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

Regina Fuchs–Godec[1], *Miomir G. Pavlović*[2*], *Milorad V. Tomić*[2]

[1] University of Maribor, Faculty of Chemistry and Chemical Engineering, Slovenia
[2] University of Eastern Sarajevo, Faculty of Technology Zvornik, Republic of Srpska
*E-mail: pavlovicmiomir@gmail.com

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The inhibitive behaviour of Vitamin C (ascorbic acid), 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 within a concentration range of 0.01 – 5.0 M HCl. Potentiodynamic polarization and electrochemical impedance spectroscopy (EIS), was used for the measurements at 25 °C. The polarization curves revealed that the studied mixtures of the chosen inhibitor represented mixed-type of the inhibitor. 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 1.0 mol L^{-1}.

Keywords: Corrosion inhibitor, green inhibitor, Vitamin C, ferritic stainless steel, inhibition efficiency

1. INTRODUCTION

Acidic solutions are extensively used within industry for industrial-equipment cleaning, oil-well acidization, and the pretreatments of compositions [1–3]. Hydrochloric acid is widely- used in pickling solutions. The addition of an inhibitor is necessary to prevent corrosion i.e. to reduce the dissolution of metals within these acidic environments. The usage of chemical corrosion-inhibitors is common during production and processing operations. The addition of high molecular weight organic compounds, such as surface active agents, to acid solutions has been proved to be an effective method to reduce the rate of corrosion of metals, as shown recently. Moreover, ionic and non-ionic surfactants have been reported to be corrosion inhibitors for metals like copper, aluminium and mild steel [4-14]. The development of new chemicals is particularly challenging, as they would need to maintain good protection of the materials under a variety of conditions, whilst being environmentally acceptable. There is increasing concern about the toxicity of corrosion-inhibitors throughout in industry. Any toxic effects not only affect living organisms but also poison the earth. Therefore, over recent years, the traditional approach regarding corrosion inhibitors has gradually changed, owing to the increasing interest and attention of the world towards environmental problems, towards protecting the environment, the hazardous effects of the using of chemicals on the ecological balance. It is believed that toxic inhibitors as widely-used within industrial processes should be replaced by new environmentally friendly ones.

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.[15–19].

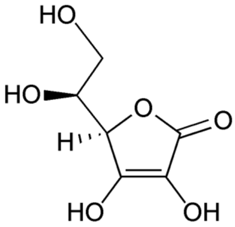
The purpose of this work was to study the inhibitive action of Vitamin C (ascorbic acid), as a type of green inhibitor, on the corrosive behaviour of stainless-steel (SS) X4Cr13 in an aqueous solution of hydrochloric acid (HCl) within a concentration range of 0.01 – 5.0 M HCl (M = mol L^{-1}). The most desirable surfactant inhibitor is the one that ensures high inhibitive efficiency at low surfactant concentrations. The chosen concentrations of added Vitamin C were 0.01 and 0.001 mol L^{-1}.

Therefore, the goal of this work was to find the highest concentration of HCl, where, the chosen concentration of added Vitamin C (0.01 or 0.001 M of Vitamin C), would be enough to achieve a satisfactory degree the inhibitive efficiency.

Two different electrochemical methods were used for this purpose, i.e. classical potentiodynamic measurement and electrochemical impedance spectroscopy.

2. EXPERIMENTAL PART

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 5 mVs^{-1}. EIS measurements were carried out within the 60 kHz –1 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. The measurements were performed using the Solartron 1287 Electrochemical interface and the Solartron 1250 Frequency response analyser. Data were collected and analysed using CorrView, CorrWare, Zplot, and ZView software, as developed by Scribner Associates Inc. The surface coverage θ, was calculated via the kinetic parameters measured during corrosion processes, as well as the polarisation resistance R_p, and the corrosion current density i_{corr}.



Vitamin – C

3. RESULTS AND DISCUSSION

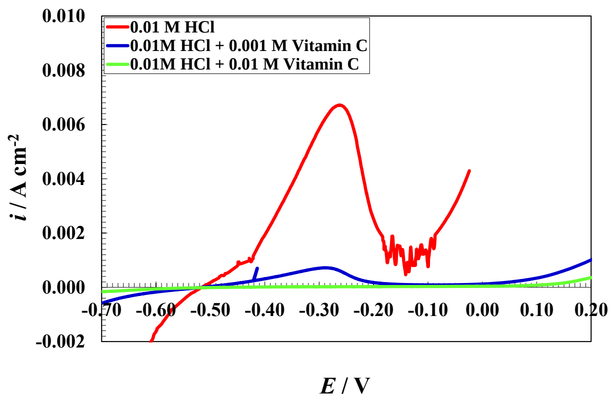
Electrochemical results

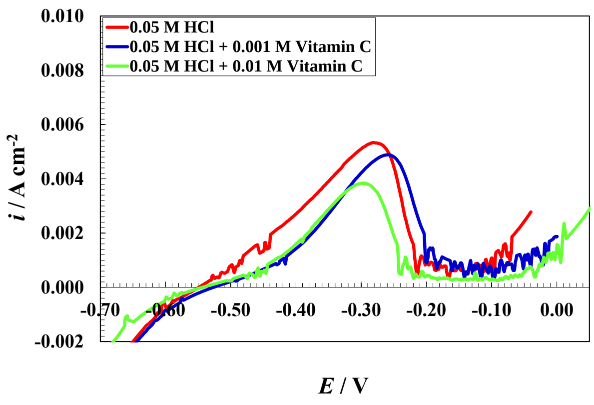
The effects of the presence of Vitamin C on the current–potential characteristics displayed by the polarisation curves of ferritic stainless steel type X4Cr13 in HCl is presented in Figs. 1 and 2.

It is clear that the addition of Vitamin C hindered any acidic attack on the steel electrode. 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}. Furthermore, an appreciable lowering of the cathodic current may be observed from these figures. This result suggests that the addition of the selected vitamin reduced anodic dissolution, and retarded the hydrogen evolution reaction (a mixed-type of inhibitor). No anodic current peak was observed at concentrations of HCl higher than 0.1 mol L^{-1}.

It is necessary to mention that at concentration of HCl c = 1.0 M with and without addition of the Vitamin C, the profiles on voltammogram (Fig. 1) obtain flat profiles. The flat portion extends to about 100 mV in both directions, with regard to the corrosion potential. The best inhibitive efficiency is expected within the potential region where the current is at minimum. The flat portion was additionally extended by about 50 mV in both directions with the addition of 0.01 M Vitamin C in the 1.0 M HCl solution. At the concentration of HCl higher than 1.0 mol L^{-1}, this effect becomes negligible.

The electrochemical parameters obtained from these polarization curves, corrosion potential (E_{corr}), corrosion current density (i_{corr}), the polarisation resistance (R_p) and the inhibition efficiency, 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. In the presence of Vitamin C, lower values of the i_{corr} we recorded. Actually, the inhibitive efficiency increased with the concentration of Vitamin C, but at concentrations of HCl higher than 0.1 mol L^{-1}, these values became negligible.





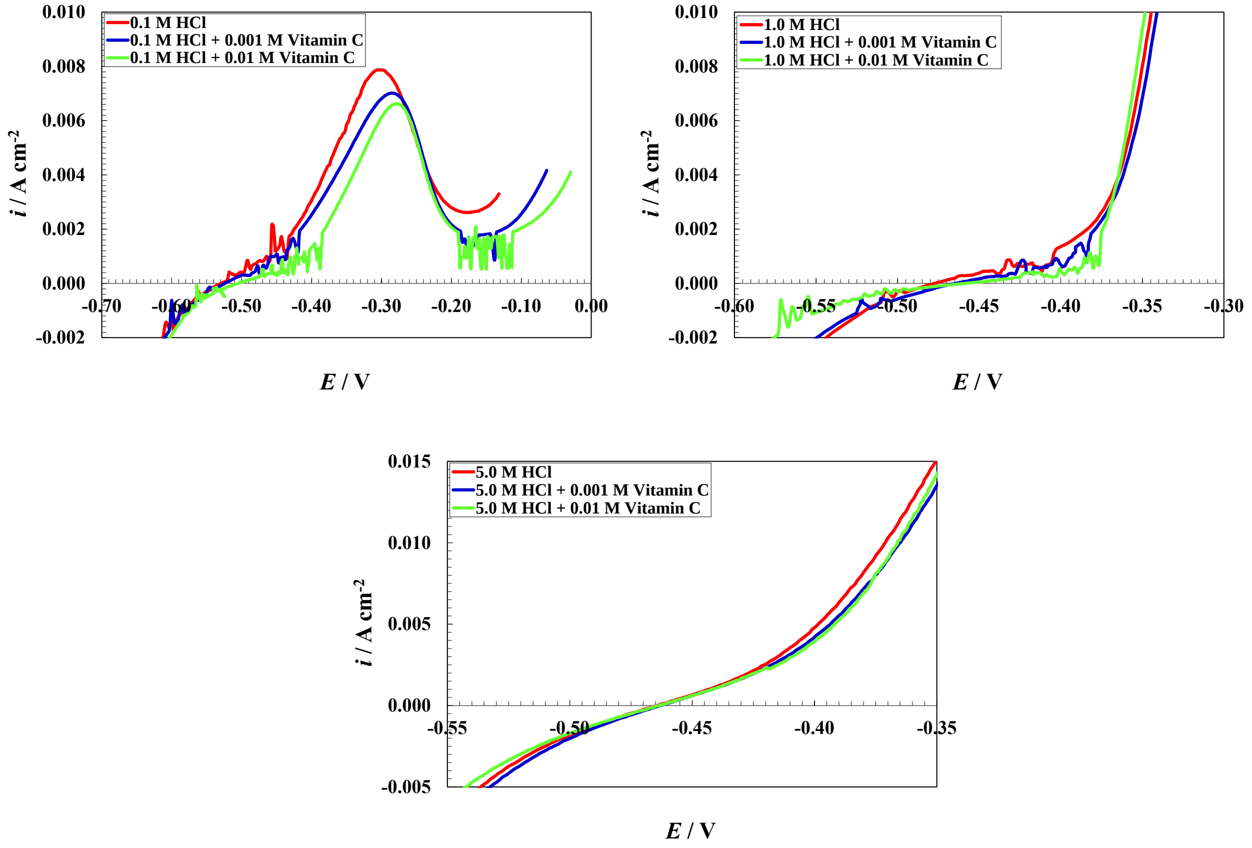
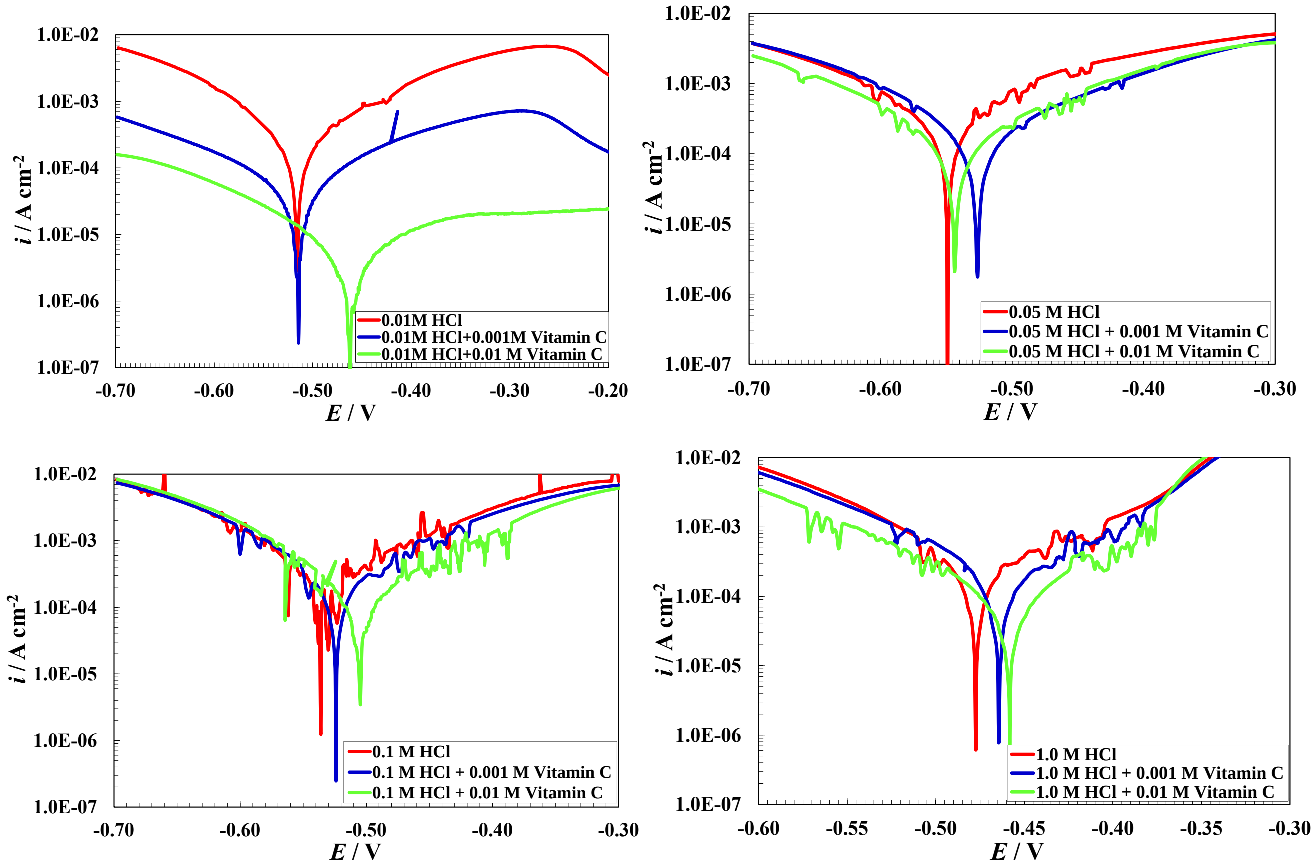


Figure 1. Potentiodynamic polarisation curves (5 mVs^{-1}) with and without addition of Vitamin C on SS type X4Cr13 in HCl.



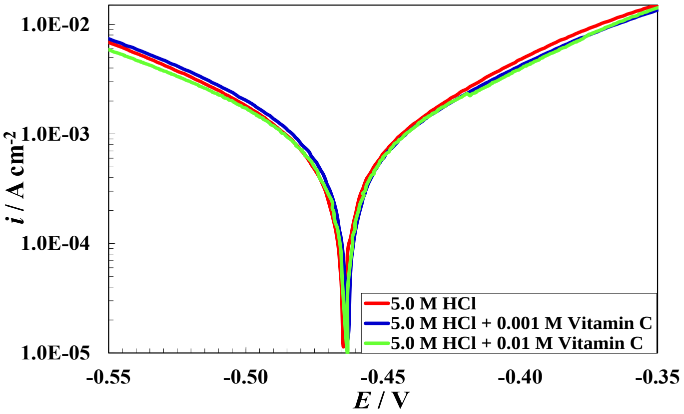


Figure 2. Influence of added Vitamin – C on the cathodic and anodic behaviour of stainless steel type X4Cr13 in HCl.

Table 1. Kinetic parameters for corrosion of stainless steel type X4Cr13 obtained from potentiodynamic polarisation curves in HCl solution with and without added x M of Vitamin C at 25ºC.

Corrosive media	i_{corr} (Acm^{-2})	E_{corr} (V vs.NKE)	R_p (Ωcm^2)	$\theta_{i_{corr}}$	θ_{R_p}
0.01 M HCl + x M Vitamin C					
0	3.21×10^{-4}	-0.521	87.179		
1.0×10^{-3}	9.210×10^{-5}	-0.515	299.830	0.713	0.709
1.0×10^{-2}	3.450×10^{-6}	-0.459	2253.90	0.984	0.961
0.05 M HCl + x M Vitamin C					
0	3.591×10^{-4}	-0.546	56.887		
1.0×10^{-3}	1.709×10^{-4}	-0.547	116.860	0.524	0.513
1.0×10^{-2}	1.370×10^{-4}	-0.542	142.412	0.618	0.600
0.1 M HCl + x M Vitamin C					
0	4.573×10^{-4}	-0.526	51.732		
1.0×10^{-3}	2.793×10^{-4}	-0.524	86.182	0.389	0.399
1.0×10^{-2}	2.120×10^{-4}	-0.532	115.330	0.536	0.551
1.0 M HCl + x M Vitamin C					
0	2.575×10^{-4}	-0.475	75.869		
1.0×10^{-3}	2.340×10^{-4}	-0.463	80.401	0.091	0.056
1.0×10^{-2}	1.703×10^{-4}	-0.457	102.400	0.338	0.259
5.0 M HCl + x M Vitamin C					
0	1.423×10^{-3}	-0.464	21.344		
1.0×10^{-3}	1.085×10^{-3}	-0.465	21.787	0.237	0.049
1.0×10^{-2}	1.025×10^{-3}	-0.468	22.851	0.279	0.152

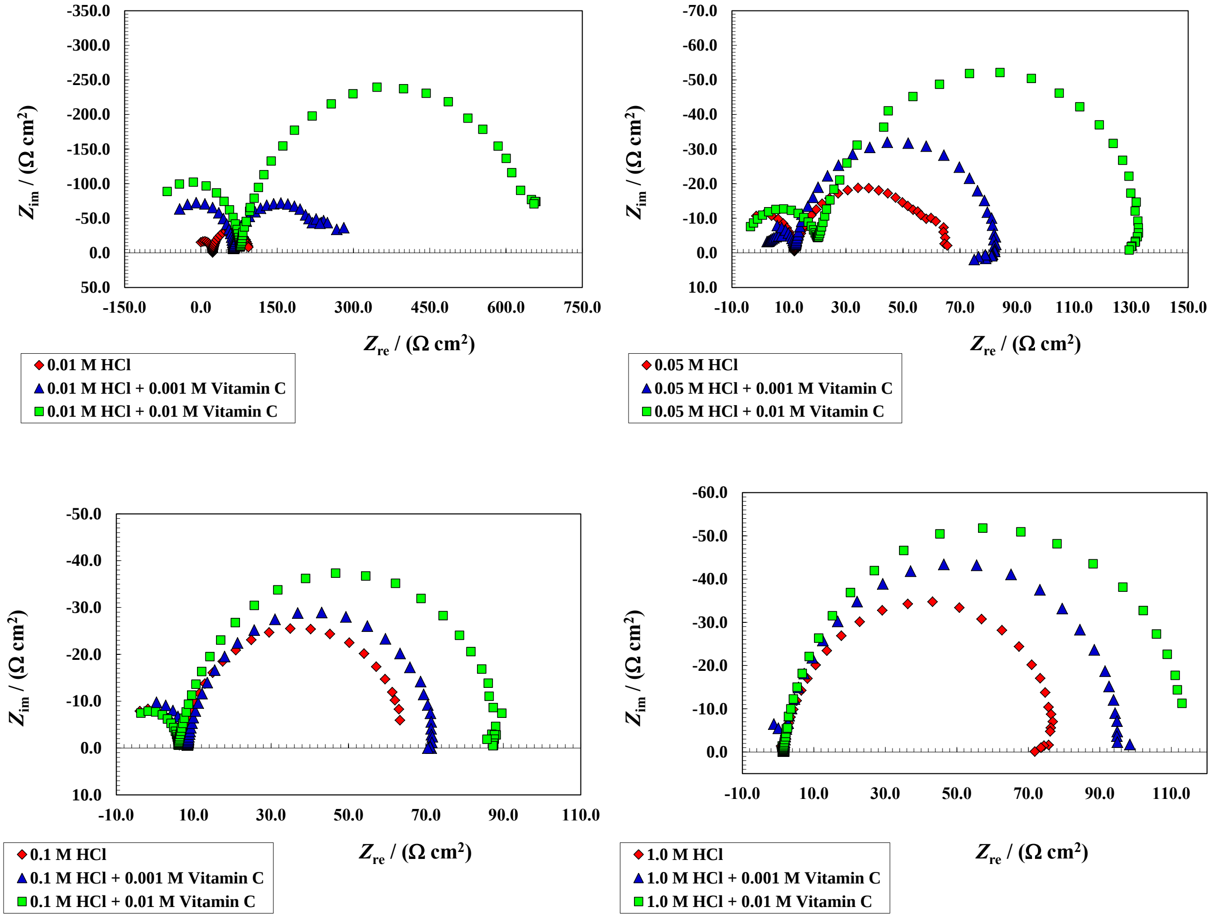
The inhibition efficiency *IE* was calculated from the measured i_{corr} and R_{p} values, using the relationship:

$$IE\% = \left[1 - \frac{i^{'}_{corr}}{i_{corr}}\right]\cdot 100 \qquad (1)$$

$$IE\% = \left[1 - \frac{R_{p}}{R^{'}_{p}}\right]\cdot 100 \quad , \qquad (2)$$

where the notations i_{corr} and R_{p} were used for those measurements without added-surfactant, whilst the primed quantities i_{corr}' and R_{p}' were applied when the Vitamin C was added to an HCl solution. The adsorption of organic molecules may be explained by the presence of an oxygen atom (a hetroatom), π electron of aromatic rings and electron donating groups. Hetro-atoms, such as oxygen, are the major adsorption centres within organic compounds because of their interactions with metal's surface [20]. Adsorption can also occur via electrostatic interaction between a negatively-charged surface, as provided by a specifically adsorbed anion (Cl^{-}) on the metal's surface (iron, steel), and the positive charge of the inhibitor [21].

Impedance measurements of the SS electrode type X4Cr13 at its open circuit potential after 2 h of immersion in HCL solution alone, and in the presence of various inhibitors' concentrations, were performed over a frequency range from 60 kHz –1 mHz.



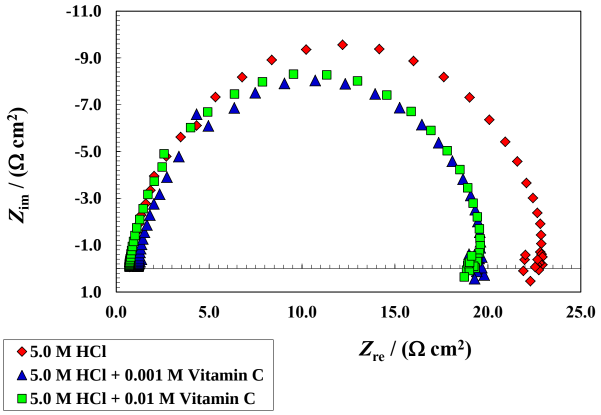


Figure 3. EIS Nyquist plots for stainless steel type X4Cr13 in HCl with and without with and without added x M of Vitamin C at 25ºC.

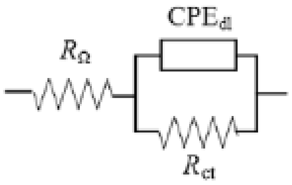


Figure 4. The electrochemical equivalent circuit used for simulating the impedance data of SS type X4Cr13 in HCl with and without with and without added x M of Vitamin C at 25ºC.

In order to compare the corrosion-behaviours of different solutions, Figs. 3 show the Nyquist diagrams of SS type X4Cr13. The charge transfer resistance (R_{ct}) and the interfacial double layer capacitance (CPE) values were derived by using the equivalent circuit, as shown in Fig. 4.

The results obtained by EIS (Table.2) in some way, confirm the interpretation mentioned above (polarization measurements). In the blank solution the C_{dl}-values have decreased with increasing concentration of HCl. On the basis of this phenomenon it could be assumed that, Cl^- anions are first adsorbed on the metal surface, they charge it negatively. In highly acidic solution, Vitamin-C exists in the protonated form. So, molecules of Vitamin-C may adsorb through electrostatic interactions between positively-charged molecules and negatively-charged metal surfaces. But, with addition of Vitamin C the C_{dl}-values were start to decrease in the opposite direction. This effect probably indicates on the porous nature of the adsorbed film at the concentration higher than c = 0.1 M of HCl.

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 1.0 mol L^{-1}.

Table 2. Electrochemical impedance parameters for SS type X4Cr13 in HCl solution with and without added x M of Vitamin C at 25°C.

Corrosive media	R_{ct} (Ω cm^2)	n	C_{dl} (□F cm^{-2})	□□R_{ct}
0.01 M HCl + x M	**Vitamin C**			
0	**72.67**	**0.858**	**615.80**	
1.0 x 10^{-3}	**176.50**	**0.871**	**21.73**	**0.589**
1.0 x 10^{-2}	**586.76**	**0.928**	**11.12**	**0.876**
0.05 M HCl + x M	**Vitamin C**			
0	**52.76**	**0.806**	**462.80**	
1.0 x 10^{-3}	**71.60**	**0.921**	**193.73**	**0.263**
1.0 x 10^{-2}	**117.61**	**0.943**	**31.50**	**0.551**
0.1 M HCl + x M	**Vitamin C**			
0	**60.14**	**0.884**	**377.58**	
1.0 x 10^{-3}	**64.72**	**0.909**	**352.06**	**0.071**
1.0 x 10^{-2}	**84.36**	**0.928**	**282.87**	**0.287**
1.0 M HCl + x M	**Vitamin C**			
0	**77.57**	**0.928**	**314.00**	
1.0 x 10^{-3}	**95.98**	**0.931**	**241.29**	**0.192**
1.0 x 10^{-2}	**116.90**	**0.946**	**253.51**	**0.336**
5.0 M HCl + x M	**Vitamin C**			
0	**22.8**	**0.885**	**189.89**	
1.0 x 10^{-3}	**18.86**	**0.899**	**256.06**	
1.0 x 10^{-2}	**19.44**	**0.903**	**288.17**	

4. CONCLUSIONS

Results 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 $c = 0.01$ mol L^{-1}. No anodic current peak was observed at the concentration of 1.0 M of HCl. In that case the flat portion extends to about 50 mV in both directions with regard to the corrosion potential. In continuation just the increasing of the current density was obtained.

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 0.1mol L^{-1}.

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