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Inhibition of mild steel corrosion in sulphuric acid using indigo dye and synergistic halide additives

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Abstract

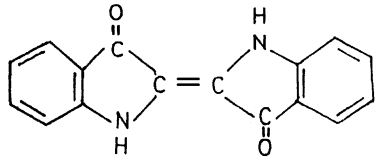
Gravimetric method was used to study the inhibitory properties of indigo dye during corrosion of mild steel in aerated sulphuric acid solutions at 30–50 °C. The effect of addition of halide salts KCl, KBr and KI was also investigated. The corrosion rates in all systems studied increased with rise in temperature. The inhibition efficiency of indigo dye increased with concentration and synergistically increased on addition of halide salts. Temperature studies revealed increased inhibition efficiency at higher temperatures, which is suggestive of chemisorption mechanism. The inhibitor adsorption characteristics were approximated by Frumkins isotherm and Flory–Huggins isotherm. Activation energy for Fe dissolution in sulphuric acid was observed to reduce from 54.6 kJ mol^{-1} in the uninhibited system to 34.9 kJ mol^{-1} in the inhibited system.

Keywords: Corrosion inhibition; Synergism; Frumkins isotherm; Flory–Huggins isotherm

1. Introduction

Organic compounds have become accepted as effective inhibitors of metal corrosion in various media [I–II]. Compounds containing nitrogen, oxygen, sulphur, phosphorous or selenium in the conjugated system have particularly been reported as efficient corrosion inhibitors [1–6]. The protective efficiency is based on adsorption ability of their molecules, where the resulting adsorption film acts as a barrier separating the metal from the corroding medium [4,5]. According to Ebenso [6], the inhibitors act at the interphase created by corrosion product between the metal and aqueous corroding solution. Thus the nature of inhibitor interaction and efficiency may be dependent on the chemical, mechanical and structural characteristics of this layer.

The study of organic dyes as potential inhibitors in metal–corrodent systems is generating a lot of interest in this laboratory. Such dyes posses molecular structures which recommend them for investigation as possible corrosion inhibitors when compared with reports on other organic inhibitors [4–6]. Indigo blue is an insoluble vat dye with structural formula as follows [7]:



In the actual practical application of corrosion inhibitors, single compounds are rarely used, rather, formulations of two or more inhibitors are usually employed [8]. Interestingly, the inhibition efficiency of organic compounds in sulphuric acid solutions has been reported to synergistically increase on addition of halide salts to the solution [3,4,9].

The present paper reports on the inhibitive action of indigo dye on the corrosion of mild steel in H_2SO_4 using gravimetric methods. The effect of temperature and addition of halide salt on the inhibition efficiency has also been examined.

2. Experimental

The experiments were performed on mild steel with weight-percentage composition as follows: C 0.05, Mn 0.6, P 0.36, Si 0.03. Indigo dye sourced from BDH Laboratory

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Supplies, England, was used without further purification, at concentrations, 0.005, 0.01, 0.05, 0.1 and 0.2 M. Sulphuric acid (Merck AR grade) solutions were prepared in the concentration range 0.1–0.5 M. The potassium halides (KCl KBr and KI) also from BDH Laboratory Supplies were used in the concentration range 10^{-4} to 10^{-1} M.

Gravimetric methods were conducted on mild steel coupons of dimension 5 cm × 2.5 cm. These were used as cut without further polishing but were however degreased in absolute ethanol, dried in acetone and weighed. Experiments were carried out under total immersion conditions in 300 ml of test solutions maintained at 30–50 °C. All tests were made in aerated solutions. The coupons were retrieved at 24-h intervals progressively for 120 h, immersed in 20% NaOH solution containing 200 g l^{-1} of zinc dust, scrubbed with bristle brush, washed, dried and weighed [9]. The results reported are averages of triplicate determinations. The corrosion rates of mild steel in different concentrations of H_2SO_4, indigo dye and halides were calculated from the expression [10]:

$$\text{Corrosion rate (mdd)} = \frac{543\,W}{DAT} \quad (1)$$

where W is the loss in weight (mg), D the density of the steel specimen (g cm^{-3}), A the area of the coupon (cm^2) and T the exposure time (h).

From the values of corrosion rate in the presence (W_{inh}) and absence (W_{blank}) of inhibitor, the inhibition efficiencies (%IE) of indigo dye, halides and indigo dye plus halides were respectively calculated from [11]

$$\%IE = \left[1 - \frac{W_{inh}}{W_{blank}}\right] \times 100 \quad (2)$$

3. Results and discussion

3.1. Weight losses and corrosion rate

The results of the gravimetric determinations of mild steel corrosion rate as a function of time and temperature in different test solutions are given in Table 1. These results show that the corrosion rate of mild steel in H_2SO_4 increased with rise in temperature in both inhibited and uninhibited solutions. The highest acid concentration studied, 0.5 M H_2SO_4, was used in subsequent tests involving the inhibitor and the halides. The weight losses for mild steel plotted against time (h) at different temperatures in 0.5 M H_2SO_4 solution containing no inhibitor (blank) and containing 0.2 M inhibitor (indigo dye) is shown in Fig. 1. Similar plots for mild steel immersed in 0.5 M H_2SO_4 solution containing 0.01 M KCl, 0.01 M KBr and 0.01 M KI, plus 0.2 M indigo dye are shown in Figs. 2–4, respectively.

Table 1
Influence of temperature and various inhibitors on the corrosion rate of mild steel in 0.5 M H_2SO_4 solutions

System	Corrosion rate (mdd)	
	30 °C	50 °C
Blank	0.969	3.72
0.01 M KCl	0.586	1.11
0.01 M KBr	0.491	0.542
0.01 M KI	0.384	0.471
Indigo	0.237	0.344
KCl + indigo	0.205	0.196
KBr + indigo	0.171	0.175
KI + indigo	0.118	0.120

3.2. Inhibition efficiency

The values obtained for the inhibition efficiency (%IE) of indigo, halides and indigo plus halides calculated from

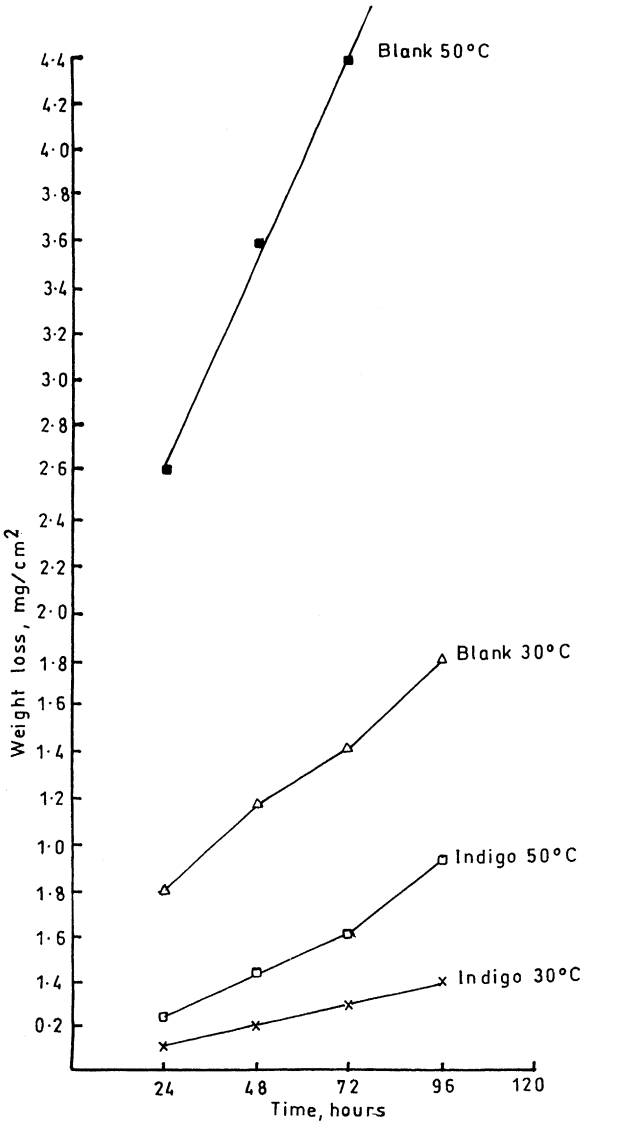

Fig. 1. Weight loss of mild Steel in halide-free 0.5 M H_2SO_4 solution and sulphuric acid plus indigo at different temperatures.

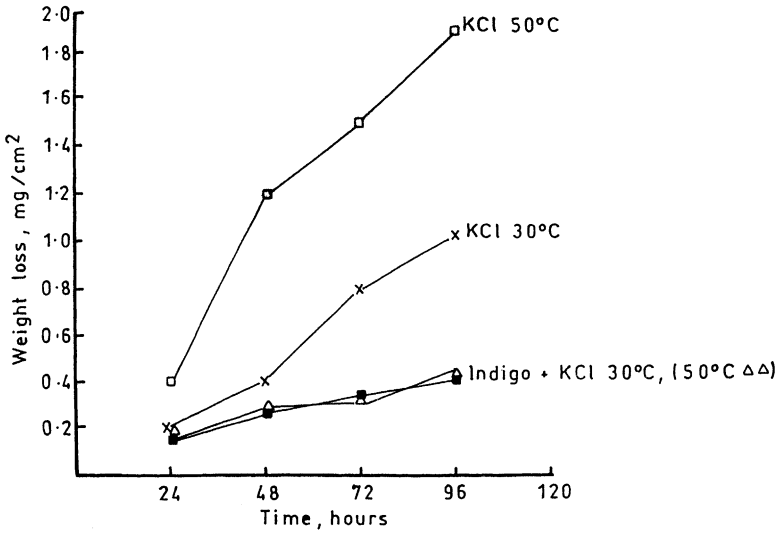

Fig. 2. Weight loss of wild steel in 0.5 M H_2SO_4 solution containing 0.01 M KCl and KCl plus indigo at different temperatures.

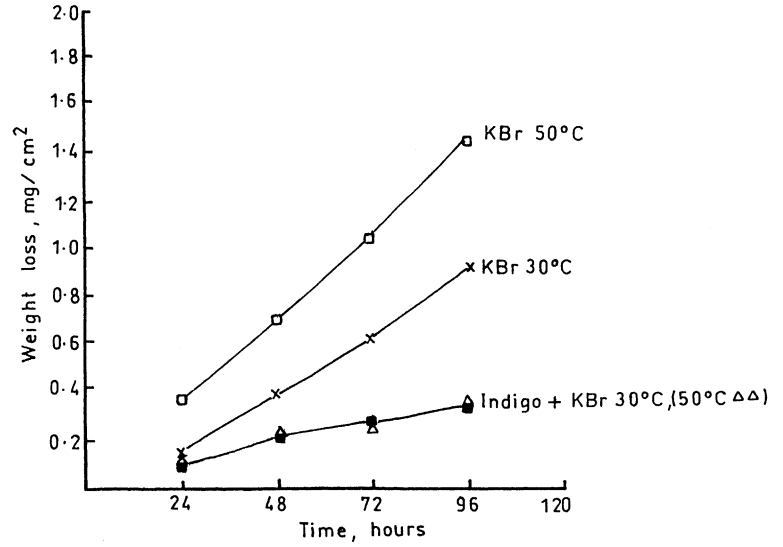

Fig. 3. Weight loss of mild steel in 0.5 M H_2SO_4 solution containing 0.01 M KBr and KBr plus indigo at different temperatures.

Eq. (2) are shown in Table 2. Organic inhibitors are known to decrease metal dissolution by forming a protective adsorption film which blocks the metal surface, separating it from the corrosive medium [9–16]. Consequently, in inhibited solutions, the corrosion rate is indicative of the number of free corroding sites remaining after some sites have been effectively blocked by inhibitor adsorption. If it is assumed that corrosion occurs only in the free sites such that the covered sites have zero corrosion rate, the degree of surface coverage, θ, can be calculated as follows:

$$\theta = I - \frac{W_{\text{inh}}}{W_{\text{blank}}} \tag{3}$$

where W_{inh} and W_{blank} are corrosion rates in the presence and absence of inhibitor, respectively. Table 2 shows that

Table 2
Calculated values of inhibition efficiency (%IE) and degree of surface coverage (θ) for mild steel in 0.5 M H_2SO_4 solution with halides, inhibitor, inhibitor + halides mixtures at different temperatures

System	Inhibition efficiency (%IE) and degree of surface coverage (θ)	
	30 °C	50 °C
0.01 M KCl	39.53 (0.40)	70.16 (0.70)
0.01 M KBr	49.33 (0.49)	85.43 (0.85)
0.0 M KI	60.37 (0.60)	87.34 (0.87)
Indigo dye	75.54 (0.76)	90.75 (0.91)
KCl + indigo	78.84 (0.79)	94.73 (0.95)
KBr + indigo	82.33 (0.82)	95.30 (0.95)
KI + indigo	87.82 (0.88)	96.98 (0.97)

Surface coverage data are given in parenthesis.

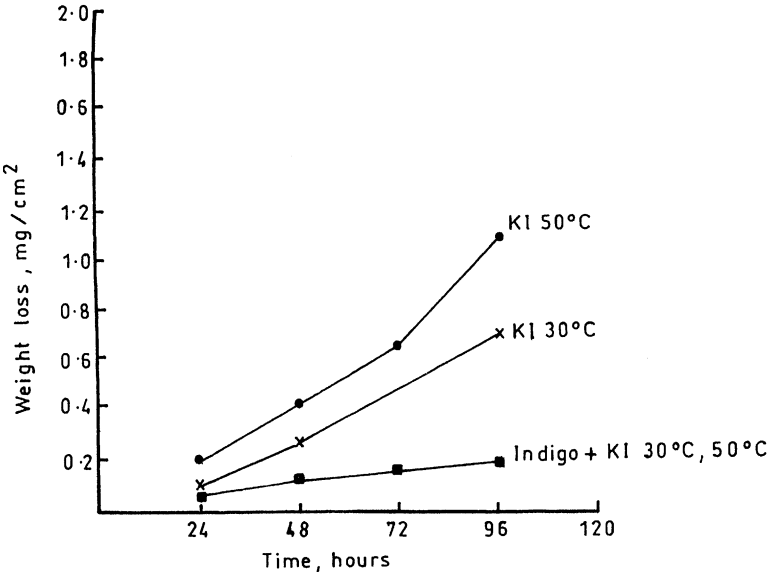

Fig. 4. Weight loss of mild steel in 0.5 M H_2SO_4 solution containing 0.01 M KI and KI plus indigo at different temperatures.

values of degree of surface coverage calculated for the various inhibited solutions increased with rise in temperature.

From Fig. 5, inhibition efficiency is observed to increase with increasing concentration of indigo dye at all temperatures studied. Inhibition efficiency also increased with rising temperature, a phenomenon which is suggestive of chemical adsorption mechanism [5,6]. Addition of halides further increased the inhibition efficiency value. This may be attributed to the stabilisation of adsorbed halide ions by means of electrostatic interaction with the inhibitor which leads to greater surface coverage and hence greater inhibition [1,9]. This synergistic effect was observed to increase in the order $Cl^- < Br^- < I^-$. Similar observations have been reported

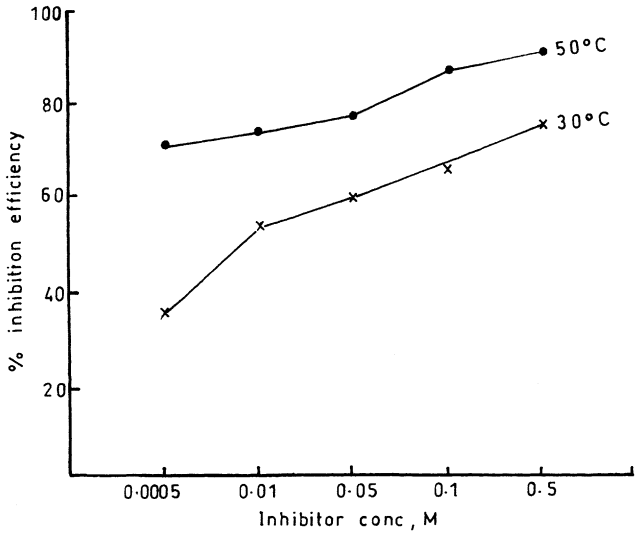

Fig. 5. Variation of inhibition efficiency with inhibitor concentration for mild steel in 0.5 M H_2SO_4 containing indigo at different temperatures.

[1,6,9,15]. The trend is suggestive of a possible role played by the radii and thus electronegativities of the halide ions. Electronegativity decreases from Cl^- to I^- ($Cl^- = 3.0$, $Br^- = 2.8$, $I^- = 2.5$). Their ionic radii also increase in the order $Cl^- < Br^- < I^-$ ($Cl^- = 0.09$ nm, $Br^- = 0.114$ nm, $I^- = 0.135$ nm). This suggests that the iodide ion radius is more predisposed to adsorption than the bromide and chloride ions.

3.3. Synergism parameter

The synergism parameter was calculated using the relationship [6,9]:

$$S_I = \frac{1 - I_{1+2}}{1 - I'_{1+2}} \tag{4}$$

where $I_{1+2} = (I_1 + I_2)$; I_1 is the inhibition efficiency of the halide, I_2, the inhibition efficiency of indigo and I' the inhibition efficiency for indigo dye in combination with halide. The value calculated in KCl was 1.92; KBr = 1.70 and KI = 1.71. These values are all greater than unity, suggesting that the enhanced inhibition efficiency resulting from the addition of halides to the inhibitor is synergistic in nature [9]. Halide ions are normally strongly adsorbed on metal surfaces, where the chemisorbed ions enter the metallic part of the double layer and the charge of the ions becomes part of the charge of the metal surface [1,12]. Thus the inhibitor is not adsorbed directly on the metal surface itself, but rather by coulombic attraction to the adsorbed halide ions on the metal surface. The process is similar to the so-called phenomenon of anion-induced adsorption [13] and may be represented by the highly simplified mechanism:

$$X_S \rightarrow X_{ads} \tag{5a}$$

$$M_S + X_{ads} \rightarrow MX_{ads} \quad (5b)$$

where X_S and M_S designate the halide ion and organic species, respectively, in the bulk solution; X_{ads} and MX_{ads} refer to the halide ion and ion-pair, respectively, in the adsorbed state. This ion-pair interaction consequently increases the surface coverage thereby reducing metal dissolution. An interesting observation in this study was that corrosion rates in test solutions containing indigo plus halides showed minimal increase with rising temperature. This suggests that chemical interactions leading to surface coverage were practically complete in these systems at lower temperature [14].

3.4. Adsorption consideration

High surface coverage suggests that a chemical bond is formed between the metal atoms and the inhibitor. Thus depending upon electron density on the functional atom of the organic inhibitor, the molecules may adsorb on the metal/solution interface by formation of either electrostatic or covalent bonds between the adsorbates and the metal surface atoms [2–6,13–21].

Surface coverage data are quite useful in determining inhibitor adsorption characteristics. Such data are applied in construction of adsorption isotherms which give detailed information on adsorption mechanisms. Classical adsorption isotherms [16] of Freundlich, Temkin and Frumkin as well as substitutional isotherms [17] of Flory–Huggins, Dhar–Flory–Huggins and Bockris–Swinkels have been used to represent the adsorption behaviour of organic compounds on steel surfaces.

Frumkins isotherm [18] represented by

$$\frac{\theta}{1-\theta}\exp(-f\theta) = KC \quad (6)$$

and Flory–Huggins isotherm [6]

$$\mathrm{Log}\left[\frac{\theta}{C}\right] = \log K + x\log(1-\theta) \quad (7)$$

were tested for their fit to the experimental data on the inhibitory action of indigo dye. θ is the degree of surface coverage, C the inhibitor concentration, x the number of inhibitor molecules occupying an active site (or the number of water molecule replaced by one molecule of inhibitor), f the factor of energetic inhomogeneity of the surface and K the equilibrium constant of adsorption. The plot of θ versus $\log C$ is shown in Fig. 6 to have the S-shape characteristic of Frumkins adsorption isotherm [18] and suggests a possible chemisorption of inhibitor molecules on the metal surface [16]. The linear plot obtained for $\log \theta/C$ as a function of $\log(1-\theta)$ in Fig. 7 supports this assertion and indicates that the experimental data fits Flory–Huggins isotherm [6]. Chemisorptive bonds would normally be formed when Fe atoms on the metal surface share an election pair with the organic inhibitor reaction centre. Considering the structure of indigo dye, with the possibility of high electron density around the oxygen and nitrogen atoms, the formation of Fe–O or even Fe–N bonds may be possible.

Further deduction of the mechanism of inhibitor adsorption requires a study of the dependence of inhibition efficiency on temperature. The observed increase in the efficiency of indigo with rise in temperature (Fig. 5) again suggests that the molecules may be chemically adsorbed on the metal surface [6,10]. Activation energy (E_a) values were calculated in both uninhibited and inhibited system using an integrated form of Arrhenius equation [19]. The value of 54.6 kJ mol^{-1} obtained in the uninhibited system is in agreement with other reports on steel dissolution in H_2SO_4 [16,20]. In inhibited solution containing indigo dye, E_a

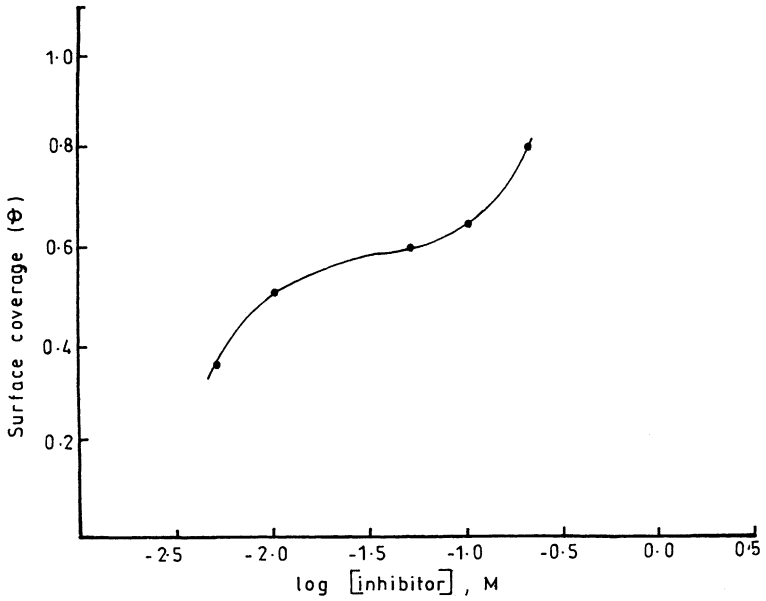

Fig. 6. Frumkin isotherm for absorption of indigo on mild steel in 0.5 M H_2SO_4 solution at 30 ± 1 °C.

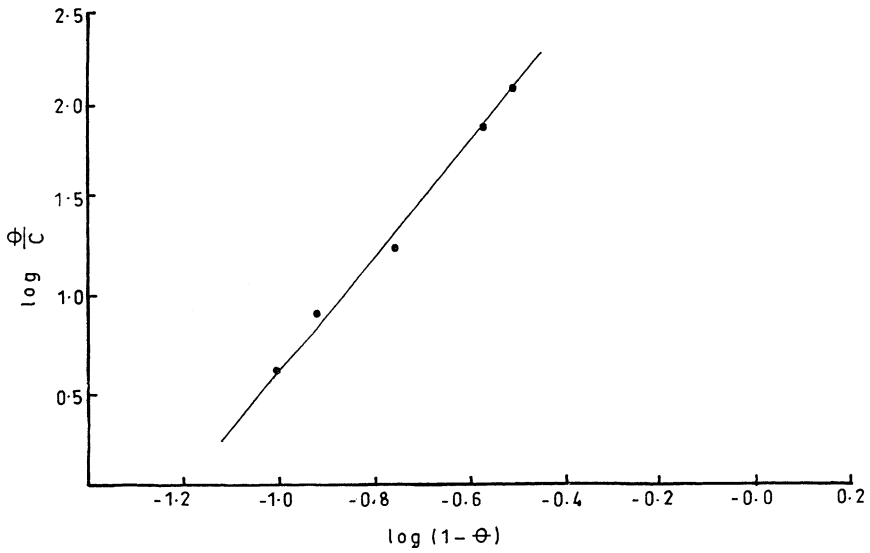

Fig. 7. Flory–Huggins isotherm for mild steel in 0.5 M H_2SO_4 containing indigo at $50 \pm 1\,^{\circ}C$.

reduced to 34.9 kJ mol^{-1}. This observation further supports the proposed chemisorption mechanism because unchanged or lowered E_a in inhibited systems compared to the blank has been reported [16,21] to be indicative of chemical adsorption mechanism, while increased E_a suggests a physical adsorption mechanism.

4. Conclusions

(i) Indigo dye effectively inhibits mild steel corrosion in sulphuric acid. The inhibition efficiency increases with inhibitor concentration at all temperatures studied and also increases with rise in temperature.
(ii) Addition of halide salts synergistically increased the inhibition efficiency of indigo in the order KCl < KBr < KI.
(iii) The inhibitive action is probably based on the adsorption ability of the inhibitor polar N or O atom bonding to the metal surface by chemical adsorption mechanism.
(iv) The adsorptive behaviour may be approximated by Frumkins isotherm as well as Flory–Huggins isotherms.

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