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Materials Chemistry and Physics 87 (2004) 212–217
MATERIALS CHEMISTRY AND PHYSICS
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Influence of halide ions on the inhibitive effect of congo red dye on the corrosion of mild steel in sulphuric acid solution

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Received 6 March 2004; received in revised form 22 May 2004; accepted 7 June 2004

Abstract

The inhibitive effect of congo red dye (CR) on mild steel corrosion in sulphuric acid solution was studied at different temperatures using gravimetric techniques. The influence of halide additives namely: KCl, KBr and KI on the inhibition efficiency of CR was also investigated. Inhibition efficiency increased with CR concentration but decreased with rise in temperature. Corrosion activation energies of 82.98 and 96.92 kJ mol^{-1} were observed in the absence and presence of CR, respectively. The observed corrosion data suggest that inhibition of mild steel corrosion is due to physical adsorption of the CR molecules on the metal surface, which follow Flory–Huggins isotherm. Inhibition antagonism and synergism were respectively observed at 30 and 60 °C on addition of halide salts to inhibited systems containing CR. The inhibition efficiency of CR in the presence of halides increased with rise in temperature and corrosion activation energy in these systems decreased to 40.63 kJ mol^{-1}. These observations indicate a chemical adsorption mechanism, thus suggesting that the halide ions reversed the mechanism of CR adsorption within the concentration range studied. The calculated values of heat of adsorption confirm physisorption and chemisorption mechanisms respectively for CR adsorption in the absence and presence of halides.

Keywords: Mild steel; Congo red dye; Halide ions; Inhibition efficiency; Physisorption; Chemisorption

1. Introduction

The corrosion behavior of mild steel has been extensively studied in various aqueous corrosive environments. The mechanism for anodic dissolution of iron in acidic solution has been found to be influenced by the anions present in solution. Perhaps the most important factor is the effect of OH^- ions, which are found in every aqueous solution. These form catalytic complexes on the metal surface which facilitate the dissolution process [1,2]. A number of mechanistic studies on the anodic dissolution of Fe in acidic sulphate solutions have been undertaken, and the hydroxyl accelerated mechanism proposed initially by Bockris and Drazic [2] has gained overwhelming acceptance

$$Fe + OH^- \rightleftharpoons FeOH_{ads} + H^+ + e \quad (1a)$$

$$FeOH_{ads} \overset{rds}{\rightarrow} FeOH^+ + e \quad (1b)$$

$$FeOH^+ + H^+ \rightleftharpoons Fe^{2+} + H_2O \quad (1c)$$

It has been suggested [2–5] that anions such as Cl^-, I^-, SO_4^{2-} and S^{2-} may also participate in forming reaction intermediates on the corroding metal surface, which either inhibit or stimulate corrosion. It is important to recognize that the suppression or stimulation of the dissolution process is initiated by the specific adsorption of the anion on the metal surface. Halide ions have been reported [6–8] to inhibit the corrosion of some metals in strong acids and this effect depends on the ion size, the electrostatic field set up by the charge of the ions on adsorption sites and the concentration of the halide ions. Indeed, this effect on mild steel is due to the ability of halide ions to replace hydroxyl ions adsorbed on the metal surface, thus reducing the catalytic effect of the hydroxyl ions [1].

Mild steel corrosion in acidic solution has been effectively controlled by the use of organic substances containing nitrogen, oxygen or sulphur in the conjugated system as inhibitors [6–12]. Corrosion inhibition occurs via the adsorption of the organic molecules on the metal surface following some known adsorption isotherms. The resulting adsorption film subsequently protects the metal from the aqueous corrodent and the inhibition efficiency depends on the mechanical, structural and chemical characteristics of the adsorption layers formed under particular experimental conditions.

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doi:10.1016/j.matchemphys.2004.06.006

The corrosion of iron may proceed, depending on the pre-history of the metal and environment conditions, via different reaction routes. Thus, a substance may be required to perform more than one function in order to be an effective corrosion inhibitor. Since acid inhibitors are known for their specificity of action, combinations of inhibitors are more likely to provide the multiple services required for effective corrosion inhibition. Interestingly, addition of halide salts to sulphuric acid solution containing any organic compound has been reported [8,13] to result in a cooperative effect which inhibits Fe dissolution.

Congo red belongs to a group of organic dyes found to be effective as inhibitors of metal corrosion [14,15]. The congo red molecule is large and contains two azo bonds having 4-amino-1-naphtalenesulphonic acid groups at each end as shown below. Talati and Joshi [16] studied the compound as an inhibitor for aluminum in aliphatic amines.

The present report investigates the corrosion of mild steel in sulphuric acid solution containing congo red using gravimetric techniques. The effect of halide ions on the mechanism of CR adsorption has also been examined.

2. Experimental

Tests were performed on mild steel sheets with weight percentage composition as follows: C, 0.05; Mn, 0.6; P, 0.36 and Si, 0.03. All reagents were BDH grade, used as sourced without further purification. 2 M sulphuric acid solution was employed as blank. For experiments involving the inhibitor, congo red dye (CR), the solid was added to the blank solution to reach final concentrations of 1×10^{-4}, 1×10^{-3}, 5×10^{-3}, 1×10^{-2} and 5×10^{-2} M. Solutions of 5×10^{-4} M concentration of the halides KCl, KBr, and Kl were prepared in the blank solution and in 5×10^{-4} M CR solution.

Gravimetric experiments were conducted on mild steel coupons of dimension 3 cm × 3 cm × 0.14 cm, used as procured without further polishing but were however degreased in absolute ethanol, dried in acetone, weighed and stored in a moisture free desiccator prior to use. Tests were conducted under total immersion conditions in 200 ml of test solutions maintained at 30–60 °C. The pre-cleaned and weighed coupons were suspended in beakers containing the test solutions using glass hooks and rods. All tests were made in aerated solutions and were run in triplicate. To determine weight loss with respect to time, the coupons were retrieved from test solutions at 2-h-interval progressively for 10 h, immersed in 20% NaOH solution containing 200 g l^{-1} of zinc dust, scrubbed with bristle brush under running water, dried and re-weighed [17]. The weight loss was taken to be the difference between the weight of the coupons at a given time and its initial weight.

3. Results and discussion

3.1. Weight losses and corrosion rate

The corrosion rates of metals and alloys can be determined using different electrochemical and non-electrochemical techniques. In this study, gravimetric techniques were employed. The weight losses of the mild steel test coupons (g dm^{-2}) in 2 M H_2SO_4 without inhibitor and in the presence of CR and CR + halides as a function of time at 30 °C are plotted in Fig. 1a, while Fig. 1b shows similar plots at 60 °C. Inspection of these plots reveal that CR inhibits corrosion of mild steel in sulphuric acid and that weight loss increased with rise in temperature in both inhibited and uninhibited solutions. Fig. 1a and b also show that the corrosion rate of mild steel in 2 M H_2SO_4 solutions containing CR was enhanced by addition of halides at 30 °C, while at 60 °C, the same halide additives diminished the corrosion rate. Fig. 2 illustrates the variation of weight loss with inhibitor concentration at 30 and 60 °C. Weight loss is observed to decrease with increase in the concentration of CR at both temperatures, suggesting that the extent of inhibition is dependent on the amount of CR present.

According to the Bockris mechanism outlined earlier, Fe electro-dissolution in acidic sulphate solutions depends primarily on the adsorbed intermediate $FeOH_{ads}$. Ashassi-Sorkhabi and Nabavi-Amri [18] proposed the following mechanism involving two adsorbed intermediates to account for the retardation of Fe anodic dissolution in the presence of an inhibitor.

$$Fe + H_2O \rightleftharpoons Fe \cdot H_2O_{ads} \quad (2a)$$

$$Fe \cdot H_2O_{ads} + Y \rightleftharpoons FeOH^-_{ads} + H^+ + Y \quad (2b)$$

$$Fe \cdot H_2O_{ads} + Y \rightleftharpoons FeY_{ads} + H_2O \quad (2c)$$

$$FeOH^-_{ads} \xrightarrow{rds} FeOH_{ads} + e \quad (2d)$$

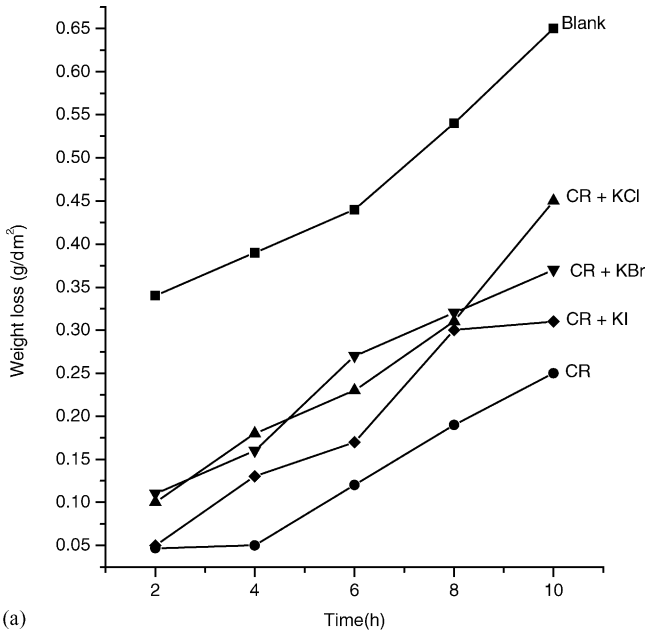
$$Fe\,Y_{ads} \rightleftharpoons FeY^+_{ads} + e \quad (2e)$$

$$FeOH_{ads} + FeY^+_{ads} \rightleftharpoons FeY_{ads} + FeOH^+ \quad (2f)$$

$$FeOH^+ + H^+ \rightleftharpoons Fe^{2+} + H_2O \quad (2g)$$

where Y represents the inhibitor species.

Considering the inhomogeneous nature of metallic surfaces resulting from the existence of lattice defects and dislocations, a corroding metal surface is generally characterized by multiple adsorption sites having definite activation energies and heats of adsorption. Inhibitor molecules may thus be adsorbed more readily at surface active sites having suitable adsorption enthalpies. According to the detailed mechanism above, displacement of some adsorbed water molecules on



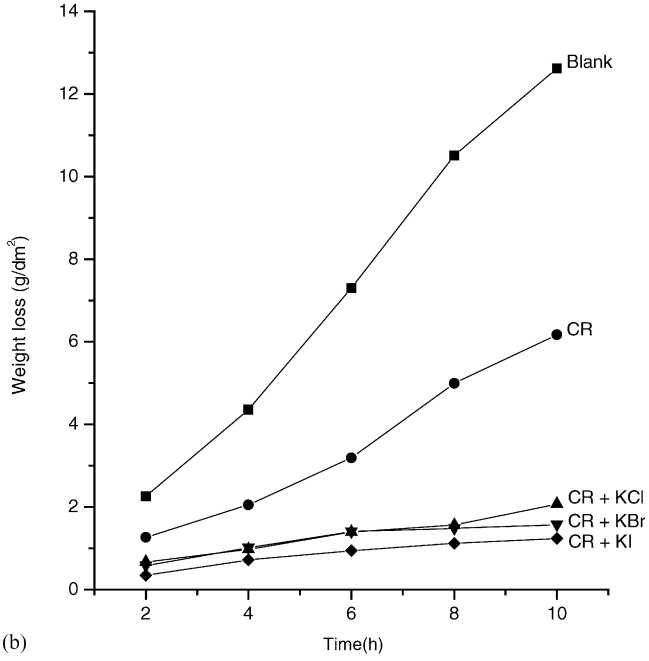


Fig. 1. (a) Variation of weight loss with time for mild steel in 2 M H_2SO_4 without inhibitor (blank) and containing CR and CR + halides at 30 °C and (b) variation of weight loss with time for mild steel in 2 M H_2SO_4 without inhibitor (blank) and containing CR and CR + halides at 60 °C.

the metal surface by inhibitor species to yield the adsorbed intermediate FeY_{ads} (Eq. 2c) reduces the amount of the species $FeOH^{-}_{ads}$ available for the rate-determining step and consequently retards Fe anodic dissolution.

3.2. Inhibition efficiency

The inhibition efficiency (1%) of CR on the electrochemical corrosion of mild steel in sulphuric acid solution and the

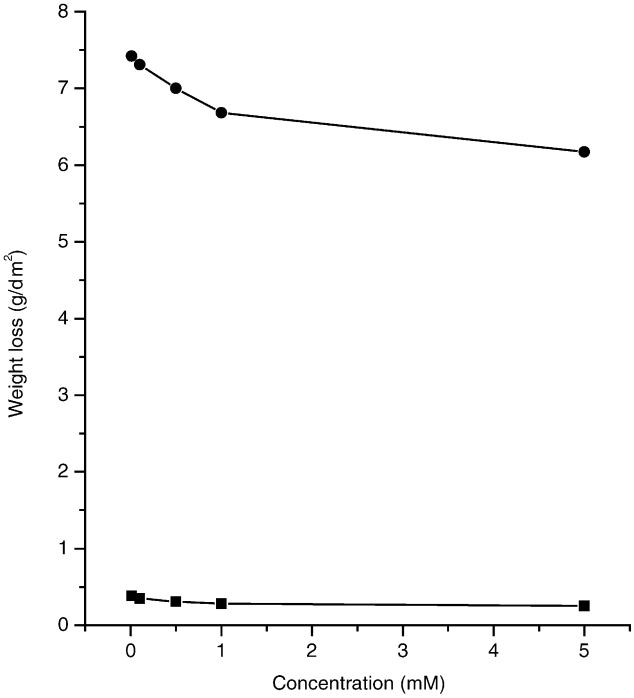


Fig. 2. Variation of weight loss with CR concentration for mild steel in 2 M H_2SO_4 at 30 and 60 °C.

degree of surface coverage (θ) were evaluated by comparing the weight losses in the presence and absence of inhibitor as follows [19]

$$1\% = \left(1 - \frac{w_1}{w_2}\right) \times 100 \quad (3)$$

$$\theta = 1 - \frac{w_1}{w_2} \quad (4)$$

where w_1 and w_2 are the weight losses in the presence and absence of inhibitor, respectively. Calculated values of inhibition efficiency and surface coverage for mild steel corrosion in 2 M H_2SO_4 containing CR, halides and CR + halide mixtures are given in Table 1. Fig. 3 illustrates the variation of inhibition efficiency with CR concentration at 30 and 60 °C. The plots show that inhibition efficiency increased with an increase in CR concentration at both temperatures. The observed corrosion inhibition may be attributed to the adsorption of CR molecules at the metal/solution interface. The inhibition efficiency however decreased with rise in temperature, suggesting that an increase in temperature resulted in desorption of some adsorbed CR molecule from the metal surface. Such behavior suggests that the inhibitor molecules are physically adsorbed on the metal surface [20,21].

3.3. Adsorption considerations

According to Eq. (2c), the adsorption of an organic inhibitor on the surface of a corroding mild steel specimen may be regarded as a substitution process between the organic compound in the aqueous phase and water molecules

Table 1
Calculated values of inhibition efficiency (1%) and degree of surface coverage (θ) for mild steel in 2 M H_2SO_4 solution with inhibitor, halides and inhibitor + halide mixtures at different temperatures

System	Inhibition efficiency (1%)		Surface coverage (θ)	
	30 °C	60 °C	30 °C	60 °C
1×10^{-5} M CR	42.41	41.21	0.42	0.41
1×10^{-4} M CR	45.67	42.10	0.46	0.42
5×10^{-4} M CR	52.26	44.52	0.52	0.45
1×10^{-3} M CR	57.12	45.53	0.57	0.46
5×10^{-3} M CR	61.71	51.11	0.62	0.51
5×10^{-4} M KCl	−6.15	42.16	−0.06	0.42
5×10^{-4} M KBr	36.92	67.74	0.37	0.68
5×10^{-4} M KI	44.62	79.00	0.45	0.79
5×10^{-3} M CR + KCl	30.77	83.60	0.31	0.84
5×10^{-3} M CR + KBr	43.08	87.56	0.43	0.88
5×10^{-3} M CR + KI	52.31	90.17	0.52	0.90

adsorbed on the metal surface. Indeed, the adsorption of CR on the mild steel surface was found to follow the substitutional isotherm of Flory–Huggins, given by [22]

$$\log\left(\frac{\theta}{C}\right) = \log K + x\log(1-\theta) \quad (5)$$

where θ is the degree of surface coverage, C the inhibitor concentration, x the number of water molecules replaced by one inhibitor molecule and K is the equilibrium constant for the adsorption process. Fig. 4 illustrates the Flory–Huggins adsorption isotherm for CR.

The corrosion behavior of the mild steel specimen in the presence of CR reveals that the inhibitor molecules are well adsorbed over the metal surface and that surface coverage

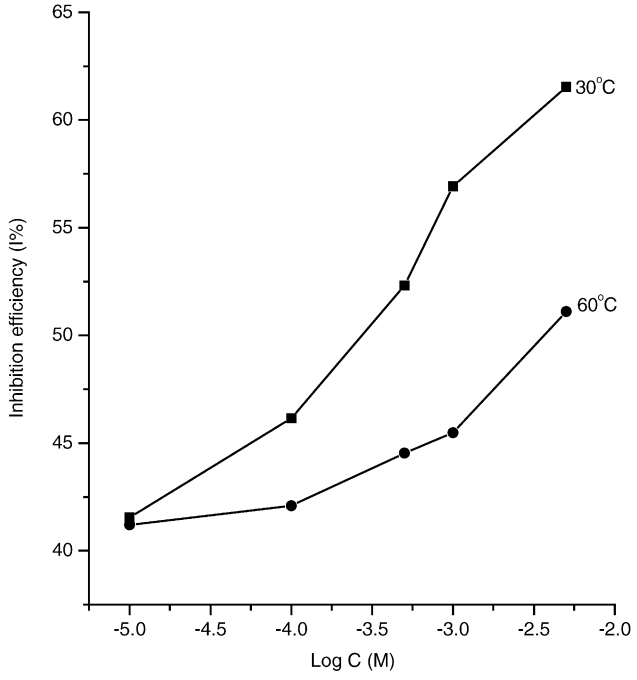


Fig. 3. Variation of inhibition efficiency with logarithmic concentration of CR for mild steel in 2 M H_2SO_4 at 30 and 60 °C.

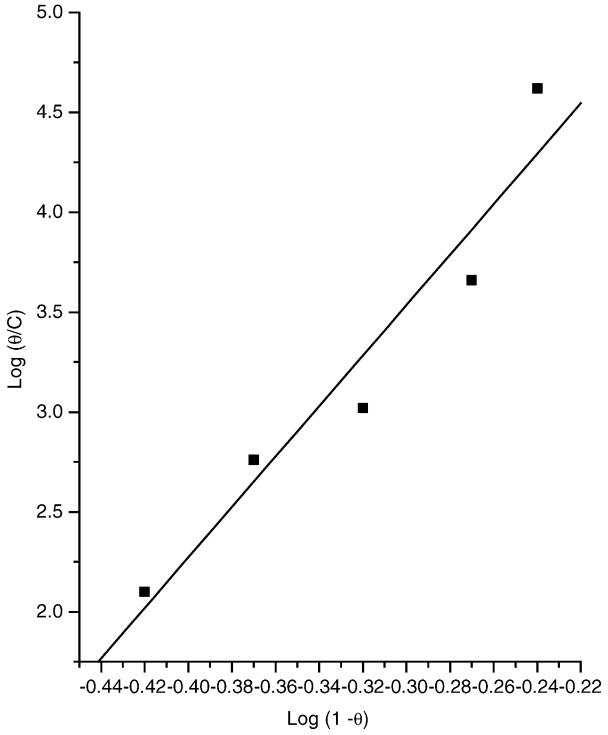


Fig. 4. Flory–Huggins isotherm for CR adsorption on mild steel in 2 M H_2SO_4 solution.

decreases with rise in temperature. This suggests that the adsorbed molecules mechanically screen the coated part of the metal surface from the action of the corrodent. This can be explained on the basis that adsorption takes place via the electron-rich nitrogen atoms of the functional azo groups [14] as well as through the delocalized pi electrons of the phenyl groups, which lie parallel to the metal surface [6], resulting in wider surface coverage. All the results obtained suggest that the CR molecules are adsorbed as aggregates in the protective film due to intermolecular association in the adsorbed layer.

3.4. Effect of halide ions

In acid solution, halides are known to both inhibit and stimulate corrosion of metals, depending on the halide ion concentration, ionic radii and/or electronegativity and prevailing experimental conditions. The data in Table 1 show that KBr and KI inhibited mild steel corrosion in 2 M H_2SO_4 at 30 °C, while KCl was found to be a corrosion accelerator. At 60 °C however, all the halides exhibited enhanced inhibition efficiencies, indicating that halide ion adsorption is enhanced at higher temperature. Inhibition efficiencies (I%) of the halides increased in the order $Cl^- < Br^- < I^-$, which on the basis of ionic radii, suggests that the iodide ion radius is more predisposed to adsorption than the bromide and chloride ions. Halide ions inhibit Fe anodic dissolution by replacing some adsorbed catalytic OH^- ions on the metal surface. The mechanism proposed by Chin and Nobe [23]

Table 2
Synergism parameter for the various halides at 60 °C

Halides	Synergism parameter (S_I)
KCl	1.12
KBr	1.36
KI	1.45

for Fe dissolution in acidic chloride solutions may thus be generalized for all the halides as follows

$$Fe + H_2O + X^- \rightleftharpoons FeXOH^-_{ads} + H^+ + e \quad (6a)$$

$$FeXOH^-_{ads} \xrightarrow{rds} FeXOH + e \quad (6b)$$

$$FeXOH + H^+ \rightleftharpoons Fe^{2+} + X^- + H_2O \quad (6c)$$

where X represents the halide ion.

Inspection of the data in Table 1 also reveals that the inhibition efficiency of CR in 2 M H_2SO_4 synergistically increased on addition of the halide salts to the solution at 60 °C. The synergism parameters (S_I) were calculated using the relationship [8,13]

$$S_I = \frac{1 - I_{1+2}}{1 - I'_{1+2}} \quad (7)$$

where $I_{1+2} = (I_1 + I_2)$; I_1 is the inhibition efficiency of the halide, I_2 the inhibition efficiency of CR and I'_{1+2} the inhibition efficiency of CR in combination with halide. The calculated values presented in Table 2 for the halides are all greater than unity, suggesting that the enhanced inhibition efficiency resulting from the addition of halides to the inhibitor is due to synergistic effect.

Corrosion inhibition synergism results from increased surface coverage arising from ion-pair interactions between the organic inhibitor and the halide ions. According to Fishtik et al. [24], two possible mechanisms account for the adsorption of such ion pairs on the metal surface. According to one mechanism, the ion-pairs are formed in the bulk of the solution and then adsorbed from the solution on to the metal surface as follows:

$$Y_s + X_s \rightarrow (YX)_s \quad (8a)$$

$$(YX)_s \rightarrow (YX)_{ads} \quad (8b)$$

In the second mechanism, the halide ion is first adsorbed on the metal surface and the inhibitor is then drawn into the double layer by the adsorbed halide ion such that the ion-pair formation occurs directly on the metal surface

$$X_s \rightarrow X_{ads} \quad (9a)$$

$$Y_s + X_{ads} \rightarrow (YX)_{ads} \quad (9b)$$

Y_s, X_s and $(YX)_s$ represent the inhibitor, halide ion and ion-pair, respectively in the bulk of the solution while Y_{ads}, X_{ads} and $(YX)_{ads}$ refer to the same species in the adsorbed state.

The data in Table 1 suggests that ion-pair interactions between CR and halide ions might have occurred via the second mechanism. It is obvious that the higher amounts of halide ions adsorbed on the mild steel surface at 60 °C may facilitate adsorption of CR via the phenomenon of anion-induced adsorption, possibly favouring the formation of CR-halide ion-pairs on the metal surface as is obvious from the greater surface coverage and higher inhibition efficiencies observed for these systems at 60 °C. This suggestion is consistent with earlier reports by Fishtik et al. [24] that the dominating factor in adsorption layer formation is the electrostatic interaction between the ions in the inner part of the double layer and as such direct adsorption of ion pairs from the bulk of the solution becomes energetically unfavourable. At 30 °C however, the halide additives diminished the inhibition efficiency of CR. The low surface coverage by halide ions at 30 °C suggests that the concentration of adsorbed halide ions may be insufficient to promote ion-pair interactions with the inhibitor. The halide ions may rather interfere with the formation of the adsorbed intermediate FeY_{ads} (Eq. (2c)), thereby reducing the concentration of CR molecules adsorbed on the metal surface.

An interesting observation in this study was the reversal in the mechanism of CR adsorption on the metal/solution interface in the presence of the halide additives. The increase in inhibition efficiency of the CR + halide systems with rise in temperature as indicated in Table 1 suggests a chemisorption mechanism for CR on the mild steel surface in the presence of halides possibly due to columbic attraction to the adsorbed halides ion on the metal surface. This is in contrast to the physisorption mechanism observed in the absence of halides.

3.5. Kinetic considerations

The apparent activation energy (E_a) for mild steel corrosion in 2 M H_2SO_4 solution in the presence and absence of inhibitor was calculated from Arrhenius equation [13,15]

$$\log\frac{\rho_2}{\rho_1} = \frac{E_a}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \quad (10)$$

where ρ_1 and ρ_2 are the corrosion rates at temperatures T_1 ands T_2, respectively. Calculated values of E_a are given in Table 3. The data shows that corrosion activation energy increased from 82.98 kJ mol^{-1} in the uninhibited solution to a mean value of 86.92 kJ mol^{-1} in inhibited solutions containing CR without halides. The difference in the activation energies may indicate that CR affects the corrosion rate by decreasing the available sites for dissolution reaction [20]. This observation is in agreement with the earlier suggestion of CR physisorption on the steel surface. On addition of halides to the inhibited system containing CR, the corrosion activation energy dropped significantly to 40.63 kJ mol^{-1}. Such reduced activation energy in inhibited systems compared to the blank has been reported [13,22] to suggest inhibitor chemisorption on the corroding metal surface. This

Table 3
Corrosion activation energies (E_a) and heats of adsorption (Q_{ads}) for mild steel in 2 M H_2SO_4 in the absence and presence of different concentrations of CR, and mixtures of CR and 5×10^{-4} M halides

System	Activation energy (E_a, kJ mol^{-1})	Heat of adsorption (Q_{ads}, kJ mol^{-1})
2 M H_2SO_4 (blank)	82.89	–
1×10^{-5} M CR	83.14	−1.16
1×10^{-4} M CR	85.02	−4.53
5×10^{-4} M CR	87.20	−7.85
1×10^{-3} M CR	89.56	−12.37
5×10^{-3} M CR	89.68	−12.6
5×10^{-3} M CR + KCl	42.68	68.72
5×10^{-3} M CR + KBr	40.43	63.61
5×10^{-3} M CR + KI	38.77	59.52

observation again indicates that the adsorption behaviour of CR is significantly reversed in the presence of halides. The huge change in the activation energy data is probably due to a difference in inhibition mechanism. Whereas physisorbed molecules retard metal dissolution by blocking cathodic areas, chemisorbed molecules protect anodic areas and reduce the inherent reactivity of the metal at the adsorption sites [25,26]. The higher E_a values in the presence of CR may thus be attributed to the decrease in degree of surface coverage with rise in temperature while lower E_a in the presence of CR + halides may be due to increased surface coverage at higher temperature [12].

To further support the assertion that halide ions alter the adsorption behaviour of CR, heats of adsorption (Q_{ads}) for the various inhibited systems were calculated from the equation [15]

$$Q_{ads} = 2.303R\left[\log\left(\frac{\theta_2}{1-\theta_2}\right) - \log\left(\frac{\theta_1}{1-\theta_1}\right)\right] \times \frac{T_1T_2}{T_2 - T_1}\ \text{kJ mol}^{-1} \quad (11)$$

where θ_1 and θ_2 are the degrees of surface coverage at temperatures T_1 and T_2, respectively. Table 3 shows negative heats of adsorption, with a mean value of -7.71 kJ mol^{-1}, for inhibited solutions containing only CR. Such negative Q_{ads} values indicate that inhibition efficiency decreases with rise in temperature [27]. For systems containing CR + halides however, the heats of adsorption were all positive with a mean value of 63.95 kJ mol^{-1}. The reason for this may be that the attainment of physical adsorption equilibrium is usually rapid and the process readily reversible whereas in chemisorption, the occurrence of chemical reactions at the metal surface makes the process relatively slow and not readily reversible. Thus, enthalpy changes for chemisorption are usually higher than for physisorption.

4. Conclusion

Congo red dye inhibits mild steel corrosion in sulphuric acid solution. The inhibition efficiency increased with concentration but decreased with rise in temperature. The inhibitor molecules are physically adsorbed on the metal surface following Flory–Huggins isotherm. Synergistic effects increased the inhibition efficiency of CR in the presence of halide additives at 60 °C while antagonistic effects were observed at 30 °C. The efficiency of the CR + halide mixtures increased with rise in temperature, indicating a chemical adsorption mechanism. This suggests that halide ions reverse the mechanism of CR adsorption on the mild steel surface. The values of activation energy and heat of adsorption confirm physisorption and chemisorption mechanisms respectively for CR in the absence and presence of halides.

Acknowledgements

The author is grateful to Ezeoke C.N. and Chijioke V.N. for helping with some measurements.

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