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Effect of iodide ions on corrosion inhibition of mild steel by 3,5-bis(4-methylthiophenyl)-4H-1,2,4-triazole in sulfuric acid solution

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Abstract

The synergistic effect of iodide ions on the corrosion inhibition of mild steel in 0.5 M sulfuric acid (H_2SO_4) in the presence of 3,5-bis(4-methylthiophenyl)-4H-1,2,4-triazole (4-MTHT) was investigated using weight loss measurements and different electrochemical techniques such as potentiostatic polarization curves and electrochemical impedance spectroscopy (EIS). The inhibition efficiency (E, %) increased with 4-MTHT concentration, but the desorption potential (E_d) remained unchanged with increasing 4-MTHT concentration. The addition of potassium iodide (KI) enhanced E considerably and increased the value of E_d. A synergistic effect was observed between KI and 4-MTHT with an optimum mass ratio of [4-MTHT]/[KI] $= 4 \times 10^{-2}$. The synergism parameters (S_θ) calculated from surface coverage were found to be more than unity. This result clearly showed the synergistic influence of iodide ions on the corrosion inhibition of mild steel in 0.5 M H_2SO_4 by 4-MTHT. The adsorption of this inhibitor alone and in combination with iodide ions followed Langmuir's adsorption isotherm.

1. Introduction

The use of inhibitors is one of the most practical methods for corrosion protection, especially in acidic media [1–3]. Inhibitors are compounds that control, reduce, or prevent reactions between a metal and its surroundings when added to the medium in small quantities. Inhibitors should be effective in low concentrations for economy. If two or more inhibitors are added to a corrosive system at the same time, the corrosion-prevention effect may be much greater than the effect of each inhibitor individually. This is called the synergistic effect. The role of synergism on the mechanism of inhibition of corrosion of steel in acidic solutions has been reported by several authors [4–8].

Substituted benzotriazoles and other triazole derivatives are well known corrosion inhibitors [9–13]. In an earlier paper, we found that the inhibiting effect of 3,5-bis(4-metylthiophenyl)-4H-1,2,4-triazole (4-MTHT) in hydrochloric acid solution is much higher than that in sulfuric acid solutions [14]. Some studies suggest that chloride ions have a stronger tendency to adsorb than do sulfate ions [15]. According to Lorenz, when an inhibited solution contains adsorbable anions, such as halide ions, these adsorb on the metal surface by creating oriented dipoles and, consequently, increase the adsorption of the organic cations on the dipoles [16].

The present study is an extension of the earlier work and reports the synergistic influence of halide ions on the performance of 4-MTHT as an inhibitor for corrosion of mild steel in 0.5 M H_2SO_4 [14]. The weight loss measurements and electrochemical methods were used to investigate the phenomena of the synergistic corrosion inhibition. For this reason we selected iodide ions as the model and studied the inhibition behaviour of 4-MTHT by adding KI to the 0.5 M H_2SO_4 solution and established the corrosion inhibition mechanism on the steel surface.

2. Experimental details

2.1. *Materials*

Mild steel strips composed of (wt %): 0.09% P, 0.38% Si, 0.01% Al, 0.05% Mn, 0.21% C, 0.05% S, and balance Fe (5 cm × 2 cm × 0.06 cm) were used for the gravimetric measurements. For the electrochemical

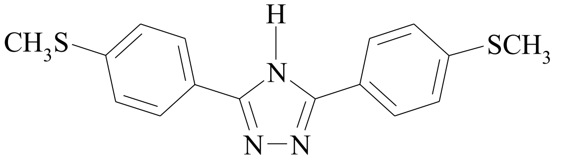

Fig. 1. Chemical structure of 4-MTHT.

steady-state measurements, mild steel strips with an exposed area of 1 cm^2 were used. Mild steel specimens were polished mechanically with emery papers SiC paper (grade 120–600–1200), rinsed with bidistilled water, degreased ultrasonically in ethanol before use and dried at room temperature. H_2SO_4 solution was prepared from an analytical reagent grade of sulfuric acid (96%) and bidistilled water and was use as a corrosion medium in the studies. Inhibitor was synthesised according to laboratory procedures reported previously [17]. Figure 1 shows molecular structure of 3,5-bis(4-methylthiophenyl)-4H-1,2,4-triazole which have been labelled 4-MTHT. The concentration range of tested inhibitor was varied from 1×10^{-5} M to 5×10^{-4} M, and the optimum inhibitor concentration was identified.

2.2. *Procedure*

The electrochemical cell used has been described in a previous paper [18]. The reference electrode was a saturated calomel electrode. All the reported potential values are referred to this type of electrode.

Polarization experiments were carried out in a conventional three-electrode glass cell with a capacity of 500 ml with a platinum counter electrode and a saturated calomel electrode (SCE) as reference with a fine Luggin capillary bridge to avoid ohmic polarization. All tests were performed in deaerated solutions under continuously stirred conditions at 30 ± 1 °C. The procedure adopted for the polarization measurements was the same as described elsewhere [18]. For a given potential, the current was usually steady within 30 min. The cathodic branch was always determined first; the open-circuit potential was then reestablished and the anodic branch determined. The anodic and cathodic polarization curves were recorded at a constant sweep rate of 0.5 mV s^{-1}. Inhibition efficiencies were determined from corrosion currents calculated by the Tafel extrapolation method and fitting the curve to the polarization equation [18].

Electrochemical impedance spectroscopy (EIS) measurements were performed using a Tacussel radiometer PGZ 301 frequency response analyser in a frequency range 10^5 Hz to 10^{-2} Hz with 10 points per decade and a Tacussel Radiometers PGZ 301 electrochemical interface. Tests were performed in a PMMA cell with a capacity of 1000 ml. Square sheets of mild steel of size (5 cm × 5 cm × 0.06 cm), which exposed a 7.55 cm^2 surface to the aggressive solution, were used as the working electrode. All tests were performed at 30 ± 1 °C in nondeaerated solutions under unstirred conditions. After the determination of steady-state current at a given potential, sine wave voltages (10 mV) peak-to-peak were superimposed on the rest potential. The impedance data were analysed and fitted using graphing and analysing impedance software (version Voltamaster 4).

Weight loss experiments were carried out to methods described previously [19]. Gravimetric experiments were carried out in a double glass cell equipped with a thermostated cooling condenser. The solution volume was 100 ml. The steel specimens used had a rectangular form (length 2 cm, width 1 cm, thickness 0.06 cm). The maximum duration of tests was 24 h at 30 °C in nondeaerated solutions. At the end of the tests the specimens were carefully washed in ethanol under ultrasound and then weighed. Duplicate experiments were performed in each case and the mean value of the weight loss is reported. Weight loss allowed calculation of the mean corrosion rate in mg cm^{-2} h^{-1}.

3. Experimental results and discussion

3.1. *Polarization curves*

3.1.1. *Influence of 4-MTHT concentrations*

Polarization behaviour of mild steel in 0.5 M H_2SO_4 in the presence and absence of different concentrations of 4-MTHT is given in Figure 2. The extrapolation method for the polarization curves was applied and the data for corrosion potential (E_{corr}), corrosion current (I_{corr}), Tafel slopes (b_c and b_a) and percentage inhibition efficiency E are shown in Table 1. The values of b_c and b_a are in reasonable agreement with literature [5, 6, 20]. 4-MTHT hindered the acid attack on the steel electrode. Its addition decreased I_{corr} with increasing inhibitor concentration (Table 1). Consequently, 4-MTHT inhibits the corrosion of mild steel in 0.5 M H_2SO_4. Percentage E increased with inhibitor concentration reaching a maximum value at 5×10^{-3} M. The corresponding efficiency value was 72.9%. Cathodic current–potential curves gave rise to parallel Tafel lines indicating that the hydrogen evolution reaction is activation controlled and the addition of 4-MTHT did not modify the mechanism of the proton discharge reaction. Its presence suppressed the cathodic reaction to greater extents than the anodic one, especially at low 4-MTHT concentration (Figure 2). Thus, 4-MTHT showed predominantly cathodic action in 0.5 M H_2SO_4.

In the anodic branches of the inhibited polarization curves, a nonmonotonic trend may be observed for sufficiently noble potentials (> -400 mV vs SCE) (Figure 2). The rapid increase in anodic current in the second polarization region may be due to desorption of 4-MTHT molecules adsorbed on the electrode surface. In this case the desorption rate is higher than its adsorption rate. Thus, a desorption potential (E_d) may be defined as attributed to the inhibitor desorption. The

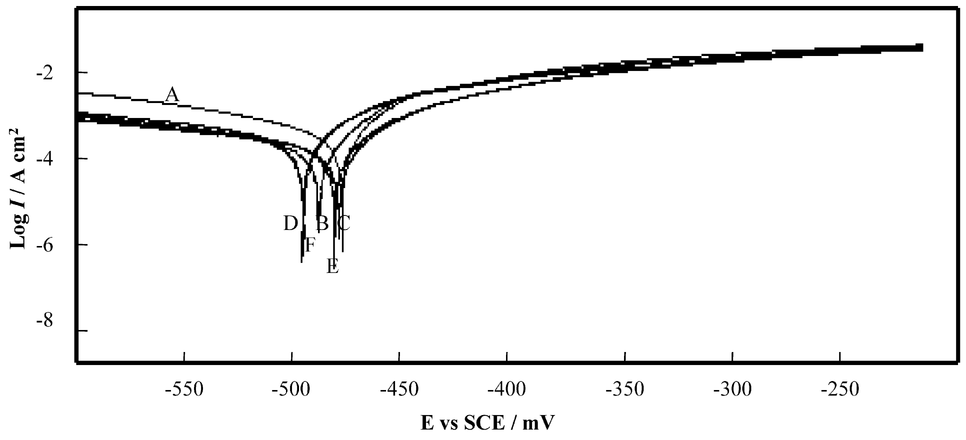

Fig. 2. Polarization curves for mild steel in 0.5 M H_2SO_4 containing different concentrations of 4-MTHT. Key: (A) blank, (B) 1×10^{-5}, (C) 2×10^{-5}, (D) 5×10^{-5}, (E) 8×10^{-5} and (F) 1×10^{-4} M.

Table 1. Polarization parameters for the corrosion of mild steel in 0.5 M H_2SO_4 containing different concentrations of 4-MTHT

Inhibitor conc./M	E_{corr} vs SCE/mV	I_{corr} /μA cm^{-2}	b_c /mV dec^{-1}	b_a /mV dec^{-1}	E /%
Blank	−477	1109	185	100	–
1×10^{-5}	−492	390	172	101	64.8
5×10^{-5}	−499	351	175	100	68.3
1×10^{-4}	−498	311	180	104	71.9
5×10^{-4}	−472	301	187	103	72.9

name 'E_d' was adopted in this work. E_d indicated the commencement of the desorption of adsorbed species on the electrode surface, above which the coverage of inhibitor decreased rapidly.

With increase in 4-MTHT concentration, the values of I_{corr} decrease markedly, indicating that a higher coverage of inhibitor on the surface was obtained in a solution with higher inhibitor concentrations. The E_d values are generally 100 mV vs SCE noble to the corrosion potential, E_{corr}. Thus, no desorption phenomenon was observed in the polarization measurements as shown in Figure 2. The desorption phenomenon may only occur when E_d is very close to, or lower than E_{corr}. In addition, the value of E_d remains almost constant with increasing 4-MTHT concentration (Figure 4). This suggests that the desorption potentials of 4-MTHT are little affected by the 4-MTHT coverage. Similar results have been reported with other organic compounds [21–23].

From these results, it is demonstrated that 4-MTHT is an effective inhibitor for mild steel in sulfuric acid. High inhibition efficiency was achieved at high 4-MTHT concentration. However, E_d remained unchanged but E_{corr} changed with increasing 4-MTHT concentration.

Therefore, the stability of the adsorbed 4-MTHT layer on the inhibited metal has become the major problem to be addressed in the improvement of the inhibition efficiency. The addition of halide ions has been shown to increase E_d [24] and may enhance the stability of 4-MTHT adsorption on the metal surface.

3.1.2. *Influence of KI concentrations*

Figure 3 illustrates the effect of addition of KI to 0.5 M H_2SO_4 solutions containing 5×10^{-5} M 4-MTHT. The E_{corr} of mild steel shifts in the positive direction with

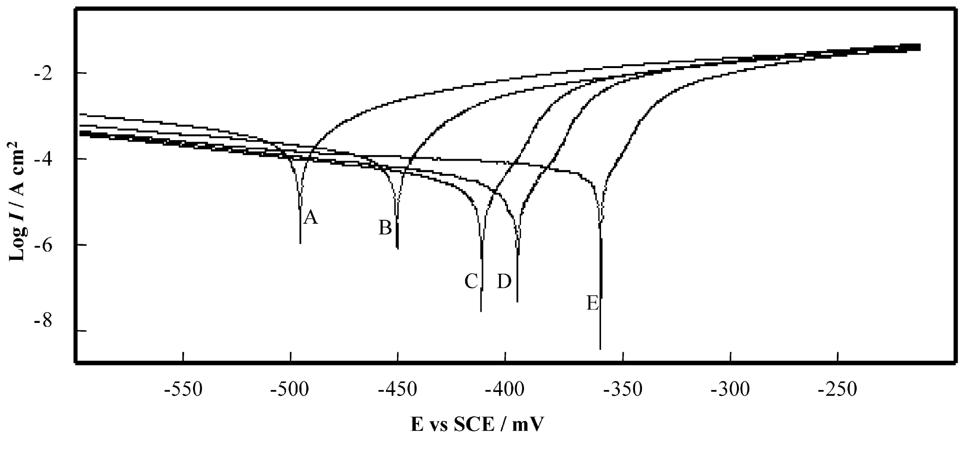

Fig. 3. Polarization curves for mild steel in 0.5 M H_2SO_4 containing 5×10^{-5} M 4-MTHT in the absence and presence of different concentrations of KI. Key: (A) 4-MTHT only, (B) 2×10^{-4}, (C) 1×10^{-3}, (D) 2×10^{-3} and (E) 1×10^{-2} M.

Table 2. Polarization parameters for the corrosion of mild steel in 0.5 M H_2SO_4 containing 5×10^{-5} M 4-MTHT in the absence and presence of different concentrations of KI

Conc. [KI]/M	E_{corr} vs SCE/mV	$I_{corr}/\mu A\ cm^{-2}$	$E/\%$
–	−499	351	68.3
2×10^{-4}	−455	82	92.6
1×10^{-3}	−416	33	97.0
2×10^{-3}	−408	25	97.7
1×10^{-2}	−348	87	92.2

addition of KI. This observation is in accord with those observed previously [25]. The shift in E_{corr} to a more positive value affords a greater tendency for the metal to adsorb anions. In addition, when only 4-MTHT was used (Figure 2), the E_u values remained almost unchanged with increase in concentration of inhibitor. When 4-MTHT and KI were used together (Figure 3), not only were both anodic and cathodic currents inhibited effectively, but the E_d values were also raised. The value of E_d is related to the amount of adsorbed iodide ions on the Fe electrode surface, according to the studies of Heusler and Cartledge [24]. Table 2 reports the corrosion kinetic parameters obtained from the polarization curves for mild steel in 0.5 M H_2SO_4 containing 5×10^{-5} M 4-MTHT for various concentrations of KI. When 5×10^{-5} M 4-MTHT only was used, I_{corr} was 82 $\mu A\ cm^{-2}$. It was reduced to 25 $\mu A\ cm^{-2}$ when 5×10^{-5} M 4-MTHT and 2×10^{-3} M KI were used together. A significant decrease in I_{corr} occurred with the addition of KI, thereby showing that synergism existed between 4-MTHT and KI. It can be seen from Table 2 that a maximum synergistic effect is observed for a combination of 5×10^{-5} M 4-MTHT and 2×10^{-3} M KI, for which maximum corrosion inhibition is obtained. A further increase in the concentration of KI decreases the value of inhibition efficiency.

From this behaviour (Figures 2 and 3), it appears that the value of E_d depends largely on the concentration of KI in the solutions. With increase in KI in the presence of 5×10^{-5} M 4-MTHT, the E_d values shift positively (Figure 3). This suggests that the iodine ions play a role in stabilising the 4-MTHT molecules adsorbed on the steel and the two species (I^- and 4-MTHT) compete for active adsorption sites. Thus, the increase in I^- ion concentration favours an increase in E_d, that is, adsorption stability [8].

3.1.3. *Synergistic effect of 4-MTHT and KI*

Figure 4 shows the polarization curves for mild steel in 0.5 M H_2SO_4 with different concentrations of 4-MTHT and 2×10^{-3} M KI. When both KI and 4-MTHT are present, a low polarization current and high E_d ($E_d \approx -375$ mV vs SCE) were observed, indicating a synergistic effect between 4-MTHT and KI. The blend inhibitor (4-MTHT + KI) combines the advantage of both KI (high E_d) and 4-MTHT (high inhibition efficiency). In this case, 4-MTHT can be classified as an inhibitor of relatively mixed effect (anodic/cathodic inhibition) in 0.5 M H_2SO_4. Table 3 lists the electrochemical parameters for various concentrations of 4-MTHT in the presence and absence of 2×10^{-3} M KI. By comparing the corrosion rates in both cases for all concentrations, it can be seen that the percentage E of 4-MTHT is greatly improved by the presence of KI. The synergistic effect between 4-MTHT and KI can be explained by the fact that the addition of KI stabilized the adsorption of 4-MTHT on the iron surface. This stabilisation may be caused by the interaction between 4-MTHT and I^- ions and the shifting of the corrosion potential due to the adsorption of iodide ions on the iron surface.

3.2. *A.C. impedance studies*

Figure 5 depicts a typical set of Nyquist plots for mild steel in 0.5 M H_2SO_4 solution in the absence and presence of various concentrations of 4-MTHT. It is apparent from these plots that the impedance response of mild steel in uninhibited H_2SO_4 solutions has significantly changed after the addition of 4-MTHT in the corrosive solutions. This indicated that the impedance of

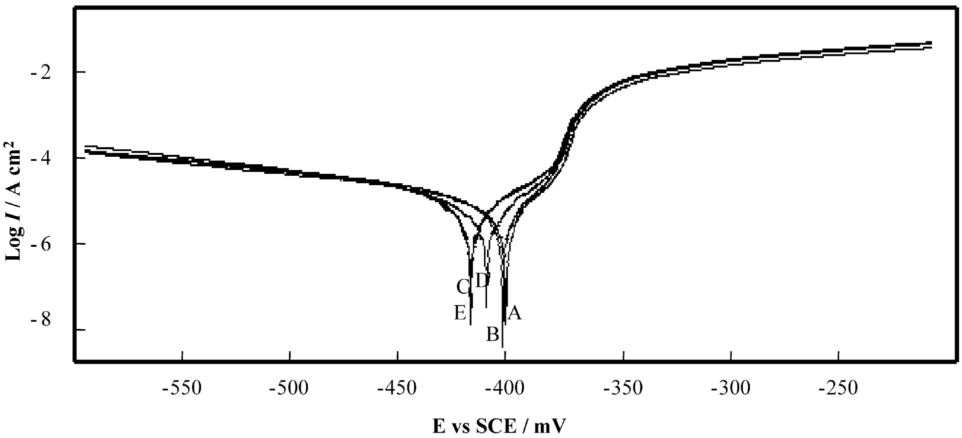

Fig. 4. Polarization curves for mild steel in 0.5 M H_2SO_4 containing different concentrations of 4-MTHT in the presence of 2×10^{-3} M KI. Key: (A) KI only, (B) 1×10^{-5}, (C) 2×10^{-5}, (D) 8×10^{-5} and (E) 1×10^{-4} M.

Table 3. Polarization parameters for the corrosion of mild steel in 0.5 M H_2SO_4 containing different concentrations of 4-MTHT in the presence and absence of 2×10^{-3} M KI

Conc. 4-[MTHT] /M	Conc. [KI]/M	E_{corr} vs SCE/mV	$I_{corr}/\mu A\ cm^{-2}$	b_c/mV dec^{-1}	b_a/mV dec^{-1}	E(%)	θ
Blank	–	−477	1109	185	100	–	–
1×10^{-5}	–	−492	390	172	101	64.8	0.65
1×10^{-5}	2×10^{-3}	−407	28	185	104	97.5	0.97
2×10^{-5}	–	−482	380	181	96	65.7	0.66
2×10^{-5}	2×10^{-3}	−422	26	170	98	97.7	0.98
5×10^{-5}	–	−499	351	175	100	68.3	0.68
5×10^{-5}	2×10^{-3}	−408	25	182	106	97.7	0.98
8×10^{-5}	–	−484	340	185	105	69.3	0.71
8×10^{-5}	2×10^{-3}	−423	23	183	103	97.9	0.98
1×10^{-4}	–	−498	311	180	104	72.0	0.72
1×10^{-4}	2×10^{-3}	−420	208	172	97	81.2	0.81

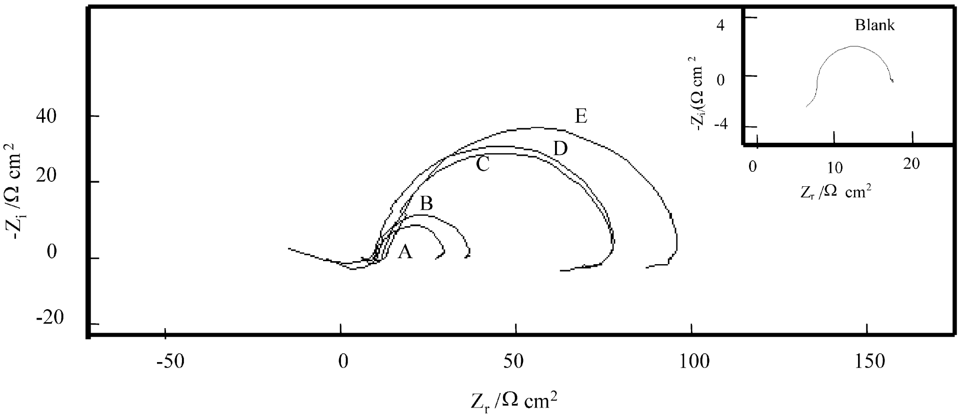

Fig. 5. Nyquist diagrams for mild steel in 0.5 M H_2SO_4 containing different concentrations of 4-MTHT. Key: (A) 1×10^{-5}, (B) 2×10^{-5}, (C) 5×10^{-5}, (D) 8×10^{-5} and (E) 1×10^{-4} M.

inhibited substrate increased with increasing inhibitor concentration.

The electrochemical parameters derived from the Nyquist plots and percentage *E* are given in Table 4. Capacitance values (*C*) and charge-transfer resistance (R_t) were calculated from Nyquist plots as described elsewhere [19]. As it can be seen from Table 4, when the inhibitor concentration increased, the R_t values increased, but the *C* values tended to decrease. This decrease in the *C*, which can result from a decrease in local dielectric constant and/or an increase in the thickness of the electrical double layer, suggested that the 4-MTHT molecules function by adsorption at the metal solution–interface [26].

Table 4. Impedance measurements and inhibition efficiency for mild steel in 0.5 M H_2SO_4 containing different concentrations of 4-MTHT at 30 °C

Inhibitor conc./M	$R_t/\Omega\ cm^2$	$E_{rest\ potential}$ vs SCE/mV	$C/\mu F\ cm^{-2}$	E/%
Blank	9	−470	1775	–
1×10^{-5}	23	−475	522	60.9
5×10^{-5}	66	−491	145	86.4
1×10^{-4}	69	−490	121	87.0
5×10^{-4}	345	−473	115	97.4

Nyquist plot for mild steel in 0.5 M H_2SO_4 containing different concentrations of 4-MTHT in combination with 2×10^{-3} M KI are shown in Figure 6. Table 5 gives values of *C*, R_t, θ and percentage *E* obtained from these plot*s*. Addition of KI enhanced the values of coverage for each concentration of 4-MTHT. The *C* values decreased and the values of R_t enhanced to the maximum in the presence of 8×10^{-5} M 4-MTHT and thereafter its values decreased with further increase in the concentration of inhibitor. This suggests that the further addition of 4-MTHT in the solution tends to reduce the *E* values, resulting in an increase in the desorption tendency of the I^- ions adsorbed on the metal surface. The excellent behaviour of 4-MTHT previously evidenced in the electrochemical steady-state measurements was again confirmed.

3.3. *Weight loss studies*

Table 6 shows the corrosion parameters such as corrosion rate (*CR*) and *E* obtained by the weight loss method at different concentrations in 0.5 M H_2SO_4 at 30 °C. 4-MTHT inhibits the corrosion of mild steel at all concentrations. Maximum *E* is obtained at a concentration of 5×10^{-4} M. The corresponding efficiency value is 80.4%.

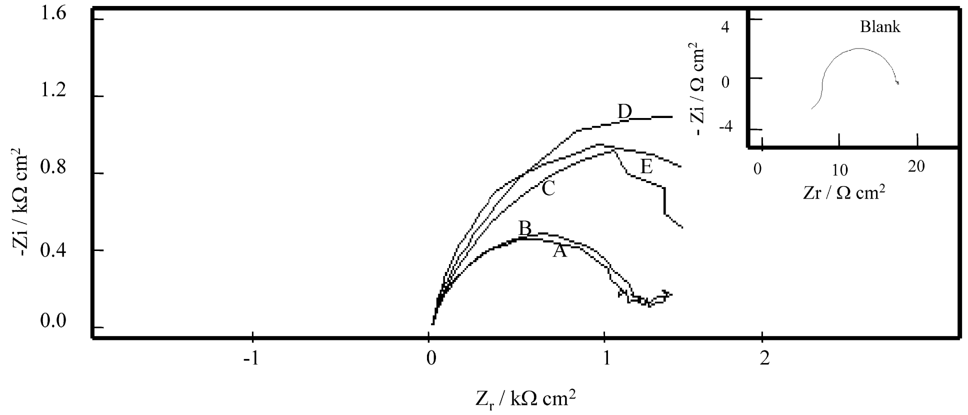

Fig. 6. Nyquist diagrams for mild steel in (0.5 M H_2SO_4 + 2×10^{-3} M KI) solution containing different concentrations of 4-MTHT. Key: (A) 1×10^{-5}, (B) 2×10^{-5}, (C) 5×10^{-5}, (D) 8×10^{-5} and (E) 1×10^{-4} M.

Table 5. Impedance measurements and inhibition efficiency for mild steel in 0.5 M H_2SO_4 containing different concentration of 4-MTHT in the presence and absence of 2×10^{-3} KI at 30 °C

Conc. [4-MTHT]/M	Conc. of [KI /M]	R_t/Ω cm^2	$E_{\text{rest potential}}$ vs SCE/mV	C/μF cm^{-2}	E/%	θ
Blank	–	9	−470	1775	–	–
1×10^{-5}	–	23	−475	522	60.9	0.60
1×10^{-5}	2×10^{-3}	1240	−472	32	99.3	0.99
2×10^{-5}	–	26	−476	403	65.0	0.65
2×10^{-5}	2×10^{-3}	1903	−468	26	99.5	0.99
5×10^{-5}	–	66	−491	145	86.4	0.86
5×10^{-5}	2×10^{-3}	2276	−455	17	99.6	0.99
8×10^{-5}	–	66	−480	145	86.2	0.86
8×10^{-5}	2×10^{-3}	3242	−449	15	99.7	0.99
1×10^{-4}	–	69	−491	121	86.8	0.87
1×10^{-4}	2×10^{-3}	1312	−476	30	99.3	0.99

Table 6. Corrosion parameters obtained from weight loss measurements for mild steel in 0.5 M H_2SO_4 containing various concentrations of 4-MTHT at 30 °C

Inhibitor conc. /M	Corrosion rate, CR/mg cm^{-2} h^{-1}	Inhibition efficiency, E/%
Blank	7.267×10^{-3}	–
1×10^{-5}	3.648×10^{-3}	49.8
5×10^{-5}	3.334×10^{-3}	54.1
1×10^{-4}	1.597×10^{-3}	78.0
5×10^{-4}	1.426×10^{-3}	80.4

Table 7. Corrosion parameters obtained from weight loss measurements for mild steel in 0.5 M H_2SO_4 containing 5×10^{-4} M of 4-MTHT in the presence and absence of various halide ions concentrations at 30 °C

Conc. [halide ion] /M	Corrosion rate, CR/mg cm^{-2} h^{-1}	Inhibition efficiency, E/%
–	1.426×10^{-3}	80.4
	KCl	
2×10^{-4}	1.088×10^{-3}	85.0
1×10^{-2}	1.064×10^{-3}	85.4
	KBr	
2×10^{-4}	7.467×10^{-4}	89.7
1×10^{-2}	4.514×10^{-4}	93.8
	KI	
2×10^{-4}	1.143×10^{-4}	98.4
1×10^{-2}	2.205×10^{-4}	97.0

We compare the effect of halide ions on corrosion inhibition of mild steel in 0.5 M H_2SO_4 by 4-MTHT. For this, the values of E for the 5×10^{-4} M 4-MTHT in combination with specific concentration of different halide ions at 30 °C in 0.5 M H_2SO_4 are given in Table 7. The addition of KI decreases the corrosion rate and increases E significantly, thereby showing that synergism exists between 4-MTHT and KI. These results agree generally with those reported by Quraichi et al. and Feng et al. [5, 8]. Comparatively, the addition of potassium chloride (KCl) or potassium bromide (KBr) are not as effective as KI. From weight loss measurements, the order of the degree of adsorption is $I^- > Br^- > Cl^-$ (Table 2). Therefore, KI is the most effective halide to be used together with 4-MTHT. This conclusion agrees with the findings of other researchers [6, 8, 24].

3.4. *Adsorption isotherm*

Figure 7 illustrates the adsorption isotherm for 4-MTHT (Figure 7A) and 4-MTHT + KI (Figure 7B)

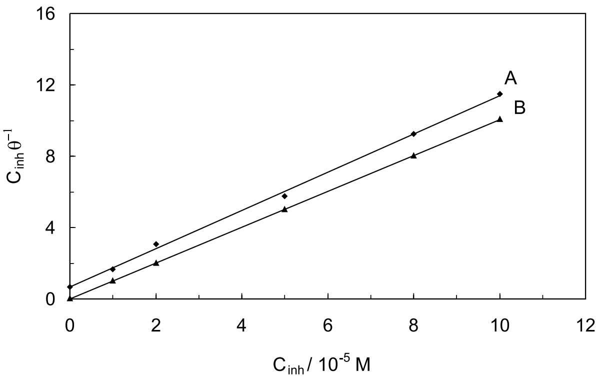

Fig. 7. Langmuir adsorption plot of C_{inh}/θ against C_{inh}, (A) 4-MTHT and (B) 4-MTHT + KI.

on mild steel in 0.5 M H_2SO_4. In this Figure, θ values are evaluated from electrochemical measurements using an equation described elsewhere [27]. The plot of C_{inh}/θ against C_{inh} is linear as shown by Figure 7, which shows that the adsorption of 4-MTHT alone and in combination with KI on the mild steel surface obeys Langmuir's adsorption isotherm.

3.5. *Synergism parameter*

Table 8 shows synergism parameter S_θ calculated at different inhibitor concentrations using the relationship given by Aramaki and Hackerman [28]:

$$S_\theta = \frac{1 - \theta_{1+2}}{1 - \theta'_{1+2}} \tag{1}$$

where $\theta_{1+2} = (\theta_1 + \theta_2) - (\theta_1\theta_2)$, θ_1 = surface coverage by anion (I^-), θ_2 = surface coverage by cation (protonated 4-MTHT) and θ'_{1+2} = measured surface coverage both anion and cation. All S_θ values are more than unity, suggesting that the phenomenon of synergism exists between 4-MTHT and iodide ions [29]. Thus, the enhancement of the inhibition efficiency caused by the addition of iodide ions to 4-MTHT is only due to a synergistic effect.

The synergistic inhibitive effect brought about by combination of 4-MTHT and KI for the corrosion of mild steel in 0.5 M H_2SO_4 can be explained as follows. The strong chemisorption of iodide ions on the metal surface is responsible for the synergistic effect of iodide ions, in attraction with protonated 4-MTHT. Iodide ion is adsorbed on the anode of the metal surface. Surface charge is changed to negative by the specific adsorption of these ions resulting in the joint adsorption of anions with triazole cations [30]. 4-MTHT is believed to be adsorbable, not only on the cathode areas by coulombic attraction using the charge of the protonated molecule, but also on the anode areas by virtue of donation of the electron-pair on the nitrogen atom of the unprotonated molecule [28]; therefore, interference adsorption can take place at the anode. Iofa has shown that I^- alone polarizes both the anodic and cathodic reaction of iron over a wide potential range [30]. It is apparent then that the effects of I^- are not due to electrostatic effects alone, but some covalent bonding to the metal must be involved. The large size and ease of polarizability of I^- facilitates electron pair bonding.

Table 8. Synergism parameter S_θ for different concentration of 4-MTHT

Concentration [4-MTHT]/M	Synergism parameter, S_θ
1×10^{-5}	9.44
2×10^{-5}	9.71
5×10^{-5}	9.69
8×10^{-5}	10.04
1×10^{-4}	1.35

4. Conclusion

The inhibition behaviour of 4-MTHT and its synergistic effect with KI for mild steel in 0.5 M H_2SO_4 has been studied. The following conclusions may be drawn:

(i) 4-MTHT is an effective inhibitor in reducing the corrosion rate for mild steel in sulphuric acid solutions and its inhibition action is due to adsorption of 4-MTHT molecules on the metal surface. In this case, the desorption potential, E_d, remains almost unchanged with concentration of 4-MTHT.

(ii) Synergistic effects between 4-MTHT and KI were observed. The addition of KI to the solution improved the percentage E of 4-MTHT significantly. The adsorption of 4-MTHT is stabilised by the presence of iodide ions in 0.5 M H_2SO_4.

(iii) 4-MTHT with KI inhibits the corrosion of mild steel in both cathodic and anodic conditions, that is, this combination is a mixed inhibitor. In this case, E_d values are markedly raised.

(iv) Adsorption of 4-MTHT alone and in combination with KI on the mild steel surface follows a Langmuir isotherm.

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