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Metavanadate(V) Anions as Corrosion Inhibitor for Carbon Steel in Acid Chloride Solution

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The influence of metavanadate(V) anions (VO_3^-) concentration on the corrosion of S235 carbon steel in acid chloride solutions were studied. The investigations were involved by electrochemical polarization methods. Tafel polarization study revealed that of VO_3^- ions were acted as a mixed-type inhibitor. The inhibition efficiency increased with an increase in the concentration of metavanadate anions. The adsorption of VO_3^- has been found to occur on the surface of S235 carbon steel according to the El-Awady isotherm. The corrosion kinetic parameters of carbon steel, and adsorption thermodynamic parameters for metavanadate(V) anions were determined and discussed.

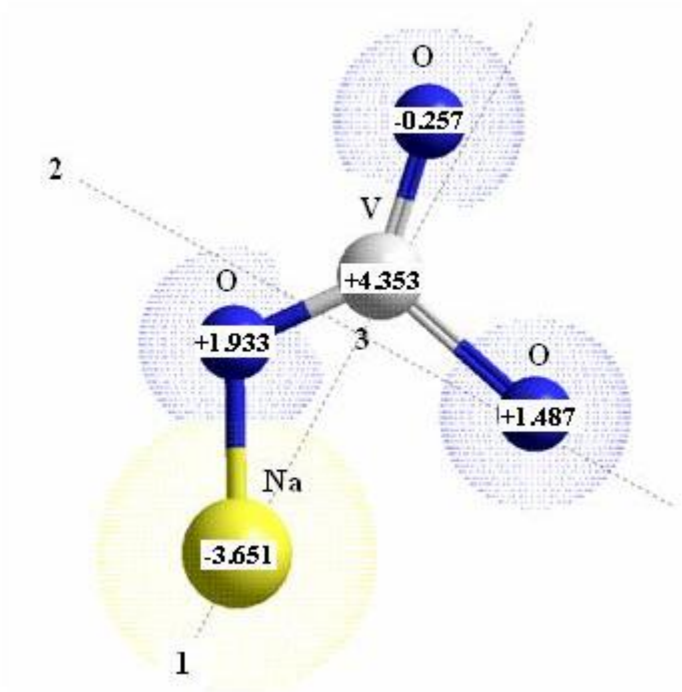
Keywords: A. S235 carbon steel; A. Metavanadate(V) anion; C. Corrosion rate; C. Kinetic parameters; C. Thermodynamic parameters, C. El-Awady isotherm

1. INTRODUCTION

Carbon steel (CS) is widely used as a construction material in many industries such as metallurgy, chemical industry and the production and refining of crude oil [1]. Unfortunately, CS undergoes corrosion under the action of hydrochloric acid used for pickling iron and its alloys [2,3]. These actions cause the corrosion of equipment, pipes and pipelines made of carbon steel. The use of organic compounds to inhibit corrosion of carbon steel has assumed great significance due to their application in preventing corrosion under various corrosive environments.

The corrosion inhibitors are compounds which, added in small quantities considerably reduce the rate of corrosion. Most of the well-known organic inhibitors are heterocyclic compounds containing π-electrons, heteroatoms like nitrogen, oxygen or sulphur and aromatic rings [4-7]. Inorganic inhibitors are not so popular. The cost of inorganic inhibitors is low, but most of them are toxic among them: mercuride, chromate, nitrite, arsenate ect. [8]. Moreover, the metavanadate compounds are not toxic, for example of sodium metavanadate(V) ($NaVO_3$) [9]. However, in the available scientific literature there is no information regarding the protective properties of metavanadate salts with regard to carbon steel especially in acid solutions.

The distribution of charge densities in the $NaVO_3$ molecule was calculated by ZINDO/1 semiempirical method using a HyperChem v. 7.5 software. The molecular structure of $NaVO_3$ is given in Scheme 1.



Scheme 1. Molecular structure of sodium metavanadate(V) obtained after a geometric optimization procedure

It was affirmed, that molecule of sodium metavanadate(V) is flat. The largest positive partial of charge density be concentrated on atom of vanadium ($\delta = +4.353$). However, the largest negative partial of charge density be situates on atom of sodium ($\delta = -3.651$).

The aim of the research concerned the influence of VO_3^- concentration on the corrosion of S235 carbon steel in an acid chloride solution. Potentiodynamic polarization methods has been used for appoint corrosion parameters of carbon steel. Moreover, the surface of the working electrode was observed by an optical microscope.

2. EXPERIMENTAL

2.1. Solutions

Sodium metavanadate(V) ($NaVO_3$) (99.9%) was purchased from Sigma-Aldrich (USA). The electrolytes were prepared using analytical grade reagents (Merck). The corrosive medium was prepared from a stock NaCl and 1.0 M HCl solution. The concentration of sodium metavanadate(V) was changed in the range from 0 to 20 mM in 1.2 M Cl^- acid solutions (pH 1.5). All solutions were prepared from double distilled water. For each experiment a freshly made solution was used. All test have been performed in naturally aerated electrolytes.

2.2. Electrodes and apparatus

Experiments were carried out in a three-electrode glass cell with a 200 cm^3 capacity. The testing material was S235 carbon steel. The elements compositions at weight percentages (wt.%) of the investigated carbon steel are show in Table 1.

Table 1. Chemical composition of S235 carbon steel

Element	C	S	P	Si	Mn	Cr	Ni	Cu	Fe
wt.(%)	<0.22	<0.050	<0.050	0.10-0.35	<1.10	<0.30	<0.30	<0.30	balance

The working electrode was prepared in the shape of rectangle which has got a surface area of 0.22 cm^2. Prior to each experiment, the working electrode surface was treated with 800, 1200, and 2000 grade emery paper to give a mirror like surface finish, and then thoroughly rinsed with double distilled water. After this the electrode was degreased with ethanol in an ultrasonic bath (about 5 min) and then rinsed with double distilled water. The electrode was taken immersed in the test electrolyte.

Electrode potentials were measured and reported against the external saturated calomel electrode (SCE) connected with solution via a Luggin capillary. The capillary tip was opposite to the end of the surface working electrode about 3 mm.

A platinum wire (99.99% Pt) was used as an auxiliary electrode.

Reference and auxiliary electrodes were individually isolated from the test solution by adjusted accordingly glass frits.

All voltammetric experiments were performed using a potentiostat/galvanostat PGSTAT 128N, AutoLab, Netherlands with NOVA 1.7 software the same firm.

The values reported in the paper represent mean values of at least three replicate measurements. Moreover, all experiments were carried out at suitably well-chosen temperature (25±0.5 ^{0}C) which was maintained by a thermostat with the forced air circulation.

2.3. Potentiodynamic experiments

The electrochemical behaviour of S235 carbon steel sample in uninhibited and inhibited solution was studied by recording potentiodynamic polarization curves. The electrode potential was changed in the range from -900 to -100 mV vs. SCE at a scan rate of 1 mV s^{-1}. The linear Tafel segments of cathodic and anodic curves were extrapolated to corrosion potential (E_{corr}) to obtain corrosion current densities (j_{corr}), and the Tafel slopes the cathodic (b_c) and anodic (b_a) were calculated.

The polarization resistance (R_p) were evaluated on the basis of j_{corr} values using the relationship [10,11]:

$$R_p = \frac{B}{j_{corr}} \tag{1}$$

where B is constant which was obtained by following equation:

$$B = \frac{b_c b_a}{2.303\ (b_c + b_a)} \tag{1a}$$

where b_c, b_a are the Tafel slopes.

Moreover, the degree of surface coverage of electrode, and the corrosion inhibition efficiency were calculated from the equations:

$$\theta = 1 - \frac{j_{corr}}{j^0_{corr}} \tag{2}$$

and:

$$IE(\%) = \frac{j^0_{corr} - j_{corr}}{j^0_{corr}} \times 100 \tag{3}$$

where j_{corr} is the corrosion current density at a particular inhibitor concentration, and j^0_{corr} is the corrosion current density in the absence of inhibitor in the solution.

All the recorded j_{corr} values are converted into the corrosion rate using the expression:

$$v_p(mm\, y^{-1}) = 3280 \times 10^{-3}\, \frac{j_{corr} M}{n\rho} \tag{4}$$

M is the molar mass of iron, n is the number of electrons transferred in the corrosion reaction, and ρ is the density of iron.

2.4. Additional measuring instrument

The surface morphology of S235 carbon steel electrode before, and after measurements were observed by an inverted optical microscope metallographic OLYMPUS GX51 BD/BF.

3. RESULTS AND DISCUSION

3.1. Potentiodynamic polarization measurements

The potentiodynamic polarization measurements were carried out in order to gain knowledge concerning the kinetics of the cathodic and anodic reactions in the aggressive chloride solutions. Therefore, the measurements begun by examining the effect of chloride ion concentrations on the corrosion of carbon steel. Therefore, the concentration of chloride ion was changed in the range from 1.2 to 2 M. For this purpose, a solution containing 1 M NaCl was supplemented by adding an appropriate volume of HCl. We found that the pH electrolytes were changed in the range from 1.5 to 0.5. The potentiodynamic polarization curves are presented in Figure 1.

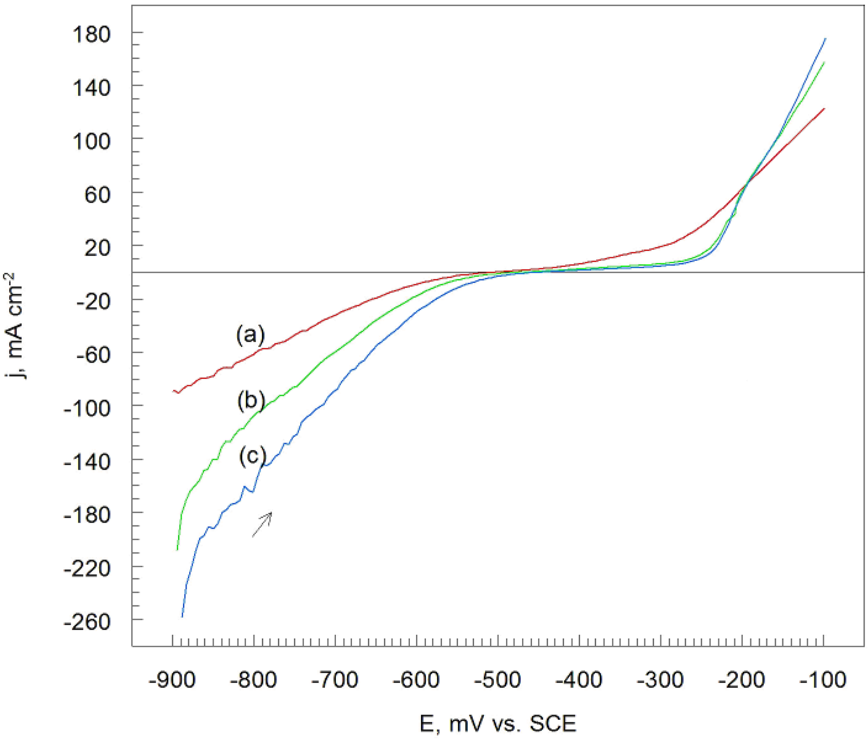


Figure 1. Potentiodynamic polarization curves for S235 carbon steel in solutions containing: (a) 1.2, (b) 1.5, and (c) 2.0 M Cl^-, scan rate 1mV s^{-1}, at 25 ^{0}C

The mechanism of corrosion process of carbon steel in aggressive solutions is well known and can be found in many publications [12-21]. The most important steps in the process corrosion of S235 carbon steel in acid chloride environments are as follows:

a) cathodic hydrogen evolution:

$$Fe + 2H^+ + 2e^- \rightarrow Fe + H_2, \quad (5)$$

b) dissolution of iron in acid environment of Cl^- ions:

$$Fe + Cl^- \rightarrow (FeCl)_{ads} + e^- \quad (6)$$

or:

$$(FeCl)_{ads} \rightarrow Fe^{2+} + Cl^- + e^-, \quad (6a)$$

c) tested electrolyte was not deoxygenated, therefore:

$$2Fe + 4H^+ + 5/2\, O_2 \rightarrow \underline{Fe_2O_3} + 2H_2O + 16e^-, \quad (7)$$

the steel indicator electrode surface was covered with a black of iron(III) oxide. We suppose that it is of γ Fe_2O_3 probably. The oxide layer is homogenous, tight and adheres well to the electrode surface. It should be noted that after exceeding the potential of approximately of -250 mV (Fig. 1) rapidly increasing current density, because the oxide layer of Fe_2O_3 was dissolved, and the electrode surface is further oxidized.

The corrosion parameters i.e. corrosion potential (E_{corr}), cathodic and anodic Tafel slopes (b_c) and (b_a), and corrosion current density (j_{corr}) were obtained from the Tafel extrapolation of the potentiodynamic polarization curves (Fig. 1), and were listed in Table 2.

Table 2. Corrosion parameters for S235 carbon steel in acid chloride solutions, at 25 ^{0}C

Concentration Cl^- M	E_{corr} mV vs. SCE	$-b_c$	b_a	j_{corr} mA cm^{-2}
		mV dec^{-1}		
1.2	-504	115	140	1.26
1.5	-463	110	215	1.08
2.0	-446	105	220	0.92

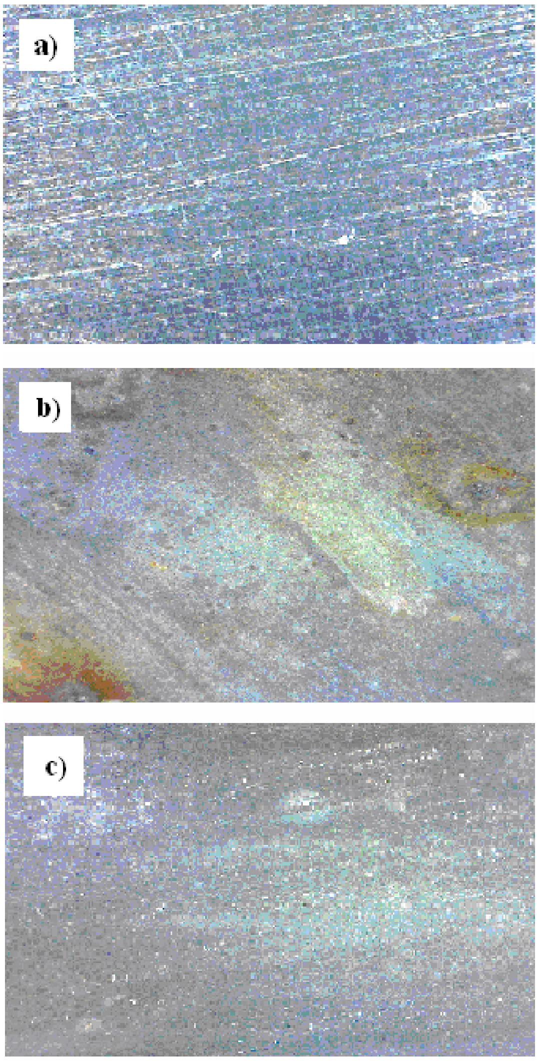


Figure 2. Surface morphology of S235 carbon steel electrode: a) before, b), and c) after measurements. Electrolytes were contained: b) 1.2, and c) 2.0 M Cl^-. Magnification 50×

It was found that E_{corr} shifted imperceptibly toward more positive values with an increase in the concentration of Cl^-. Moreover, a decrease cathodic (b_c), and increase anodic (b_a) Tafel slopes indicated a mixed effect of Fe_2O_3 inhibition corrosion mechanism of carbon steel. Moreover, the corrosion current density (j_{corr}) decreased when the concentration of Cl^- were increased.

With increasing concentration of Cl^- ions strongly increases the anticorrosive effect of the oxide layer on the electrode surface.

In order to confirm this assumption we made photos (using an inverted optical microscope metallographic) of the surface morphology of S235 carbon steel electrode before, and after measurements Figure 2. The electrolyte was contain 1.2 and 2.0 M of Cl^-, respectively. Figure 2a) revels that after electrochemical measurements the surface of S235 carbon electrode was strongly damaged in acid of 1.2 M Cl^- solution. On the other hand of carbon electrode (Fig. 2b)) which worked in 2.0 M Cl^- electrolyte was much less destroyed.

Therefore, for the next investigations as corrosive environment were applied solutions which contained 1.2 M Cl^- ions (pH 1.5) because this electrolyte proved to be the most aggressive environment in studied potential range that is, to reach value of -250 mV (Fig. 1).

The potentiodynamic polarization curves for S235 carbon steel in corrosive solution in the absence and presence of sodium metavanadate(V) are shown in Figure 3.

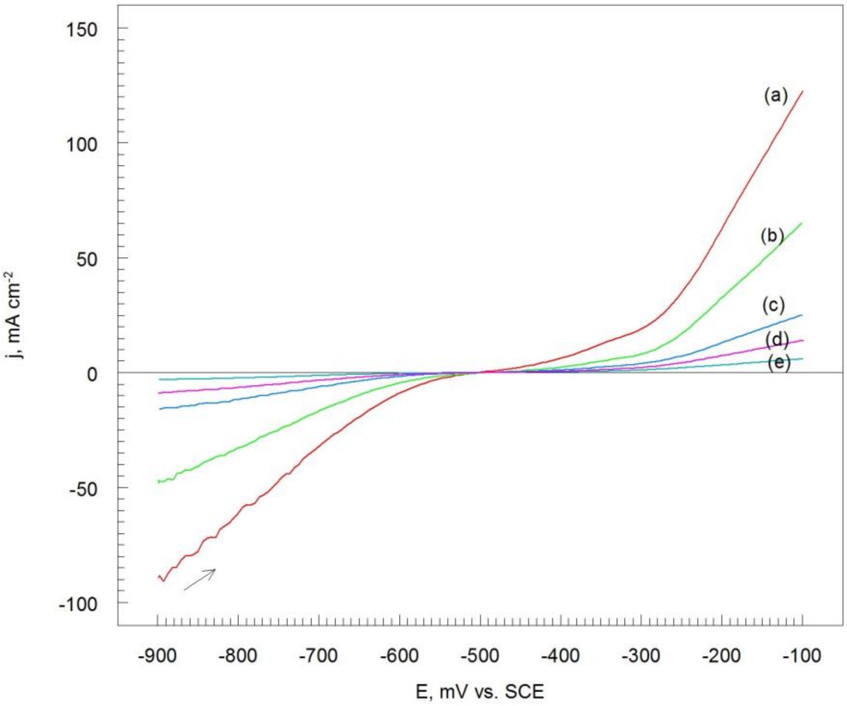


Figure 3. Potentiodynamic polarization curves for S235 carbon steel. Solution containing 1.2 M Cl^- and: (a) 0, (b) 5, (c) 10, (d) 15, and (e) 20 mM $NaVO_3$, scan rate 1 mV s^{-1}, at 25 ^{0}C

It could be observed that both the cathodic and anodic reactions were suppressed with the addition of sodium metavanadate(V) which suggested that VO_3^- ions were reduced the hydrogen evaluation (reaction (5)) and also retarded anodic dissolution of carbon steel (reactions (6) - (7)). The corrosion parameters [14,16-21], and were given in Table 3.

Table 3. Corrosion parameters for S235 carbon steel in 1.2 M Cl^- solution at different concentrations of sodium metavanadate(V), at 25 ^{0}C

Concentration $NaVO_3$ mM	E_{corr} mV vs. SCE	$-b_c$	b_a	j_{corr} mA cm^{-2}
		mV dec^{-1}		
0	-504	115	140	1.26
5	-489	130	145	0.60
10	-494	140	150	0.29
20	-475	160	155	0.18
25	-491	160	155	0.079

It should be noted that E_{corr} shifted imperceptibly (about 13 mV) toward more positive values with an increase in the concentration of sodium metavanadate(V). The slight increase in the corrosion potential means that of VO_3^- should be classified as mixed type inhibitor in the acid chloride environment. Moreover, a increase in both cathodic (b_c) and anodic (b_a) Tafel slopes (Table 3) indicated that the addition of $NaVO_3$ to the electrolyte changes the mechanism of corrosion of the S235 carbon steel. The corrosion current density (j_{corr}) decreased when the concentration of VO_3^- was increased (Table 3) which indicates that the inhibiting effect of VO_3^- increases with increasing concentration of inhibitor.

The polarization resistance (R_p) (Eq. (1)), and the degree of surface coverage (Θ) (Eq. (2)) of S235 carbon steel electrode in the environment electrolytes are showed in Figure 4.

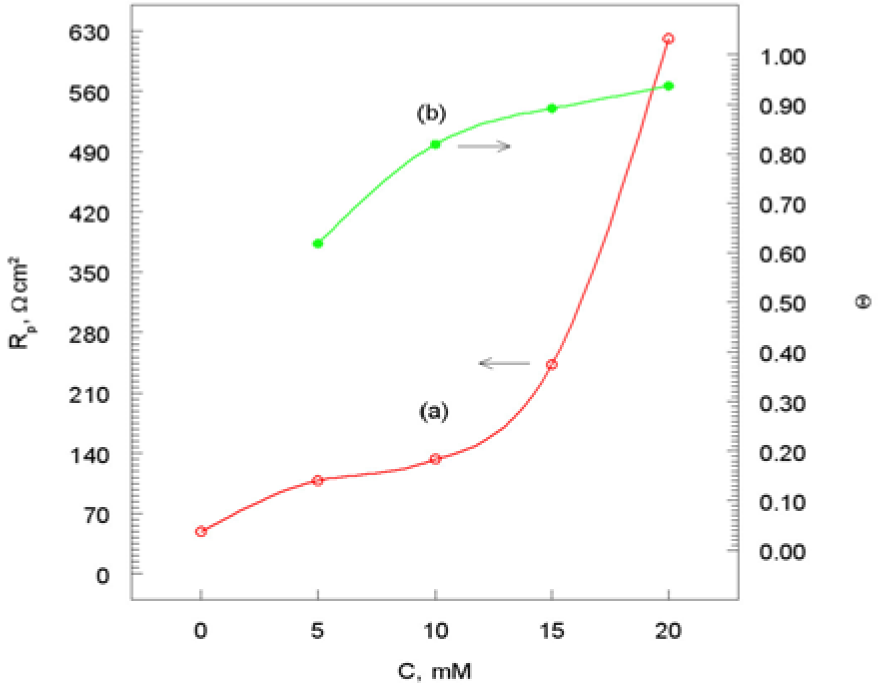


Figure 4. Effect of concentration of $NaVO_3$ on: (a) polarization resistance, and (b) degree of surface coverage of S235 carbon steel electrode. Solution containing 1.2 M Cl^-, concentrations of inhibitor were changed in the range from 0 to 20 mM

The polarization resistance, and degree of surface coverage values of S235 carbon steel were increased with an increase in the concentration of inhibitor (Fig. 4, curves (a) and (b)). Therefore that, the surface of electrode was covered by VO_3^- ions making difficult the exchange the charge and mass with depth of electrolyte. Moreover, we suppose that of metavanadate(V) ions are adsorbed on S235 carbon steel surface.

Figure 5 presented the surface morphology of S235 carbon steel electrode: a) before, and b) – d) after measurements. The electrolyte was contained 1.2 M Cl^-, and the concentration of $NaVO_3$ amounted to 5 or 20 mM, respectively.

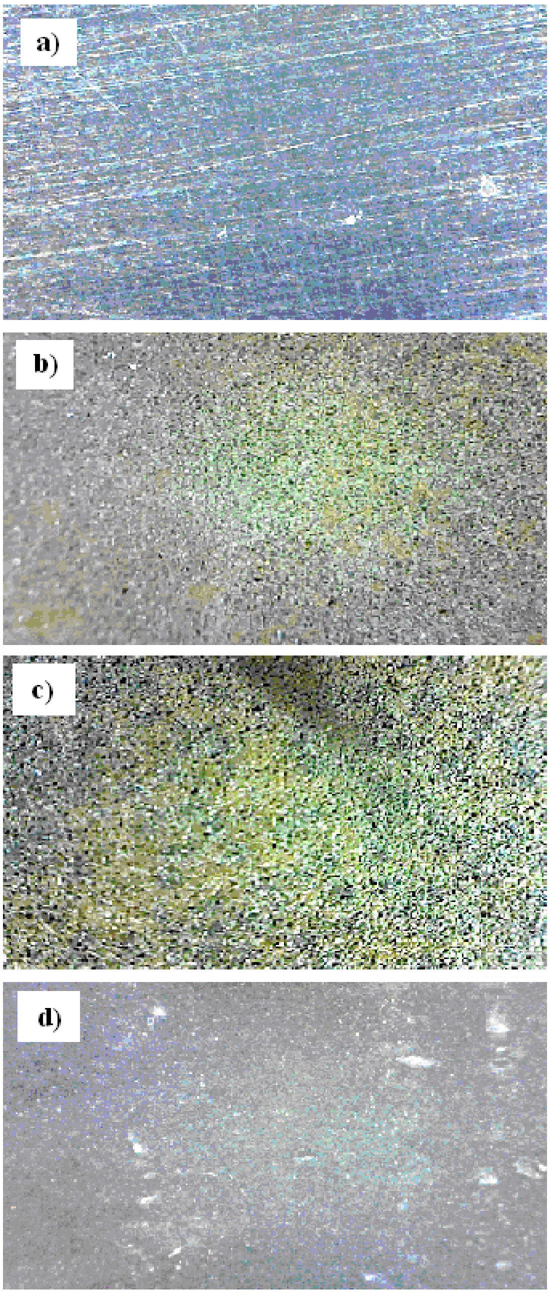


Figure 5. Surface morphology of S235 carbon steel electrode: a) before, and after measurements. Electrolytes were contained 1.2 M Cl^- and: b) 5, c) 20 mM $NaVO_3$, d) after removal of the inhibitor. Magnification 50×

The photographs b) and c) demonstrated that the surface electrodes were covered by VO_3^- film. The inhibitor layers were adhered well to the electrode surface. Moreover, in the case of 20 mM of $NaVO_3$ the film was more thicker, and better protect the surface of S235 carbon steel against the corrosive action of the electrolyte. The Figure 5d) presents surface of electrode after the removal of the inhibiting film. It should be noted that the electrode surface has been slightly damaged as a result of the corrosion process.

Consequently, the corrosion inhibition efficiency values (Eq. (3)) were also calculated on basis polarization tests. The values *IE* are presented in Figure 6.

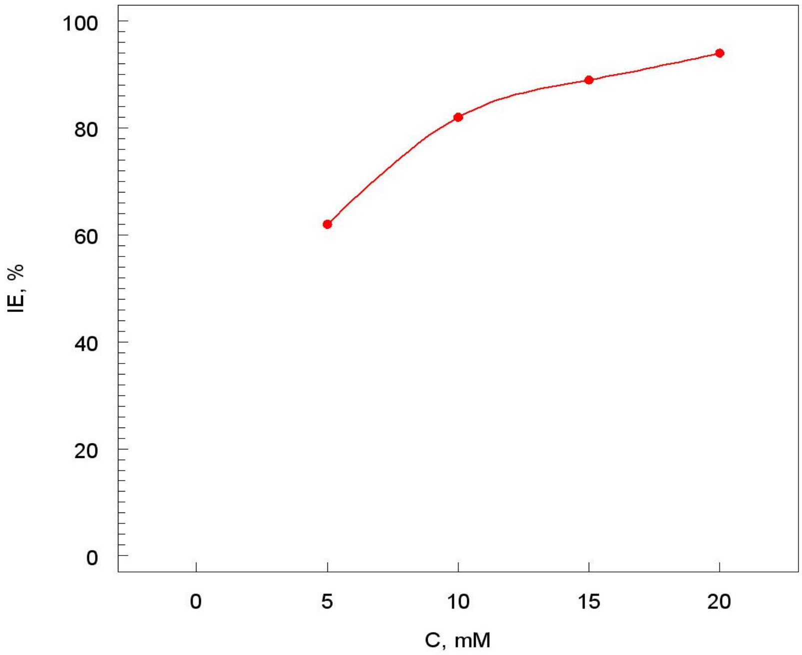


Figure 6. Corrosion inhibition efficiency of S235 carbon steel. Electrolyte was contained 1.2 M Cl^-, and concentrations of inhibitor were changed in the range from 5 to 20 mM

We have shown that in the presence of $NaVO_3$ the inhibition efficiency increases with an increase in the concentration of inhibitor. For the inhibitor concentration of 20 mM the *IE* reaches of 90% value.

3.2. Corrosion rate

The corrosion current densities values (Table 3) were converted into the corrosion rates (Eq. (4)) of S235 carbon steel in acid chloride environments [11,21]. The values of the corrosion rates of S235 carbon steel in the absence and presence of sodium metavanadate(V) are shown in Figure 7.

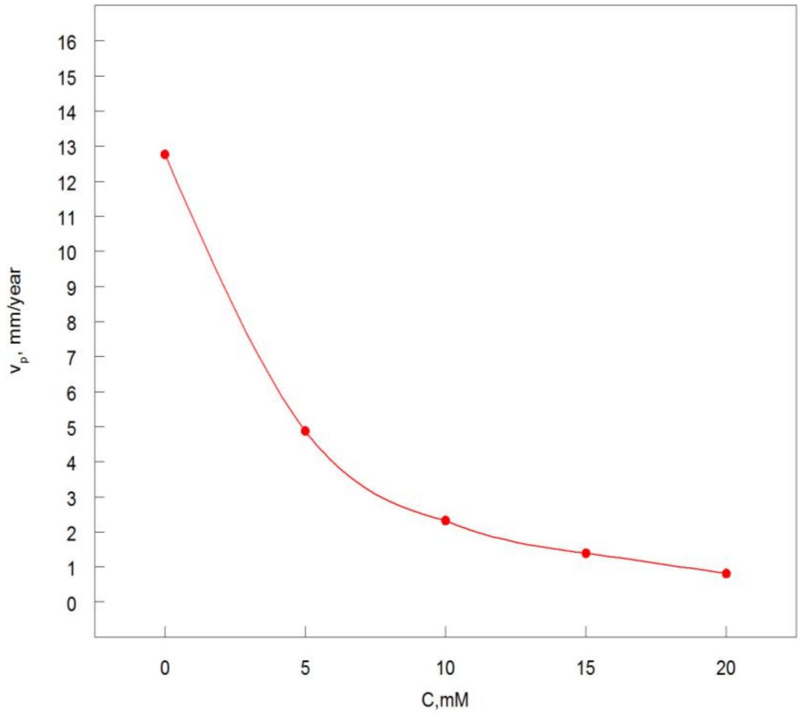


Figure 7. Corrosion rate of S235 carbon steel in absence and presence of sodium metavanadate(V), at 25 ^{0}C

The corrosion rates of S235 carbon steel gradually decrease with increasing of $NaVO_3$ concentration in the acid chloride solutions. However, in solution without inhibitor the corrosion rate was 12.75 mm/year, while in the case of solution with 20 mM of sodium metavanadate(V) the corrosion rate decreases about fifteen times. Therefore, it is clear that of VO_3^- to be counted as efficient inhibitor corrosion of S235 carbon steel in acid chloride aggressive environment.

3.3. Activation parameters of the corrosion process

The effect of temperature (in range 30 – 60 ^{0}C) on the S235 carbon steel general corrosion inhibition by VO_3^- ions were studied. Figure 8 were showed Tafel polarization plots recorded for investigated steel in presence of 20 mM of sodium metavanadate(V) at different temperatures. The similar curves were recorded for other concentrations of inhibitor but not shown.

The chosen values of the corrosion parameters for studied temperatures are listed in Table 4. We have found that for the same concentration of the inhibitor with increasing electrolyte temperature corrosion potential moves slightly to the negative values. In contrast, the corrosion current densities values are increased. Moreover, the degree of surface coverage and corrosion inhibition efficiency values, Figure 9 were decreased with rise in temperature suggests the physical adsorption mechanism of inhibitor on steel surface.

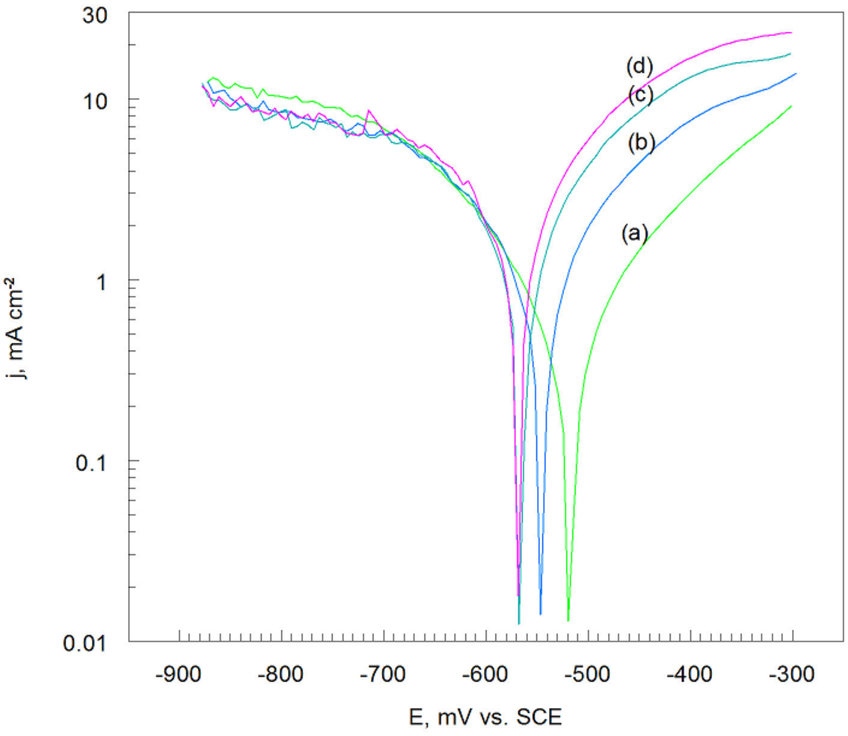


Figure 8. Tafel polarization plots for S235 carbon steel in 1.2 M Cl^- solution additionally containing 20 mM of sodium metavanadate(V) at different temperatures: (a) 30, (b) 40, (c) 50, and (d) 60 ^{0}C, scan rate 1mV s^{-1}

Table 4. Corrosion parameters, degree of surface coverage, and corrosion inhibition efficiency for S235 carbon steel in 1.2 M Cl^- solution with different concentrations of sodium metavanadate(V), at different temperatures

Temperature ^{0}C	Concentration $NaVO_3$ mM	E_{corr} mV vs. SCE	j_{corr} mA cm^{-2}	Θ	*IE* %
30	0	-506	4.40	–	–
	5	-509	2.40	0.454	45
	10	-512	1.16	0.736	74
	15	-515	0.88	0.800	80
	20	-519	0.64	0.854	85
40	0	-508	9.20	–	–
	5	-518	5.91	0.358	36
	10	-529	2.75	0.701	70
	15	-537	2.39	0.740	74
	20	-546	2.01	0.781	78
50	0	-519	15.70	–	–
	5	-534	10.60	0.352	32
	10	-550	5.60	0.643	64
	15	-559	4.61	0.706	71
	20	-568	3.70	0.764	76
60	0	-530	35.50	–	–
	5	-548	25.24	0.289	29
	10	-566	13.99	0.606	61
	15	-568	11.33	0.681	68
	20	-573	9.80	0.724	72

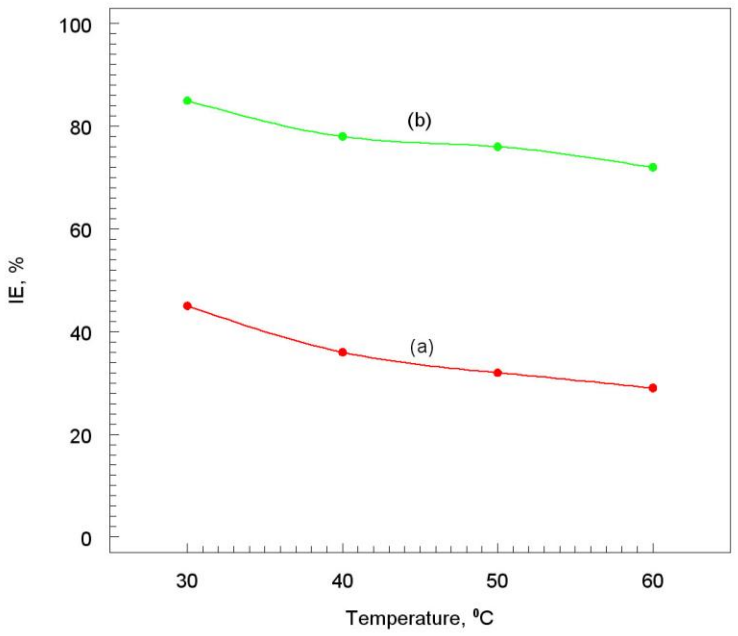


Figure 9. Effect of temperature on corrosion inhibition efficiency of S235 carbon steel. Electrolyte was contained 1.2 M Cl^-, concentrations of inhibitor: (a) 5, and (b) 20 mM

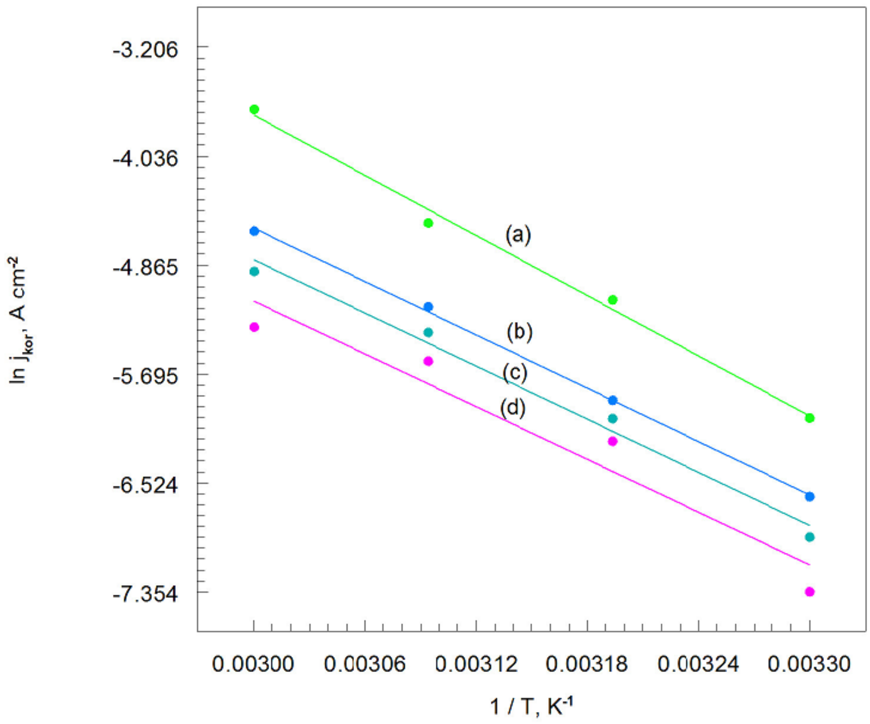


Figure 10. Arrhenius plots for S235 carbon steel in 1.2 M Cl^- solution containing different concentrations of sodium metavanadate(V): (a) 5, (b) 10, (c) 15, and (d) 20 mM

The activation parameters such as: the activation of energy (E_a) the enthalpy of activation (ΔH_a) and the entropy of activation (ΔS_a) were calculated from Arrhenius – type plot [22-24]:

$$j_{corr} = A \exp\left(\frac{-E_a}{RT}\right) \quad (8)$$

and transition – state equation:

$$j_{corr} = \left(\frac{RT}{Nh}\right) \exp\left(\frac{\Delta S_a}{R}\right) \exp\left(\frac{-\Delta H_a}{RT}\right) \quad (9)$$

where A is the Arrhenius constant, E_a is the apparent activation energy, N is the Avogadro's constant, h is the Planck's constant, ΔS_a is the change of entropy for activation, ΔH_a is the change of enthalpy for activation.

The plots of ln (j_{corr}) vs. 1/T, Figure 10 and ln (j_{corr}/T) vs. 1/T, Figure 11 give straight lines with slopes of $-E_a$/R and $-\Delta H_a$/R respectively. The intercepts which can them be calculated, will be ln (A) and [ln ($R/N\,h$) + (ΔS_a/R)] for the Arrhenius and transition-state equations, respectively.

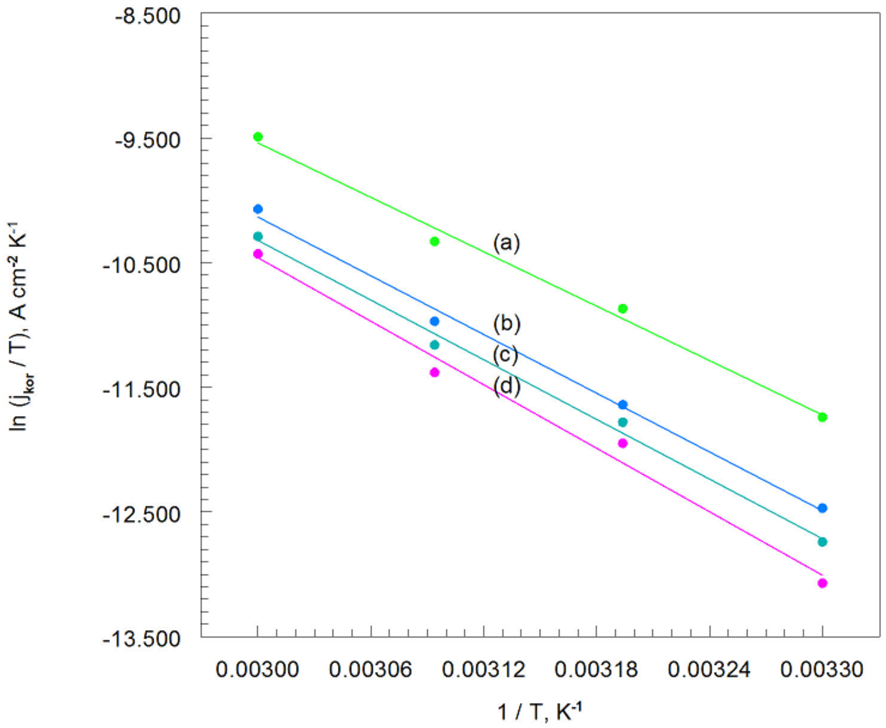


Figure 11. Transition state plots for S235 carbon stainless steel in 1.2 M Cl^- solution containing different concentrations of sodium metavanadate(V): (a) 5, (b) 10, (c) 15, and (d) 20 mM

The calculated values of Ea, ΔHa and ΔSa are summarized in Table 5.

In the presence increasing of sodium metavanadate(V) concentration the decrease of E_a values were observed. The decrease in apparent activation energy arises from a shift of the net corrosion reaction, from one on the uncovered surface to one directly involving the adsorbed sites [25]. The values Ea and ΔHa are nearly the same (Table 5) and are smaller in the presence of sodium metavanadate(V) than in a blank solution, indicating that the energy barrier of the corrosion reaction decreased in the presence of inhibitor without changing the mechanism of dissolution of metal.

Table 5. Activation parameters for S235 carbon steel in 1.2 M Cl^- solution at different concentrations of sodium metavanadate(V)

Concentration $NaVO_3$ mM	E_a kJ mol^{-1}	ΔH_a kJ mol^{-1}	ΔS_a J mol^{-1} K^{-1}
0	65.43	62.75	-84.62
5	64.16	61.53	-92.02
10	56.98	54.34	-120.75
15	56.64	53.79	-123.75
20	56.30	53.67	-127.40

The entropy of activation, ΔSa in the absence and presence of $NaVO_3$ are negative, implying that the rate-determining step for the activated complex is the association rather than the dissociation step. In the presence of the inhibitor, ΔSa moves in direction of negative values (Table 5) which implies that the adsorption process is accompanied by an decrease in entropy, which is the driving force for the adsorption of adenine onto the S235 carbon steel surface.

3.4. Thermodynamic parameters of the adsorption isotherm

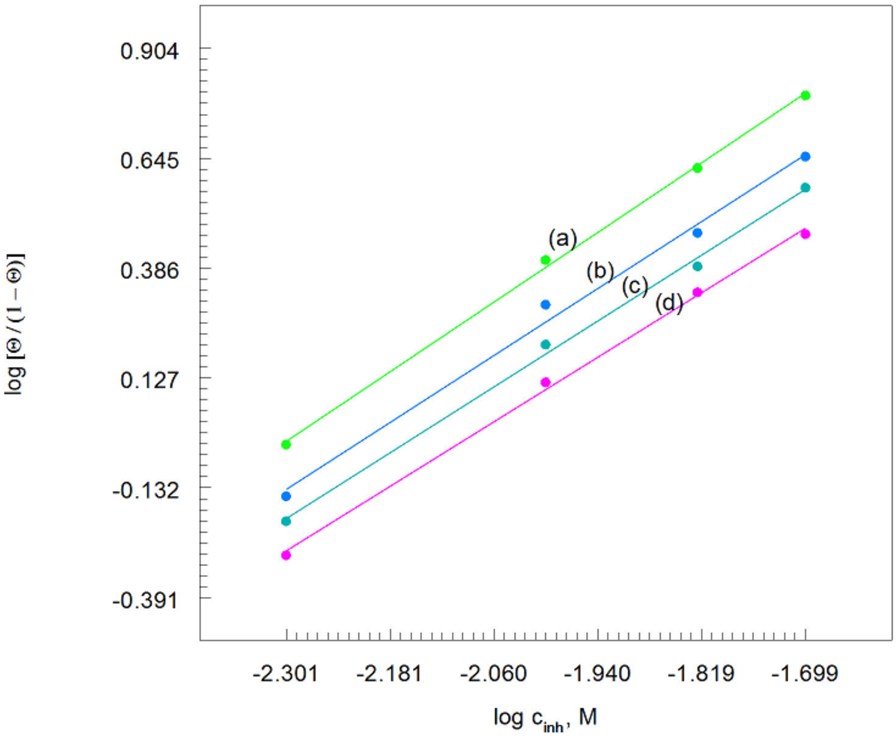


Figure 12. El-Awady adsorption plots of sodium metavanadate(V) onto the S235 carbon steel in the presence of 1.2 M Cl^- solution at different temperatures: (a) 30, (b) 40, (c) 50, and (d) 60 ^{0}C

The efficiency of inorganic molecules as good corrosion inhibitors depends mainly on their adsorption ability on the metal surface. Basic information about the interaction between inhibitor and metal can be provided by the adsorption isotherm. The investigation of the relation between corrosion inhibition and adsorption of inhibitor is of great importance.

The surface coverage and the concentration of sodium metavanadate(V) solution were tested by fitting to various isotherms like: Langmuir, Langmuir-Freundlich, and El-Awady. However, the best fit was obtained with El-Awady isotherm as shown in Figure 12 which is given by following equation [26,27]:

$$\log\left[\frac{\theta}{(1-\theta)}\right] = \log K_{ads} + y\log C_{inh} \qquad (10)$$

where *K*ads is the equilibrium constant of the adsorption/desorption processes, and it reflects the affinity of the inhibitor molecules towards surface adsorption sites.

The El-Awady adsorption isotherm has a very good fit curve (correlation 0.999). The slope of the curve, that is, parameter 1/y represents the number of active sites that are occupied by one molecule of the inhibitor. In this case the parameter 1/y is 1.46, which means that of VO_3^- adsorbed on the surface of S235 carbon steel to form a multilayered and occupies more than one active site. The parameters determined on basis of the El-Awady isotherm are presented in Table 6.

The equilibrium constant of the adsorption/desorption (K_{ads}) were related to the standard free energy of adsorption according to equation [28]:

$$\Delta G^o_{ads} = -RT\ln(55.5\,K_{ads}) \qquad (11)$$

where R is the universal gas constant, T is the absolute temperature, and value 55.5 is concentration of water in solutions.

Table 6. Equilibrium constant adsorption/desorption and standard free energy, enthalpy, and entropy of the adsorption onto the S235 carbon steel in the presence of 1.2 M Cl^- solution and of sodium metavanadate(V) at different temperatures

Temperature ^0C	K M^{-1}	ΔG_{ads}^0 kJ mol^{-1}	ΔH_{ads}^0 kJ mol^{-1}	ΔS_{ads}^0 J mol^{-1} K^{-1}
30	1.29×10^3	-27.70	-30.51	-9.44
40	7.59×10^2	-26.38		-13.86
50	5.74×10^2	-25.69		-16.18
60	4.24×10^2	-24.92		18.70

According to the assumptions El – Awady isotherm, the adsorption of the inhibitor on the surface of metal will be according to the mechanism:

$$Fe + 3\,VO_3^- \rightarrow \underline{Fe(VO_3)_3} + 3\,e^-. \qquad (12)$$

The standard free energy of adsorption of VO_3^- were calculated and listed in Table 6. Generally the standard free energy of adsorption values of -20 kJ mol^{-1} or less negative are associated with an electrostatic interaction between charged metal surface (physical adsorption), those of -40 kJ mol^{-1} or more negative involves charge sharing or transfer from the inhibitor molecules to the metal surface to form a co-ordinate covalent bond (chemical adsorption) [29,30].

The values of standard free energy of adsorption of VO_3^- ions onto the S235 carbon steel surface were found as -27.70, and -24.92 kJ mol^{-1} at temperatures 30 and 60 ^0C, respectively (Table 6). Therefore, it can be concluded that the adsorption of metavanadate(V) ions onto the steel surface takes place through both physical and chemical adsorption, namely mixed type with predominant physical one [31-33].

Voluble information about the mechanism of corrosion inhibition can be provided by the values of thermodynamic parameters for the adsorption of inhibitor. Thermodynamically, ΔG^0_{ads} were related to the standard enthalpy, ΔH^0_{ads} and standard entropy, ΔS^0_{ads} according to [34,35]:

$$\Delta G^0_{ads} = \Delta H^0_{ads} + T\,\Delta S^0_{ads} \quad (13)$$

and the standard enthalpy of adsorption can be calculated on basis the Van’t Hoff formula:

$$\Delta G^0_{ads} = \frac{\Delta H^0_{ads}}{RT} + const \quad (14)$$

or:

$$\log K_{ads} = \frac{\Delta H^0_{ads}}{2{,}303\,RT} + \frac{\Delta S^0_{ads}}{2{,}303\,RT} \quad (15)$$

A plot of ln K_{ads} vs. 1/T gives a straight line, as shown in Figure 13. The slope of the straight line $-\Delta H^0_{ads}/R$.

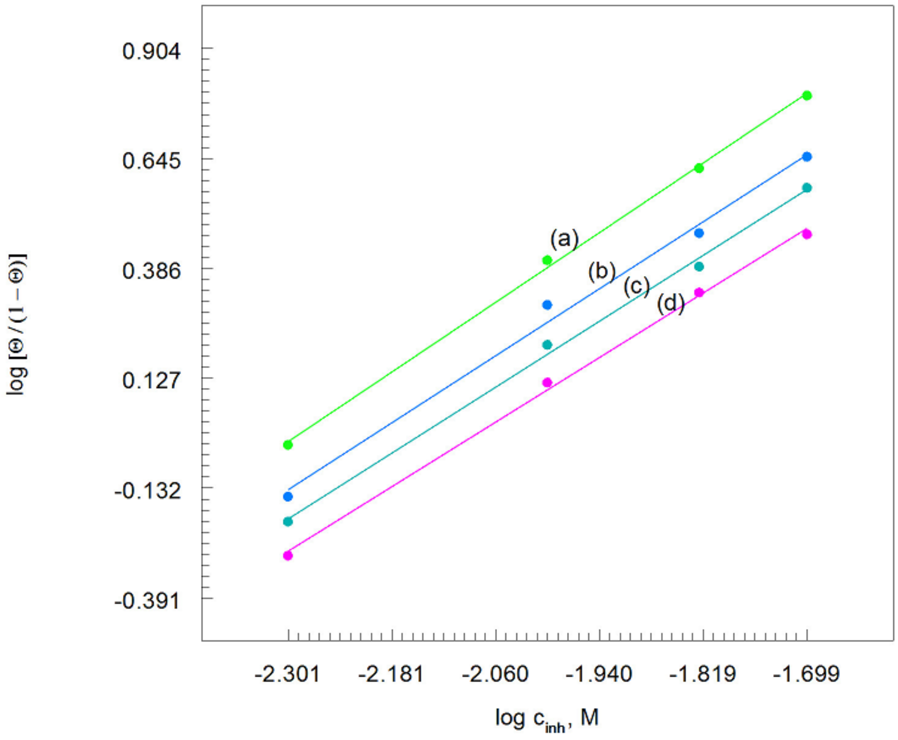


Figure 13. Van’t Hoff plot for S235 carbon steel in 1.2 M Cl^- solution containing of sodium metavanadate(V)

The value of standard enthalpy adsorption is given in Table 6. Since the ΔH^0_{ads} value is negative the adsorption of metavanadate(V) ions onto the carbon steel surface is an exothermic process. In a exothermic process chemisorption is distinguished from physisorption by considering the absolute value of ΔH^0_{ads} for the chemisorption process it approaches 100 kJ/mol while for the physisorption process it is less than 40 kJ/mol. In the present study (Table 6) the ΔH^0_{ads} value is slightly lower than the common physical adsorption heat once again implying that physical adsorption of VO_3^- is taking place.

The standard entropy adsorption, ΔS^0_{ads} of inhibitor can be calculated from [22]:

$$\log S^0_{ads} = \frac{\Delta H^0_{ads} - \Delta G^0_{ads}}{T} \tag{16}$$

The calculated values of ΔS^0_{ads} are recorded in Table 6. Negative values ΔS^0_{ads} indicate on free and chaotic movement of the molecules inhibitor in the bulk solution (are chaotic) before adsorption on the carbon steel surface, while as adsorption progresses of VO_3^- adsorbed onto the S235 carbon steel surface become more orderly resulting in a decrease in entropy. The increase temperature causes a decrease entropy and ordered adsorption organic compounds on surface steel [36].

4. MECHANISM OF INHIBITION

The corrosion inhibition mechanism in acid medium the most often depends on the adsorption of an inhibitor onto the metal surface. The inhibitive action of inhibitors depends on the electron densities around the adsorption centers. The higher the electron density at the centre, the more efficient is the inhibitor. The adsorption of the inhibitor on metal surface is the first step in the action mechanism of inhibition. Physical adsorption requires presence of both electrically charged surface of the metal and charged species in the bulk of the solution. Moreover, chemical adsorption requires in the presence of a metal to have a vacant low-energy electron orbital, and an inhibitor with molecules having relatively loosely bond electrons or heteroatom with lone pair electrons.

In the presence of chloride ions, the protective layer on the surface steel was formed. The protective layer consists of $(FeCl)_{ads}$ (reaction (6)). The formed film was dissolved for more positive values potential of electrode (Fig. 1 or 2, and reaction (6a)). As a result of the oxidation of iron oxide layer of Fe_2O_3 was formed (reaction (7) which did not have passivation properties. When was added of $NaVO_3$ to the aggressive chloride solution was disappeared layer of Fe_2O_3. Moreover, on surface electrode was appeared green protective layer of iron(III) metavanadate(V) (reaction (12), and Fig. 5b) or c)). The physical adsorption of VO_3^- ions depend on electrostatic interaction between atoms of vanadium ($\delta = +4.353$), and the negatively charged surface of S235 carbon steel electrode, Figure 14. Therefore, protective layer was formed by the chemical and physical interaction of the inhibitor with the steel surface.

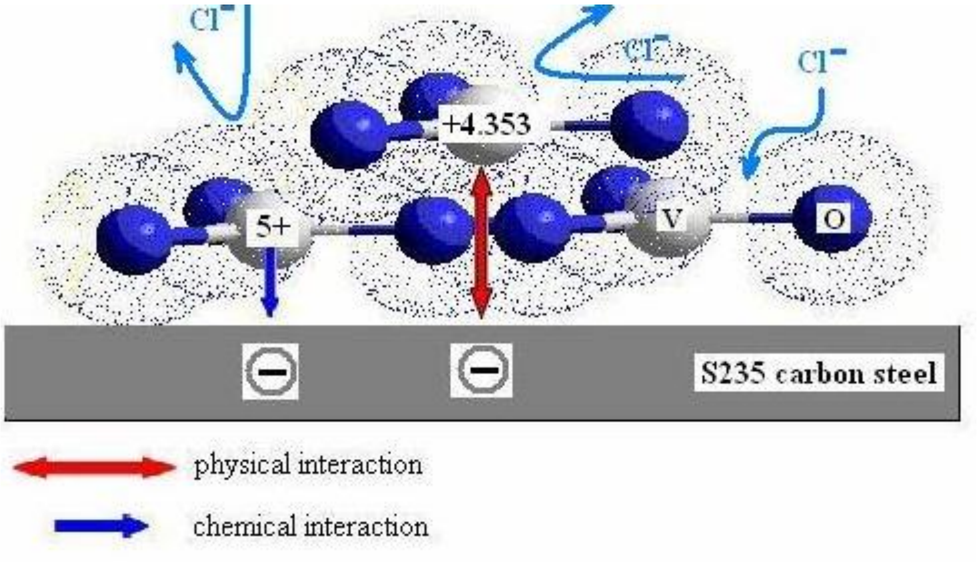


Figure 14. Proposal of model protective layer of VO_3^- on S235 carbon steel surface

The effectiveness of the protective layer depends on the orientation of VO_3^- ions, relative to the steel surface. In this case, the ions of the inhibitor set horizontally with respect to the electrode surface. In this way, on the steel surface protective layer of $Fe(VO_3)_3$ was formed. However, the protective layer adhere well to the S235 carbon steel surface to provide effective protection against corrosion in aggressive environment of chloride.

5. CONCLUSION

The inhibition effect of VO_3^- on the corrosion of S235 carbon steel in chloride acid solution was studied. From the data obtained the following points can be emphasized:

(1) The sodium metavanadate(V) has good inhibition effect for the corrosion of S235 carbon steel in 1.2 M Cl^- acid solution, and inhibition efficiency was increased with inhibitor concentration.

(2) The corrosion inhibition efficiencies of investigated carbon steel were decreased with temperature for the same concentrations of sodium metavanadate(V).

(3) The values of E_a and ΔH_a indicate that the energy barrier of the corrosion reaction decreased in the presence of VO_3^- without changing the mechanism of dissolution of S235 carbon steel. The negative values of ΔS_a implying that the rate-determining step for the activated complex is the association rather than the dissociation step.

(4) The El – Awady adsorption isotherm exhibited the best fit to the experimental data. The values of adsorption equilibrium constant suggested that of VO_3^- strongly adsorbed on the surface, forming a protective film.

(5) The negative sign of ΔG^0_{ads} and ΔH^0_{ads} indicate that the adsorption process of VO_3^- is spontaneous and exothermic. The negative of ΔS^0_{ads} can be attributed to the increase in the solvent entropy and more positive water desorption entropy.

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