

Effect of Ions Y^{+3} Inhibitor on Mild Steel Corrosion in 0.5 N NaCl Under Hydrostatic and Hydrodynamic Regime

Sihem OUCHENANE, Sihem ABDERRAHMANE, Abdelaziz HIMOUR

Laboratoire d'Ingénierie des Surfaces (L. I. S.)-Université Badji Mokhtar,

B. P. 12 -23000 Annaba, Algérie

E-mail: abderrahmanesihem@yahoo.fr

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Abstract: The corrosion inhibition of mild steel by Yttrium salt $Y(NO_3)_3 \cdot 6H_2O$ at different concentrations in 0.5 N NaCl, has been carried out by potentiodynamic tests and electrochemical impedance spectroscopy (EIS). In ions Y^{+3} presence, the ions OH^- formation at the interface (electrode / electrolyte) by water and oxygen reduction ,precipitates oxide and hydroxyde composite in passive film. The current density decreases as a function of the inhibitor concentration; it varies from the value without inhibitor ($i = 0.2139 \text{ m A /cm}^2$) to the minimal value ($i = 7.4.10^{-4} \text{ m A/cm}^2$) for 600 ppm concentration; the corresponding inhibitive efficiency reaches 99.65 %. On laminar hydrodynamic regime ($\omega \leq 3000 \text{ rpm}$), steel inhibition depends on rotation speed. It has been showed that passive film formation is all the more slowly than the rotation speed increases. *Copyright © 2014 IFSA Publishing, S. L.*

Keywords: Inhibitor, Yttrium, Rare earth, Corrosion, Hydrodynamic effect, EIS.

1. Introduction

Steel consumption has known these last year's an important increase, provoked by the growing world demand; therefore, steel price increased from (20 to 50) %. Steels remain the more required materials in almost all application fields, due to the competitive price and the existence of product large scale that allows an adequate choice for each use. Among this scale, mild steels, which are iron carbon alloys, constitute most metallic structures and canalizations .These installations are often set up in corrosive medium. Steel is susceptible to be damaged by corrosion phenomena; thus, it frequently happens that initial mechanical properties of steel infrastructures are deteriorated provoking accidents and production

stops. The cost related to loss due to corrosion for networks and metallic structures has been evaluated about (3-4) % of Gross National Product (GNP) [1].

The campaign against steel corrosion is the subject of several works. It remains the major concern that led to the implementation of several protection methods, among them: the coating application, electrochemical protection and inhibitor use. This latter aim an energy and matter economy. Medium corrosive effect decrease by inhibitors adjunction has known an industrial broad application. The inhibitor use is well- known as being excellent, like the chromates, became difficult because of their toxicity [2-7]. Actually, corrosion inhibitor use is subject to more and more severe regulations in terms of environment protection.

One alternative consists to use structure composites related to those of non ecotoxic nature chromates, such as Yttrium and the lanthanides like Cerium that are considered as new inhibitory substances [8]. The Yttrium anticorrosive properties towards steels are relatively well-known, whereas its action mode and the optimal conditions of its use are not completely elucidated yet [9-10].

In this work, we have characterized the behaviour to mild steel corrosion in 0.5 N NaCl at pH=6, under potentiostatic regime with and without inhibitor. After that, we have studied the ions Y^{+3} inhibitor effects on mild steel corrosion under hydrodynamic regime.

The electrochemical characterization has been carried out by potentiodynamic and electrochemical impedance spectroscopy tests. These methods which have been proved to be very useful in different corrosive mediums.

2. Experimental

The study medium is 0.5 N NaCl solution whose pH is adjusted to 6 by hydrochloric acid. The used inhibitor is a salt of rare earth whose chemical formula is: $Y(NO_3)_3 \cdot 6H_2O$, manufactured by Monsanto with the appellation Desquest 2010. The chemical composition in weight percentage (wt %) is: 0.17C, 1.40Mn, 0.045P, 0.045S, 0.009N, balance Fe.

The electrochemical characterization well performed with a potentiostat/galvanostat Voltalab 40 Analytical Radiometer - France), linked to electrolytic thermostated cell which is composed of three electrodes: mild steel working electrode, platinum counter electrode of 1 cm² section and saturated calomel reference electrode (SCE) with $E=0.241$ V/SHE, supplied with Luggin capillary whose extremity is placed near the working electrode in order to minimize the ohmic drop influence. In hydrostatic and hydrodynamic regimes, the working electrode is placed on rotative electrode. It has circular section of 0.2 cm² that was polished mechanically with abrasive Silicon carbide SiC paper up to grade 1200, then finished with diamond paste (1 μ m).

For polarization measurements, the potential was scanned from - 1000 mV/ECS to 1000 mV/ECS at $v=1$ mV/s rate. These quasi-stationary conditions allow to have reproducible results. The polarization resistance (R_p) is measured from polarisation curves, obtained at interval voltage ± 10 mV which is centred on the free potential. Electrochemical impedance spectroscopy (EIS) measurements were carried out in the frequency range of 100 KHz-10 MHz, at the open potential using the amplitude of 10 mV. Impedance data consisting of charge transfer resistance (R_t) and electrical double layer capacitance (C_{dl}) were extracted from Nyquist diagrams.

All tests were carried out at 25 °C after 2 h working electrode immersion in 200 ml corrosive solution under atmospheric conditions.

3. Results and Discussion

3.1. Steel Electrochemical Characterization in 0.5 N NaCl at pH = 6 under Hydrostatic Regime

3.1.1. Free Potential

Fig. 1 represents steel corrosion free potential in 0.5 N NaCl at inhibitor concentrations (200; 400; 600 and 800 ppm) in terms of immersion time. We observe that free circuit potential evolves towards negative values and then tends to be stabilized. This behaviour is normal in a solution without inhibitor; it could be attributed to superficial layer reorganization with anodic process acceleration. Whereas, the explanation is more complex with inhibitor use; the free potential shifts towards more electronegative values may be attributed to: (a) cathodic reaction inhibition; (b) reaction acceleration of anodic oxidation; (c) less resistant superficial layer reorganization to corrosion. When the inhibitor concentration increases, the corrosion free potential tends towards positive values, and reaches maximal values from - 535 mV/ ECS and - 545 mV/ ECS respectively for 600 ppm and 800 ppm.

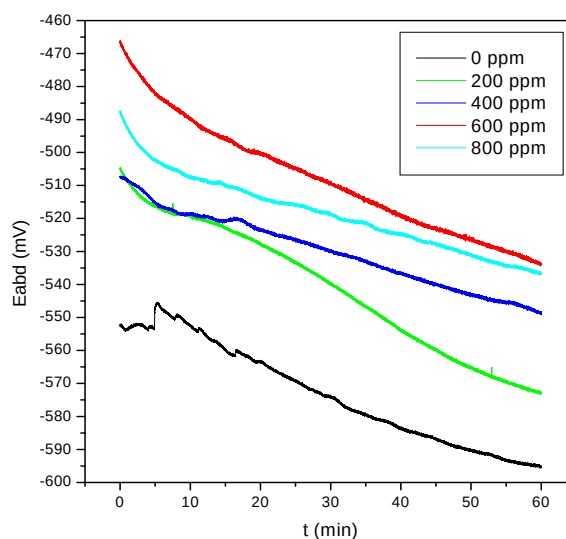
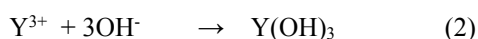
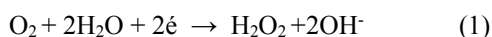


Fig. 1. Free potential in 0.5 N NaCl + ions Y^{+3} at different concentrations.

3.1.2. Polarization Curves

The polarization curves are regrouped in Fig. 2, for 600 ppm concentration, the corrosion potential reaches -500 mV/ECS; this value is noble than those obtained for the other concentrations 200, 400 and 800 ppm. The ions Y^{+3} act to corrosion potential proximity by reduction speed decreasing of dissolved oxygen ;during the cathodic polarization, the ions OH^- , formed at the electrode surface by

oxygen and water reduction, take part to $Y(OH)_3$ compound precipitation reaction, according to the equations [11]:



For cathodic potentials with regard to E_{corr} , we note a slope abrupt augmentation ($\Delta E / \Delta \log I$) = 50 mV/dec. This current variation cannot be attributed to the reduction of Yttrium oxidation degree IV which is not known, contrary to the cerium case [12].

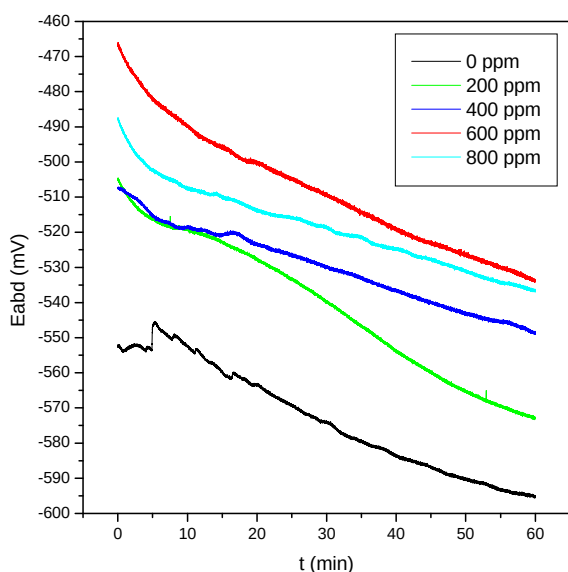


Fig. 2. Polarisation curves in 0.5 N NaCl + ions Y^{+3} at different concentrations.

In ions Y^{+3} presences, the anodic curve decreases slightly with regard to those without inhibitors. For 600 ppm concentration, we note a current density decrease. This can be attributed to anodic dissolution of formed passive film during the corrosion potential. The inhibitive efficiency has been calculated from current density values following the relation:

$$E_{corr} = [(i'_{corr} - i_{corr}) / i'_{corr}] \times 100, \quad (3)$$

where i'_{corr} and i_{corr} are the current density values in both respectively inhibitor absence and presence.

According to electrochemical data deduced from potentiostatic polarization curves, in Table 1, we observe that: (a) The corrosion potential (-496.0 mV/ECS) remains noble in inhibitor absence with regard to the other concentrations. Whereas, the current density take minimum value ($7.4 \cdot 10^{-4}$ mA/cm²) for 600 ppm concentration and maximum value ($2139 \cdot 10^{-4}$ mA/cm²) without inhibitor; (b) the inhibitive efficiency is raised for all concentrations; it is especially (99.65 %) for 600 ppm.

Table 1. Parameter values (E_{corr} ; i_{corr} ; E_r and E_{icorr}) in 0.5 N NaCl + ions Y^{+3} at different concentrations.

Ci (ppm)	E_{corr} (mV/ECS)	i_{corr} (mA/cm ²)	E_r (mV/ECS)	E_{ic} (%)
0	-496.0	0.2139	452.6	/
200	-650.6	0.0236	451.2	88.9
400	-573.2	0.0198	361.0	90.7
600	-517.2	0.00074	336.9	99.65
800	-636.6	0.0046	402.8	97.84

3.1.3. Impedance Diagrams

Impedance measurements have been effected to corrosion free potential, after 2 hours of immersion in 0.5N NaCl at pH = 6, with sinusoidal perturbation of 5 mV in a frequency scale from 100 kHz to 10 MHz. The Nyquist diagrams corresponding respectively to Yttrium concentrations (0, 200, 400, 600) ppm, are showed in Fig. 3a- Fig. 3d. Thus, we can put into evidence the phenomena of: charge transfer, species adsorption and diffusion; and also determine the parameters: charge transfer resistance (R_t), polarization resistance (R_p) and double layer capacity (C_{dl}) relative to each one of these processes. Fig. 3a shows a half-centered capacitive loop on the real axis; the transfer resistance value (277.8 Ohm.cm²) indicates an important steel corrosion from the first immersion hours. And, the double layer capacity value is about 40 μ F.cm⁻². This latter is inferior to 50 μ F.cm⁻² which is generally attributed to corrosion product conductive layer [13]. Either in Fig. 3b or 3c, we observe only one well centered capacitive loop on real axis.

Their loop's diameters are similar to the loop's one without inhibitor. According to Fig. 3d diagram, we note two intermingled loops. The higher one probably corresponds to pure charge transfer loop. The calculated capacity for the frequency maximum value is about 76 μ F.cm⁻². The second one at lower frequencies can be attributed to an intermediary reaction, represented by complex species between ferrous cations and chloride anions. We observe in Fig. 3e, that the loop's diameter is being reduced with an inductive loop obtention. The impedance curves data deduced from impedance diagrams are regrouped in Table 2.

Table 2. Parameter values R_t ; C_{dl} et E_{Rt} (%) according to the inhibitor concentration.

Ci (ppm)	C_{dl} (μ F.cm ⁻²)	R_t (Ohm.cm ²)	E_{Rt} (%)
0	14.33	277.8	/
200	14.08	282.7	1.73
400	0.89	443.3	3.73
600	0.02	10535.0	97.36

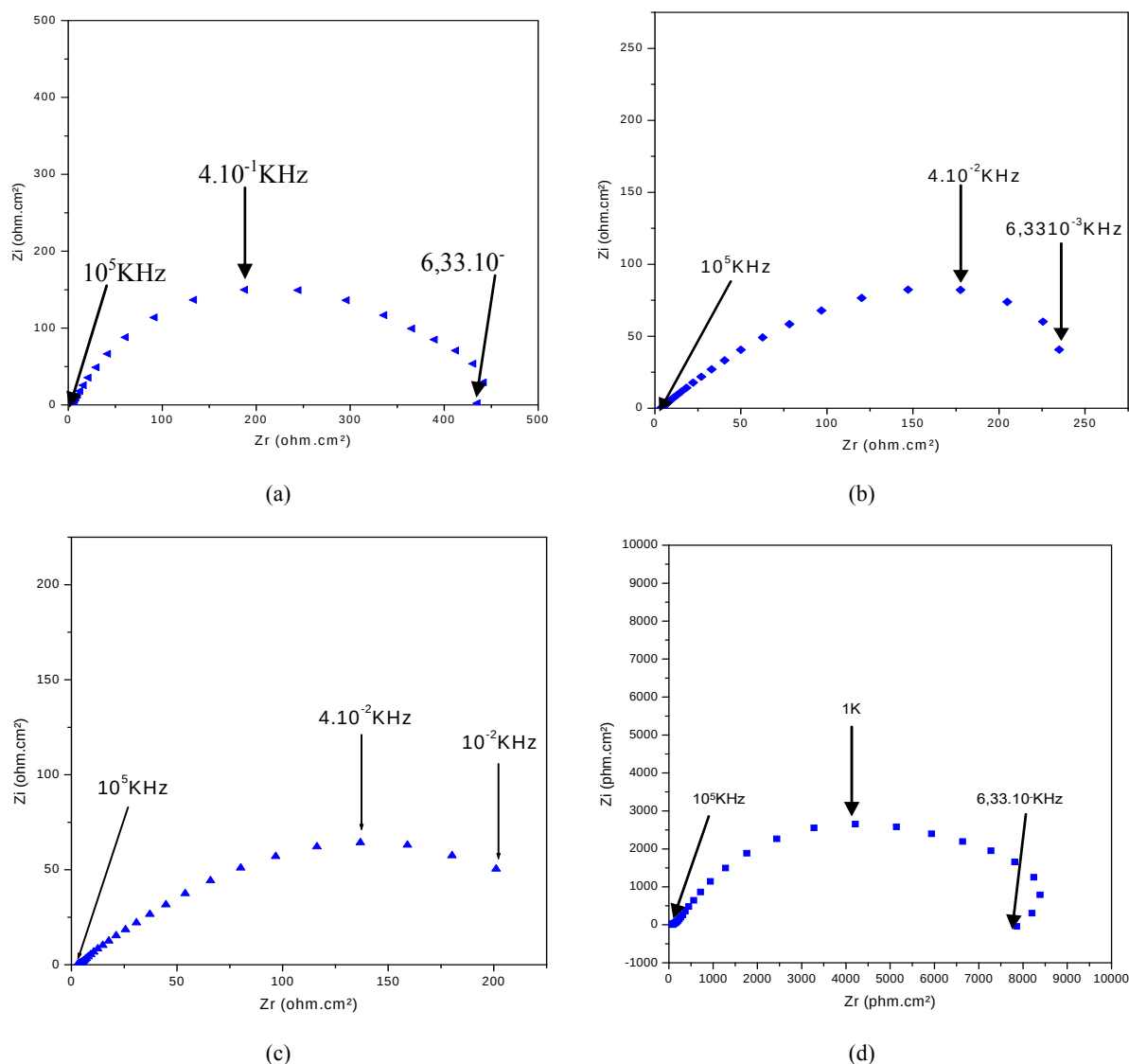


Fig. 3. Nyquist diagrams in 0.5 N NaCl + ions Y^{+3} at (0, 200, 400, 600) ppm.

The double layer capacities (C_{dl}) have been calculated according to the following relation:

$$C_{dl} = 1 / 2\pi R_t f \quad (4)$$

$$R_t = Z_{r(max)} - Z_{r(min)} \quad (5)$$

R_t is the transfer resistance value which is equal to the difference between the maximal real impedance value $Z_{r(max)}$ and the minimal real impedance value $Z_{r(min)}$. f is the frequency value that corresponds to the maximal imaginary impedance value $Z_{i(max)}$. The inhibitive efficiency values have been calculated following the relation:

$$E(\%) = [(R_t - R_t') / R_t] \times 100, \quad (6)$$

where R_t and R_t' are the transfer resistance values in presence and absence of inhibitor respectively.

When the inhibitor concentration increases, R_t increases too, but C_{dl} decreases. These respective evolutions characterized in one hand by the charge

transfer increasing blocking at the electrode surface and, in an other hand, a contact surface diminution linked to the inhibitor adsorption. The best inhibitive efficiency 97.36 % is obtained for 600 ppm concentration, in accordance with polarization curves.

3.2. Steel Electrochemical Characterization in 0,5 N NaCl at pH = 6 Under Hydrodynamic Regime

3.2.1. Hydrodynamic Regime Type

In order to characterize the electrochemical behavior of protector film under hydrodynamic regime, EIS and polarization curves have been established at different working electrode rotation speeds. The flowing regime type is defined by the following three parameters: Reynolds number (Re), Sherwood number (Sh) and the friction force (F_e). The characteristic equations are:

$$Re = (\omega r^2 / \nu) \quad (7)$$

$$Sh = 0.62.Re^{0.5}Sc^{1/3} \quad (8)$$

$$F_e = \rho.\omega.D.Sh.Sc^{0.644} \quad (9)$$

where r (m) is the electrode ray; ν (m²/s) is the kinematic viscosity; ω (rad/s or rpm) is the electrode rotation speed; for $\omega \leq 3000$ rpm: the flowing regime is laminar; ρ (Kg/cm³) is the fluid volumic mass; D (m²/s) is the electroactive specie diffusion coefficient. Re , Sh and F_e values calculated according to the electrode rotation speed are reported in Table 3.

Table 3. Hydrodynamic parameters in rotating electrode case.

ω (rad/s)	Re	Sh	F_e (N/m ²)
10	65	56	0.05
52	327	126	0.5
105	654	179	1.4
209	1308	253	4.0
314	1963	309	7.3
419	2618	357	11.3

3.2.2. Free Potential

The steel corrosion free potential has been followed in 0,5 N NaCl with 600 ppm Yttrium. The hydrodynamic effect on the passive film behaviour is measured (Fig. 4) according to the electrode speed rotation during 60 min. At $\omega = 0$ rpm, the free potential decreases then stabilizes at -545 mV/ ECS after 30 minutes. When the rotation speed increases, we observe a slight free potential increasing for 500 rpm and 2000 rpm. Whereas for $\omega = 1000$ rpm and $\omega = 3000$ rpm, the free potential reaches the respective values -475 mV/ ECS and -400 mV/ ECS.

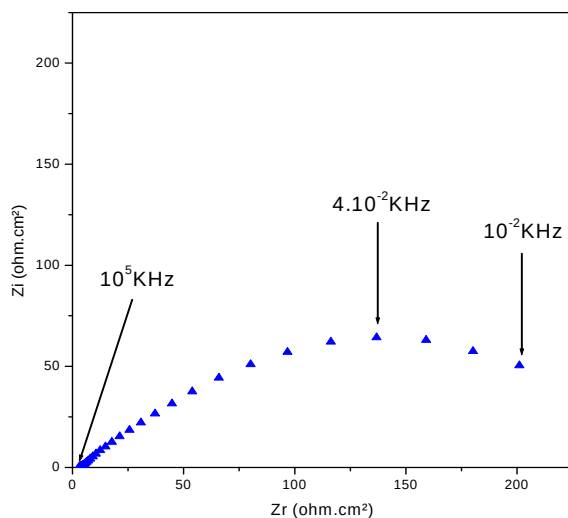


Fig. 4. Free potential in 0.5 M NaCl solution + 600 ppm ions Y³⁺ at different rotation speeds.

This behaviour can be attributed to inhibitor rapid diffusion, with an increasing of dissolved oxygen mass transfer towards the interface. This phenomenon has an effect of oxygen reduction current increasing, and therefore a balance potential moving towards more noble values.

3.2.3. Polarization Curves

Fig. 5 shows the polarization curves obtained in potential interval (-1000 ÷ +1000) mV/ ECS at different rotation speeds. In anodic and cathodic field, the current densities have close values for different rotation speeds, only the one at $\omega = 3000$ rpm in the anodic field. In this case, this high current density decrease can be explained by an anodic reaction speed decrease. The electrochemical data deduced from polarization curves are regrouped in Table 4. At $\omega = 0$ rpm, the current density takes a minimum value 0.74 μ A/cm², then increases considerably when rotation speed increases; the diffusion phenomena in solution and through layers are complexes. For the rotation speeds 500 rpm and 3000 rpm, the corrosion potentials move towards electropositive values, whereas for $\omega = 1000$ rpm and $\omega = 2000$ rpm, they move towards electronegative values.

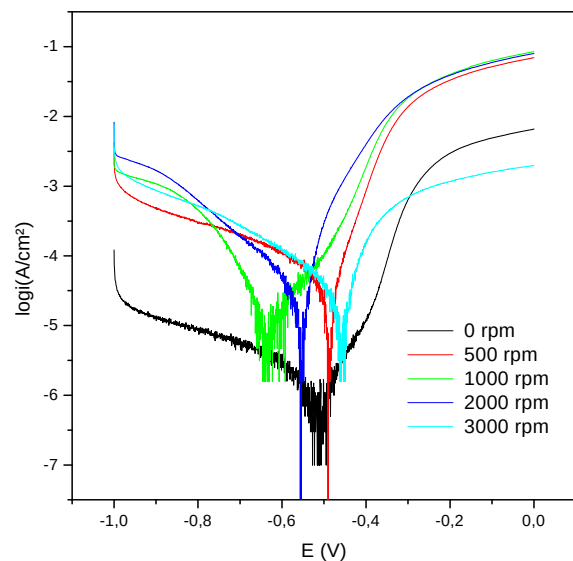


Fig. 5. Polarization curve in 0.5 N NaCl + 600 ppm ions Y³⁺ at different rotation speeds.

Table 4. Parameter values (E_{corr} ; i_{corr} and E_r) in 0.5 N NaCl + 600 ppm ions Y³⁺ at different rotation speeds.

ω (rpm)	E_{corr} (mV/ECS)	i_{corr} (mA/cm ²)	E_r (mV/ECS)
0	-517.2	0.74	-336.9
500	-448.3	25.80	-393.2
1000	-438.4	1.50	-404.6
2000	-558.0	106.10	-435.1
3000	-459.7	33.90	-298.9

3.2.4. Impedance Curves

The electrochemical impedance diagrams (Fig. 6) measured at different electrode rotation speeds, in 0,5 N NaCl, after 2 hours immersion.

They are characterized by only one capacitive loop which height decreases with the rotation speed increasing. The capacitive loop diameter decreasing expresses diffusionnal process existence linked to oxygen transfer towards the electrode which is added

to charge transfer. In these conditions, it is difficult to determine the charge resistance transfer (R_t); the transfer and diffusion processes, prevent diagram deconvolution in two loops.

The obtained parameter values by impedance diagrams are regrouped in Table 5. When the electrode rotation speed increases, R_t decreases whereas C_{dl} increases; which indicates a film protector power decreasing. So, the hydrodynamic effect acts negatively on the film formation.

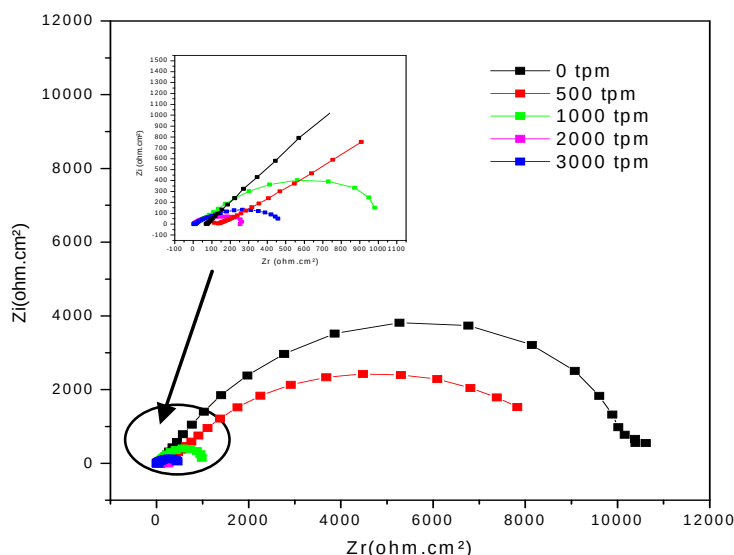


Fig. 6. Nyquist curve in 0.5 N NaCl solution + 600 ppm ions Y^{+3} at different rotation speeds, after 2 h of immersion.

Table 5. Parameter values R_t ; C_{dl} in 0.5 N NaCl + 600 ppm ions Y^{+3} according to the rotation speed.

ω (rpm)	C_{dl} ($\mu F.cm^{-2}$)	R_t ($k\Omega.cm^{-2}$)
0	23.87	10.530
500	171.80	9.260
1000	3.59	1.107
2000	2.34	0.271
3000	1.97	0.509

4. Conclusion

The results of this study have shown that Yttrium salt $Y(NO_3)_3 \cdot 6H_2O$ inhibit carbon steel corrosion in 0,5N NaCl at pH = 6, under hydrostatic and hydrodynamic regimes. Under hydrostatic regime ($\omega = 0$ rpm), the corrosion free potential moves towards negative values as a function of immersion time, in the solution with or without inhibitor. This behaviour is attributed to superficial layer reorganization with anodic process acceleration.

The potentiodynamic tests have showed that at 600 ppm concentration, the corrosion potential values

and the current density are respectively -517.20 mV/ECS and $7.4 \cdot 10^{-4}$ mA/cm². The corresponding inhibitive efficiency is 99.65 %. EIS measurements confirm ions Y^{+3} inhibitor effect; in this case, the charge transfer resistance increases at the same time that the double layer capacity decreases.

Under hydrodynamic regime, the experimental conditions have showed that the protector film electrochemical characterization has been realized under laminar flowing ($\omega \leq 3000$ rpm). The double layer capacity values and charge transfer resistance, obtained after 2 hours of immersion, indicate that the film is being formed slowly when the electrode rotation speed increases. And for an average rotation speed 1000 rpm, the passive film corrosion resistance increases after 24 h of immersion.

According to these results, these non-ecotoxic ions Y^{+3} inhibitor can be an alternative to the chromates use.

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References

- [1]. <http://www.CortecVPCI.com>
- [2]. K. Aramaki, Preparation of chromate-free, self-healing polymer films containing sodiumsilicate on zinc pretreated in a cerium(III) nitrate solution for preventing zinc corrosion at scratches in 0.5 M NaCl, *Corrosion Science*, 2002, Vol. 44, pp. 1375–1389.
- [3]. K. Aramaki, The inhibition effects of cation inhibitors on corrosion of zinc in aerated 0.5M NaCl, *Corrosion Science*, Vol. 43, 2001, p. 1573-1588.
- [4]. K. Aramaki, Protection of zinc from corrosion by coverage with a hydrated cerium (III) oxide layer and ultrathin polymer films of a carboxylate self-assembled monolayer modified with alky ltrieth oxysilanes, *Corrosion Science*, 2007, Vol. 49, pp. 1963-1980.
- [5]. B. R. W. Hinton, D. R. Arnott, The characteristics of corrosion inhibiting film formed in the presence of rare earth cations, *Microstructural Science*, 1989, Vol. 17, Issue 12, pp. 311-320.
- [6]. B. R. W. Hinton, Corrosion inhibition with rare earth metal salts, *Journal of Alloys and Compounds*, 1992, Vol. 180, pp. 15-25.
- [7]. M. Bethencourt, F. J. Botana, J. J. Calvino, M. Marcosc, M. A. Rodriguez-Chadon, Lanthanide compounds as environmentally-friendly corrosion nhibitors of aluminum alloys, *Corrosion Science*, 1998, Issue 11, Vol. 40, pp. 1803.
- [10]. D. Briggs, M. P. Seah (Eds.), Practical 6Surface Analysis: Auger and X-ray Photoelectron Spectroscopy, Wiley, Cichester, UK, 1990.
- [11]. M. A. Arenas, A. Conde, J. J. de Damborenea. Growth mechanisms of cerium layers on galvanised steel, *Corrosion Science*, 2002, Vol. 44, p. 511.
- [12]. J. T. Lu, H. J. Wu, G. Kong, C. S. Che, Q. Y. Xu. Growth and corrosion behavior of rare earth film on hot-dip galvanized steel. *Transactions of Nonferrous Metals Society of China*, 2006, Vol. 16, p.1397.
- [13]. M. G. S. Ferreira, R. G. Duarte, M. F. Montemor, A. M. P. Simões, Silanes and rare earth salts as chromate replacers for pre-treatments on galvanised steel. *Electrochimica Acta*, Vol. 49, 2004, pp. 2927-2935.

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