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Corrosion control of vanadium in aqueous solutions by amino acids

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Abstract

The electrochemical behavior of vanadium in amino acid free and amino acid containing aqueous solutions of different pH was studied using open-circuit potential measurements, polarization techniques and electrochemical impedance spectroscopy (EIS). The corrosion current density, i_{corr}, the corrosion potential, E_{corr} and the corrosion resistance, R_{corr}, were calculated. A group of amino acids, namely, glycine, alanine, valine, histidine, glutamic and cysteine has been investigated as environmentally safe inhibitors. The effect of Cl^- on the corrosion inhibition efficiency especially in acid solutions was investigated. In neutral and basic solutions, the presence of amino acids increases the corrosion resistance of the metal.

The electrochemical behavior of V before and after the corrosion inhibition process has shown that some amino acids like glutamic acid and histidine have promising corrosion inhibition efficiency at low concentration (≅25 mM). The inhibition efficiency (η) was found to depend on the structure of the amino acid and the constituents of the corrosive medium. The corrosion inhibition process is based on the adsorption of the amino acid molecules on the metal surface and the adsorption process follows the Freundlich isotherm. The adsorption free energy for valine on V in acidic solutions was found to be −9.4 kJ/mol which reveals strong physical adsorption of the amino acid molecules on the vanadium surface.

Keywords: Amino acids; Corrosion inhibition; EIS; Polarization; Vanadium

1. Introduction

Vanadium is a light transition metal, largely used in metallurgical applications and fabrication of batteries. It is also well known as catalyst in combination with oxygen and phosphorous for the oxidation of light alkanes [1]. Vanadium chemistry is of interest because of its applications in vanadium-based redox flow batteries. The redox flow batteries are electrochemical energy storage systems where the energy rather than being stored at the electrodes like in conventional batteries it is stored by chemical changes to species dissolved in a working fluid [2]. Contrary to many transition metals, vanadium shows active behavior [3–7]. The electrode potential of vanadium and the effect of oxygen on its potential were the subjects of early studies [8,9]. The active behavior of vanadium and its anodic dissolution in aqueous solutions was investigated [10,11]. It was found that the rate of metal dissolution is independent of the hydrogen ion concentration or the nature of the present anions. The rate determining step was a monovalent adsorbed intermediate (V^+/ads) [11]. The behavior of the metal in both acidic and basic media was found to obey the Tafel approximation of the Butler–Volmer equation over a wide range of potentials [12].

In this work some naturally occurring amino acids were used as inhibitors for the corrosion of vanadium electrode in aqueous acidic, neutral and basic solutions. The corrosion rate was calculated and the corrosion inhibition process was investigated using the different amino acids as environmentally safe corrosion inhibitors. For these investigations conventional electrochemical techniques such as open-circuit, potential measurements, potentiodynamic polarization techniques and electrochemical impedance spectroscopy (EIS) were used. Fitting of the experimental impedance data to theoretical values according to equivalent circuit models enables understanding

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of the corrosion inhibition mechanism and the suggestion of the suitable electrical model that explains the behavior of the metal under different conditions.

2. Experimental details

The working electrodes were made from spectroscopically pure vanadium rods (Alderich-Chemie). The metal rods were mounted into glass tubes by two-component epoxy resin leaving a surface area of 0.302 cm^2 to contact the solution. The electrochemical cell was a three-electrode all-glass cell, with a platinum counter electrode and a saturated calomel reference electrode. Before each experiment, the working electrode was polished mechanically using successive grades of emery paper up to 2000 grit, rubbed with a smooth polishing cloth, then washed with triple distilled water and transferred quickly to the electrolytic cell. The electrochemical measurements were carried out in aqueous solutions of different pH, namely, 2, 7 and 12, where analytical grade reagents and triple distilled water were used. The solutions were prepared according to the following series.

pH	Composition
2(Cl^-, in)	250 ml HCl (0.1 M)
2*(Cl^-, free)	62.5 ml (0.2 M) boric acid + 62.5 ml (0.05 M) borax + 62.5 ml (0.4 M) H_3PO_4 and complete to 250 ml, with triple distilled water
7	127.8 ml (0.1 M) $COOKC_6H_4COOH$ + 122.2 ml (0.1 M) HCl and complete to 250 ml, with H_2O
12	100 ml (0.2 M) KH_2PO_4 + 163.7 ml (0.2 M) NaOH

The pH of the prepared solution was measured and controlled using a standard microprocessor pH meter.

The electrochemical impedance investigations and polarization measurements were performed using the voltalab 10 PGZ 100 “All-in-one” potentiostat/galvanostat. The amplitude of the superimposed ac-signal was 10 mV peak to peak. The method involves direct measurements of the impedance Z and the phase shift θ of the electrochemical system in the frequency range from 0.1 to 10^5 Hz. To achieve reproducibility, each experiment has been carried out at least twice. Unless otherwise stated, all experiments have been carried out at room temperature, 25 ± 1 °C and the potentials were measured against and referred to the saturated calomel electrode (SCE). The experimental details are as described elsewhere [13,14].

All potentiodynamic polarization measurements were carried out using a scan rate of $10\,mV\,s^{-1}$ in the potential range from −450 to 0 mV. The amino acids used in these investigations include:

1. Aliphatic amino acids: glycine, alanine and valine.
2. Sulfur containing amino acids: cysteine.
3. Acidic amino acids: glutamic acid.
4. Basic amino acids: histidine.

The corrosion inhibition efficiency, η, was calculated from the measured values of the corrosion current densities of the metal in the different solutions before and after the addition of the amino acids to the corrosive medium.

3. Results and discussion

3.1. Open-circuit potential measurements

The open-circuit potential (OCP) of vanadium was traced over a period of 180 min from the electrode immersion in amino acid free and amino acid containing solutions of different pH. A constant concentration of the different amino acids of 0.025 M was used. The results of these measurements are presented in Fig. 1 and the values of the steady state potentials, E_{ss}, in absence and presence of amino acids are presented collectively in Table 1. The open-circuit potential shows the same trend in all solutions, it gets more positive (more noble) with time until it reaches a steady state value (cf. Fig. 1A). Generally, the steady state potential, E_{ss}, was reached within 60 min from the electrode immersion in the test solution. The values of E_{ss} show a straight line relationship with the pH of the solution with an inflection at pH 7 as presented in Fig. 1B. Such a linear relation suggests the use of the V electrode as a pH indicator electrode [15]. The presence of the amino acid in the solution shifts the E_{ss} value most likely in the more noble direction. The value of the shift in the OCP and the E_{ss} is related to the structure of the amino acid and the constituents of the electrolyte. The presence of chloride ions in the solution shifts the steady potential to more negative values and higher rates of corrosion were recorded.

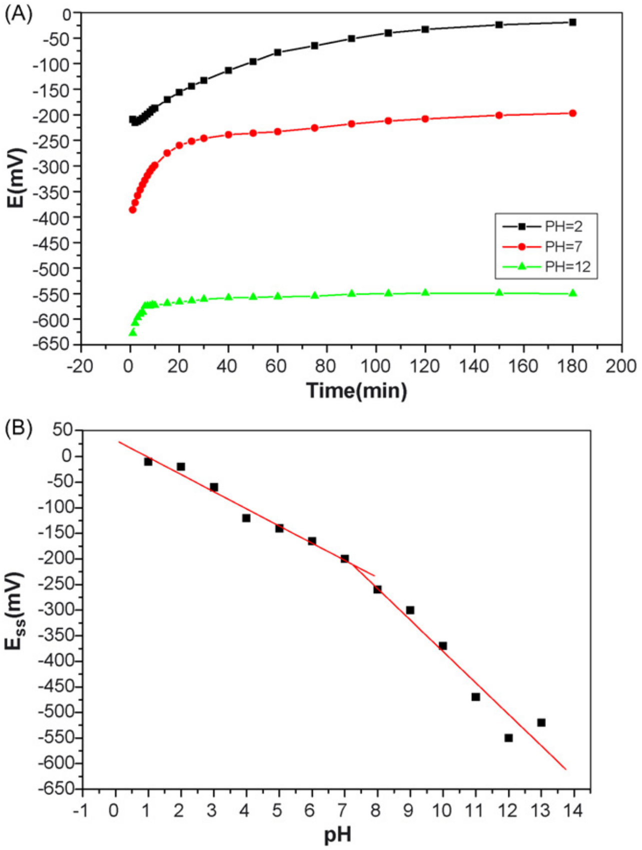


Fig. 1. (A) Variation of the open-circiut potential with time for V electrode after immersion in aqueous solutions at different pHs at 25 °C. (a) pH 2 (b) pH 7 (c) pH 12. (B) Variation of the steady state potential of V electrode with the solutions pH (1–13) at 25 °C>.

3.2. Potentiodynamic polarization measurements

The effect of different amino acids on the corrosion rate of vanadium in aqueous solutions was investigated using the potentiodynamic technique. The potentiodynamic polarization curves of these investigations in chloride free acidic solutions of pH

Table 1
Corrosion parameters of V after 60 min of electrode immersion in amino acid free and amino acid containing aqueous solutions of different pHs at 25 °C

	E_{corr} (mV)	R_{corr} (kΩ cm^2)	i_{corr} (μA/cm^2)	β_a (mV/dec)	β_c (mV/dec)	Corrosion rate (μm/Y)	Ess (mV)	η (%)
pH 2*(Cl$^-$, free)	−238.1	1.74	6.68	228.3	−15.1	91.11	−111	–
Glycine	−276.9	1.99	4.22	111.6	−11.0	57.56	−155	36.82
Alanine	−357.1	2.28	1.77	38.5	−20.1	24.20	−158	73.43
Valine	−355.5	1.88	2.12	31.7	−17.5	28.98	−210	68.19
Histidine	−369.6	2.23	2.15	37.1	−20.1	29.29	−134	67.85
Glutamic	−327.2	2.61	1.65	37.0	−19.8	22.49	−122	75.31
Cysteine	−361.6	4.21	1.93	76.5	−21.3	26.32	−199	71.10
pH 2(0.1 M Cl$^-$)	−318.1	6.84	1.51	66.8	−56.9	20.60	−190	–
Glycine	−334.3	2.91	1.65	80.7	−24.6	22.45	−163	−8.9
Alanine	−372.7	3.85	1.95	61.2	−31.9	26.63	−220	−29.1
Valine	−341.6	3.56	1.69	49.2	−31.7	23.00	−190	−11.9
Histidine	−392.2	3.66	2.39	71.0	−35.1	32.58	−247	−58.2
Glutamic	−344.6	3.80	2.46	73.8	−41.3	33.52	−205	−62.9
Cysteine	−328.2	4.93	2.89	127.8	−61.2	39.40	−200	−91.3
pH 7	−545.0	2.33	2.15	43.0	−22.1	25.17	−337	–
Glycine	−534.2	2.15	1.86	30.3	−18.1	21.72	−335	13.7
Alanine	−518.6	3.70	0.898	23.7	−19.2	10.50	−342	58.3
Valine	−536.4	2.43	1.94	41.4	−20.1	22.69	−353	9.8
Histidine	538.6	2.06	2.09	33.2	−18.3	24.48	−356	2.7
Glutamic	−429.1	3.67	1.28	47.3	−22.9	15.01	−342	40.4
Cysteine	−522.9	4.04	1.03	47.3	−22.5	12.06	−350	52.1
pH 12	−712.3	1.81	2.5	33.5	−27.1	29.67	−537	–
Glycine	−680.3	1.37	2.16	35.0	−14.3	25.23	−553	13.7
Alanine	−631.2	3.72	1.48	33.7	−42.7	17.27	−516	40.9
Histidine	−649.4	3.64	1.56	47.8	−41.4	18.25	−540	37.6
Glutamic	−580.1	3.08	1.36	81.6	−29.1	15.85	−525	45.76

The amino acid concentration was kept constant at 0.025 M.

2 containing three representative amino acids are presented in Fig. 2. In general, the presence of the amino acid has a little effect on the general shape of the potentiodynamic polarization curves of V in these solutions, but the corrosion current density is affected and in most cases a remarkable decrease in its value was recorded. The values of the corrosion parameters, corrosion current density, i_{corr}, corrosion potential, E_{corr}, and the corrosion inhibition efficiency (η%) of V in the different solutions were calculated and presented in Table 1.

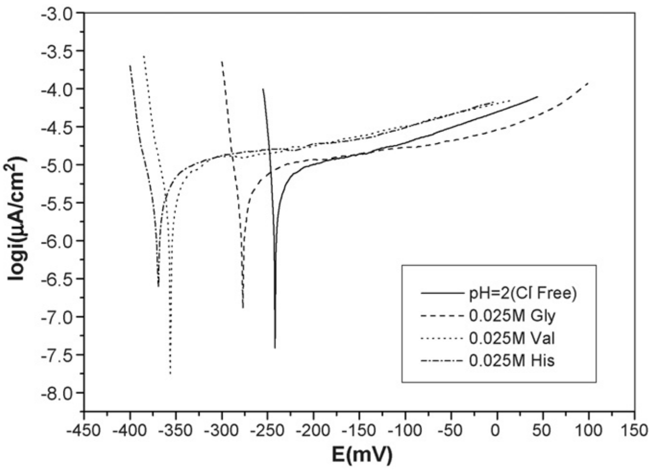


Fig. 2. Potentiodynamic polarization curves of V after 60 min of the electrode immersion in amino acid free and amino acid containing aqueous solutions of pH 2 (Cl$^-$, free) at 25 °C.

The corrosion resistance, R_{corr} is related to the corrosion rate as corrosion current density i_{corr}.

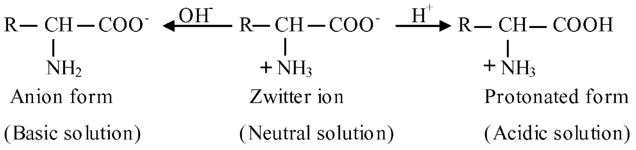
$$R_{corr} \equiv \left(\frac{dE}{di}\right)_{i\to 0} \equiv \frac{\beta_a\beta_c}{2.3(\beta_a+\beta_c)i_{corr}} \tag{1}$$

where β_a and β_c are the anodic and cathodic Tafel slopes, respectively. The values of R_{corr} and i_{corr} were calculated directly after reaching the steady state [16].

The inhibition efficiency is calculated using the following equation:

$$\eta = \left[\frac{i - i_{inh}}{I}\right] \times 100 \tag{2}$$

where i and i_{inh} are the corrosion current densities before and after the corrosion inhibition process, respectively. The inhibition effect of the amino acid is due to the adsorption of its molecules on the metal surface [17], and the adsorption process depends on both the nature and state of the surface and also on the structure of the amino acid. In general, the amino acid molecule occurs in its protonated form in acidic solution according to


$$\underset{NH_2}{R-CH-COO^-} \xleftarrow{OH^-} \underset{+NH_3}{R-CH-COO^-} \xrightarrow{H^+} \underset{+NH_3}{R-CH-COOH} \tag{3}$$

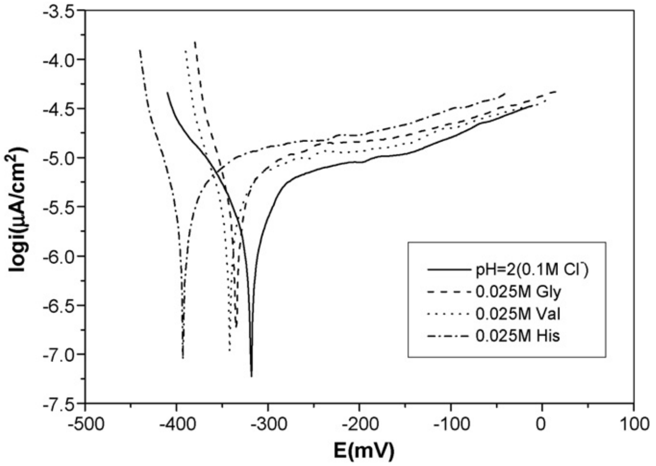


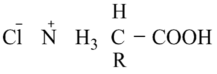
Fig. 3. Potentiodynamic polarization curves of V after 60 min of the electrode immersion in amino acid free and amino acid containing aqueous solutions of pH 2 (0.1 M Cl^-) at 25 °C.

It could be electrostatically attracted to the cathodic sites on the metal surface [17]. Since, the electrostatic adsorption of inhibitors may be increased in halide-containing solutions [18], so it is interesting to study the corrosion inhibition of amino acids in acidic solutions containing Cl^- ions.

The effect of different amino acids on the corrosion rate of vanadium in acidic solutions of pH 2 containing 0.1 M Cl^- was investigated. The potentiodynamic polarization curves for V in amino acid free and amino acid containing solutions are presented in Fig. 3. The calculated corrosion parameters are presented in Table 1.

In chloride containing solutions higher corrosion currents were recorded, which can be attributed to the aggressiveness of the Cl^- ions. The presence of Cl^- leads to the formation of the hydrochloride salt of the amino acid, which prevents the adsorption of the amino acids to the cathodic regions.

At the same time, the halide ions are adsorbed at the anodic regions leading to continuous dissolution of the metal and hence, higher rates of corrosion were recorded.



$$\overset{-}{Cl}\ \ \overset{+}{N}\ \ H_3\ \ \underset{R}{\overset{H}{C}} - COOH$$

In neutral and basic solutions, similar potentiodynamic polarization curves are obtained. The values of the corrosion parameters are similarly calculated and presented in Table 1. In neutral solutions, the presence of the amino acid molecules shifts the corrosion potential, E_{corr}, to more positive values. The positive shift of E_{corr} is an indication that the addition of the amino acids influences the anodic process, leading to the corrosion inhibition effect. It can be seen that the presence of the amino acid decreases the corrosion rate of metal. In neutral solutions, the amino acid molecules are presented as Zwitter ions, that leads to the suggestion that the amino acid molecules can be electrostatically attracted through the carboxylic groups to the anodic regions on the metal surface and block the active sites for corrosion, since the lone pair of electrons on the N atom are no longer available, and so the amino acids act as anodic inhibitors in neutral solutions.

In basic solutions, the amino acid decreases the anodic current density values and shifts the corrosion potential to more positive values. In such cases the amino acid is considered as anodic inhibitor. The corrosion rate decreases and the amino acid molecule is present in its anionic form, so that it can be adsorbed on the electrode surface through two centers, the amino group and the carboxylic group [19].

The effectiveness of the different amino acids as corrosion inhibitors is related to the extent of the adsorption of their molecules and how these molecules can cover the metal surface and protect it from continuous corrosion. The adsorption process depends on the structure of the inhibitor molecules, the surface charge of the metal, and the constituents of the electrolyte [20]. For neutral and basic solutions, alanine and glutamic acid show, relatively higher inhibition efficiency η (%). Since the glutamic acid molecules are relatively large, their surface coverage ability is high and hence higher corrosion inhibition is recorded. For histidine the presence of the heterocyclic ring and π-electron character is likely to enhance the adsorption of its molecules on the metal surface, especially in basic solutions [21]. In the case of glycine, alanine and valine being amino acids with non-polar hydrocarbon side chain, the inhibition efficiency will increase with increasing the chain length of the side group due to the increase of the covered surface area. So, alanine has higher η than glycine. The degree of chain branching appears to have the opposite effect to chain length. The chain branching prevents the dense packing of the adsorbed layer, thus valine show lower inhibition efficiency than alanine. In the presence of halide ions and due to the formation of the amino acid hydrochloride the adsorption process on the cathodic active sites is prevented and hence an increased dissolution of the metal from the anodic active regions takes place.

3.3. Electrochemical impedance measurements

The potentiodynamic polarization experiments were confirmed by EIS. The experimental results obtained with V after

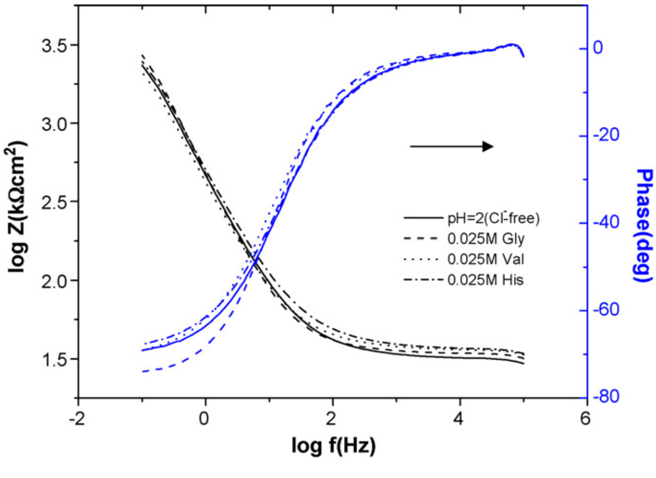


Fig. 4. Bode plots for V after 60 min of the electrode immersion in aqueous solutions of pH 2(Cl^-, free) using different amino acids at 25 °C.

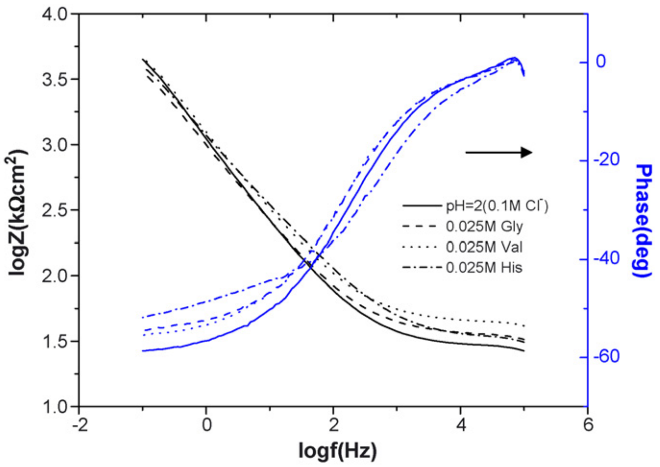


Fig. 5. Bode plots for V after 60 min of the electrode immersion in aqueous solutions of pH 2(0.1 M Cl^-)using different amino acids at 25 °C.

Table 2

Equivalent circuit parameters for V after 60 min of electrode immersion in chloride free and chloride containing acidic solutions of pH 2 in absence and presence of constant concentration (0.025 M) of the amino acid at 25 °C

	R_s (Ω cm^2)	R_{corr} (kΩ cm^2)	C_{dl} (μF/cm^2)	α
pH 2*(Cl^-, free)	26.26	6.12	259.9	0.953
Glycine	32.49	24.3	65.40	0.994
Alanine	34.73	37.6	42.22	0.999
Valine	36.73	34.5	45.99	0.999
Histidine	37.55	40.0	39.70	1
Glutamic	35.73	40.1	39.64	0.999
Cysteine	18.81	7.64	208.0	0.976
pH 2(Cl^-, in)	28.51	50.3	9.997	1
Glycine	40.59	33.9	46.92	0.999
Alanine	51.39	28.99	54.89	0.997
Valine	42.41	28.7	5.54	1
Histidine	30.39	46.4	34.27	1
Glutamic	37.01	52.4	30.33	1
Cysteine	26.98	21.5	74.02	1

60 min of the electrode immersion in amino acid free and amino acid containing chloride free aqueous acidic solutions of pH 2 are presented as Bode plots in Fig. 4. In these plots one phase maximum was recorded at lower frequencies. The effect of chloride ions was also investigated and the impedance results for V after 60 min of electrode immersion in chloride containing acidic solutions are presented in Fig. 5. The presence of chloride ions in the solutions has led to a decrease in the phase maximum and the corrosion resistance was also decreased, which indicates an increase in the corrosion rate.

The impedance results were fitted to a simple equivalent circuit consisting of a parallel combination representing the electrode capacitance, C, and the corrosion resistance, R_{corr}, in series with a resistor, R_s, representing the ohmic drop in the electrolyte (cf. Fig. 6).

The equivalent circuit parameters were calculated and presented in Table 2. It is clear that the presence of amino acid increases the corrosion resistance and hence the corrosion inhibition effect is pronounced. Also, the decrease of the capacitance is due to the thickening of the barrier layer which is responsible for the decrease of the corrosion rate. The barrier layer thickness is directly proportional to $1/C$, [22,23]. This value increases remarkably in the presence of the amino acid, which can be attributed to the adsorption of amino acid molecules on the electrode surface [17]. Similar results have been obtained in neutral and basic solutions and equivalent circuit parameters of these measurements are summarized in Table 3.

For basic solution, pH 12, the Bode plots for V with different amino acids show that the total impedance values increase in the presence of the amino acids. In addition to that, the phase maximum broadens in the presence of the amino acid, which reveals the formation of a passive film on the electrode surface.

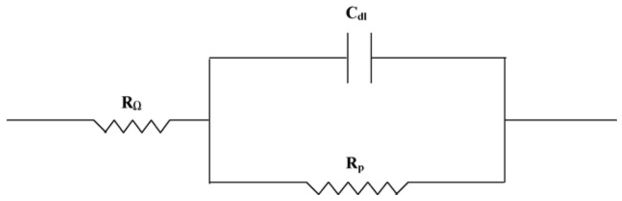


Fig. 6. Equivalent circuit model for the electrode/electrolyte interface.

3.4. Adsorption isotherm

Since the corrosion inhibition process is based on the adsorption of the amino acid molecules on the metal surface. It is essential to know the mode of adsorption and the adsorption isotherm that fits the experimental results. Many attempts have been made to fit the surface coverage data to different adsorption isotherms. Among the investigated amino acids the adsorption isotherm for valine, with different concentrations in acidic solutions was studied as a representative example under the same experimental conditions. The corrosion inhibition efficiency of valine reached about 70% at low concentration of 25 mM and its adsorption on vanadium was found to be best fitted to the Freundlich isotherm, according to

$$\theta = KC^n \tag{4}$$

Table 3

Equivalent circuit parameters for V after 60 min of electrode immersion in amino acid free and amino acid containing neutral and basic solutions at 25 °C

	R_s(Ω cm^2)	R_{corr}(kΩ cm^2)	C_{dl}(μF/cm^2)	A
pH 7	40.16	32.96	48.28	0.998
Glycine	40.62	35.93	44.28	0.998
Alanine	36.30	40.15	39.63	1
Valine	33.95	48.44	32.85	0.999
Histidine	41.37	34.74	45.80	0.998
Glutamic	38.23	72.93	21.82	1
Cysteine	37.46	67.50	23.56	1
pH 12	52.26	1.52	468.3	0.976
Glycine	21.40	1.61	988.4	0.999
Alanine	55.35	1.96	812.6	0.999
Valine	22.13	1.58	1009.0	1
Histidine	54.62	3.41	467.0	0.998
Glutamic	42.24	3.79	419.6	0.996
Cysteine	18.01	1.67	94.90	0.996

The amino acids concentration was 0.025 M.

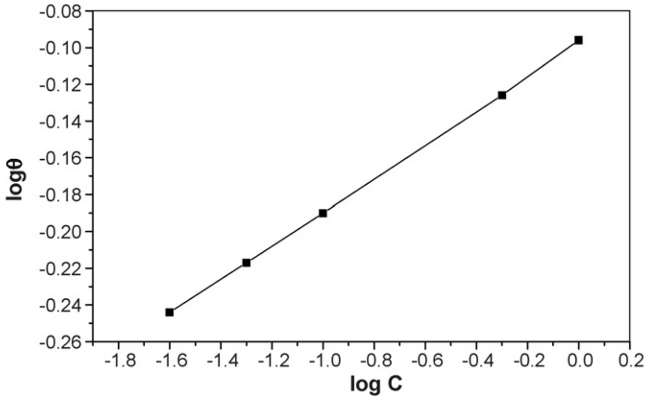


Fig. 7. Adsorption isotherm for V in acidic solutions of pH 2 containing 0.1 mM valine at 25 °C.

where C is the equilibrium concentration of the amino acid, θ the fraction of the surface coverage and was calculated from the corrosion inhibition efficiency η (%) as being equal to

$$\theta = \eta(\%) \times 10^{-2} \tag{5}$$

n is a constant depending on the characteristics of the adsorbed molecule, where $0 < n < 1$ [24] and K is the equilibrium constant for adsorption/desorption process. K is related to the free energy of adsorption, ΔG, as follows:

$$K = \frac{1}{C_{\text{solvent}}} \exp\left(\frac{-\Delta G}{RT}\right) \tag{6}$$

where, C_{solvent} is the molar concentration of the solvent, which is 55.5 mol/L for aqueous solutions. The logarithmic form of the isotherm presented by Eq. (3) is given by:

$$\log\theta = \log K + n \log C \tag{7}$$

This linear relation can be used for the calculation of the values of both K and n for the inhibitor used. The adsorption isotherm for valine in acidic solutions is presented in Fig. 7. The equilibrium constant K is calculated and the free energy of adsorption, ΔG, is obtained. The calculated value is −9.4 kJ/mol, which reveals a physisorption based mechanism for the adsorption of valine on the metal surface.

4. Conclusion

Amino acids can be used as environmentally safe inhibitors for the corrosion of vanadium in halide free aqueous solutions. The corrosion inhibition efficiency of the amino acid depends on its chemical structure and the constituents of the corrosive medium. The corrosion inhibition process is based on the adsorption of the amino acid molecules on the metal surface. The presence of chloride ions prevents the adsorption of the amino acid on the cathodic areas leading to increased corrosion rates. The adsorption of valine follows the Freundlich adsorption isotherm and the free energy of adsorption was calculated to be −9.4 kJ/mol which reveals strong physical adsorption. The thickness of the adsorption layer, as obtained from the impedance measurements, increases as the time of immersion of the metal in the amino acid containing solution increases.

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