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Inhibitory mechanism of mild steel corrosion in 2 M sulphuric acid solution by methylene blue dye

E.E. Oguzie*, G.N. Onuoha, A.I. Onuchukwu

Electrochemistry and Materials Science Research Laboratory, Department of Chemistry, Federal University of Technology,
PMB 1526 Owerri, Nigeria

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Abstract

Methylene blue dye (MB) was investigated as a corrosion inhibitor for mild steel in 2 M sulphuric acid solution using gravimetric and thermometric techniques. The inhibition efficiency of MB increased with concentration and synergistically increased in the presence of the halide additives, namely KCl, KBr and KI. The trend of inhibition efficiency with temperature suggests that inhibitor molecules are physically adsorbed on the corroding metal surface at lower concentration (0.01–0.5 mM), and chemically adsorbed at higher concentration (1.0–5.0 mM). These results were further corroborated by kinetic and activation parameters for corrosion and adsorption processes evaluated from experimental data at the temperatures studied. MB was found to obey Langmuir and Frumkin adsorption isotherms in the concentration range investigated.

Keywords: Mild steel; Methylene blue; Inhibition efficiency; Physisorption; Chemisorption; Adsorption isotherm

1. Introduction

The study of corrosion inhibitors gives insight into the mechanisms by which materials added to a fluid aggressive environment retard the reaction between the corrodent and the metal [1,2]. Corrosion inhibitors may be divided into three broad classes, namely oxidizing, precipitation and adsorption inhibitors [3]. Adsorption inhibitors are usually organic substances containing polar functions with nitrogen, sulphur and/or oxygen in the conjugated system [4–8]. Such substances have been reported to function by adherence to the metal surface through metal ions still in place in the lattice and thereby retard metal dissolution by virtue of adsorption, with the polar group acting as the reaction centre for the adsorption process [6–11]. The adsorption bond strength is dependent on the composition of the metal and corrodent, inhibitor structure and concentration as well as temperature [10–13]. Generally, inhibitor molecules may either physically or chemically adsorb on a corroding metal surface. It has been suggested [14,15] that physisorbed molecules are attached to the metal at local cathodes and essentially retard metal dissolution by stifling the cathodic reaction, whereas chemisorbed molecules protect anodic areas and reduce the inherent reactivity of the metal at the sites where they are attached. The more efficient inhibitors appear to protect anodic areas preferentially by chemisorption [3]. In any case, adsorption is general over the metal surface and the resulting adsorption layer functions as a barrier, isolating the metal from the corrodent [16,17].

In recent times, in this laboratory, attention has been focused on the investigation of organic dyes as potential inhibitors in metal–corrodent systems. The results so far obtained reveal that the processes involved in corrosion inhibition are not uniform with respect to all the classes of compounds studied, and are not even constant or consistent with one inhibitor in a given system. Indeed, the overall process is a function of the metal, corrodent, inhibitor structure and concentration, as well as temperature. Again, efficiency of inhibition is closely related to inhibitor adsorption abilities [18–20],

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* Corresponding author. Tel.: +234 8037026581; fax: +234 83233948.
E-mail address: oguziemeka@yahoo.com (E.E. Oguzie).

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which was observed in most cases to be enhanced in the presence of halide ions. Methylene blue, the inhibitor chosen for this study, has been assessed as an inhibitor for aluminium corrosion in acidic and alkaline media. The compound is a heterocyclic dye with molecular structure as follows:

The corrosion rates of metals and alloys can be determined using different electrochemical and non-electrochemical techniques. In the present study, the corrosion behaviour of mild steel in 2 M sulphuric acid solution in the presence and absence of methylene blue dye was investigated by gravimetric and thermometric techniques. The effects of temperature and halide additives were also determined. The activation parameters that govern steel corrosion in acidic media were also 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, 0.03. Each sheet, which was 0.14 cm in thickness, was mechanically pressed-cut into coupons of dimension 3 cm × 3 cm. These coupons were used as procured without further polishing, but were degreased in absolute ethanol, dried in acetone, weighed and stored in a moisture-free desiccator prior to use. All reagents were BDH grade, and used as source without further purification. Distilled water was used for all solution preparations. 2 M H_2SO_4 solution was employed as blank. For experiments involving methylene blue dye (MB), the solid was added to the blank solution to reach final concentrations of 0.01, 0.1, 0.5, 1.0 and 5.0 mM. Solutions of 0.1 mM of the halides KCl, KBr and Kl were prepared in the blank solution and in 5.0 mM MB solution.

Gravimetric experiments were conducted under total immersion conditions in 250 ml of test solutions maintained at 30–60 °C. All tests were made in aerated solutions. Test coupons were retrieved at 2 h intervals progressively for 10 h, immersed in 20% NaOH solution containing 200 g l^{-1} of zinc dust, scrubbed with bristle brush, washed, dried and reweighed. The weight loss was taken as the difference between the weight at a given time and the initial weight of the coupon.

The reaction vessel used in the thermometric experiments has been described elsewhere [21]. Test coupons of dimension 1.0 cm × 6.0 cm were immersed in 15 ml of the test electrolyte and the initial temperature was maintained at 30 °C. Temperature change was measured to ±0.05 °C on a calibrated thermometer. This allowed for the evaluation of the reaction number as follows:

$$\mathrm{RN}(^{\circ}\mathrm{C\,min^{-1}}) = \frac{T_m - T_i}{t} \tag{1}$$

where T_m is the maximum temperature and T_i the initial temperature of the system studied when put into the reaction vessel, and t is time interval (min).

3. Results and discussion

3.1. Weight losses and corrosion rates

The anodic dissolution of iron in acidic solutions has been reported to proceed according to the mechanism [22–25]:

$$\mathrm{Fe} + \mathrm{OH}^- \rightleftharpoons \mathrm{FeOH_{ads}} + \mathrm{H}^+ + \mathrm{e} \tag{2a}$$

$$\mathrm{FeOH_{ads}} \xrightarrow{\mathrm{rds}} \mathrm{FeOH}^+ + \mathrm{e} \tag{2b}$$

$$\mathrm{FeOH}^+ + \mathrm{H}^+ \rightleftharpoons \mathrm{Fe}^{2+} + \mathrm{H_2O} \tag{2c}$$

As a consequence of these reactions, including the high solubility of the corrosion products, the metal loses weight in the solution. Corrosion inhibition is initiated by the displacement of adsorbed water molecules by inhibitor species leading to the specific adsorption of the inhibitor on the metal surface [6,22]. The weight loss of the mild steel coupons in 2 M H_2SO_4 was determined for different inhibitor mixtures as shown in Table 1.

Fig. 1a and b show plots of weight loss (g dm^{-2}) versus time (h) in the blank corrodent and in the presence of 5.0 mM MB at 30 and 60 °C, respectively. The plots indicate that MB actually retarded mild steel corrosion in 2 M H_2SO_4 and that corrosion rates in both inhibited and uninhibited corrodent increased with rise in temperature. The plots also suggest that the inhibitor is more effective at higher temperature. Plots of weight loss as a function of MB concentration at 30 and 60 °C are given in Fig. 2. Weight loss decreases with increasing MB concentration at any given temperature, indicating that the extent of corrosion inhibition depends on the amount of MB present.

3.2. Inhibition efficiency

The characterization of the free corrosion of mild steel in the different inhibitor/corrodent solutions was carried out by an assessment of the inhibition efficiency (I, %) defined by:

$$I\,(\%) = \left(1 - \frac{W_1}{W_2}\right) \times 100 \tag{3}$$

Table 1
Different inhibitor systems studied for mild steel corrosion in 2 M H_2SO_4

Methylene blue conc. (mM)	Halide conc. (mM)
0.01–5.0	0.00
0.00	0.5 (KCl, KBr, KI)
5.0	0.5 (KCl)
5.0	0.5 (KBr)
5.0	0.5 (KI)

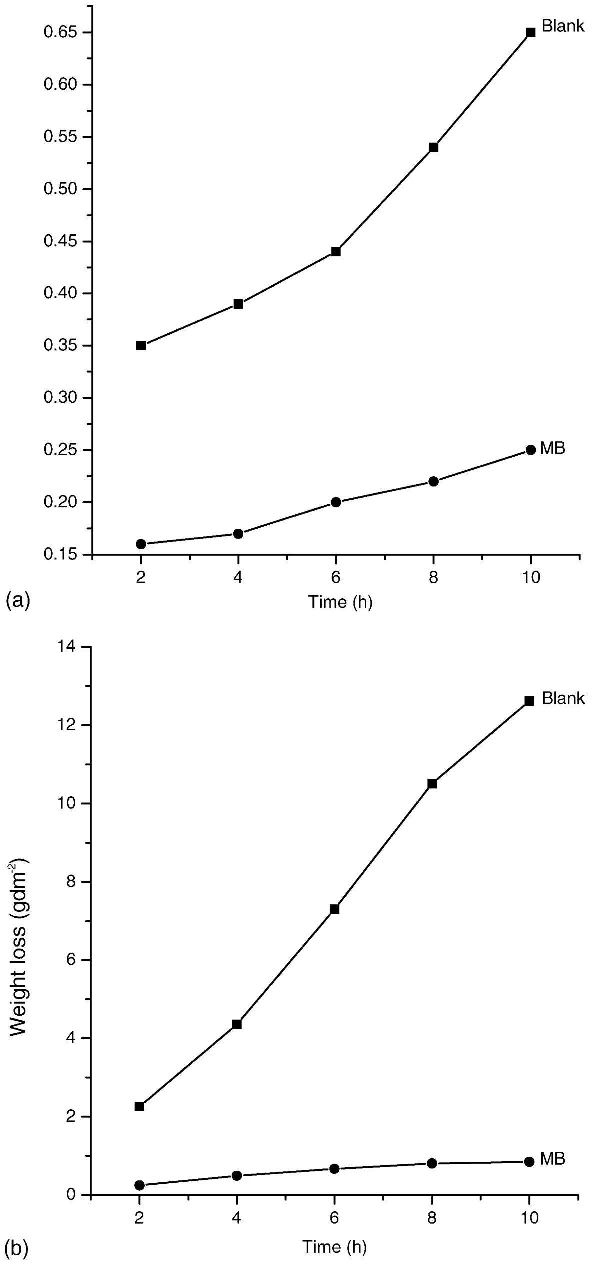

Fig. 1. (a) Variation of weight loss with time for mild steel corrosion in 2 M H_2SO_4 in the presence and absence of MB at 30 °C. (b) Variation of weight loss with time for mild steel corrosion in 2 M H_2SO_4 in the presence and absence of MB at 60 °C.

where W_1 and W_2 are the corrosion rates in inhibited and uninhibited corrodent, respectively. The calculated values are given in Table 2. In Fig. 3, the inhibition efficiency of MB is compared at various levels of concentration at different temperatures. The plots show that efficiency increased with an increase in MB concentration at any given temperature. This suggests that more inhibitor molecules were adsorbed on the metal surface at higher concentration, leading to greater surface coverage. Fig. 3. also reveals that adsorption rate at lower MB concentrations is diminished by an increase in temperature, whereas adsorption is enhanced by an increase in temperature at higher MB concentrations.

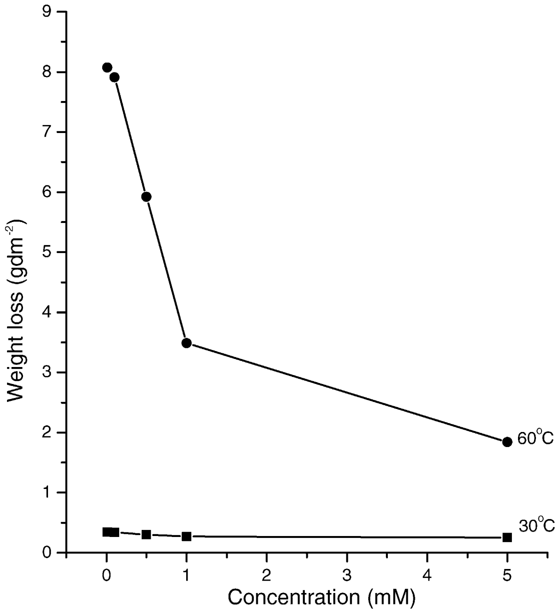

Fig. 2. Variation of weight loss of mild steel in 2 M H_2SO_4 with MB concentration at different temperatures.

The inhibition efficiency of MB in 2 M H_2SO_4, as determined by thermometric method, was assessed from the percentage reduction in the reaction number as follows [26]:

$$I\,(\%) = \frac{RN_1 - RN_2}{RN_1} \times 100 \qquad (4)$$

where RN_1 and RN_2 are the reaction numbers in the presence and absence of inhibitor, respectively. A comparison of I, % calculated from gravimetric and thermometric methods, as given in Table 3, indicates that the two techniques give almost identical values for all systems studied.

3.3. Adsorption considerations

An investigation of the influence of temperature on the protective effect of an inhibitor is important in elucidating

Table 2
Calculated values of inhibition efficiency (I, %) for different concentrations of MB and 5.0 mM MB + 0.5 mM halide mixtures at different temperatures

System	Inhibition efficiency (I, %)	
	30 °C	60 °C
0.01 mM MB	46.15	36.05
0.1 mM MB	47.69	37.72
0.5 mM MB	53.85	53.09
1.0 mM MB	58.46	72.35
5.0 mM MB	61.54	85.42
0.5 mM KCl	−6.15	42.16
0.5 mM KBr	36.92	64.74
0.5 mM KI	44.62	79.00
MB + KCl	73.85	91.36
MB + KBr	80.00	92.63
MB + KI	84.62	97.46

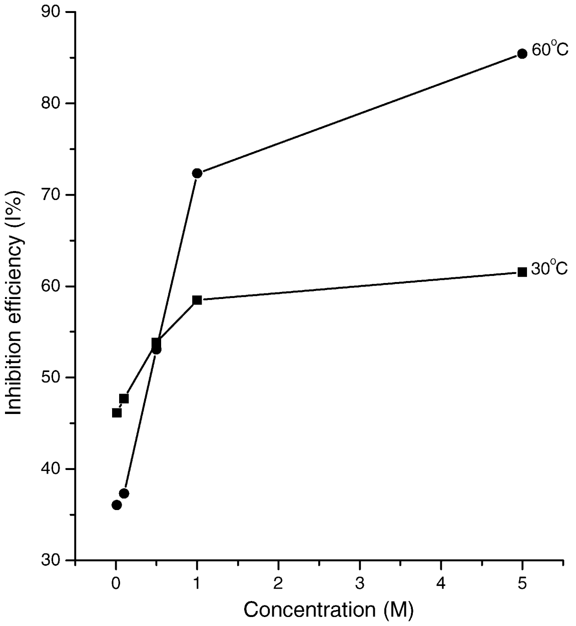

Fig. 3. Variation of inhibition efficiency with mild concentration for mild steel corrosion in 2 M H_2SO_4 at different temperatures.

the mechanism of adsorption on a corroding metal surface. Although the border line between chemical and physical adsorption is blurred and their distinction difficult, a number of experimental criteria make this possible. According to Ebenso [5], Oguzie et al. [10], El Rehim et al. [27] and Al-Mayouf [28], a decrease in inhibition efficiency with rise in temperature suggests that inhibitor molecules are physically adsorbed on the metal surface, while the reverse behaviour suggests chemisorption. Accordingly, the trend of inhibition efficiency with temperature as illustrated in Table 2 and Fig. 3 suggests that MB molecules were physically adsorbed at the lower concentration range (0.01–0.5 mM) and chemically adsorbed at higher concentrations (1.0–5.0 mM). The reason for this behaviour is still not quite clear and several factors may possibly play a role.

Orientation of adsorbed aromatics is a function of several variables among which are adsorbate molecular structure and solute concentration, and the reactivity of these adsorbed intermediates is a sensitive function of their orientation [29]. For heterocyclic compounds, adsorption normally occurs with the aromatic ring parallel to the metal surface and the degree of adsorption depends mainly on the electronic structure of the molecule [30]. Generally, the mechanism by which a given inhibitor may attach to a metal depends on the functional group present in its molecule. Some functional groups are normally held more firmly than others. According to Fragnani and Trabanelli [31], sulphur-containing substances easily chemisorb onto the surface of iron in acid media whereas nitrogen-containing compounds tend to favour physisorption. This suggestion is corroborated by the results of other authors [8-12]. Hackerman [14] also reported that the presence of more than one functional group in a molecule might influence its adsorption by causing changes in the electron density of the molecule. Considering structure of the methylene blue molecule, it is thus possible to suggest that at lower concentrations, the adsorbed molecules are oriented with the nitrogen atom functioning as the reaction centre for the adsorption process, and as concentration is increased, reorientation of adsorbed molecules takes place and the sulphur atom becomes the anchor. This behaviour is consistent with the earlier suggestion by Shaw [32] that a molecule may first physically adsorb and then slowly react with the metal surface to form a chemisorbed layer. Thus, MB functions by dual inhibitory mechanism and, depending on the concentration, inhibits both cathodic and anodic reactions.

Table 3
Comparison of inhibition efficiency values obtained from gravimetric and thermometric techniques

System	Inhibition efficiency (*I*%)	
	Gravimetric (30 °C)	Thermometric
5.0 mM MB	61.54	59.89
MB + KCl	73.85	72.26
MB + KBr	80.00	82.04
MB + KI	84.62	83.57

The corrosion behaviour of the mild steel specimen in the presence of MB indicates that the inhibitor molecules were well adsorbed over the metal surface, and that surface coverage changed with temperature as well as inhibitor concentration. The results suggest that the adsorption intermediate formed at the metal solution interface at lower MB concentration becomes soluble at elevated temperature, leading to desorption of some adsorbed molecules. This leaves an uncovered area of the metal surface, facilitating the attack of the corrodent. At higher MB concentrations, however, the adsorbed layer becomes insoluble, possibly due to reaction with the metal surface. In addition, since reaction rates normally increase with temperature, MB adsorption at higher concentrations is also enhanced, resulting in the observed increase in inhibition efficiency with rise in temperature.

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. Fig. 4 represents the Langmuir isotherm given by the equation [9,12]:

$$\left[\frac{\theta}{1-\theta}\right] = A\,C\exp\left(\frac{Q_{\text{ads}}}{RT}\right) \tag{5}$$

where A is a constant; C, the inhibitor concentration; Q_{ads}, the heat of adsorption and θ, the degree of surface coverage related to the inhibition efficiency I, %, as follows:

$$\theta = \frac{I\,(\%)}{100} \tag{6}$$

A linear plot was obtained with a slope of 0.12. Deviation of the slope from unity suggests interaction between adsorbed molecules on the metal surface [9]. The existence of molecular interactions on the adsorbed layer was further

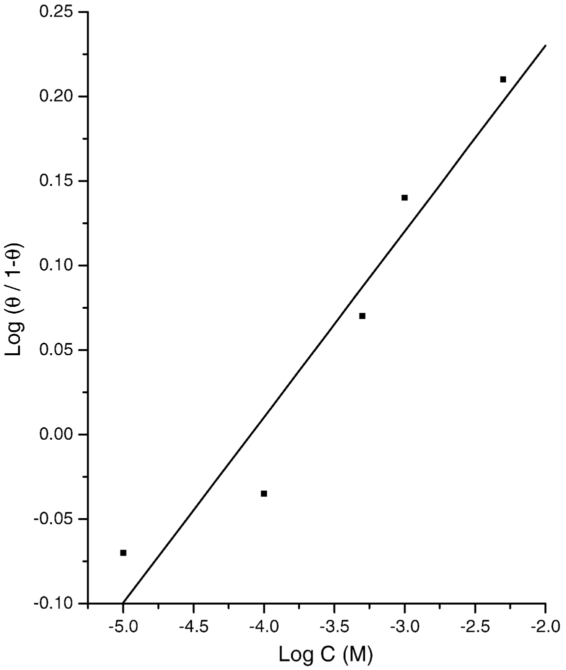

Fig. 4. Curve fitting of the corrosion data of mild steel in 2 M sulphuric acid solution in the presence of MB to Langmuir isotherm.

confirmed by the fit of the experimental data into Frumkin isotherm given by [10,12]:

$$\left[\frac{\theta}{1-\theta}\right]\exp(-f\theta) = K\,C \tag{7}$$

and plotted as θ versus log C in Fig. 5. K is the equilibrium constant for adsorption and f represents the variation of adsorption potential with coverage, which depends upon molecular interactions in the adsorption layer. The fit of the experimental data to the above isotherms suggests an occurrence of multilayer physical adsorption on top of the chemisorbed monolayer formed at higher MB concentrations [32].

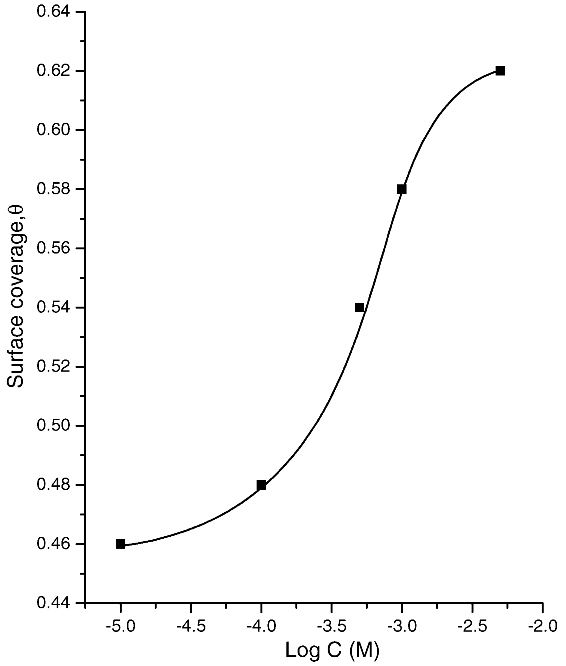

Fig. 5. Curve fitting of the corrosion data of mild steel in 2 M sulphuric acid solution in presence of MB to Frumkin isotherm.

3.4. Synergism parameter

Inspection of the data in Table 2 reveals that the halide additives further enhanced inhibitor chemisorption on the metal/solution interphase, thus increasing the inhibition efficiency of methylene blue. The surface of iron is positively charged in sulphuric acid solutions [30] and halide ions will be strongly adsorbed on the metallic part of the double layer, where they form intermediate bridges between the metal surface and the inhibitor [33]. Hence, the inhibitor molecules are not directly adsorbed on the metal surface itself, but rather by coulombic attraction to the adsorbed halide ions on the metal surface. This synergistic effect increased with rise in temperature and was observed to increase in the order $Cl^- < Br^- < I^-$, suggesting a possible role by the radii of the halide ions, which also increase in the order Cl^- (0.09 nm) < Br^- (0.114 nm) < I^- (0.135 nm).

The synergism parameter S_1 was evaluated from the equation [7]:

$$S_1 = \frac{1 - I_{1+2}}{1 - I'_{1+2}} \tag{8}$$

where $I_{1+2} = (I_1 + I_2)$; I_1 is the inhibition efficiency of the halide, I_2 the inhibition efficiency of MB and I'_{1+2} the inhibition efficiency of MB in combination with halide. The values obtained are given in Table 4. Synergism parameter greater than unity suggests that the enhanced inhibition efficiency resulting from addition of halides to the inhibitor is only due to synergistic effect [7].

3.5. Kinetic considerations

The apparent activation energies (E_a) for mild steel corrosion in 2 M H_2SO_4 solution in the absence and presence of inhibitor were evaluated from Arrhenius equation [18].

$$\log\frac{\rho_2}{\rho_1} = \frac{E_a}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{9}$$

Table 4
Synergism parameter (S_I) for various halides at 30 and 60 °C

Halide	Synergism parameter (S_I)	
	30 °C	60 °C
KCl	0.83	1.40
KBr	1.23	1.61
KI	1.26	1.69

Table 5
Calculated values of activation energy E_a (kJ mol^{-1}), heat of adsorption Q_{ads} (kJ mol^{-1}) and rate constant k (s^{-1}) for mild steel corrosion in 2 M H_2SO_4 with MB as inhibitor

System	Activation energy E_a (kJ mol^{-1}), 30–60 °C	Heat of adsorption Q_{ads} (kJ mol^{-1}), 30–60 °C	Rate constant k (s^{-1}) × 10^{-2}, 30 °C
2 M H_2SO_4	82.98	–	0.915
0.01 mM MB	87.89	−10.19	0.505
0.1 mM MB	88.03	−12.63	0.501
0.5 mM MB	83.42	−1.12	0.496
1.0 mM MB	71.60	17.40	0.390
5.0 mM MB	55.04	34.80	0.386

where ρ_1 and ρ_2 are the corrosion rates at temperatures T_1 and T_2, respectively. An estimate of heat of adsorption can be obtained from the trend of surface coverage with temperature as follows [34].

$$Q_{ads}\left(\mathrm{kJ\,mol^{-1}}\right) = 2.303R\left[\log\left(\frac{\theta_2}{1-\theta_2}\right) - \log\left(\frac{\theta_1}{1-\theta_1}\right)\right] \times \frac{T_1 T_2}{T_2 - T_1} \qquad (10)$$

where θ_1 and θ_2 are the degrees of surface coverage at temperatures T_1 and T_2. The rate constant for the initial dissolution of the mild steel specimen in 2 M H_2SO_4 containing different concentrations of MB was assessed from the relationship:

$$k_1\,(\mathrm{s^{-1}}) = \frac{1}{t}\ln\frac{y}{y_0} \qquad (11)$$

where y is the experimental net weight of the mild steel coupons at various time intervals, t, of the corrosion process and y_0 is the initial weight of the coupon. Table 5 shows calculated values of activation energy, heat of adsorption and rate constant for mild steel corrosion in the different test solutions. The results obtained further support the earlier suggestions of MB physisorption at lower concentration and chemisorption at higher concentration. According to Martinez [35] and El Rehim et al. [27], unchanged or lowered activation energy in inhibited system compared to the blank is indicative of chemisorption possibly, because some of the energy is used up in chemical reaction. Increased activation energy in inhibited system suggests physisorption, where the adsorbed inhibitor molecules mechanically screen the active sites on the metal surface from the action of the corrodent. The trend of Q_{ads} is consistent with earlier suggestions [32] that heats of physisorption are usually lower than heats of chemisorption. In fact, according to Bhajiwala et al. [36], negative Q_{ads} values indicate physical adsorption on the metal surface while positive values indicate chemisorption. The rate constants for the corrosion process decreased with increasing MB concentration, indicating that the inhibitory action is concentration-dependent.

4. Conclusion

(i) Methylene blue effectively inhibits mild steel corrosion in 2 M H_2SO_4 solution and the inhibition efficiency increases with MB concentration at all temperatures studied.
(ii) Halide additives synergistically increased the inhibition efficiency of MB in the order KCl < KBr < KI.
(iii) The trend of inhibitor adsorption with temperature suggests that MB molecules are physically adsorbed on the mild steel surface at lower concentrations and chemically adsorbed at higher concentration.
(iv) The adsorptive behaviour of MB was approximated by Langmuir and Flory–Huggins adsorption isotherms.

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