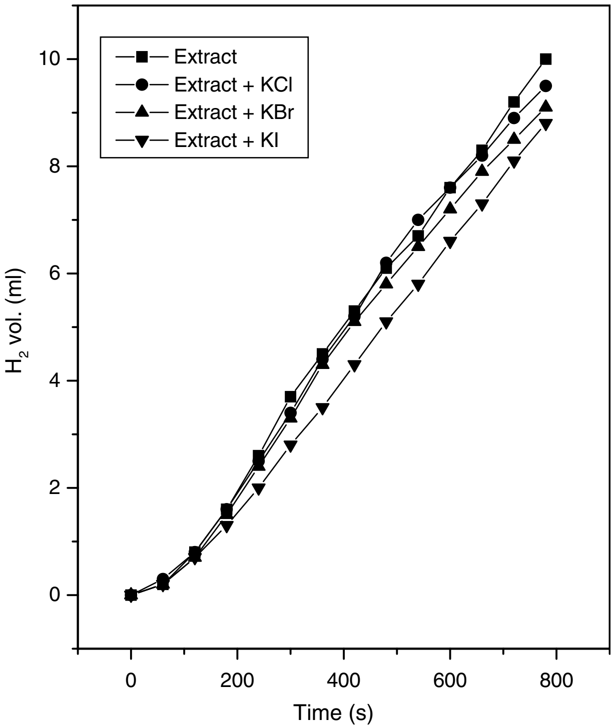

Fig. 7. Influence of halide additives on the inhibitive effect of *Sansevieria trifasciata* extract during aluminium corrosion in 2 M KOH at 30 °C.

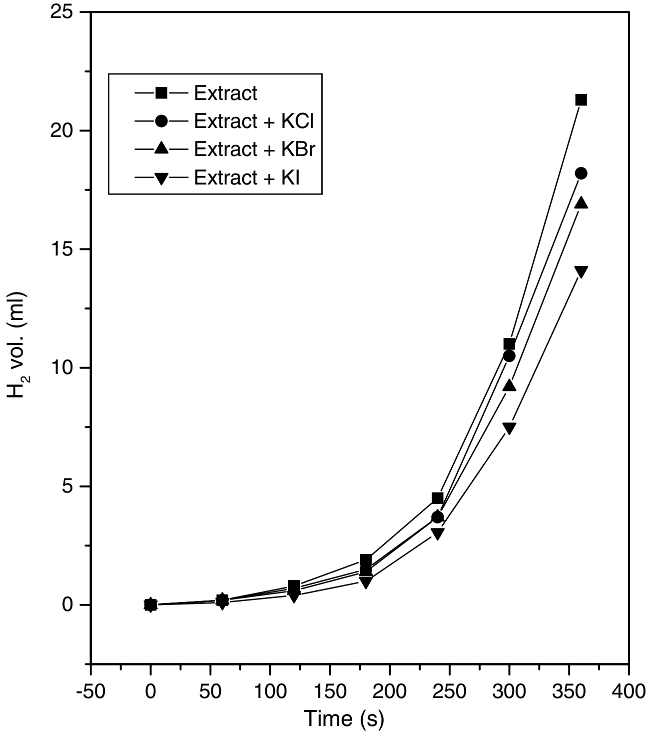

Fig. 8. Influence of halide additives on the inhibitive effect of *Sansevieria trifasciata* extract during aluminium corrosion in 2 M HCl at 60 °C.

Table 3 compares the inhibition efficiency of the extract with and without the halide additives. It is clear that the halide ions generally have a beneficial effect upon the performance of the extract. The synergistic effect increased in the order; $Cl^- < Br^- < I^-$, suggesting a possible role by ionic radii of the halides which also increase in the same order.

3.4. Effect of temperature

To gain insight into the nature of inhibitor adsorption, the effect of temperature (30 and 60 °C) on the corrosion behaviour of aluminium in the presence of *S. trifasciata* extract was studied. The results obtained indicate that the rates of aluminium corrosion in absence and presence of the extract increased with temperature while the inhibition efficiency decreased. This may be attributed to the higher dissolution rates of aluminium at elevated temperature and a possible desorption of adsorbed inhibitor due to increased solution agitation resulting from higher rates of H_2 gas evolution, which may also reduce the ability of the inhibitor to be adsorbed on the metal surface. Such behaviour, which was observed in both corrodents, suggests physical adsorption of the extracts on the corroding aluminium surface [4].

The apparent activation energies (E_a) for the corrosion process in absence and presence of inhibitor were evaluated from Arrhenius equation

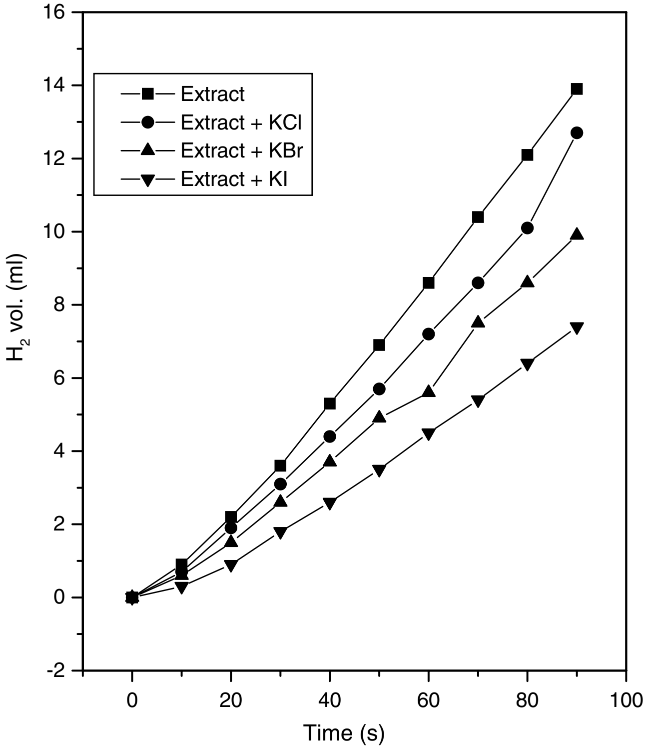

Fig. 9. Influence of halide additives on the inhibitive effect of *Sansevieria trifasciata* extract during aluminium corrosion in 2 M KOH at 60 °C.

Table 3
Influence of halide additives (0.5 mM) on the inhibition efficiency of 10% *Sansevieria trifasciata* at different temperatures

System	Inhibition efficiency			
	2 M HCl		2 M KOH	
	30 °C	60 °C	30 °C	60 °C
10% extract	87.3	53.9	76.8	72.1
Extract + KCl	86.9	59.5	80.6	75.4
Extract + KBr	90.9	62.8	81.3	80.1
Extract + KI	93.6	68.8	82.3	84.7

$$\log\frac{\rho_2}{\rho_1} = \frac{E_a}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{6}$$

where ρ_1 and ρ_2 are the corrosion rates at temperatures T_1 and T_2, respectively. An estimate of the heats of adsorption (θ) was obtained from the trend of surface coverage with temperature as follows [28]:

$$Q_{\mathrm{ads}} = 2.303R\left[\log\left(\frac{\theta_2}{1-\theta_2}\right) - \log\left(\frac{\theta_1}{1-\theta_1}\right)\right] \times \frac{T_1T_2}{T_2 - T_1} \tag{7}$$

Table 4
Calculated values of activation energy (E_a) and heat of adsorption (Q_{ads}) for aluminium corrosion in 2 M HCl and 2 M KOH with *Sansevieria trifasciata* extract as inhibitor

System	E_a (kJ mol^{-1})	Q_{ads} (kJ mol^{-1})
2 M HCl (blank)	65.18	–
2 M HCl + 10% extract	101.20	−49.50
2 M HCl + 50% extract	108.21	−49.97
2 M KOH (blank)	65.53	–
2 M KOH + 10% extract	70.69	−6.92
2 M KOH + 50% extract	93.63	−15.78

θ_1 and θ_2 are the degrees of surface coverage at temperature T_1 and T_2. The calculated values of both parameters are given in Table 4.

E_a increased in the presence of the extract in both 2 M HCl and 2 M KOH, hence leading to reduction in the corrosion rates. It has been suggested that adsorption of an organic inhibitor can affect the corrosion rate by either decreasing the available reaction area (geometric blocking effect) or by modifying the activation energy of the anodic or cathodic reactions occurring in the inhibitor-free surface in the course of the inhibited corrosion process [29]. The experimental observations suggest that the *S. trifasciata* extract does not alter the rate determining hydrogen adsorption step [2,18] of the corrosion process. Rather, corrosion inhibition occurs primarily through physical adsorption on the aluminium surface, giving rise to the deactivation of these surfaces to hydrogen atom recombination. Additional information on the inhibition mechanism could be realised from analysis of the adsorbed layer and detailed study of the corrosion morphology.

The negative Q_{ads} values indicate that the degree of surface coverage decreased with rise in temperature, supporting the earlier proposed physisorption mechanism.

4. Conclusions

1. *S. trifasciata* extract was found to be a good green inhibitor of aluminium corrosion in very aggressive acidic and alkaline environments.
2. The corrosion process is inhibited by adsorption of the extract on the aluminium surface following the Freundlich isotherm and inhibition efficiency increased with an increase in extract concentration but decreased with rise in temperature suggesting physical adsorption.
3. Addition of halide salts synergistically increased the inhibition efficiency of the extract in the order KCl < KBr < KI.
4. The presence of the extract increased the corrosion activation energy in both media and the adsorption heats gave negative values.

Acknowledgement

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