

Synergistic Effect of Iodide Ion and Methyl Violet on the Corrosion Inhibition of Carbon Steel in Phosphoric Acid

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The corrosion inhibition effects of iodide ion and its synergistic effect with methyl violet (MV) on carbon steel in 1.0 mol/L phosphoric acid solution have been investigated using potentiodynamic polarization, electrochemical impedance spectroscopy and weight loss measurements. The results show that there is an excellent synergistic effect between iodide ion and MV for carbon steel corrosion inhibition in 1.0 mol/L H₃PO₄. The electrochemical studies reveal that single iodide ion or combination of iodide ion and MV acts as a mixed-type inhibitor and the corrosion reaction is controlled by charge transfer process. Adsorption of iodide ion on the steel surface obeys Langmuir adsorption isotherm in the absence or presence of MV. The values of K_{ads} , ΔG_{ads}° , ΔH_a , ΔS_a and E_a were obtained and discussed. The adsorption of inhibitor molecules on the steel surface is a spontaneous process containing a mixed physical and chemical adsorption mechanism.

Keywords: Carbon steel, Corrosion, Phosphoric acid, Iodide ion, Methyl violet, Synergistic inhibition.

1. INTRODUCTION

As an important alloy material in existence carbon steel has a wide variety of industrial applications [1-2]. Carbon steel has also been confront with a problem of corrosion, in acidic surroundings especially. Sulfuric acid, hydrochloric acid and phosphoric acid are usually used in many industries such as acid cleaning, acid pickling and acid descaling procedures of metallic materials [3-4]. It is a convenient and effective measurement that the corrosion inhibitors are used to protect metal materials against corrosion caused by acid solutions. Some of the efficient inhibitors are organic compounds containing nitrogen [5-8], sulfur [9-12], oxygen [13-14], π -electrons or aromatic rings [15-17].

It has been reported by Lagrenée that nitrogen-containing organic compounds showed more effective inhibition in hydrochloric acid than in sulphuric acid for the steel corrosion [18]. The research indicated that there is a synergistic inhibition between nitrogen-containing compounds and chloride ions for steel corrosion in hydrochloric acid. Synergistic action is a useful way to enhance the inhibition ability of the inhibitor, to reduce the amount of usage and to extend the application of the inhibitor in acidic solution. Synergistic techniques have been frequently used in practice for its efficiency and economy [19-20]. Iodine and chlorine are the same main group elements. Compared with chloride ion, iodide ion (I^-) should be adsorbed on the metal surface and provide better synergistic effect because iodide ion has larger radius and present the better polarizability and even bigger steric effect [19, 21-22].

Abdel Rehim et al have researched the synergistic inhibition effect of iodide ions and adenine on the corrosion of low carbon steel in sulphuric acid solution [23]. They have observed that the combination of adenine and I^- improved the inhibition efficiency greatly because of synergistic effects. Musa et al have studied that the synergistic inhibition between pathalazone and I^- for mild steel in hydrochloric acid solution [24]. They have found that the synergism of pathalazone and I^- promoted improvement of inhibition efficiency significantly and observed that a cooperative mechanism exists between the iodide anion and pathalazone cations.

Methyl violet (MV) is an indicator and contains nitrogen atoms unshared electron pairs and abundant π -electrons aromatic rings. We have studied the inhibition of MV and chloride ion for the cold rolled steel corrosion in sulphuric acid solution [25]. The results indicated that MV and chloride ion show up a better synergistic inhibition effect for the steel corrosion. Phosphoric acid is a medium strong acid and shows strong aggressiveness for ferrous and ferrous alloys [26-27]. The metallic material equipment are vulnerable to corrosion attack in the wet process of phosphoric acid manufacture and the production of ammonium phosphate fertilizer. The aim of the present work is to research the synergism of MV and I^- for carbon steel corrosion inhibition in phosphoric acid solution using potentiodynamic polarization, electrochemical impedance spectroscopy (EIS) and weight loss measurements. We look forward to some useful results to guide the composing of inhibitors for phosphoric acid system.

2. EXPERIMENTAL

2.1. Materials

The carbon steel specimens have a chemical composition of (wt%): 0.18% C, 0.016% S, 0.021% P, 0.053% Si, 0.38% Mn and Fe balance.

Bidistilled water was used to prepare the experimental solutions and AR grade H_3PO_4 and potassium iodide (KI) were used too. Methyl violet was supplied by Merck Chemicals. Figure 1 gives its structure.

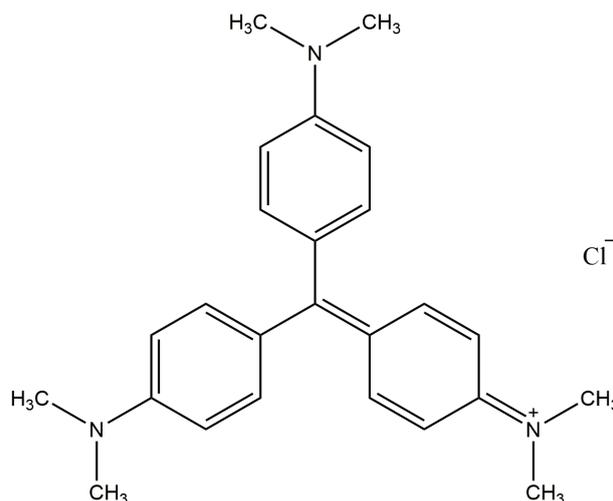


Figure 1. Structure of MV

2.2. Electrochemical measurements

The electrochemical measurements were conducted in a conventional three-electrode cell. The auxiliary electrode and reference electrode were a platinum foil and saturated calomel electrode (SCE), respectively. The working electrodes were embedded in PVC holder using epoxy resin with an exposed area of 1.0 cm². Each working electrode was polished using emery papers (300 - 1200 grade) on the test face, washed with distilled water, degreased with acetone, and dried with a warm air stream. Before each measurement, the working electrode was immersed for two hours in the 250 ml experimental solution at open circuit potential until corrosion potential reached a steady state.

All the electrochemical experiments were performed using PARSTAT 2263 Potentiostat/Galvanostat (Princeton Applied Research). The potentiodynamic polarization curves were gained by changing the electrode potential from -250mV to + 250mV versus the open circuit potential, at a scanning rate of 0.5 mVs⁻¹. EIS experiments were performed in the frequency range of 100 kHz to 10 mHz using a 10 mV peak to peak voltage excitation. Each experiment was performed in triplicate to ensure reproducibility.

2.3. Weight loss measurements

The specimens (40 mm × 15 mm × 0.4 mm) were successively polished with emery papers (300 - 1200 grade), washed in distilled water, degreased in acetone and dried in a stream of air.

The specimens were weighed accurately before immersion in experimental solutions (150 ml) for four hours in air without bubbling. At the end of the run the specimens were taken out, washed with distilled water then acetone, dried and immediately weighed. Each measurement was performed on three separate samples and the average weight loss was taken.

3. RESULTS AND DISCUSSION

3.1. Polarization measurements

The polarization curves for carbon steel in 1.0 mol/L H_3PO_4 solution in the absence (a) and presence (b) of 0.4 mmol/L MV at 40°C are shown in Figure 2.

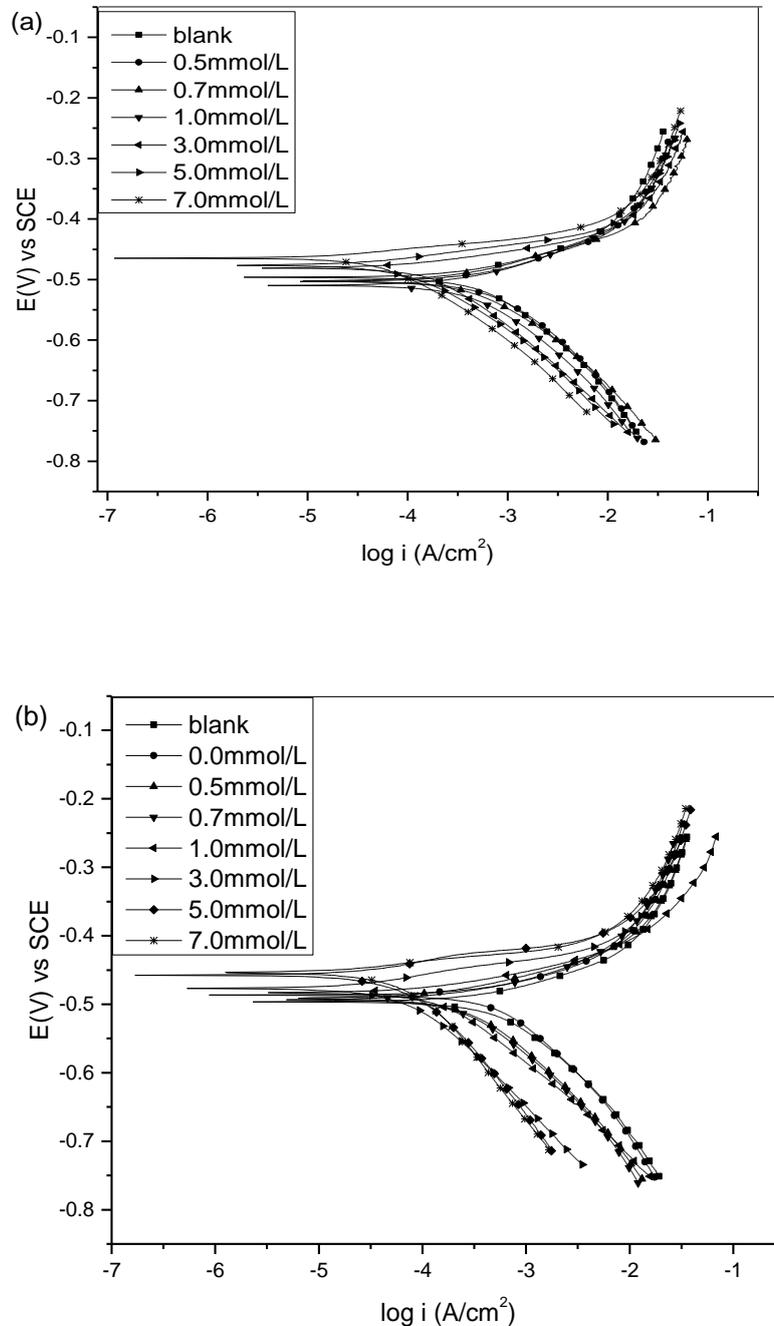


Figure 2. Potentiodynamic polarization curves of carbon steel containing different concentrations of I⁻ without (a) and with (b) 0.4 mmol/L MV in the 1.0 mol/L H_3PO_4 at 40°C.

From Figure 2 (a), It can be seen that the presence of increasing amounts of Γ caused a decrease in both anodic and cathodic current densities, but cathodic polarization was dominant. The presence of single Γ slightly shifted the corrosion potential to both negative and positive directions. These showed that Γ could retard the hydrogen evolution reaction and reduce anodic dissolution, which means that Γ is a mixed-type inhibitor. By Figure 2 (b), with addition of 0.4 mmol/L MV, the E_{corr} were slightly shifted to positive and the changes of anodic and cathodic branches were approximate with those without MV, but it is clear that the shifting levels of cathodic and anodic are obviously larger. These results indicated that the combination of MV and Γ is also a mixed-type inhibitor for carbon steel corrosion in H_3PO_4 .

The inhibition efficiency (IE) could be calculated from the following formula:

$$IE = \frac{I_{\text{corr}}^0 - I_{\text{corr}}^{\text{inh}}}{I_{\text{corr}}^0} \times 100 \quad (1)$$

where I_{corr}^0 and $I_{\text{corr}}^{\text{inh}}$ are the corrosion current density values without and with inhibitors, respectively.

The electrochemical polarization parameters: anodic and cathodic Tafel slopes (β_a , β_c), corrosion current density (I_{corr}), corrosion potential (E_{corr}), and the inhibition efficiencies for the carbon steel corrosion in 1.0 mol/L H_3PO_4 are illustrated in Table 1. As seen, the change of Tafel slopes showed no regularity with the change of Γ concentrations, which means that the reactions of anodic metal dissolution and cathodic hydrogen evolution were both inhibited by the inhibitors through merely blocking the reaction active centers of steel surface without influencing the anodic and cathodic reaction mechanism [28-29].

Table 1. Electrochemical polarization parameters obtained for carbon steel in 1.0 mol/L H_3PO_4 containing different concentrations of Γ without and with 0.4 mmol/L MV at 40 °C.

KI (mmol/L)	MV (mmol/L)	E_{corr} (vs. SCE) (mV)	I_{corr} ($\mu\text{A}/\text{cm}^2$)	β_a (mV/dec)	$-\beta_c$ (mV/dec)	$IE(\%)$
0	0	-496.2	689.3	73.6	163	—
0.5	0	-503.1	678.8	67.5	144	1.5
0.7	0	-502.1	644.6	85.8	167	6.48
1.0	0	-509.6	540.0	73.8	150	21.7
3.0	0	-480.9	292.3	89.2	160	45.9
5.0	0	-476.4	187.6	58.4	133	72.8
7.0	0	-464.7	108.4	40.3	124	84.3
0	0.4	-486.6	654.6	68.7	170	5.0
0.5	0.4	-493.3	429.4	88.8	179	37.7
0.7	0.4	-491.1	355.1	70.1	162	48.2
1.0	0.4	-483.6	214.1	65.0	144	68.9
3.0	0.4	-476.8	75.05	55.3	154	89.1
5.0	0.4	-457.4	63.05	43.7	168	91.0
7.0	0.4	-453.7	58.20	35.8	172	91.6

Compared with the values of I_{corr} and IE only in the presence of I^- or MV, decreases of I_{corr} and improvements of IE could be observed clearly in the co-existence of I^- and MV, which means that combination of MV and I^- is effective corrosion inhibitor for the carbon steel in H_3PO_4 solution. For instance, the IE of the combination of MV and I^- reached 91% at 5 mmol/L I^- and 0.4 mmol/L MV.

3.2. Electrochemical impedance spectroscopy

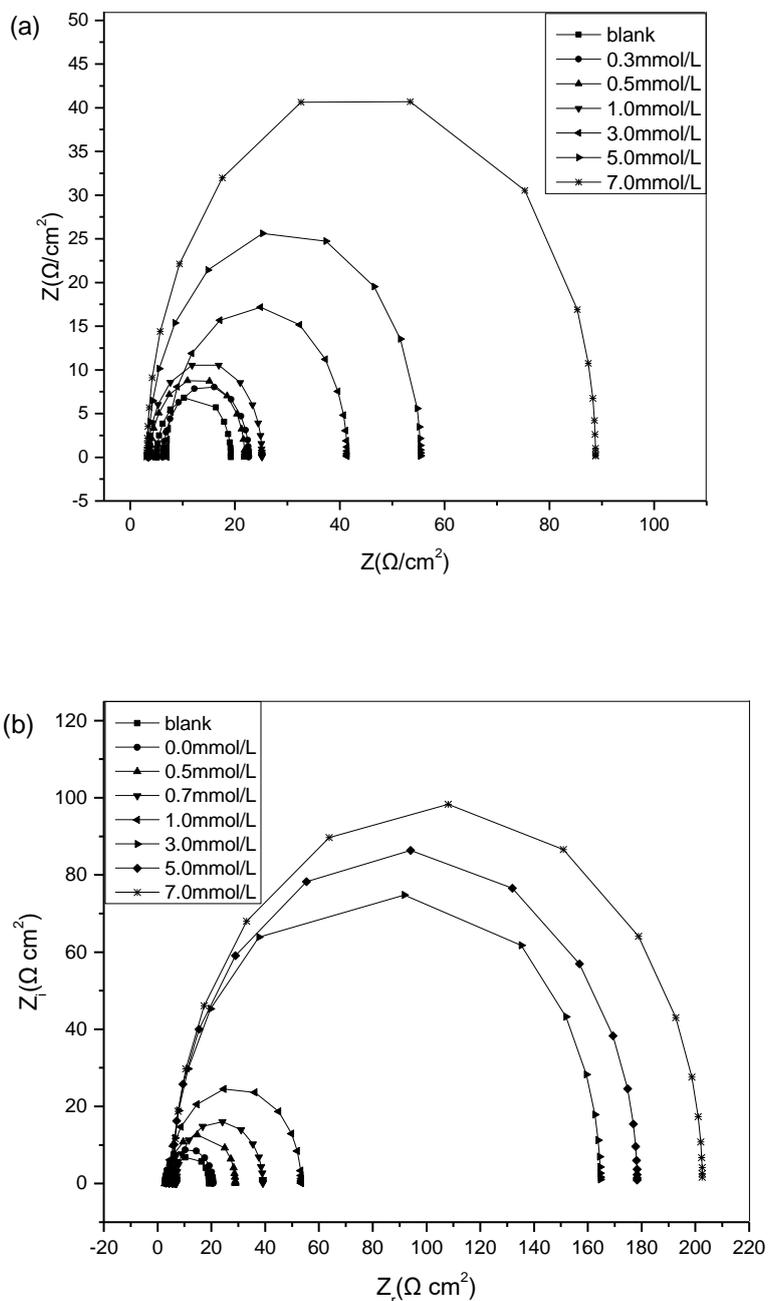


Figure 3. Nyquist plots of the carbon steel containing different concentrations of I^- without (a) and with (b) 0.4 mmol/L MV in the 1.0 mol/L H_3PO_4 at 40°C.

The Nyquist plots for carbon steel in the absence and presence of different concentrations of I alone (a) and in combination with 0.4 mmol/L MV (b) in 1.0 mol/L H₃PO₄ at 40°C are given in Figure 3.

From figure 3, a single depressed capacitive loop could be observed in the absence and presence of inhibitors in H₃PO₄, which shows that the charge transfer is the main controlling factor for corrosion reaction process. The result indicates that the corrosion inhibition of carbon steel was affected mainly by charge-transfer process and the inhibitor did not change the mechanism of carbon steel dissolution [30]. The imperfect semicircles of capacitive loops are related to the frequency dispersion effect because of the roughness and inhomogeneous of the electrode surface [31]. Comparing the semicircles in the absence of MV with those in the presence of MV, the diameters of the capacitance loops are clearly larger with MV than without MV, indicating that the presence of MV could improve inhibition performance of I effectively. The impedance spectra for different Nyquist plots were analyzed on the basis of an equivalent circuit model which is well-known Randle cell, which includes a constant phase element (CPE), charge transfer resistance (R_{ct}) and solution resistance (R_s), given in figure 4. The value of double layer capacitance (C_{dl}) influenced by the surface imperfections is simulated via CPE [32].

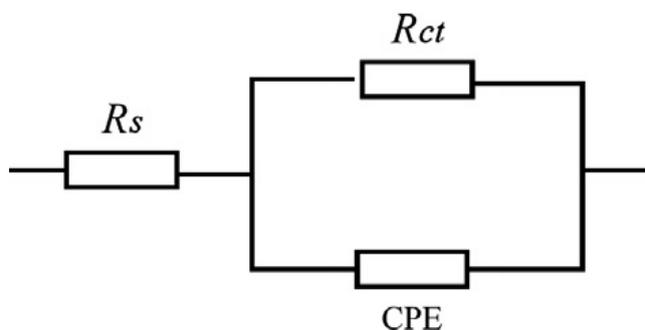


Figure 4. Equivalent circuit model used to fit the EIS experiment data.

The CPE is composed of a component Q_{dl} and a coefficient b which quantifies different physical phenomena such as surface inhomogeneous, porous layer formation, inhibitor adsorption, etc. The C_{dl} could be obtained from the formula [18]:

$$C_{dl} = Q_{dl} \cdot (2\pi f_{max})^{b-1} \quad (2)$$

where f_{max} represents the frequency at which the imaginary component of the impedance is maximal on the Nyquist plot.

The inhibition efficiency (IE_{ct}) could be determined according to the relation:

$$IE_{ct} = \frac{R_{ct(inh)} - R_{ct(0)}}{R_{ct(inh)}} \times 100 \quad (3)$$

where $R_{ct(inh)}$ and $R_{ct(0)}$ are the charge-transfer resistances in the presence and absence of inhibitor, respectively. Table 2 illustrates the values of R_s , C_{dl} , R_{ct} , and IE_{ct} .

According to Table 2, the values of C_{dl} is decrease in the presence of inhibitors compare to the blank solution, indicating that the adsorption of the inhibitors on the surface of steel formed an

adherent film and increased the thickness of the electrical double layer, which could be reason of decrease in C_{dl} [33-35]. Furthermore, the values of R_{ct} and IE_{ct} both increase with increasing I^- concentration in the presence or absence of MV. However, the increase of R_{ct} or IE_{ct} is clearly larger in the presence of MV than in the absence of MV. These results have a good consistency with those obtained from polarization methods.

Table 2. Electrochemical impedance parameters obtained for the carbon steel in 1.0 mol/L H_3PO_4 containing different concentrations of I^- without and with 0.4 mmol/L MV at 40 °C.

KI (mmol/L)	MV (mmol/L)	R_s ($\Omega\text{ cm}^2$)	C_{dl} ($\mu\text{F cm}^{-2}$)	R_{ct} ($\Omega\text{ cm}^2$)	$IE_{ct}(\%)$
0	0	5.057	172.7	15.87	
0.5	0	6.316	163.6	16.34	2.88
0.7	0	3.877	140.0	17.98	11.7
1.0	0	3.480	117.8	21.68	26.8
3.0	0	7.005	146.4	34.40	53.8
5.0	0	3.471	110.1	51.90	69.4
7.0	0	3.229	73.65	83.70	81.0
0	0.4	2.854	133.9	17.73	10.9
0.5	0.4	3.464	142.5	25.47	37.7
0.7	0.4	7.017	152.5	32.18	50.7
1.0	0.4	3.829	77.00	49.65	68.0
3.0	0.4	5.523	40.61	159.1	90.0
5.0	0.4	5.540	47.60	172.8	90.8
7.0	0.4	5.377	39.33	203.4	92.2

3.3. Weight loss measurements

The inhibition efficiency (IE_w) by weight loss was calculated using following equation:

$$IE_w = \frac{V_0 - V_i}{V_0} \times 100 \quad (4)$$

where V_0 and V_i are the corrosion rates in the absence and presence of the inhibitors, respectively.

Table 3 illustrates the corrosion rates and inhibition efficiencies of carbon steel for alone I^- and mixture of MV and I^- in 1.0 mol/L H_3PO_4 at 40 °C.

The corrosion rate decreases gradually and the inhibition efficiency increases with the increase of I^- concentration no matter without or with MV. It is also very clear that the corrosion inhibition of carbon steel in the combination of MV and I^- are greatly promoted in comparison with those only in the presence of single MV or I^- . These results are also in good agreement with those obtained from polarization curves and electrochemical impedance spectroscopy measurements.

Table 3. Corrosion rates and inhibition efficiencies obtained by weight loss for the carbon steel in 1.0 mol/L H₃PO₄ containing different concentrations of I⁻ without and with 0.4 mmol/L MV at 40 °C.

KI (mmol/L)	MV (mmol/L)	V (g/m ² h)	IE _w (%)
0	0	20.99	
0.5	0	17.59	16.2
0.7	0	16.56	21.1
1.0	0	15.09	28.1
3.0	0	10.27	51.1
5.0	0	7.744	63.1
7.0	0	4.996	76.2
0	0.4	17.14	18.3
0.5	0.4	10.47	50.1
0.7	0.4	7.452	64.5
1.0	0.4	6.152	70.7
3.0	0.4	1.700	91.9
5.0	0.4	1.341	93.6
7.0	0.4	1.091	94.8

3.4. Effect of temperature

Temperature is an important parameter on the progress of metal dissolution in acid solution. The effects of different temperature (30-45 °C) on the corrosion rate of carbon steel in the 0.7 mmol/L I⁻ with and without 0.4 mmol/L MV in 1.0 mol/L H₃PO₄ solution were researched by weight loss method. The results are illustrated in Table 4.

Table 4. The effect of temperature on the corrosion of carbon steel in the absence and presence of 0.7 mmol/L KI without and with 0.4 mmol/L MV in 1.0 mol/L H₃PO₄.

T (°C)	blank V(g/m ² h)	I ⁻ V(g/m ² h)	IE _w (%)	I ⁻ +MV V(g/m ² h)	IE _w (%)
30	8.701	6.590	24.3	1.932	77.8
35	14.22	10.77	24.2	3.953	72.2
40	20.99	16.56	21.1	7.452	64.5
45	30.55	24.62	19.4	11.18	63.4

It is observed that the inhibition efficiencies decreases with increasing temperature, which implies the inhibition of I⁻ or I⁻+MV for carbon steel corrosion could be caused by the adsorption of I⁻ or I⁻+MV on the steel surface. With the increase in temperature, the inhibitors could desorb from the surface of the steel, which leads to the reduction of surface coverage of I⁻ or I⁻+MV on the surface of carbon steel and the greater area of the carbon steel being exposed to the acidic solution [36]. Kinetic model can be used to elucidate the mechanism of the inhibitors action. The values of the apparent activation parameters can be obtained by the Arrhenius equation:

$$\ln V = \frac{-E_a}{RT} + \ln A \quad (5)$$

where E_a is apparent activation energy, R is the gas constant, T is the absolute temperature and A is pre-exponential factor. Figure 5 shows the Arrhenius plots for carbon steel containing Γ or Γ +MV in 1.0 mol/L H_3PO_4 . The E_a values could be calculated by the slopes of the Arrhenius plots.

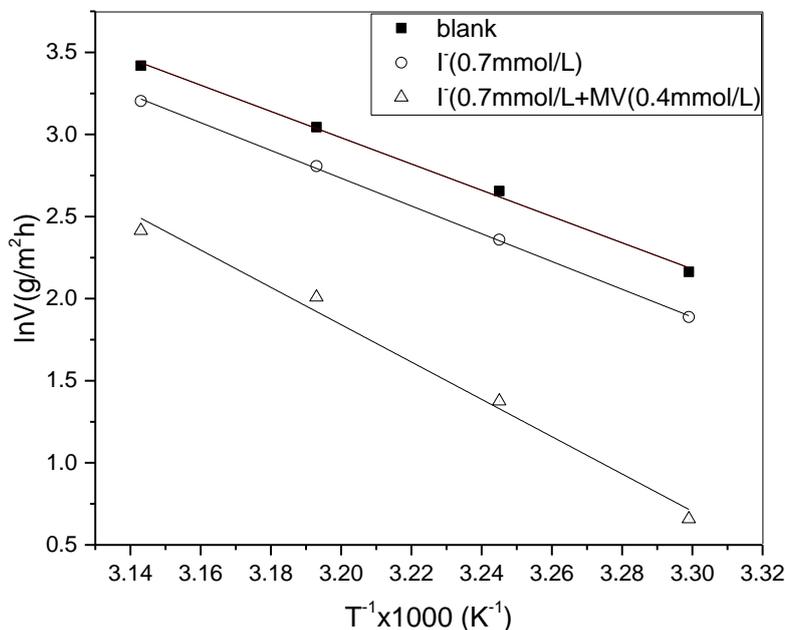


Figure 5. Arrhenius plots of the carbon steel in 1.0 mol/L H_3PO_4 .

The enthalpy of activation (ΔH_a) and entropy of activation (ΔS_a) for the corrosion of carbon steel were calculated by the transition state equation [37]:

$$V = \frac{RT}{Nh} \exp\left(\frac{\Delta S_a}{R}\right) \exp\left(\frac{-\Delta H_a}{RT}\right) \quad (6)$$

Where N is Avogadro's number and h is Plank's constant. Equation (6) can be rearranged to another kind of expression form in order to carry simple calculation:

$$\ln\left(\frac{V}{T}\right) = \left[\ln\left(\frac{R}{Nh}\right) + \frac{\Delta S_a}{R} \right] - \frac{\Delta H_a}{RT} \quad (7)$$

A straight line with the slope ($-\Delta H_a/R$) and intercept [$\ln(R/Nh) + (\Delta S_a/R)$] can be given from a plot of $\ln(V/T)$ against $1/T$. The plots from equation (7) for carbon steel containing Γ or Γ +MV in 1.0 mol/L H_3PO_4 are shown in Figure 6.

The calculated values of E_a , ΔH_a and ΔS_a are tabulated in Table 5. It is noticed that the values of ΔH_a and E_a in the presence of inhibitor is greater than that in the absence of inhibitor, indicating that the corrosion rate of carbon steel is mainly decided by the apparent activation energy and the energy barrier for the corrosion reaction increases with addition of inhibitor. There is a greater energy barrier in the presence of $\Gamma + MV$ than in the presence of Γ alone. The increase in E_a with the presence of

inhibitor may be attributed to the physical adsorption mechanism of the inhibitor on the metal surface [38-39]

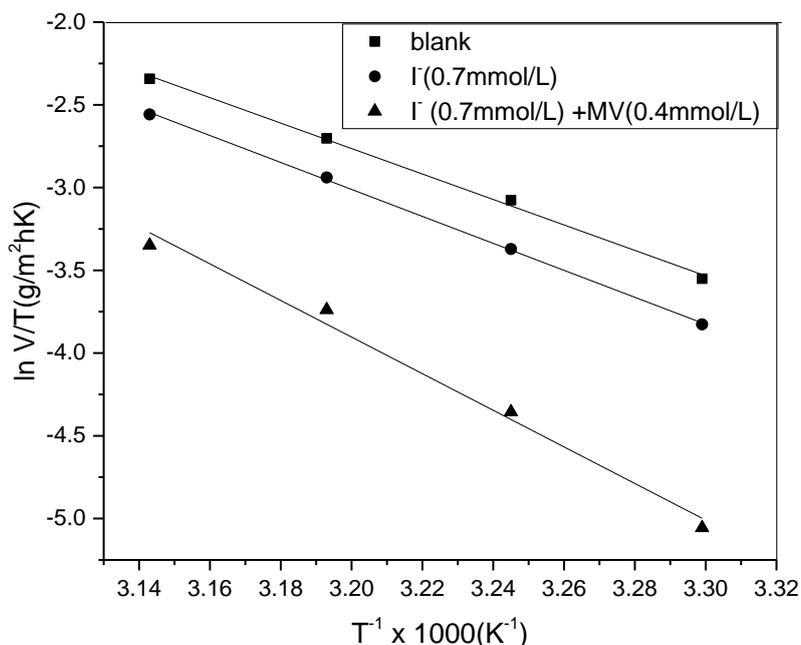


Figure 6. Transition state plots of the carbon steel in 1.0 mol/L H₃PO₄.

Table 5. Activation parameters for the corrosion of carbon steel in 1.0 mol/L H₃PO₄ without and with KI or KI + MV.

I^- (mmol/L)	MV (mmol/L)	E_a (kJ/mol)	ΔH_a (kJ/mol)	ΔS_a (J/mol)
0	0	66.63	63.94	-15.83
0.7	0	70.42	67.74	-5.746
0.7	0.4	94.66	91.95	64.31

The negative values of ΔS_a in the absence of the inhibitor means that the activated complex represents association rather than the dissociation step [40]. In the presence of I^- or $I^- + MV$, the values of ΔS_a becomes less negative or more positive. The adsorption of inhibitor is accompanied by desorption of water molecules from the steel surface and the increase of solvent entropy causes the increasing in entropy of activation [41]. The increase of entropy is the driving force for the adsorption of the inhibitor onto the carbon steel surface [42].

3.5. Adsorption isotherm

Adsorption isotherms are usually used to investigate the corrosion inhibition mechanism of the inhibitor molecules on the metal surface. It is assumed that the adsorption of I^- or $I^- + MV$ on the surface of carbon steel follows the Langmuir adsorption isotherm where:

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \quad (8)$$

Where C is the concentration of the inhibitor, θ is the degree of surface coverage and K_{ads} is the adsorptive equilibrium constant. The θ was calculated using the following formula [43]:

$$\theta = \frac{V_0 - V}{V_0 - V_m} \quad (9)$$

where V_m is the smallest corrosion rate.

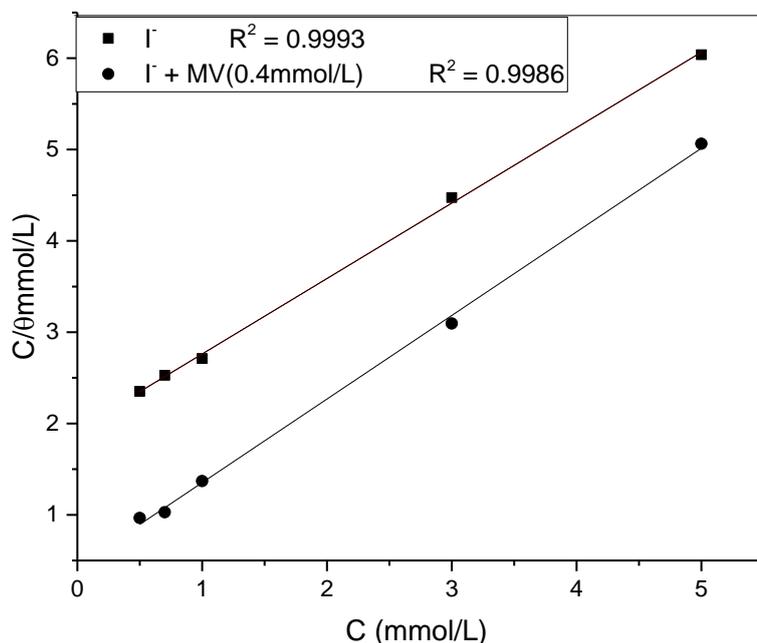


Figure 7. The plot of C/θ against C in 1.0 mol/L H_3PO_4 at 40°C.

Figure 7 shows the plot of C/θ against C in the different concentration of I^- with or without 0.4 mmol/L MV in 1.0 mol/L H_3PO_4 at 40°C by weight loss measurements. The linear regression coefficient values of the plot are close to unity, indicating that the adsorption of I^- with or without MV on the surface of carbon steel in 1.0 mol/L H_3PO_4 obeys Langmuir adsorption isotherm. The values of K_{ads} calculated are

$0.5167 \times 10^3 \text{ (M}^{-1}\text{)}$ in the presence of I^- alone and $2.288 \times 10^3 \text{ (M}^{-1}\text{)}$ in the presence of $I^- + MV$, respectively. The value of K_{ads} is greater in the presence of MV than the absence, showing that the tendency of adsorption of mixture of MV and I^- is more intense than single I^- on the steel surface.

The standard free energy of adsorption (ΔG_{ads}°) could be obtained from the formula [44-45]:

$$K_{ads} = \frac{1}{55.5} \exp\left(\frac{-\Delta G_{ads}^{\circ}}{RT}\right) \quad (10)$$

where the value of 55.5 is the concentration of water in the solution in mole units. Normally, the values of ΔG_{ads}° up to -20 kJ/mol are associated with the electrostatic interactions (physisorption), whereas those around -40 kJ/mol or more negative are assigned for chemisorption which means charge

sharing or transferring from the inhibitor molecules to the metal surface to form a coordinate bond [46-47]. The calculated values of $\Delta G_{\text{ads}}^{\circ}$ for Γ without and with 0.4 mmol/L MV are -26.75 kJ/mol and -30.36 kJ/mol, respectively. These $\Delta G_{\text{ads}}^{\circ}$ values obtained suggest that the adsorption process of Γ on the carbon steel without and with MV in 1.0 mol/L H_3PO_4 may involve both physisorption and chemisorption and the physisorption is dominant in the presence of Γ alone. The results of $\Delta G_{\text{ads}}^{\circ}$ values and decrease of inhibition efficiency with increasing temperature indicate that the adsorption of the inhibitor on the carbon steel surface in H_3PO_4 is unfavorable at higher temperature and hence can be regarded as predominantly physical adsorption.

3.6. Synergism effect

The above studies indicate that the inhibition efficiencies for solution in the presence of MV exhibit higher values in comparison with solution in the absence of MV. This means that there may be a synergistic inhibition effect of Γ and MV on corrosion process of carbon steel in 1.0 mol/L H_3PO_4 , which can be described from synergism parameters (S), obtained as follows [30]:

$$S = \frac{1 - (IE_1 + IE_2)}{1 - IE_{1+2}} \quad (11)$$

where IE_1 and IE_2 are the inhibition efficiencies in the presence of inhibitor 1 or inhibitor 2 alone, respectively. IE_{1+2} is the inhibition efficiency for combination of inhibitor 1 and inhibitor 2.

Generally, value of $S > 1$ indicates a synergistic effect and value of $S < 1$ implies antagonistic behavior leading to competitive adsorption prevails [22, 48]. The calculated values of S from three experimental methods are listed in Table 6. It is clear that all of S values are greater than unity and behave larger, which clearly shows that there is a stronger synergistic inhibition effect between Γ and MV for carbon steel corrosion in 1.0 mol/L H_3PO_4 , leading to inhibition efficiency improved greatly.

Table 6. Synergism parameters of Γ with 0.4 mmol/L MV for the carbon steel corrosion inhibition in 1.0 mol/L H_3PO_4 at 40°C from the three methods.

KI (mmol/L)	Synergism parameters(S)		
	polarization	EIS	weight loss
0.5	1.50	1.38	1.31
0.7	1.72	1.57	1.71
1.0	2.36	1.95	1.83
3.0	4.51	3.53	3.78
5.0	2.46	2.14	2.91
7.0	1.27	1.03	1.09

In acid solution, steel surface contains positive charge due to $E_{\text{corr}} - E_q = 0$ (zero charge potential) > 0 [49], Iodide ions can be specifically adsorbed on the steel surface charged positively through the electrostatic force. In this case, zero charge potential becomes less negative, which enhances the adsorption of inhibitors in cationic form [50]. MV could be protonated as to $[\text{MVH}_x]^{x+}$ in

H₃PO₄. With addition of MV, the positively charged MV can also be easily approach the steel surface and the MV molecules can also be adsorbed through donor-acceptor interactions between the abundance π -electrons or nitrogen atom of MV and the unoccupied d-orbital of the iron atoms. So, chemisorption and physisorption could be combined action on the carbon steel surface.

4. CONCLUSION

(1) Single Γ or MV does not show desirable inhibition efficiency for carbon steel corrosion in 1.0 mol/L H₃PO₄. The addition of MV enhances the inhibition efficiency of Γ obviously. The synergism parameters indicate that there is a stronger synergistic inhibition effect between Γ and MV for carbon steel corrosion in 1.0 mol/L H₃PO₄.

(2) The adsorption of Γ on the surface of carbon steel obeys the Langmuir adsorption isotherm in the absence or presence of MV. The adsorption of inhibitor molecules is a spontaneous process containing combination of physical and chemical adsorption.

(3) Single Γ or mixture of Γ and MV retards the cathodic and anodic reaction for carbon steel corrosion in 1.0 mol/L H₃PO₄, however the cathodic polarization is dominant for the presence of Γ alone. Γ and Γ + MV act as mixed type inhibitor and retard cathodic hydrogen evolution reaction and reduce anodic steel dissolution. EIS shows that the corrosion reaction is controlled by charge transfer.

The results obtained from polarization, EIS and weight loss measurements show good consistency.

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