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Studies on the inhibitive effect of *Occimum viridis* extract on the acid corrosion of mild steel

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Abstract

Corrosion inhibition of mild steel in 2 M HCl and 1 M H_2SO_4 by leaf extracts of *Occimum viridis* (OV) was studied using the gasometric technique at temperatures of 30 and 60 °C. The results indicate that the extracts inhibit the corrosion process in both acid media and inhibition efficiency increased with concentration. Synergistic effects increased the inhibition efficiency in the presence of halide additives namely KCl, KBr, KI. Temperature studies revealed a decrease in efficiency with rise in temperature and corrosion activation energies increased in the presence of the extract, probably implying that physical adsorption of cationic species may be responsible for the observed inhibition behaviour. Comparative analysis of the inhibitor adsorption behaviour in 2 M HCl and 1 M H_2SO_4 as well as the effect halide additives suggest that cationic species may not be the only constituents responsible for the inhibiting action of the extract.

Keywords: Mild steel; Acid corrosion; *Occimum viridis*; Cationic species; Halide ions; Synergism

1. Introduction

Mild steel corrosion in acidic solution has been effectively controlled by the use of organic inhibitors [1–7]. Such substances usually contain polar functions with nitrogen, oxygen and/or sulphur in a conjugated system and the inhibiting action is attributed as a first stage, to the adsorption of the additives to the metal/solution interface. Inhibitor adsorption is influenced by factors such as the nature and surface charge on the metal, the type of aggressive media, the structure of the inhibitor and the nature of its interaction with the metal surface. Inhibitor adsorption in acid solution usually leads to a structural modification in the double layer with subsequent reduction in the rates of the electrochemical half cell reactions—the anodic metal dissolution and the cathodic reduction of hydrogen ions.

The increase in inhibition efficiency of organic compounds in the presence of some ions has been reported by some authors and was ascribed to the synergistic effect [8–10]. Synergism has become a very important effect in corrosion inhibition processes and serves as the basis for most modern inhibitor formulations. Kalman et al. [11] reported the synergistic increase in inhibition efficiency of hydroxyl-ethane-1,1-diphosphonic acid (HEDP) in the presence of divalent cations such as Zn^{2+}. Rajendran et al. [12] also observed the synergistic effect of calcium gluconate and Zn^{2+}. Similar effects have been observed in the presence of some anions, particularly halide ions. Gomma [8] studied the effect of halide ions on the inhibition efficiency of pyrazole derivatives and observed that the synergistic effect increased in the order $Cl^- < Br^- < I^-$. Oguzie [10] reported similar observation for the influence of halide ions on the inhibitive action of some organic dyes. Zhang et al. [13] reported the synergistic effect of iodide ions on the efficiency of benzotriazole. El-Hosary and Saleh [14] also reported the synergistic effect of iodide ions on the inhibition efficiency of molasses. It is thought that the initial specific adsorption of the halide ions on the metal surface improves adsorption of the organic cations in acidic solution by forming intermediate bridges between the positively charged 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.

Recently, due to increasing environmental awareness and the need to develop environmentally friendly processes, attention has been focused on the corrosion inhibiting properties of natural products of plant origin. This area of research is of much importance because in addition to being environmentally friendly and

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ecologically acceptable, plant products are inexpensive, readily available and renewable sources of materials. Zucchi and Omar [15] studied a variety of plant extracts and reported that *Auforpio turkiale* and *Azydracta indica* reduced the corrosion of steel in 1N HCl with an efficiency of 88–96%. Saleh et al. [16] reported that aloe leaves and peels from mangoes and oranges gave adequate protection to steel in hydrochloric acid solutions. Quraishi [17] even observed possible synergism of HEDP with some plant extracts.

The present study investigates the inhibiting effect of leaf extracts of *Occimum viridis* on mild steel corrosion in 1 M H_2SO_4 and 2 M HCl solutions using the gasometric technique. The plant is popularly called scent leaf and belongs to the Lamiaceae or mint family. 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

The experiments were performed on mild steel sheets with weight percentage composition as follows: C 0.05, Mn 0.6 P 0.36, Si 0.0.03 and thickness 0.14 cm. The metal specimen were prepared, degreased and cleaned as previously described [10].

All chemicals and reagents used were of analytical grade. The blank corrodents were respectively 2 M HCl and 1 M H_2SO_4 solutions. Stock solutions of the plant extract were prepared by boiling weighed amounts of the dried and ground leaves of *O. viridis* (OV) for 3 h in the 2 M HCl and 1 M H_2SO_4, respectively. The solutions were cooled and then filtered and stored. The filtrates from both acid extractions had a reddish brown appearance. 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 gasometric setup is essentially an apparatus that measures the volume of gas evolution from a reaction system. The reaction vessel was a two-necked flask connected via a delivery tube to a burette, which was in turn connected to a reservoir of paraffin oil. Two hundred and fifty millilitres of the test solution was then introduced into the flask and the initial volume of air in the burette recorded. Thereafter, two mild steel test coupons were dropped into the test solution and the reaction vessel immediately closed. The volume of hydrogen gas evolved by the corrosion reaction was estimated by the volume change in the level of the paraffin oil in the burette. 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 spontaneous corrosion of mild steel in acidic solutions can be represented by the anodic dissolution reaction

$$Fe \rightarrow Fe^{2+} + 2e \quad (1)$$

Accompanied by the corresponding cathodic reaction

$$2H^{+} + 2e \rightarrow H_2 \quad (2)$$

The corrosion rates of the test coupons in absence and presence of inhibitor was thus assessed 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 [18–20]. Figs. 1 and 2 depict plots of the evolved H_2 volume as a function of time for mild steel corrosion in 2 M HCl and 1 M H_2SO_4, respectively, in absence and presence of inhibitor (10

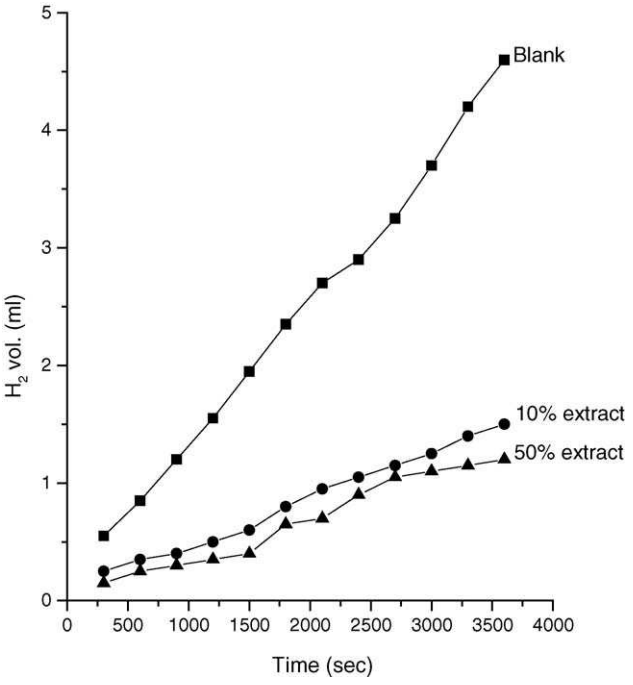

Fig. 1. Hydrogen evolution during mild steel corrosion in 2 M HCl at 30 °C in absence and presence of *Occimum viridis* extract.

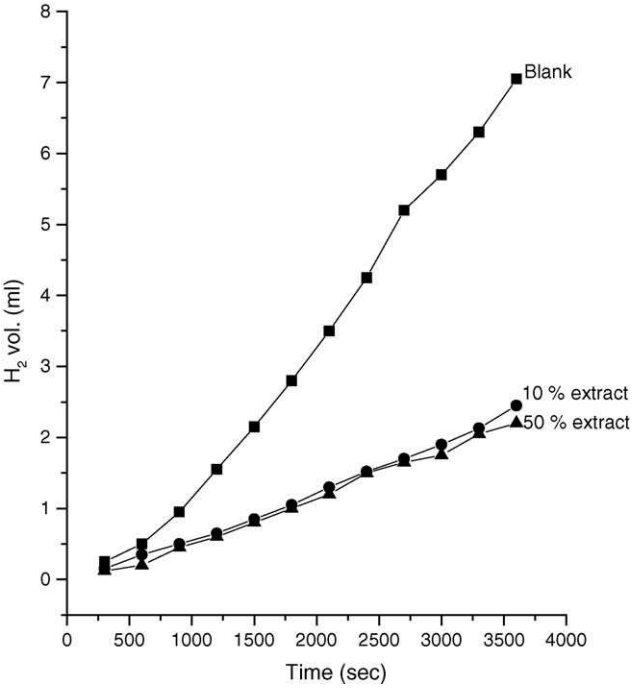

Fig. 2. Hydrogen evolution during mild steel corrosion in 1 M H_2SO_4 at 30 °C in absence and presence of *O. viridis* extract.

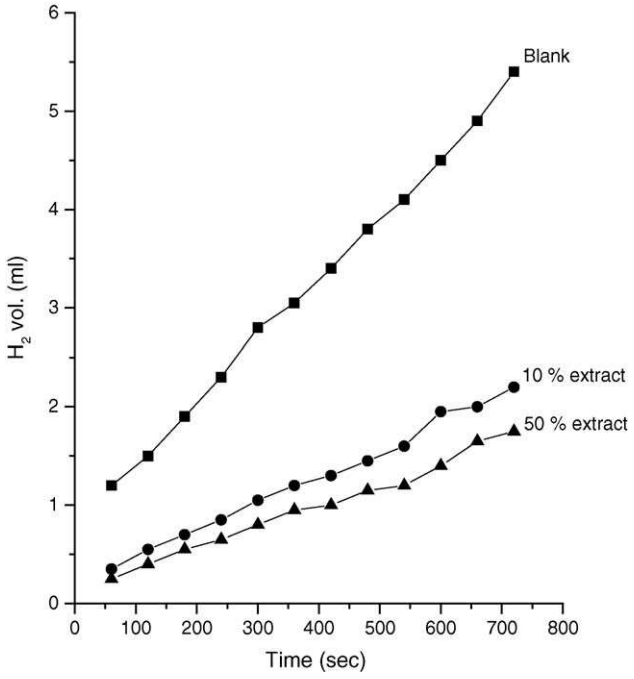

Fig. 3. Hydrogen evolution during mild steel corrosion in 2 M HCl at 60 °C in absence and presence of *O. viridis* extract.

and 50% *O. viridis* extract) at 30 °C. Figs. 3 and 4 show similar plots at 60 °C. The results illustrate the decreased deflection of H_2 gas evolution rate on introduction of the extract into the corrodents, indicating that the leaf extracts of OV actually affords corrosion inhibition of mild steel in the acidic 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 metal

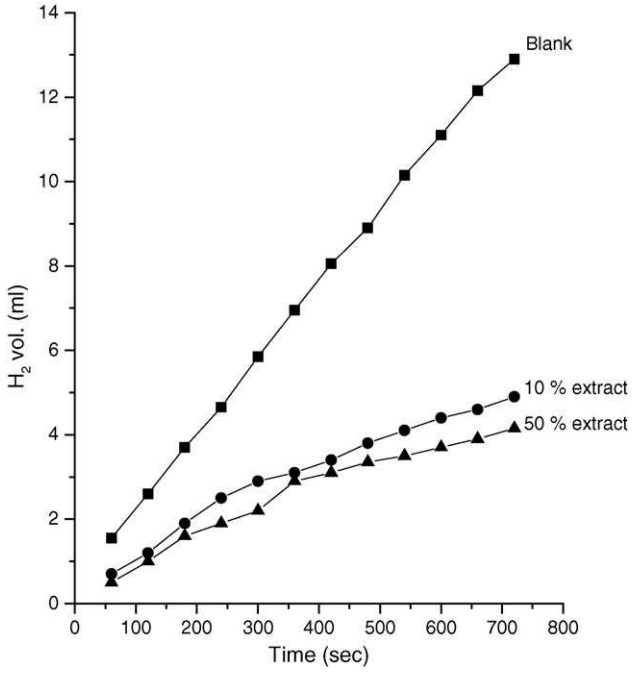

Fig. 4. Hydrogen evolution during mild steel corrosion in 1 M H_2SO_4 at 60 °C in absence and presence of *O. viridis* extract.

Table 1
Corrosion rates of mild steel in 2 M HCl and 1 M H_2SO_4 in absence and presence of *Occimum viridis* extract

System	Corrosion rate ($\times 10^{-3}$ H_2 gas vol ml s^{-1})	
	30 °C	60 °C
2 M HCl	1.22	6.26
2 M HCl + 10% extract	0.404	2.75
2 M HCl + 50% extract	0.353	2.19
1 M H_2SO_4	2.25	17.80
1 M H_2SO_4 + 10% extract	0.70	6.54
1 M H_2SO_4 + 50% extract	0.67	3.58

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, mild steel is observed to exhibit higher corrosion susceptibility in 1 M H_2SO_4.

3.2. Inhibition efficiency

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. The degree of surface coverage (θ) and hence the inhibition efficiency (I, %) was calculated from the equations:

$$\theta = 1 - \frac{R_{\text{inh}}}{R_{\text{free}}} \tag{3}$$

$$I\,(\%) = \left(1 - \frac{R_{\text{inh}}}{R_{\text{free}}}\right) \times 100 \tag{4}$$

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.

Fig. 5 illustrates the variation of inhibition efficiency with OV extract concentration in both corrodents at 30 and 60 °C. The plots show that the extract actually inhibits the acid corrosion of mild steel and that inhibition efficiency increased with an increase in the extract concentration at both temperatures.

Plant products are organic in nature and some of the constituents including tannins, organic and amino acids, alkaloids, pigments are known to exhibit inhibiting action. In addition, leaf extracts of *O. viridis* have been reported to contain of ascorbic acid, carotenoids and aromatic oils [21,22]. Species in the same family have also been reported to contain monoterpene glycosides and terpenoids [23]. Owing to the complex chemical composition of the OV extract, it is quite difficult to assign the inhibitive effect to a particular constituent. The adsorption of these compounds on the metal surface reduces the surface area available for corrosion. The degree of protection increases with an increase in extract concentration due to higher degree of surface coverage resulting from enhanced inhibitor adsorption.

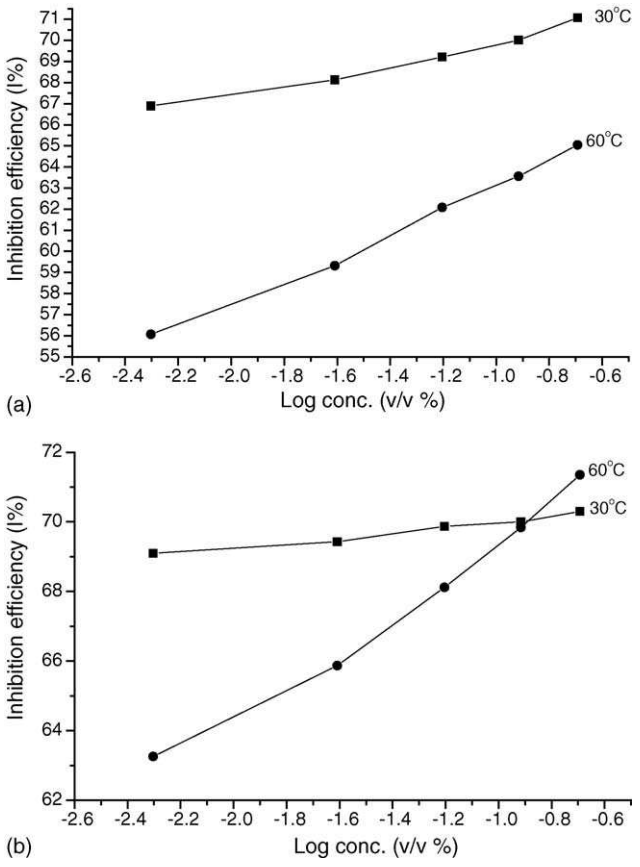

Fig. 5. Variation of inhibition efficiency with logarithmic concentration of OV extract for mild steel corrosion in 2 M HCl and 1 M H_2SO_4 at different temperatures.

3.3. 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 mild steel in the presence of *O. viridis* extract was investigated. The results suggest that the extract was adsorbed on the mild steel surface at all temperatures studied. The data in Table 1 indicate that the rates of steel corrosion in absence and presence of the extract increased with rise in temperature in both acid media. This is because an increase in temperature usually accelerates corrosive processes, particularly in media in which H_2 gas evolution accompanies corrosion, giving rise to higher dissolution rates of the metal. The plots in Fig. 5 show that inhibition efficiency generally decreased with rise in temperature, apart from the observed increase in the highest inhibitor concentration in 1 M H_2SO_4. This suggests a possible shift of the adsorption–desorption equilibrium towards desorption of adsorbed inhibitor. In addition, the boost in solution agitation resulting from higher rates of H_2 gas evolution as well as the roughening of the metal surface as a result of enhanced corrosion may also reduce the ability of the inhibitor to be adsorbed on the metal surface at elevated temperature [24].

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

Table 2
Calculated values of activation energy (E_a) and heat of adsorption (Q_{ads}) for mild steel corrosion in 2 M HCl and 1 M H_2SO_4 with *O. viridis* extract as inhibitor

System	E_a (kJ mol^{-1})	Q_{ads} (kJ mol^{-1})
2 M HCl (blank)	45.97	–
2 M HCl + 10% extract	53.70	−12.82
2 M HCl + 50% extract	51.10	−7.73
1 M H_2SO_4 (blank)	57.91	–
1 M H_2SO_4 + 10% extract	62.91	−7.34
1 M H_2SO_4 + 50% extract	56.90	1.50

Arrhenius equation:

$$\log\frac{\rho_2}{\rho_1} = \frac{E_a}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \quad (5)$$

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 [25]:

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

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 2.

E_a increased in the presence of the extract at all the studied concentrations in 2 M HCl suggesting that the adsorbed organic matter creates a physical barrier to charge and mass transfer, leading to reduction in corrosion rate. The negative Q_{ads} values also signify that the degree of surface coverage decreased with rise in temperature. Similar behaviour is observed at low extract concentrations in 1 M H_2SO_4 while the reduction in activation energy at high inhibitor concentration is consistent with the trend of inhibition efficiency with temperature in this medium and may signify that a chemisorbed film is gradually formed on the metal surface at high extract concentration [6,24].

3.4. Adsorption mechanism

The data obtained from the temperature dependence of the inhibition process suggest a physical or coulombic type of adsorption. To further elucidate the mechanism of inhibitor adsorption, it is necessary to establish the adsorption modes of the inhibiting species (whether molecular or ionic). The predominant adsorption mode will be dependent on factors such as the extract composition, type of acid anion as well as chemical changes to the extract. In the acid extractions used in this study, it is expected that some of the organic constituents may exist in the protonated form and some as molecular species. The protonated species can be adsorbed on cathodic sites on the mild steel and reduce H_2 gas evolution. Zucchi and Omar [15] attributed the inhibiting effect of acid extractions of some plant materials on the protein hydrolysis products. The physical adsorption mechanism, suggested by the results obtained so far, results from electrostatic attractive forces between inhibiting

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

System	Inhibition efficiency			
	2 M HCl		1 M H_2SO_4	
	30 °C	60 °C	30 °C	60 °C
10% extract	66.89 (0.67)	56.07 (0.56)	69.10 (0.69)	63.26 (0.63)
10% extract + KCl	−8.20	54.31 (0.54)	87.00 (0.87)	79.89 (0.80)
10% extract + KBr	87.13 (0.87)	57.51 (0.58)	87.54 (0.88)	87.75 (0.88)
10% extract + KI	91.56 (0.92)	56.71 (0.57)	94.50 (0.95)	90.00 (0.90)

NB: surface coverage data are given in parenthesis.

organic ions or dipoles and the electrically charged surface of the metal due to the electric field existing at the metal/solution interface. A negative surface charge will favour the adsorption of cations whereas anion adsorption is favoured by a positive surface charge. A corroding mild steel specimen carries a positive surface charge in both sulphuric and hydrochloric acid solutions and as such, protonated species should be poorly adsorbed. On the other hand, the ability of Cl^- ions in hydrochloric acid to be strongly adsorbed on the metal surface and hence facilitate physical adsorption of inhibitor cations is an important consideration. Accordingly, a comparison of the inhibiting characteristics of the extract in 2 M HCl and 1 M H_2SO_4 could very well give an insight into the mode of adsorption of the inhibiting species. Both solutions have identical anion concentration. If corrosion inhibition is due exclusively to protonated species which adsorb electrostatically, the inhibitor should be less effective in 1 M H_2SO_4 and exhibit improved efficiency in 2 M HCl, alternatively, if they adsorb as molecules, the inhibiting effect in both acid solutions should be comparable. A similar interpretation has been adduced by Popova et al. [26]. Again, it is generally accepted that halide ions facilitate adsorption of organic inhibitors during mild steel corrosion in acidic media. It is thought that the halide ions, which become specifically adsorbed on the metal surface, 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. Thus, if the inhibiting effect is due to the protonated species, a synergistic increase in inhibition efficiency should be observed in the presence of the halide additives. The calculated values of inhibition efficiency and degree of surface coverage for mild steel corrosion in 2 M HCl and 1 M H_2SO_4 containing 10% OV as well as 10% OV + 5.0 mM halide mixtures at different temperatures are given in Table 3.

Analyses of all the results yield a number of interesting observations. Although the slightly higher efficiency of the extract in 2 M HCl as well as the synergistic action of the halides supports the proposed physisorption of protonated organic species, the close similarity in inhibition efficiency values in both acid solutions at 30 °C implies that these may not be the only species responsible for the observed inhibiting effect. Rather such behaviour suggests the participation of both protonated and neutral species in the inhibiting process, with the former having a predominating effect. In addition, Table 3 demonstrates that adsorption of these cationic species was further enhanced in the presence of halide ions resulting in improved surface coverage and hence high inhibition efficiencies observed in the extract + halide systems.

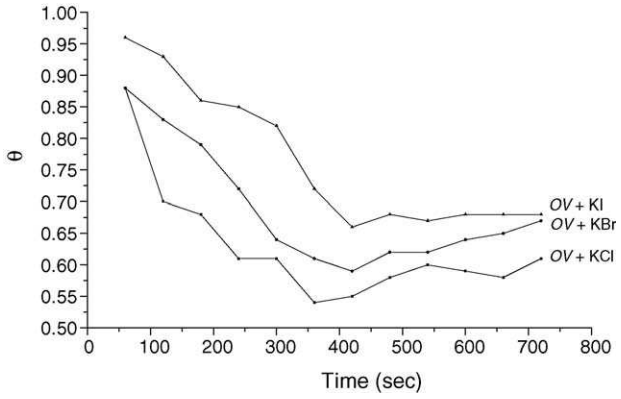

Fig. 6. Variation of surface coverage with for OV + halide mixtures at 60 °C.

The results also indicate that the enhancement of extract efficiency due to the halide additives was significantly diminished at higher temperature in 2 M HCl. This may be attributed to formation of soluble adsorption intermediates which exhibit fast dissolution rates as temperature rises as illustrated in Fig. 6.

4. Conclusion

O. viridis extract inhibited mild steel corrosion in 2 M HCl and 1 M H_2SO_4 at the temperatures studied. Inhibition efficiency increased with an increase in extract concentration and synergistically increased in the presence of halide ions. Temperature studies revealed a decrease in efficiency with rise in temperature and corrosion activation energies were higher in the presence of the extract. Comparative analyses of the results from both acid solutions suggest that protonated and neutral organic species in the extract may be responsible for the observed inhibitive behaviour, the predominant effect being the physical adsorption of protonated species.

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