

The Inhibitive Effect of Vitamin-C on the Corrosive Performance of Steel in HCl Solutions - Part II

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The inhibitive behaviour of Vitamin C, as a type of green inhibitor, on the corrosive behaviour of stainless-steel (SS) X4Cr13 within an aqueous solution of hydrochloric acid (HCl) was studied at concentration of $c = (0.01, 0.1 \text{ and } 1.0) \text{ mol L}^{-1}$. Potentiodynamic polarization and electrochemical impedance spectroscopy (EIS), was used for the measurements at 25 °C. To observe the morphology and microstructures of sample surfaces, after the electrochemical measurements a Scanning electron microscopy (SEM) was used. On the basis of the EDAX analysis within the solution of hydrochloric acid (0.01 mol L^{-1}) with addition of Vitamin-C (0.005 mol L^{-1}) the presence of the ferri-chelates on the metal surface could be confirmed. The polarization curves revealed that the studied mixtures of the chosen inhibitor represented mixed-type of the inhibitor. The results show that the inhibition efficiency increases with the increase of the inhibitor concentration. This valid especially in the case of the lowest concentration of HCl ($c=0.01 \text{ mol L}^{-1}$). In addition to this at higher HCl concentration ($c=1.0 \text{ mol L}^{-1}$) the immersion time has a noticeable influence on the inhibitive response. Furthermore, the results obtained in this study showed that the inhibitory effect of Vitamin-C to a great extent on electrode potential.

Keywords: green inhibitor, acid corrosion, steel, adsorption

1. INTRODUCTION

Acid pickling, chemical and electrochemical etching, and oil well acidizing are industrial processes where the role of acidic solutions are undoubtable. Among various anticorrosion methods for protection of metals, exposing aggressive environments, corrosion inhibitors due to their easy application, reasonable cost and their sufficient efficiency are popular choices for many applications and environments. The adsorption of organic molecules on the surface of metal can reduce its

corrosion rate by blocking active corrosion spots. Unfortunately, many of these compounds are toxic and do not fulfil completely the requirements imposed by the environmental protection standards. The new generation of environmental regulations requires the replacement of toxic chemicals with the so-called "green or eco-friendly chemicals". For the last couple of years big efforts have been made by researchers in this area and many studies have been carried out to find suitable compounds to be used as corrosion inhibitors [1–7].

As certain types of vitamins have similar structures to those of conventional organic inhibitors, research efforts have therefore begun to focus on non-toxic, or green corrosion. Heteroatoms, such as P, S, N, and O, which can donate lone pairs of electrons, can be found in Vitamins such as Vitamin B (thiamine), C (ascorbic acid), E (tocopherol) etc.[8-10].

Part of the present study is an extension of our previous work in which we investigated the inhibition abilities of Vitamin C, as a type of green inhibitor, on the corrosive behaviour of stainless-steel (SS) X4Cr13 in an aqueous solution of hydrochloric acid (HCl) within a concentration range of 0.01 – 5.0 M HCl ($M = \text{mol L}^{-1}$) [10]. The chosen concentrations of added Vitamin C were 0.01 and 0.001 mol L⁻¹. It was found that a good inhibitive efficiency for Vitamin C at chosen concentration of 10⁻² and 10⁻³ mol L⁻¹ on the SS type X4Cr13 in HCl was limited to concentrations of HCl below 0.1 mol L⁻¹.

It was therefore natural to extend these studies within the concentration range of HCl that is actually around the previously mentioned concentrations of HCl i.e. 0.1 mol L⁻¹. From this reason the chosen concentrations of hydrochloric acid (HCl) were $c = (0.01, 0.1 \text{ and } 1.0) \text{ mol L}^{-1}$. The experimental concentrations of added Vitamin C were; $c = (0.005, 0.001, 0.005 \text{ and } 0.01) \text{ mol L}^{-1}$. Potentiodynamic polarization and electrochemical impedance spectroscopy techniques were performed, in order to examine the corrosion-inhibition process of the chosen system. Surface characterization of metal surface, after exposure in chosen corrosion media with and without added Vitamin C, was carried out using scanning electronic microscope.

2. EXPERIMENTAL

The conventional three-electrode configuration was applied in order to conduct the potentiodynamic studies. All the potentials were measured against the saturated calomel electrode (SCE), and the counter electrode was made from Pt. The potentiodynamic current-potential curves were recorded by automatically changing the electrode potential from -0.7 to not more than -0.1V with a scanning-rate of 2 mVs⁻¹. EIS measurements were carried out within the 60 kHz –10 mHz frequency range at a steady open circuit potential (OCP) disturbed by an amplitude of 10 mV. Nyquist and polarization plots were obtained from the results of these experiments 120 mins after the working electrode had been immersed in the solution, in order to allow stabilization of the stationary potential. All the experiments were carried at 25°C ± 1°C. For electrochemical measurements the test specimens were fixed within a PTFE holder, and the geometric area of the electrode exposed to the electrolyte was 0.785 cm².

The measurements were performed using the Solartron 1287 Electrochemical interface and with a Gamry 600™ potentiostat/galvanostat controlled by electrochemical program, respectively. Data were collected and analysed using CorrView, CorrWare, Zplot and ZView software, developed by Scribner Associates, Inc. Scanning electron microscope (SEM; JEOL JSM 840 A was used to characterise the morphologies of the surfaces of SS type X4Cr13.

3. RESULTS AND DISCUSSION

3.1. Electrochemical results

The effects of the presence of Vitamin C on the current–potential characteristics displayed by the polarisation curves of ferritic stainless steel type X4Cr13 in HCl is presented in Figs. 1,2 and 3 (Figs 1,2 and 3 show 1st, 2nd and 5th consecutive measurements). Moreover, the stability of the formed layer was also goal of our research. For this purpose five following polarisations curves were performed. The electrochemical parameters obtained from these polarization curves, corrosion potential (E_{corr}), corrosion current density (i_{corr}), the polarisation resistance (R_p) and the corrosion rate are shown in Table 1. The polarisation resistance was obtained from linear polarisation within the potential range of ± 10 mV with respect to E_{corr} . Extrapolation of the Tafel line allowed us to calculate the corrosion current density i_{corr} . All the parameters were determined simultaneously by CorrView software.

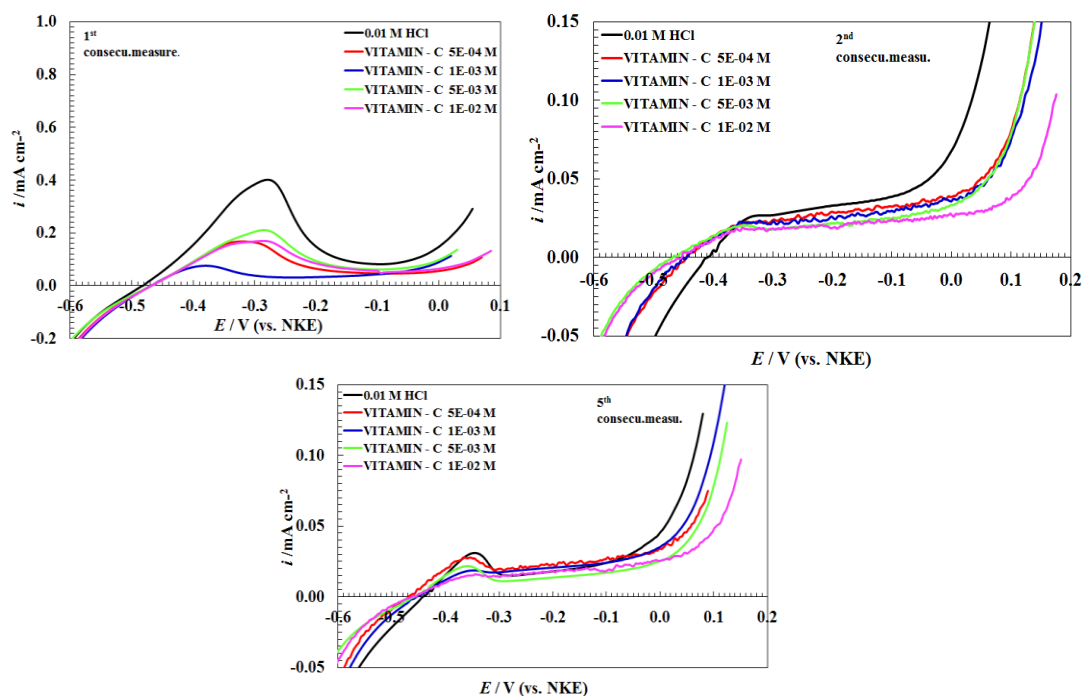


Figure 1. Potentiodynamic polarisation curves (2 mVs^{-1}) with and without addition of Vitamin C on SS type X4Cr13 in 0.01 M HCl (1st, 2nd and 5th consecutive measurement).

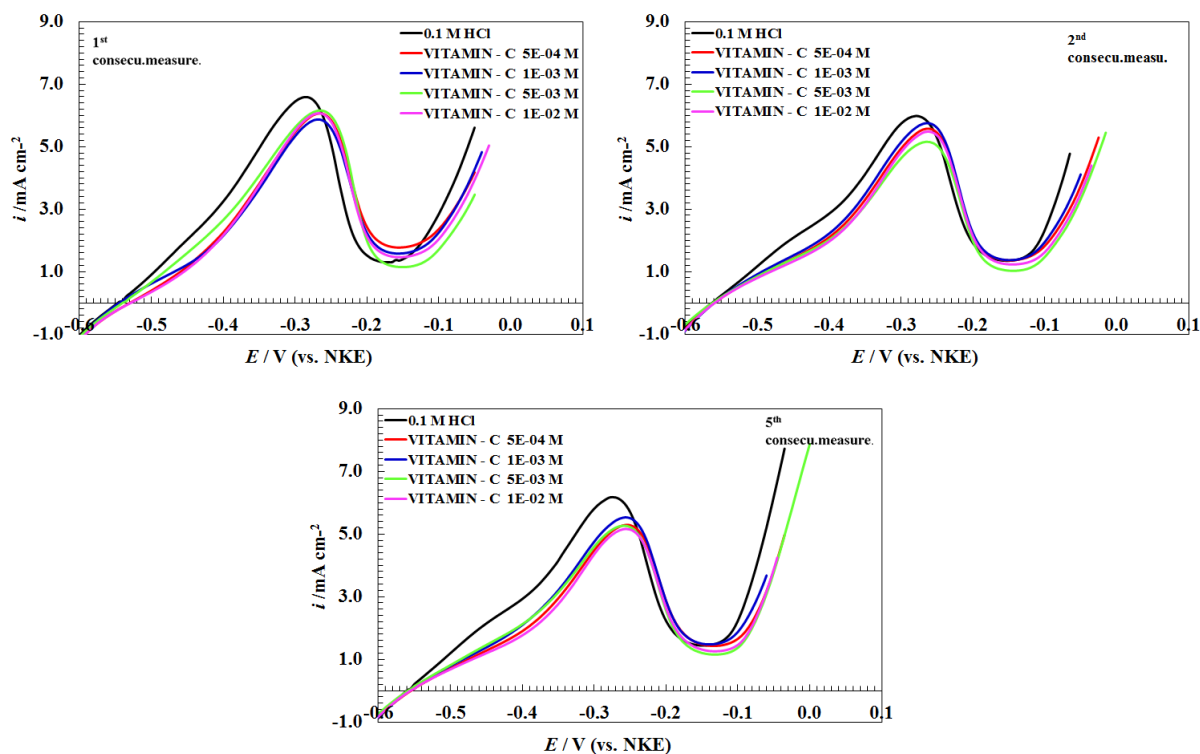


Figure 2. Potentiodynamic polarisation curves (2 mVs^{-1}) with and without addition of Vitamin C on SS type X4Cr13 in 0.1 M HCl (1st, 2nd and 5th consecutive measurement).

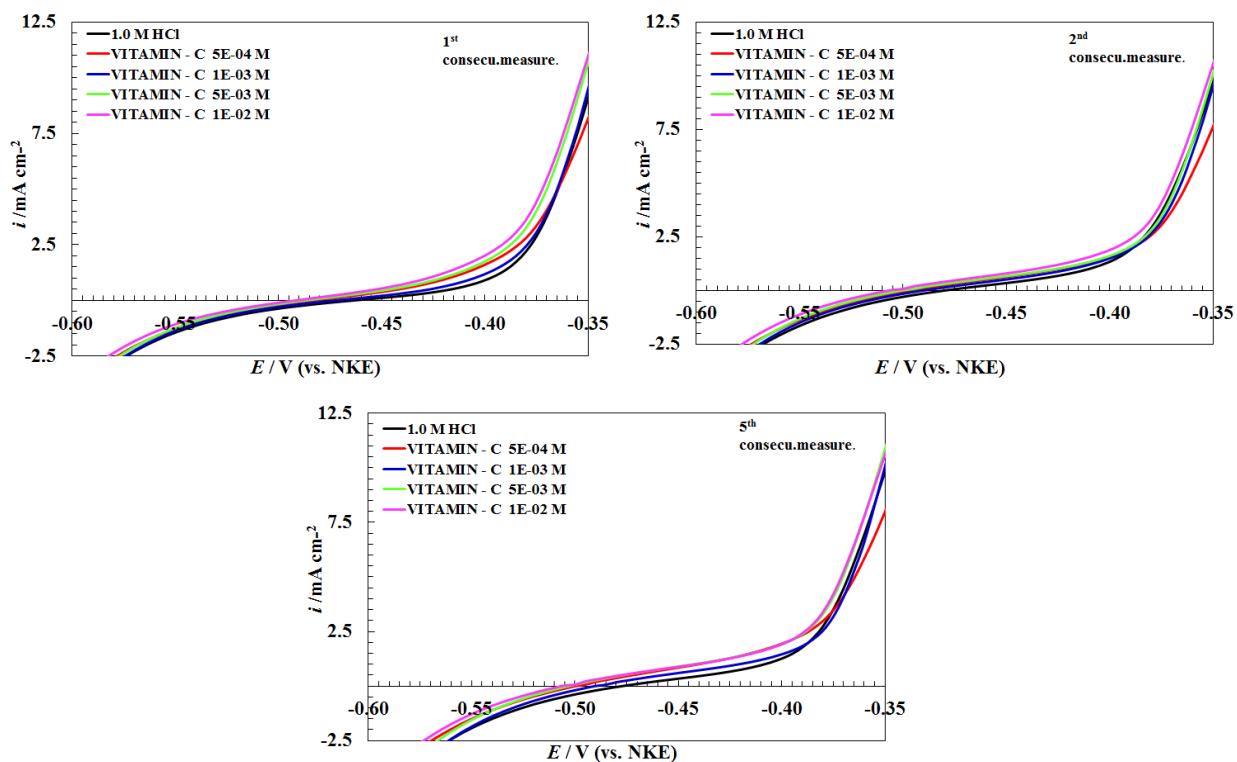
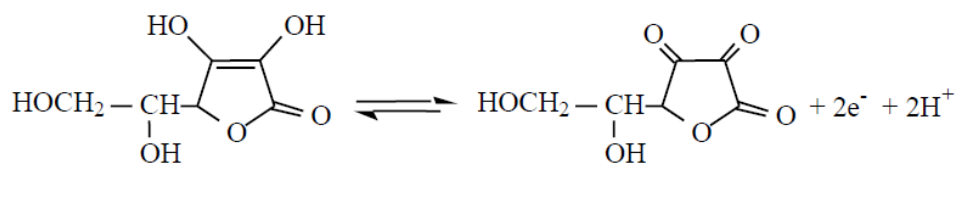


Figure 3. Potentiodynamic polarisation curves (2 mVs^{-1}) with and without addition of Vitamin C on SS type X4Cr13 in 1.0 M HCl (1st, 2nd and 5th consecutive measurement).

It is clear that the addition of Vitamin C hindered any acidic attack on the steel electrode especially in the case when corrosive media was 0.01M HCl. A comparison of curves showed that, with respect to the blank, a noticeable decrease in the anodic current-peak was observed at concentration of HCl from 0.01 to 0.1 mol L⁻¹ and thus the charge under the oxidation part of the curve. It also reduces the cathode current density. This result suggests that the selected vitamin reduced anodic dissolution, and retarded the hydrogen evolution reaction a mixed-type of inhibitor or inhibitor with 'dual-action'. In the anodic part a lower plateau is observed, which shows on the surface passivation. As was expected, that mentioned decrease was more pronounced in case when concentration of used HCl was $c = 0.01$ M. Although, this effect is not such pronounced as it is the case when classical inhibitors were used. But it has to be taken into account that the majority of classical inhibitors are harmful as well as not environmentally friendly.

No anodic current peak was observed at concentrations of HCl, $c = 1.0$ but the characteristic flat profiles. The flat portion extends to about 100 mV in anodic directions and 50 mV in cathodic direction with regard to the corrosion potential. It can be assumed that the inhibition process begins with electrostatically adsorption of chloride ions on the positively-charged surface within the anodic region (dissolution Fe to Fe²⁺). Being specially adsorbed, these anions create an excess negative charge towards the solution and favour more adsorption of the cations. The feasible adsorption of organic cations in the presence of halide ions may be due to formation of intermediate bridge, the negative ends of the halide metal dipoles being oriented towards the solution. It is known that Vitamin-C exists in acid solution in protonated form (see reaction 1). Therefore, it could be possible that due to electrostatic interaction, strong adsorption of protonated Vitamin-C with halide covered surface takes place.



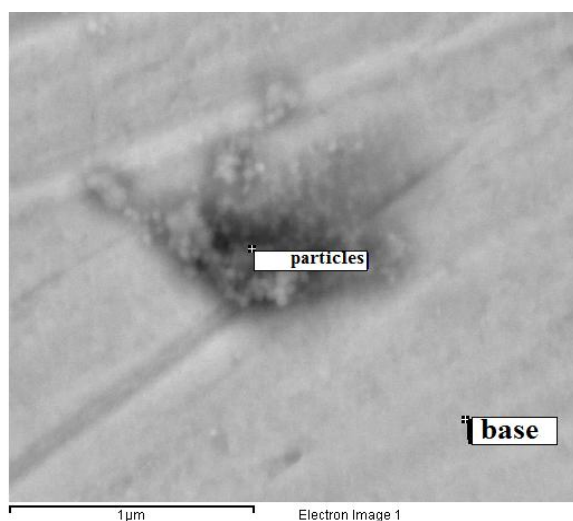
Some authors have confirmed that Vitamin-C can form chelates with ferric or ferro ions [12-14]. Martell and Khan have performed pioneering work on the catalytic effects of iron(III) and copper(II), and their chelate complexes on the oxidation of ascorbic acid [14]. Joshua et al. have stated that ascorbic acid binds to the metal ion through the carbonyl and C-2 hydroxy groups of the ascorbic acid. Complexation through the C-2 enolic hydroxy group is possible because its acidic nature. Type of chelate which has been synthesized in their research using the metal chloride solution has the following structure - [Fe (Asc)₂ (H₂O)₂] Cl, bi-ascorbate-di-aqua iron (III) chloride) [12].

Formation of ferri-chelates on stainless steel surface should lead to the chemisorption mechanism. Which of the possible processes are to a great extent depends also on the concentration of acid, since the results show the so-called dual character of Vitamin-C. It acts as an inhibitor or as an activator of corrosion processes.

In case when the concentration of HCl is equal to $c = 0.01$ M the formation of ferri -chelates on the surface of SS type X4Cr13 is possible to a great extent.

This presumption can be confirmed on the basis of obtained values for polarisation resistance R_p . These values have increased during the repetitions of the consecutive measurements and also with increasing concentration of added Vitamin-C.

SEM photograph obtained from ferritic SS type X4Cr13 surface after polarization test within the solution of hydrochloric acid (0.01 mol L^{-1}) with addition of Vitamin-C (0.005 mol L^{-1}) is shown in Fig.4. The EDAX analysis shows the increasing of the amount of C and O on the places where the small spherical particles are visible, while in the vicinity of the spherical particles the amount of carbon noticeable falls and the content of O either. On the basis of the EDAX analysis the presence of the feri-chelates on the metal surface could be confirmed.



Processing option : All elements analysed (Normalised)

Spectrum	In stats.	C	O	Si	Cr	Fe		
particles	Yes	47.67	15.04	1.03	4.53	31.73		
base	Yes	4.31	15.04	0.95	17.33	77.40		
Max.		47.67	15.04	1.03	17.33	77.40		
Min.		4.31	15.04	0.95	4.53	31.73		

All results in atomic%

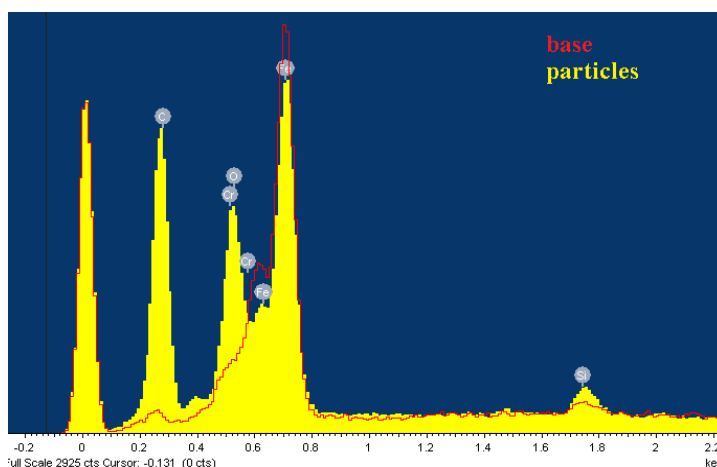


Figure 4. EDAX analysis and micrograph of the ferritic SS type X4Cr13 obtained by scanning electron microscopy after polarization within the mixture of hydrochloric acid (0.01 mol L^{-1}) with addition of Vitamin-C (0.005 mol L^{-1}).

Table 1. Kinetic parameters for corrosion of stainless steel type X4Cr13 obtained from potentiodynamic polarisation curves in HCl solution ($c_{\text{HCl}} = 0.01, 0.1$ and 1.0 mol L^{-1}) with and without added $x \text{ M}$ of Vitamin C at 25°C ($1^{\text{st}}, 2^{\text{nd}}$ and 5^{th} consecutive measurement).

Corrosive media	E_{corr1} (V vs.SCE)	E_{corr2} (V vs.SCE)	E_{corr5} (V vs.SCE)	i_{corr1} ($\mu\text{A cm}^{-2}$)	i_{corr2} ($\mu\text{A cm}^{-2}$)	i_{corr5} ($\mu\text{A cm}^{-2}$)	R_{p1} ($\Omega \text{ cm}^2$)	R_{p2} ($\Omega \text{ cm}^2$)	R_{p5} ($\Omega \text{ cm}^2$)	r_1 mm y^{-1}	r_2 mm y^{-1}	r_5 mm y^{-1}
0.01 M HCl + xM Vitamin C												
0	-0.482	-0.410	-0.442	46.01	12.85	10.43	647.2	2319.0	2853.0	0.534	0.149	0.120
5.0×10^{-4}	-0.468	-0.436	-0.460	44.01	11.73	6.74	787.3	2890.0	4760.0	0.511	0.136	0.078
1.0×10^{-3}	-0.469	-0.439	-0.454	42.55	9.06	6.09	773.2	3267.0	4881.0	0.494	0.105	0.071
5.0×10^{-3}	-0.468	-0.425	-0.459	39.14	8.52	5.36	825.6	3217.0	5050.0	0.454	0.099	0.062
1.0×10^{-2}	-0.468	-0.443	-0.472	37.69	9.35	6.25	790.0	2926.0	3992.0	0.415	0.108	0.072
0.1 M HCl + x M Vitamin C												
0	-0.526	-0.555	-0.549	456.00	597.71	616.00	68.14	53.13	60.33	5.293	6.937	5.728
5.0×10^{-4}	-0.530	-0.560	-0.555	389.83	406.40	353.14	76.37	58.32	66.49	4.524	4.717	4.092
1.0×10^{-3}	-0.534	-0.545	-0.557	402.97	371.89	464.80	66.73	65.22	61.68	4.676	4.315	5.395
5.0×10^{-3}	-0.531	-0.562	-0.559	489.60	451.66	450.51	65.15	64.09	65.91	5.682	5.243	5.230
1.0×10^{-2}	-0.529	-0.560	-0.556	361.14	368.34	440.46	82.46	65.00	67.60	4.191	4.275	5.113
1.0 M HCl + x M Vitamin C												
0	-0.464	-0.479	-0.471	171.43	370.63	434.74	116.7	80.34	68.49	1.989	4.300	5.044
5.0×10^{-4}	-0.482	-0.496	-0.500	233.14	389.71	446.86	85.75	61.71	48.08	2.703	4.524	5.189
1.0×10^{-3}	-0.473	-0.490	-0.490	226.29	332.00	457.14	105.2	67.47	56.41	2.621	3.853	5.306
5.0×10^{-3}	-0.487	-0.500	-0.503	283.09	501.83	632.91	83.50	59.34	47.04	3.284	5.824	7.346
1.0×10^{-2}	-0.492	-0.506	-0.506	275.43	429.71	536.00	80.38	55.98	49.35	3.190	4.991	7.003

Impedance spectra measured after 2, 4, and 10 h of immersion at the open-circuit potential are given in Figures 5, 6 and 7 in HCl solution alone, and in the presence of various concentrations of the chosen inhibitor. EIS measurements were performed over a frequency range from 60 kHz –10 mHz. The results obtained by EIS (Table.2) in some way, confirm the interpretation mentioned above (polarization measurements).

At the lowest concentration of HCl; $c = 0.01$ M the low frequency response is connected to the diffusion and the adsorption process of the reactants. The diffusion tail may indicate on the porosity of the adsorbed layer. In continuation with increasing acid concentration, this phenomenon is becoming less pronounced, which is reflected in the fall of double layer capacitance especially between 0.1 and 1.0 M HCl.

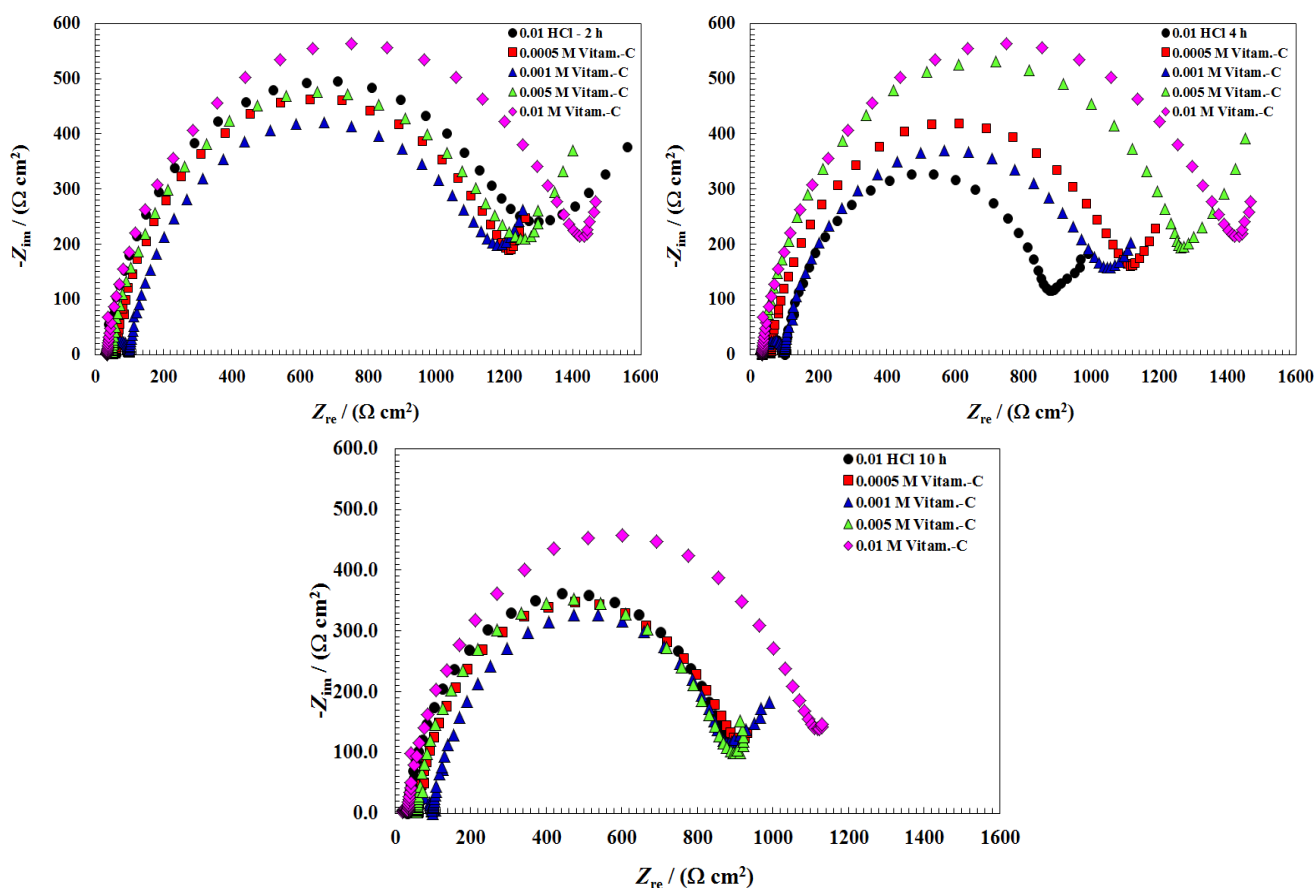


Figure 5. EIS Nyquist plots for stainless steel type X4Cr13 in 0.01 M HCl with and without with and without added x M of Vitamin C at 25°C (after 1h, 4h and 10 h of immersion).

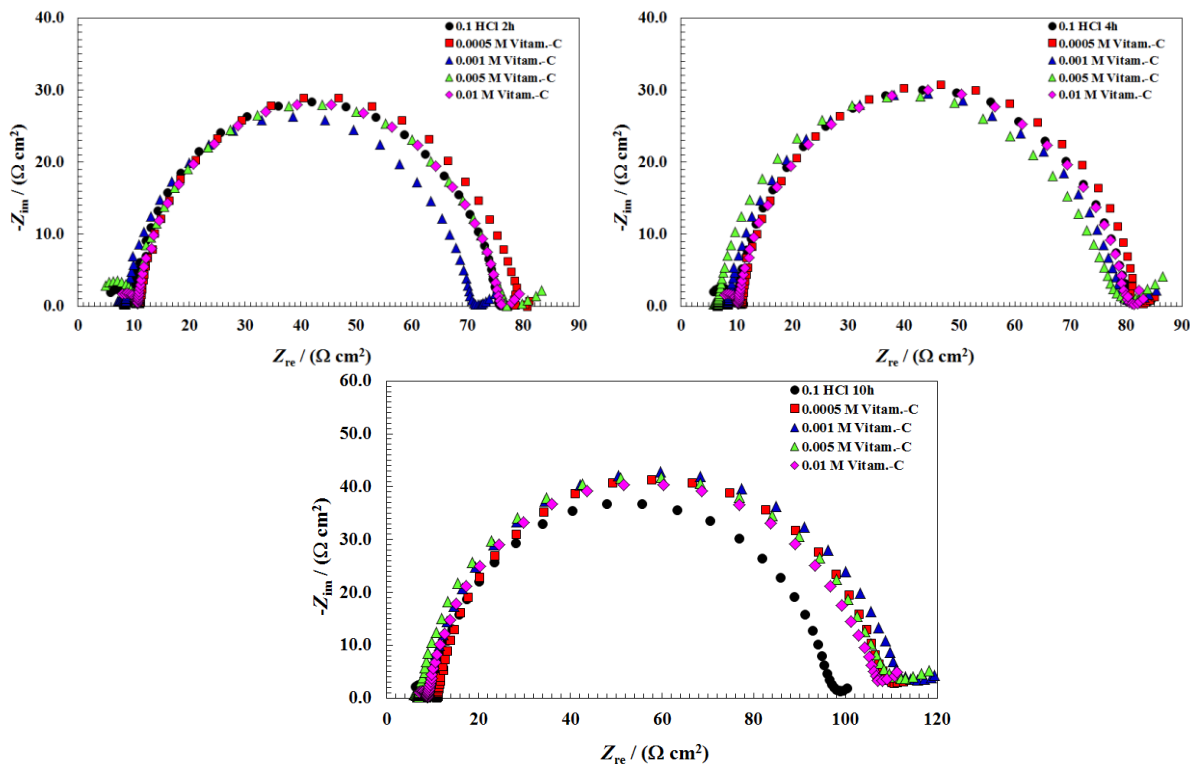


Figure 6. EIS Nyquist plots for stainless steel type X4Cr13 in 0.1 M HCl with and without with and without added x M of Vitamin C at 25°C (after 1h, 4h and 10 h of immersion).

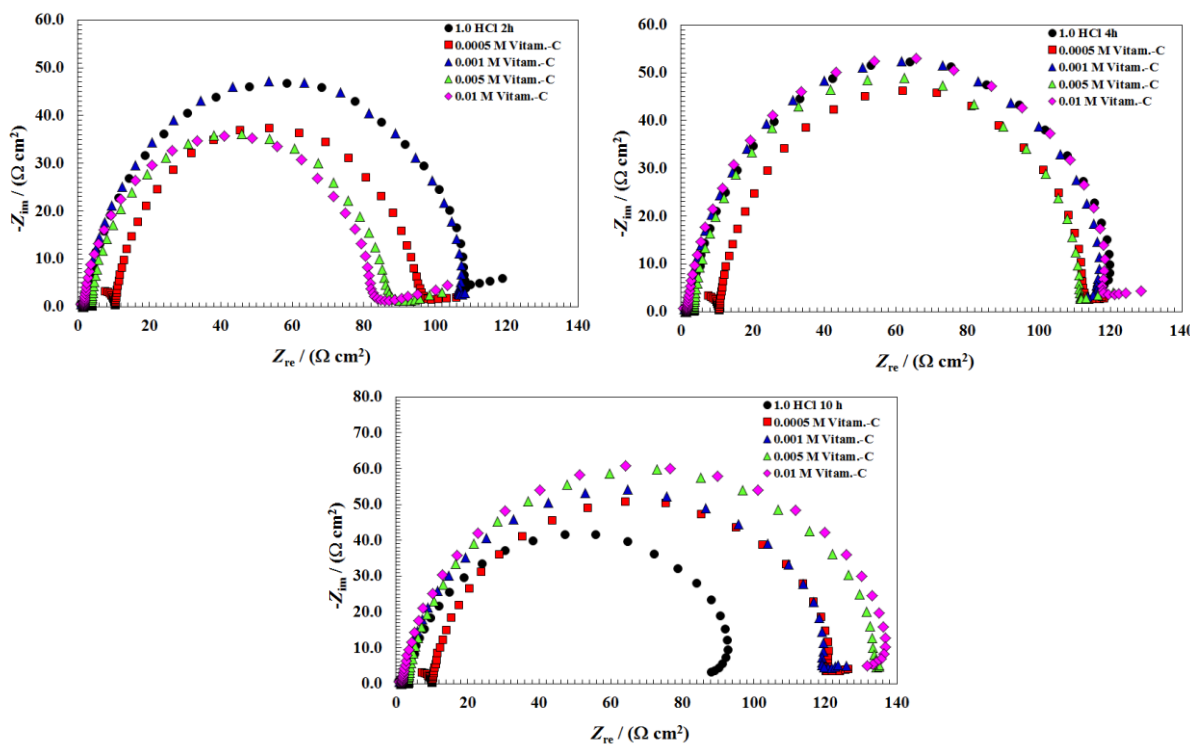


Figure 7. EIS Nyquist plots for stainless steel type X4Cr13 in 1.0 M HCl with and without with and without added x M of Vitamin C at 25°C (after 1h, 4h and 10 h of immersion).

Table 2. Electrochemical impedance parameters for SS type X4Cr13 in HCl solution ($c_{\text{HCl}} = 0.01, 0.1$ and 1.0 mol L^{-1}) with and without added $x \text{ M}$ of Vitamin C at 25°C (after 1h, 4h and 10 h of immersion).

Corrosive media	R_{ct1} ($\Omega \text{ cm}^2$)	R_{ct2} ($\Omega \text{ cm}^2$)	R_{ct5} ($\Omega \text{ cm}^2$)	n_1	n_2	n_5	C_{dl1} ($\mu\text{F cm}^{-2}$)	C_{dl2} ($\mu\text{F cm}^{-2}$)	C_{dl5} ($\mu\text{F cm}^{-2}$)
0.01 M HCl + x M Vitamin C									
0	1310.0	995.0	877.5	0.826	0.881	0.879	100.26	80.66	79.79
5.0×10^{-4}	1215.0	1100.0	877.3	0.837	0.831	0.856	75.67	74.76	79.07
1.0×10^{-3}	1150.0	1002.0	698.5	0.822	0.820	0.848	88.45	82.99	99.94
5.0×10^{-3}	1239.0	1295.0	839.3	0.839	0.845	0.890	85.19	76.27	79.69
1.0×10^{-2}	1454.0	1463.0	1099.0	0.839	0.842	0.888	77.79	73.45	69.35
0.1 M HCl + x M Vitamin C									
0	65.70	70.59	87.41	0.901	0.899	0.899	500.35	607.81	848.03
5.0×10^{-4}	67.98	70.73	98.30	0.901	0.913	0.898	446.90	562.07	862.85
1.0×10^{-3}	62.36	71.10	104.1	0.889	0.880	0.882	536.86	712.98	998.59
5.0×10^{-3}	66.29	76.19	125.5	0.891	0.901	0.889	479.19	631.47	986.10
1.0×10^{-2}	69.36	78.96	110.6	0.912	0.900	0.902	421.30	596.84	915.64
1.0 M HCl + x M Vitamin C									
0	108.20	121.0	105.5	0.907	0.910	0.932	347.91	393.93	408.79
5.0×10^{-4}	86.21	103.3	112.7	0.910	0.940	0.941	368.40	382.18	453.85
1.0×10^{-3}	107.40	117.2	120.9	0.925	0.930	0.935	365.07	389.33	458.59
5.0×10^{-3}	83.79	109.9	132.5	0.909	0.929	0.933	374.76	414.29	454.96
1.0×10^{-2}	81.20	119.3	138.9	0.918	0.925	0.915	404.68	484.49	516.06

4. CONCLUSIONS

The inhibiting effect of Vitamin-C is dependent on the electrode potential, concentration of the corrosive medium such as on concentration of Vitamin C, and also on the time of exposure to the media.

For the chosen corrosion system it has been proved that selecting an appropriate inhibitor and also its concentration for a specific environment and metal must be done with great care: it is known that an inhibitor that protects one particular system may accelerate the corrosion of another. Results of presented research show that Vitamin-C exhibits a dual character. In some cases it acts as corrosion

inhibitor and in the other as an activator of corrosion processes. A comparison of curves showed that, with respect to the blank, a noticeable decrease in the anodic current-peak was observed at concentration of HCl $c = 0.01 \text{ mol L}^{-1}$. No anodic current peak was observed at the concentration of 1.0 M of HCl. The flat portion extends to about 100 mV in anodic directions and 50 mV in cathodic direction with regard to the corrosion potential. In continuation just the increasing of the current density was obtained. It can be assumed that the inhibition process begins with electrostatically adsorption of chloride ions on the positively-charged surface within the anodic region (dissolution Fe to Fe^{2+}). Being specially adsorbed, these anions create an excess negative charge towards the solution and favour more adsorption of the cations.

On the basis of the EDAX analysis the presence of the ferri-chelates on the metal surface could be confirmed. It seems to suggest that the existence of the insoluble surface chelate formation on SS surface represents the inhibitive action of Vitamin-C. Good inhibition efficiency of Vitamin-C on SS type X4Cr13 was limited to the concentration of HCl below $c = 0.1 \text{ mol L}^{-1}$ and also the concentration of added Vitamin-C has to be lower than $c = 0.01 \text{ mol L}^{-1}$.

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