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Original scientific paper

Corrosion inhibition of carbon steel by sodium metavanadate

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Abstract

The inhibition efficiency of sodium metavanadate (SMV)-adipic acid (AA) system in controlling corrosion of carbon steel in an aqueous solution containing 60 ppm of Cl^- has been evaluated by weight-loss method; 250 ppm of SMV exhibits inhibition efficiency of 56 %. Addition of adipic acid to SMV improves the inhibition efficiency of the system. The formulation consisting of 250 ppm of SMV and 250 ppm of adipic acid has inhibition efficiency of 98 %. A synergistic effect exists between SMV and adipic acid with the synergism parameters greater than 1. Mechanistic aspects of corrosion inhibition have been studied by electrochemical methods like potentiodynamic polarization and electrochemical impedance spectroscopy. FTIR spectra reveal that the protective film consists of Fe^{2+}-SMV complex and Fe^{2+}-adipic acid complex. The protective film has been analyzed by fluorescence spectra, SEM and EDAX.

Keywords

Carbon steel, corrosion inhibition, fluorescence, synergism parameters, SEM, adipic acid, sodium metavanadate**.**

Introduction

Vanadium based oxy-anion, also referred to as vanadate, has been investigated as corrosion inhibitor for Al alloys [1-4]. Smith *et al.* explored the release kinetics and protection performance of vanadate based pigments in epoxy-coated AA 2014-T6 panels [5]. Cook *et al*. investigated several corrosion inhibitors including vanadates, molybdates and ions of rare earth elements like Ce, Y and La [6]. Blanc *et al.* developed a surface conversion process for aluminium alloy based on acidic vanadium formulations which imparted protection to AA 2024-T3 coated panel [7]. These

coating can be characterized by optical microscopy and scanning electron microscopy. Schumz and Frankel performed several AFM Scraching experiments on pure Al and AA 2024-T3 [8-10]. Buchheit *et al.* noticed that vanadates from the coating can impart active corrosion protection [11]. ^{51}V nuclear magnetic resonance spectroscopy (NMR) has been used to prove that the inhibition efficiency of vanadate strongly depends on the speciation [12-14]. It was shown that the clear meta vanadate solutions inhibited AA 2024-T3 corrosion to an extent similar to chromate while orange decavanadate solution was poor inhibitor

Experimental

Preparation of the specimens

Carbon steel specimens, containing 0.02 - 0.03 % S, 0.03 - 0.08 % P, 0.4 - 0.5 % Mn, 0.1 - 0.2 % C, of the dimensions 40×10×2 mm were polished to a mirror finish, degreased with trichloroethylene, and used for weight-loss and surface examination studies. For potentiodynamic polarization studies, carbon steel encapsulated in Teflon, with an exposed cross section of 5 mm diameter, was used as the working electrode. The working electrode surface was polished to a mirror finish and it was degreased with trichloroethylene.

Solution preparation

Clear metavanadate solution was prepared by dissolving 1 g $NaVO_3$ in 100 ml double distilled water. The adipic acid solution was prepared by dissolving 1 g $COOH\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}COOH$ in 100 ml double distilled water.

Weight-loss method

Three mild steel specimens were immersed for a period of three days in 100 ml of the neutral aqueous test solutions (with a chloride content of 60 ppm) containing various concentrations of adipic acid as the inhibitor in the absence and presence of SMV. After the exposure, corrosion products were removed with Clarke's solution [15], and the weights of the specimens before and after the immersion were determined using a SHIMADZU AY62 electronic balance.

The percentage of inhibition efficiency (*IE*) was calculated using the following equation:

$$IE = \frac{W_1 - W_2}{W_1} 100 \quad (1)$$

W_1 = corrosion rate (CR) in the absence of inhibitor and

W_2 = corrosion rate (CR) in the presence of inhibitor

The corrosion rate was calculated using the following formula:

$$\text{Corrosion rate, mm year}^{-1} = \frac{\text{Loss in weight, mg}}{\text{Surface area of specimen, dm}^2 \times \text{period of imersion, day}} \times \frac{0.0365}{\rho} \quad (2)$$

ρ-density of the metal in g cm^{-2} (7.86).

Potentiodynamic polarization studies

The polarization studies were carried out in a three-electrode cell assembly, using carbon steel as the working electrode, platinum as the counter electrode and saturated calomel electrode (SCE) as the reference electrode. Electrochemical impedance and polarization curve measurements were achieved using H & CH model CHI 660A provided with *iR* compensation option. Polarization curve measurements were carried out at scan rate of 0.01 V s^{-1}. The exposed area (1 cm^2) was

mechanically polished with a series of emery sheets of variable grade. The samples were washed thoroughly with double distilled water before insertion in the cell. During the polarization study, the scan rate was 0.01 V s^{-1}; hold time at *Ef* was 0 s and quiet time was 2 s.

AC impedance spectra

AC impedance spectra were recorded using the same instrument as for polarization study and the same type of three electrode cell assembly. The real part *Z*' and imaginary part *Z*'' of the cell impedance were measured in Ω for various frequencies. The charge transfer resistance (R_t) and double layer capacitance (C_{dl}) values were calculated.

$$R_t = (R_s + R_t) - R_s \quad (3)$$

$$C_{dl} = ½ \pi R_t f_{max} \quad (4)$$

where R_s = solution resistance, f_{max} = maximum frequency.

AC impedance spectra were recorded with dc potential E = 0 V, in the frequency range $1x10^5$ - 10 Hz, amplitude = 0.005 V, and quiet time = 2 s.

Analysis of the protective film

The carbon steel samples were immersed in various test solutions for a period of three days. After three days samples were taken out and dried up. The film formed on the metal surface was carefully removed, mixed thoroughly with KBr and made as pellets samples which were recorded using Perkin Elmer FTIR 1600 spectrometer. The UV and Fluorescence spectra were recorded using Hitachi F-4500 fluorescence spectrophotometer. Surface analysis by SEM was recorded with JOEL MODEL 6390 to study the surface smoothness of the metal.

Synergism parameter

The synergism parameter can be calculated by using the equation indicating the synergistic effect existing between the inhibitors [16-18]:

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

where $\theta_{1+2} = (\theta_1 + \theta_2) - (\theta_1\theta_2)$,

θ_1 = Surface coverage by substance 1

θ_2 = Surface coverage by substance 2

θ'_{1+2} = combined surface coverage for substance 1 and substance 2

Let the surface coverage be represented by θ; $\theta = IE/100$.

If synergistic effect exists between the inhibitors, S_I value will be greater than 1.

Analysis of variance (F-test)

An F-test was carried out to investigate whether the synergistic effect existing between inhibitor systems is statistically significant [19]. If *F*-value is greater than 5.32 for 1,8 degrees of freedom, the synergistic effects proves to be statistically significant. If it is less than 5.32 for 1,8 degrees of freedom, it was statistically insignificant at a 0.05 level of significance.

Results and Discussion

Weight-loss method

Corrosion rate of carbon steel in an aqueous solution containing 60 ppm of Cl^- in the presence and absence of inhibitor was obtained by weight loss method.

The inhibition efficiency is given in Table 1. It is observed that sodium metavanadate (SMV) has good inhibition efficiency (IE), *i.e*. as the concentration of SMV increases the inhibition efficiency also increases: 250 ppm of SMV has *IE* = 56 % and 250 ppm of adipic acid (AA) has *IE* = 61 %, but the combination of 250 ppm of SMV and 250 ppm of adipic acids show *IE* = 98 %. This suggests a synergistic effect between the binary inhibitor formulation of SMV and AA.

Table 1. *Corrosion rates (CR) of carbon steel in aqueous solution containing 60 ppm Cl^- in the presence of inhibitor obtained by weight-loss method. Inhibitor: SMV – AA, immersion period: 3 days*

Amount of SMV, ppm	Amount of AA, ppm	*IE* / %	*CR* / mm $year^{-1}$
0	0	-	1.0374
50	0	8	0.9544
100	0	12	0.9544
150	0	29	0.6933
200	0	32	0.5765
250	0	56	0.4564
0	50	33	0.7261
0	100	40	0.6221
0	150	48	0.5390
0	200	56	0.4564
0	250	61	0.4044
250	50	64	0.3697
250	100	92	0.0826
250	150	96	0.0411
250	200	96	0.0411
250	250	98	0.0310

Synergism parameter

The value of synergism parameter is shown in Table 2, here values of S_I are greater than 1 suggesting a synergistic effect. S_I approaches 1 when no interaction exists between the inhibitor compounds. If $S_I > 1$ it shows that the synergistic effect exists between the inhibitor compounds. In the case of $S_I < 1$ the negative interaction of inhibitor prevails (*i.e.* the corrosion rate increases).

Table 2. *Inhibition efficiencies and synergism parameters for various concentrations of AA-SMV (250 ppm) system, when carbon steel is immersed in aqueous solution containing 60 ppm of Cl^-. Immersion period: 3 days, pH 7*

Amount of AA, ppm	*IE* / %	θ_1	Amount of SMV, ppm	*IE* / %	θ_2	I'_{1+2}	θ_{1+2}	S_I
50	33	0.33	250	56	0.56	64	0.64	0.75
100	40	0.40	250	56	0.56	92	0.92	3.3
150	48	0.48	250	56	0.56	96	0.96	5.72
200	56	0.56	250	56	0.56	96	0.96	4.84
250	61	0.61	250	56	0.56	98	0.98	8.8

Analysis of variance (ANOVA)

F-test is used to confirm if the synergistic effect existing between SMV and AA is statistically significant. The results are given in Table 3. The influence of various concentrations of adipic acid (50, 100, 150, 200, 250 ppm) on the inhibition efficiency 250 ppm of SMV is tested in Table 3 for the statistical significance. The observed F-value 6.17 is greater than the critical F-value (5.32) for 1,8 degrees of freedom at 0.05 level of significance so it was concluded that the synergistic effect existing between sodium metavanadate and AA is statistically significant.

This is in agreement with conclusion derived from the calculation of synergism parameter.

Table 3. *Distribution of F-Value between the inhibition efficiencies of the influence of SMV-AA*

Source of variance	Sum of squares	Degree of freedom	Mean square	F	Level of significance
Between the sample	1708	1	1708	6.17	$p < 0.05$
With the sample	521	8	278		

Analysis of FTIR spectra

The FTIR spectrum of pure SMV is shown in Fig 1a. The vanadate stretching frequency of the sodium metavanadate appears at 1385 cm^{-1}. The FTIR spectrum of pure adipic acid (AA) is shown in Fig 1b. The -C=O stretching frequency appears at 1650 cm^{-1}, $-OH^-$ stretching frequency at 3413 cm^{-1}, and -CH stretching frequency appears at 2900 cm^{-1}. The FTIR spectrum of film formed on the carbon steel surface after immersion in solution containing 250 ppm of SMV and 250 ppm of adipic acid is shown in Fig. 1c. The vanadate frequency of sodium metavanadate increased from 1385 cm^{-1} to 1389 cm^{-1}. The $-OH^-$ stretching frequency shifted from 3413 cm^{-1} to 3434 cm^{-1}. The stretching frequency of carboxylic acid shifted from 1650 cm^{-1} to 1639 cm^{-1}. This indicates that the oxygen atom of carboxyl group has coordinated with Fe^{2+}-AA and Fe^{2+}-SMV complex on the metal surface [20].

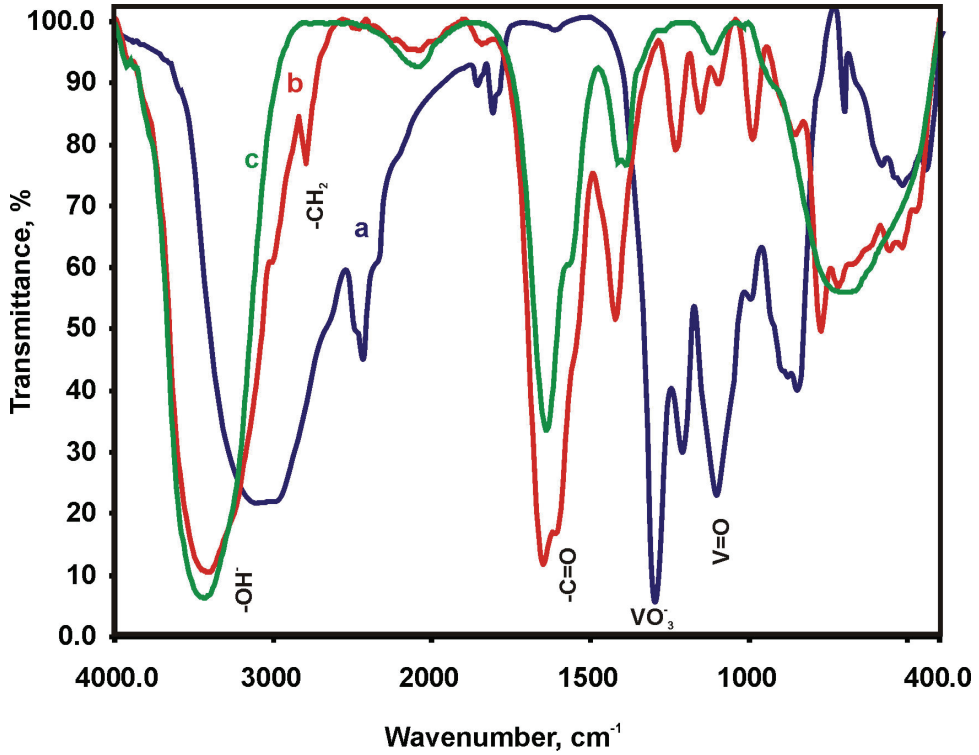

Figure 1. *FTIR spectra of* ***(a)*** *Pure SMV.* ***(b)*** *Adipic Acid,* ***(c)*** *Film formed on the metal surface after immersion in the solution containing 50 ppm of* Cl^- *+ 250 ppm of SMV + 250 ppm of AA*

Analysis of fluorescence spectra

The analysed formulation contains 250 ppm of SMV and 250 ppm of adipic acid. Its emission spectrum (λ_{ex} = 300 nm) is shown in Fig 2a. The peak appears at 400 nm.

Solution containing 250 ppm of SMV and 250 ppm of adipic acid were mixed with a few drops of freshly prepared Fe^{2+} ions (ferrous sulphate) solution. After drying, its emission spectrum (λ_{ex} = 300 nm) is shown in Fig 2b. The intensity of the peak shifted from 400 to 403 nm [21]. The increase in intensity of the peak is due to the fact that the metal surface, after the formation of the protective film, is very bright and the film is very thin. Only one peak is obtained. Hence it is inferred that the complex is somewhat highly symmetric in nature.

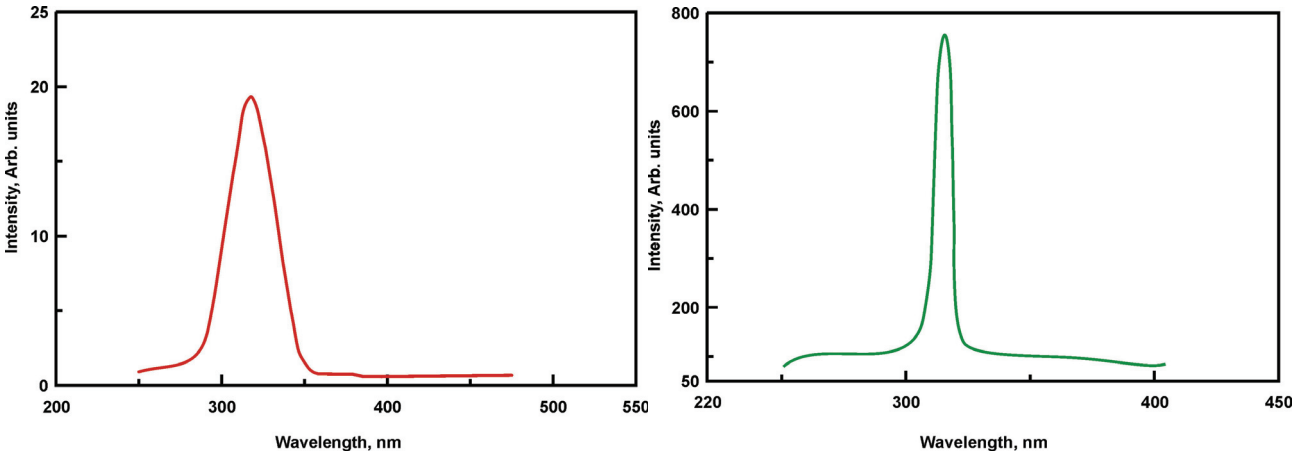

Figure 2. *Fluorescence spectra of: (a) SMV + Fe^{2+}, (b) SMV + AA + Fe^{2+}*

Analysis of potentiodynamic polarization curve

Polarization study has been carried out to confirm the formation of protective film formed on the metal surface during the corrosion inhibition process. If a protective film is formed on the metal surface, the linear polarization resistance value (LPR) increases and the corrosion current value (I_{corr}) decreases.

The potentiodynamic polarization curves of carbon steel immersed in aqueous solution containing 60 ppm of Cl^- are shown in Fig. 3 and the corrosion parameters are given in Table 4. When sodium metavanadate and adipic acid were added to the above system, the corrosion potential shifted to the anodic sites of the metal surface. This film controls the anodic reaction by forming Fe^{2+}-SMV and Fe^{2+}-AA complex on the anodic sites of the metal surface.

The formation of a protective film on the metal surface is further supported by the fact that the anodic Tafel slope (b_a) increases from 198 to 288 mV. Furthermore, the linear polarization resistance (LPR) value increases from $2.0157\times10^4\ \Omega\ cm^2$ to $4.0990\times10^4\ \Omega\ cm^2$; the corrosion current decreases from 2.025×10^{-6} A cm^{-2} to 1.120×10^{-6} A cm^{-2}. Thus the polarization study confirms the formation of the protective film on the metal surface [22-23].

Table 4. *Corrosion parameters of carbon steel immersed in an aqueous solution containing 60 ppm of Cl^- in the absence and presence of inhibitors obtained by polarization method*

Amount of		E_{corr}	b_c	b_a	I_{corr}	LPR / Ω cm^2
AA, ppm	SMV, ppm	mV *vs.* SCE	mV $decade^{-1}$	mV decade-1	A cm^{-2}	
0	0	-542	193	198	2.025×10^{-6}	2.0157×10^4
250	250	-554	166	288	1.120×10^{-6}	4.0990×10^4

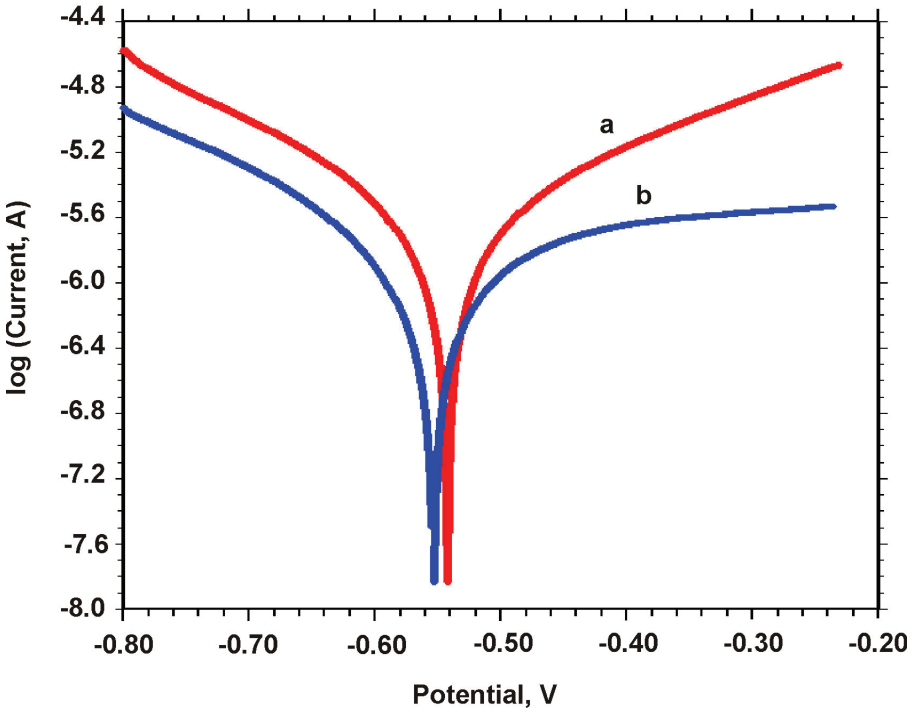

Fig.3. *Polarization curves of carbon steel immersed in various test solutions (a) 60 ppm of Cl^-. (b) 60 ppm of Cl^- + 250 ppm of SMV + 250 ppm of AA*

Analysis of AC impedance spectra

AC impedance spectra (electrochemical impedance spectra) have been carried out to confirm the formation of the protective film on the metal surface since charge transfer resistance (R_{ct}) increases, double layer capacitance value (C_{dl}) decreases and the impedance log (Z/Ω) value increases. The AC impedance spectra of carbon steel immersed in aqueous solution containing 60 ppm of Cl^- in the absence and presence of inhibitors are shown in Figs. 4a,b (Nyquist plots) and in Figs. 5a,b (Bode plots). The impedance log (Z/Ω) values derived from Bode plots are also given in Table 4.

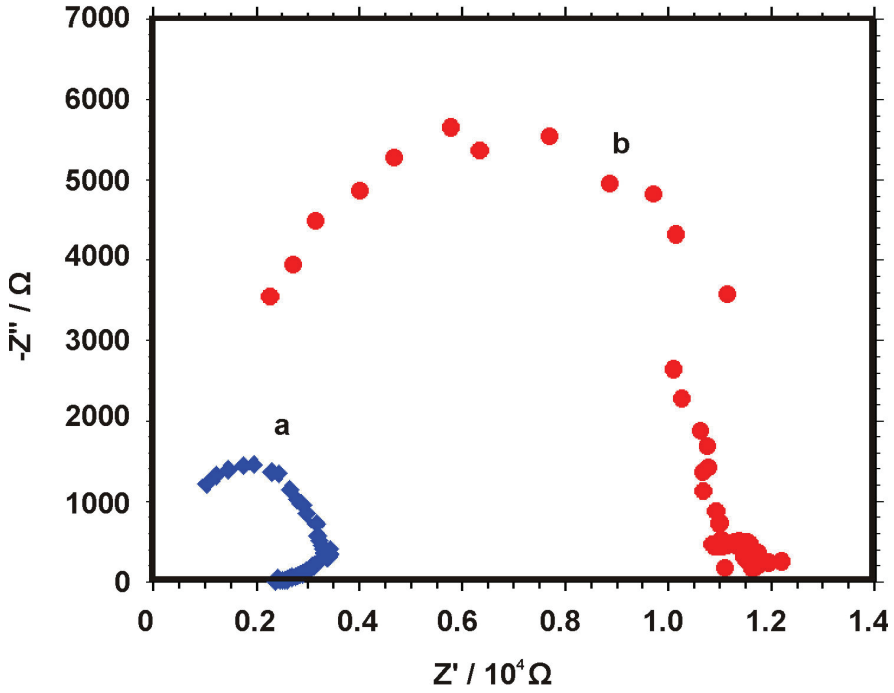

Figure 4. *AC impedance spectra (Nyquist plot) of carbon steel immersed in various test solutions:* ***(a)*** *60 ppm of Cl^-.* ***(b)*** *60 ppm of Cl^- + 250 ppm of SMV + 250 ppm of AA*

AC impedance parameters, namely, charge transfer resistance (R_{ct}) and double layer capacitance (C_{dl}) are given in Table 5 for the aqueous solution containing 60 ppm of Cl^- . The obtained values are: R_{ct} 2500 Ω cm^2 and C_{dl} value of 2.04×10^{-8}. When adipic acid and SMV are added to aqueous solution containing 60 ppm Cl^-, R_{ct} value increases from 2500 Ω cm^2 to 3500 Ω cm^2. The C_{dl} value decreased from 2.04×10^{-8} to 1.45×10^{-8} F cm^{-2}. This suggests that the protective film is formed on the metal surface.

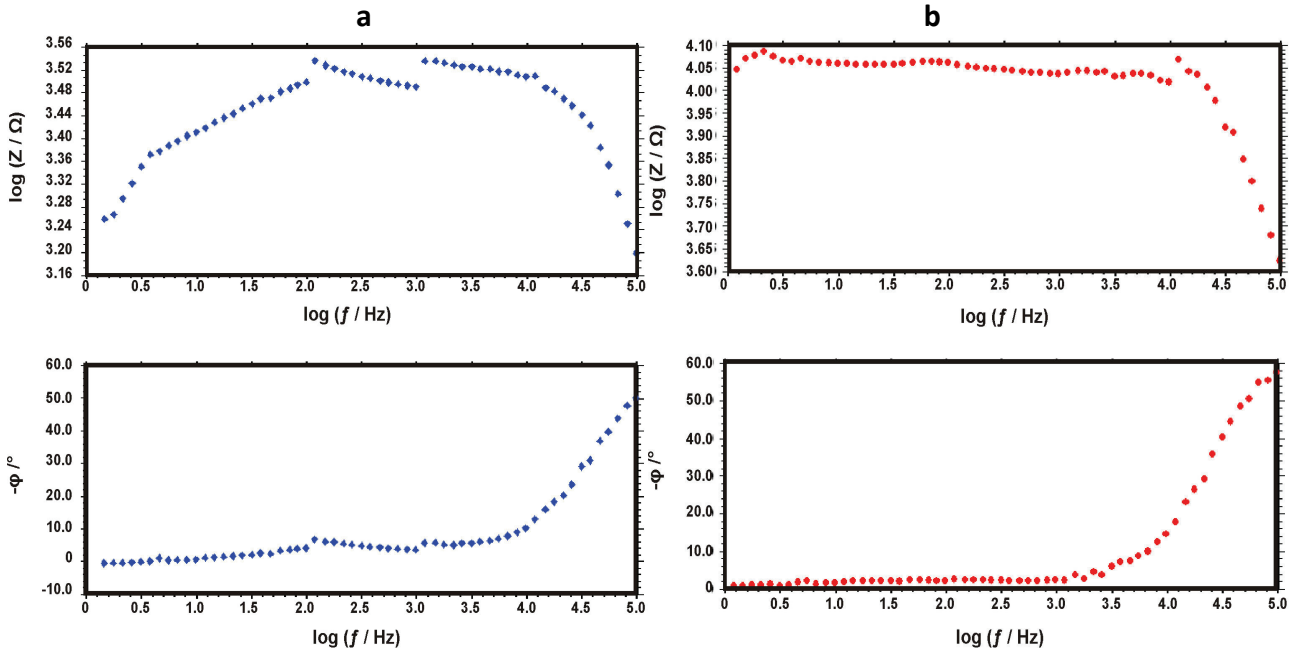

Figure 5. *AC impedance spectra (Bode plots) of carbon steel immersed in various test solutions:* ***(a)*** *60 ppm of Cl^-* ***(b)*** *60 ppm of Cl^- + 250 ppm of SMV + 250 ppm of AA*

Table 5 : *Corrosion parameters of carbon steel immersed in an aqueous solution containing 60 ppm Cl^- in the absence and presence of inhibitors obtained by AC impedance spectra*

Amount of AA, ppm	Amount of SMV ppm	Nyquist plot		Bode plot
		R_t /Ω cm^2	C_{dl} / F cm^{-2}	log (Z / Ω)
0	0	2500	2.04×10^{-8}	3.125
250	250	3500	1.45×10^{-8}	3.44

Scanning electron microscopy (SEM)

The SEM images of different magnification (×500, ×1000) of carbon steel specimen immersed in an aqueous solution containing 60 ppm Cl^- for 3 days in the absence and presence of inhibitor systems are shown in Figs. 6(b,d) and 6(c,f), respectively.

The SEM micrographs of polished carbon steel in Figs. 6(a,b) show the smooth surface of the metal. The carbon steel surface immersed in aqueous solution containing 60 ppm Cl^-, Figs. 6(b,d), shows the roughness of the metal surface that indicates the corrosion of carbon steel. Figs. 6(c,f) indicate that in the presence of inhibitor the rate of corrosion is suppressed, as it can be seen from the decrease of the corroded area. In the presence of SMV + AA, the surface is covered by a thin layer of inhibitors, which effectively controls the dissolutions of carbon steel [24].

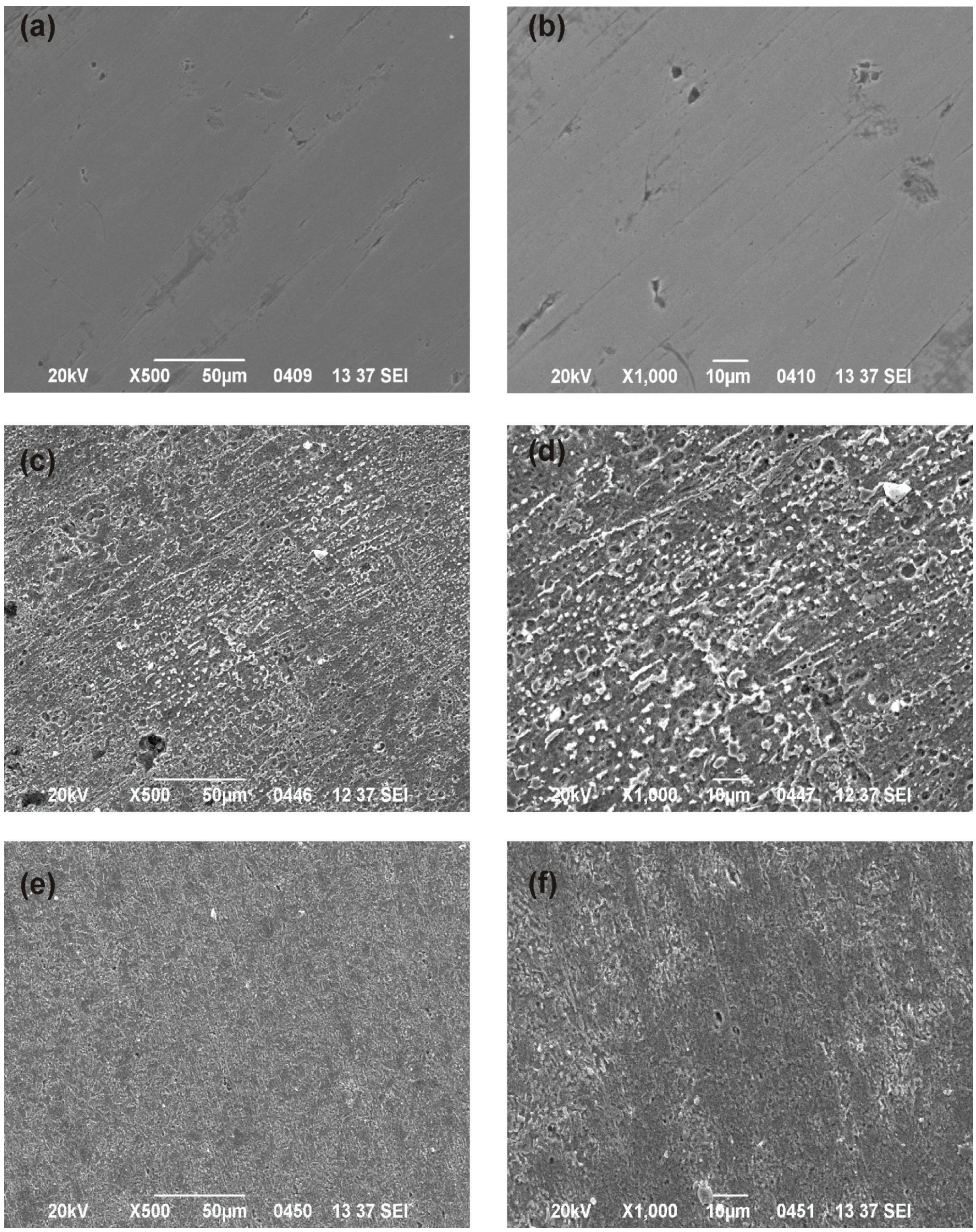

Figure 6. *SEM micrographs of* ***(a)*** *Polished carbon steel (Control) (magnification ×500);* ***(b)*** *Polished carbon steel (Control) (magnification ×1000),* ***(c)*** *60 ppm of Cl^- (magnification ×500),* ***(d)*** *60 ppm of Cl^- (magnification ×1000),* ***(e)*** *Cl^- 60 ppm + AA 250 ppm + SMV 250 ppm (magnification ×500),* ***(f)*** *Cl^- 60 ppm + AA 250 ppm + SMV 250 ppm (magnification ×1000)*

EDAX analysis

EDAX analysis of various surfaces is shown in Fig. 7. The EDAX analysis of polished carbon steel is shown in Fig.7a.

The EDAX analysis of polished carbon steel immersed in an aqueous solution containing 60 ppm of Cl^-, 250 ppm of AA and 250 ppm of SMV is shown in Fig. 7(b). Due to the formation of Fe-inhibitor complexes formed on the metal surface in presence of AA and SMV, the observed Fe signal is high in Fig 7a and low in Fig 7b. Thus the presence of vanadate on the metal surface is confirmed. It is also found that the intensity due to oxygen increases in Fig. 7b. This is due to the adsorption of carboxyl group of adipic acid of the inhibitor system. Thus it is concluded that the protective film consists of Fe^{2+}-adipic acid complex and Fe^{2+}-vanadate complex.

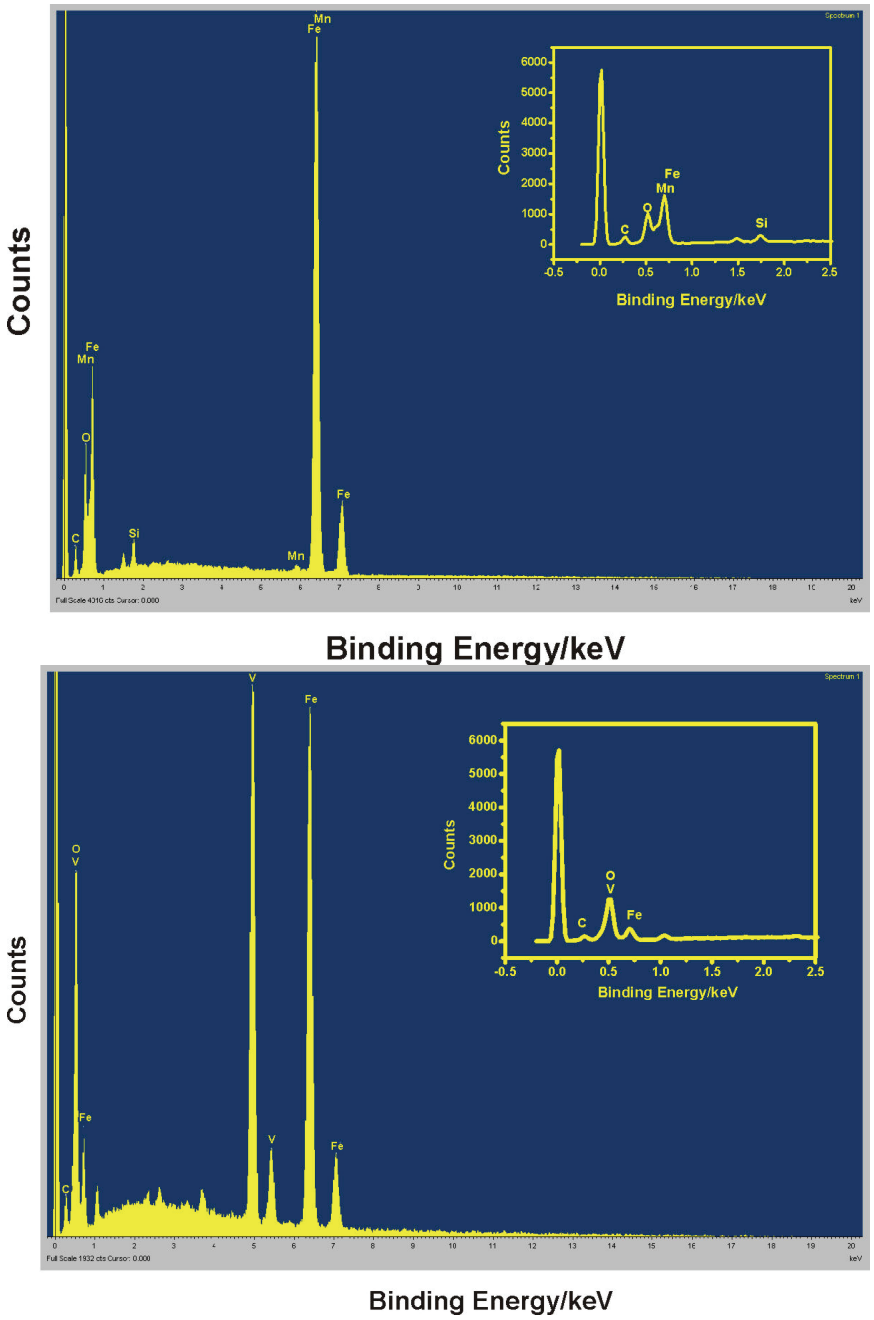

Figure 7. *EDAX* ***(a)*** *Polished carbon steel (blank)*
(b) *Carbon steel in the solution containing 60 ppm Cl^- + 250 ppm of AA + 250 ppm of SMV*

Conclusions

The corrosion inhibition by sodium metavanadate and adipic acid in aqueous solution containing 60 ppm of Cl^- in the presence and absence of inhibitor was studied by weight-loss study and electrochemical measurements. The results show that inhibitor has the ability of reducing the corrosion rate of carbon steel in aqueous solution containing 60 ppm of Cl^-, and it acts as an anodic inhibitor. This effectiveness is confirmed by electrochemical impedance spectra and potential polarization analysis. The SEM image in the presence of the inhibitor shows the formulation of the inhibitor layer. EDAX analysis revealed that vanadium is adsorbed on the metal surface. The formulation consisting of 250 ppm of SMV and 250 ppm adipic acid shows more than 96 % inhibition efficiency and no pitting tendency.

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