

Electrochemical behavior of indole for AISI 430 stainless steel in changing the media from 1 mol L⁻¹ H₂SO₄ to 1 mol L⁻¹ HCl

Comportamento eletroquímico do indol para o aço inoxidável AISI 430 com a mudança do meio de H₂SO₄ 1 mol L⁻¹ para HCl 1 mol L⁻¹

Martha Tussolini¹, Aline Viomar², Everson do Prado Banczek³, Maico Taras da Cunha⁴ e Paulo Rogério Pinto Rodrigues⁵.

¹Master in Applied Chemistry, ²Bachelor in Chemistry, ⁴Master and ³⁻⁵Doctor in Science. UNICENTRO - State University in the Midwest, Guarapuava - Paraná, Brazil.

Abstract

The adsorption of organic substances in metals and in different media has been attributed to different effects, such as the carbon chain size, type or number of heteroatom in the molecule structure, reactivity, steric effect, among others. The objective of this work is to study the electrochemical indole behavior for AISI 430 stainless steel (SS), when changing the study media from H₂SO₄ 1 mol L⁻¹ to HCl 1 mol L⁻¹. The experimental techniques used are as follows: the open circuit potential, anodic and cathodic potentiodynamic polarization, electrochemical impedance spectroscopy, optical microscopy and scanning electron microscopy. These results suggest that the adsorption of indole in the presence of SO₄⁻² is lower than in the medium containing Cl⁻, which is justified by the indole action as a weak acid, because it has only a single pair of electrons, which is displaced and takes part in the π-electron aromatic system, thus the first step of the indole reaction in acid media is the protonation and generation of an indole cation.

Keywords: corrosion inhibitor, adsorption, protonation.

Resumo

A adsorção das substâncias orgânicas nos metais em diferentes meios tem sido atribuída a diferentes efeitos, tais como: ao tamanho da cadeia carbônica, tipo ou número de heteroátomo presente na estrutura da molécula, reatividade, efeito estérico, entre outros. O objetivo deste trabalho é estudar o comportamento eletroquímico do Indol (C₈H₇N) para o aço inoxidável AISI 430, quando se muda o meio de estudo de H₂SO₄ 1 mol L⁻¹ para HCl 1 mol L⁻¹. Experimentalmente foram empregadas como técnicas: medida de potencial de circuito aberto, curvas de polarização potenciodinâmica anódica e catódica, espectroscopia de impedância eletroquímica, microscopia óptica e eletrônica de varredura. Estes resultados sugerem que a adsorção do indol em presença de SO₄⁻² é menor em relação ao meio que contém íons Cl⁻, justificado pela ação do indol como ácido fraco, pois o mesmo possui apenas um único par de elétrons, o qual é deslocado e participa do sistema π-eletron aromático, desta forma a primeira etapa da reação do indol em meio ácido é a protonação e geração de um indol cátion.

Palavras-chave: inibidor de corrosão, adsorção, protonação.

Introduction

The metallic corrosion is a technology subject well studied since the economic loss of companies and governments in the replacement of corroded metal parts are quite significant (ANUNZIATO, 2010). To minimize the problem of corrosion, corrosion inhibitors are used, these

are substances that when added to aggressive media minimize the oxidation reactions (RODRIGUES, 1998). There are several studies about inhibitors, mainly on the adsorption effect of these compounds considering the influence of the heteroatom present in the carbon chain, the polar groups effect, the electron density in aromatic compost, the position of the heteroatom in the aromatic ring, the nature and charge of the metal surface, the type of electrolyte, among others (RODRIGUES, 1997). It was observed that the inhibition depends on the chemical and electronic structures of the compounds, the latter being more important when different azoles were studied, but with similar surface areas, differing only in the number and type of heteroatom, the oxidation of carbon steel in media $1 \text{ mol L}^{-1} \text{ HCl}$ (POPOVA, 2006). The study of the indole effect on the corrosion behavior of 316 L solution of sodium chloride 0.3 mol L^{-1} at different pH values (4, 8 and 10) showed that change occurs in inhibitory efficiency (DÜDÜKCÜ, 2004). For these changes, the objective is to study the electrochemical behavior of Indole ($\text{C}_8\text{H}_7\text{N}$) for AISI 430 SS, when changing the aggressive medium from $1 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ to $1 \text{ mol L}^{-1} \text{ HCl}$ (TUSSOLINI, 2010).

Materials and Methods

The electrochemical behavior was evaluated using the following techniques: open circuit potential (Eca) tests, anodic and cathodic potentiodynamic polarization measurements, electrochemical impedance spectroscopy (EIS), the surface of the sample was analyzed by scanning electron microscopy (SEM). All tests were performed at $22 \pm 2^\circ \text{ C}$. In electrochemical tests a three-electrode cell was employed: using the platinum as counter-electrode with a 35 cm^2 average area, saturated mercurous sulfate ($\text{Hg}/\text{Hg}_2\text{SO}_4$) and silver-silver chloride (Ag / AgCl) as reference electrode and working electrode (square plate 430 steel Stainless (SS) with a 2 cm^2 average area).

Before tests were carried out, the working electrode was polished with SiC sandpaper with grit sizes 320, 400, 600 and 1200 mesh successively; after that it was rinsed with ultrapure water and dried in cold air jet. A scanning electron microscope Philips brand, model XL 30 was used for SEM, and the analysis was followed by polishing with diamond paste 1μ . All solutions used were prepared with analytical reagents and ultra pure water. The concentrations of sulfuric acid and hydrochloric acid were 1 mol L^{-1} in the presence and absence of indole at 1×10^{-3} , 5×10^{-4} and $1 \times 10^{-4} \text{ mol L}^{-1}$ concentrations.

Tests of the open circuit potential (Eca) were obtained performing a stable potential of $\pm 5 \text{ mV}$ in the interval time of 30 minutes before each test electrochemical impedance spectroscopy was carried out. The curves of anodic and cathodic potentiodynamic polarization were obtained in the two media studied with $1 \text{ mV} / \text{s}$ scan rate. The electrochemical impedance spectroscopy curves were obtained from the kinetic equilibrium with $\pm 10 \text{ mV}$ potential perturbation.

Results

The open circuit potential curves of 430 SS in different media are shown in Figure 1.

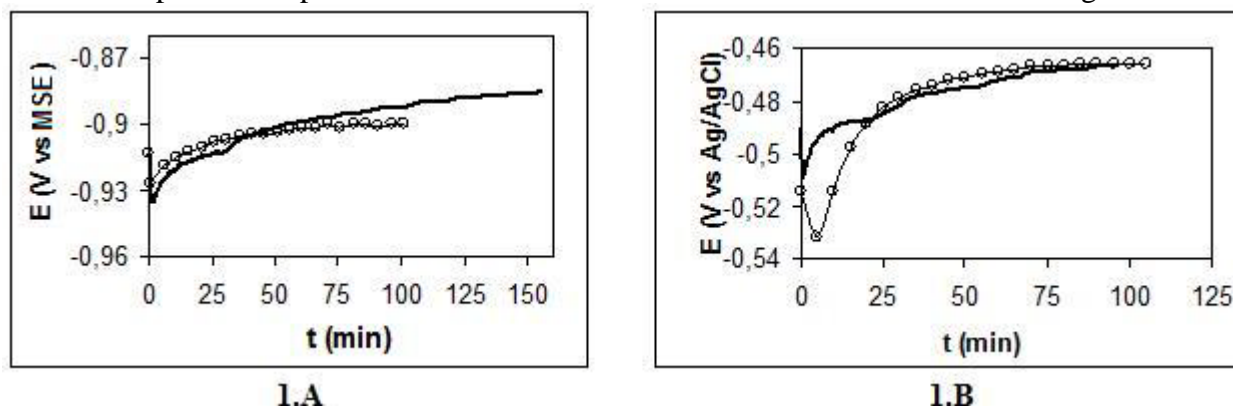


Figure 1: Open circuit potential curves of 430 SS, in absence (\circ) and in the presence of azoles in $1 \times 10^{-3} \text{ mol L}^{-1}$ (—) concentration in media: (1.A) $1 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$; and (1.B) $1 \text{ mol L}^{-1} \text{ HCl}$.

The reason why two different reference electrodes were used is the different media, so in the H_2SO_4 media the MSE employed contains sulfate ion and in the HCl media SCE was employed that contains chloride ion, the common ion present in the reference electrode and in the media allows to minimize de junction potential. The E_{corr} values for the system in the absence and presence of indole in $1 \text{ mol L}^{-1} \text{H}_2\text{SO}_4$ and $1 \text{ mol L}^{-1} \text{HCl}$ media are presented in the table below.

Table 1: Corrosion potential of indole at different concentrations in the $1 \text{ mol L}^{-1} \text{H}_2\text{SO}_4$ and $1 \text{ mol L}^{-1} \text{HCl}$ media for 430 SS.

| Indole / mol L^{-1} | E_{corr} / mV vs SHE (vs. MSE) in $1 \text{ mol L}^{-1} \text{H}_2\text{SO}_4$ | E_{corr} / mV vs SHE (vs. Ag/AgCl) in $1 \text{ mol L}^{-1} \text{HCl}$ |
|------------------------------|--|--|
| 0 | -1514 ± 5 (-900) | -683 ± 9 (-462) |
| 1×10^{-4} | -1498 ± 3 (-884) | -681 ± 6 (-459) |
| 5×10^{-4} | -1501 ± 3 (-887) | -672 ± 8 (-450) |
| 1×10^{-3} | -1508 ± 8 (-894) | -682 ± 9 (-460) |

In figures 2 and 3 the anodic potentiodynamic polarization curves for 430 SS are presented in the absence and presence of indole in $1 \text{ mol L}^{-1} \text{H}_2\text{SO}_4$ and $1 \text{ mol L}^{-1} \text{HCl}$ media.

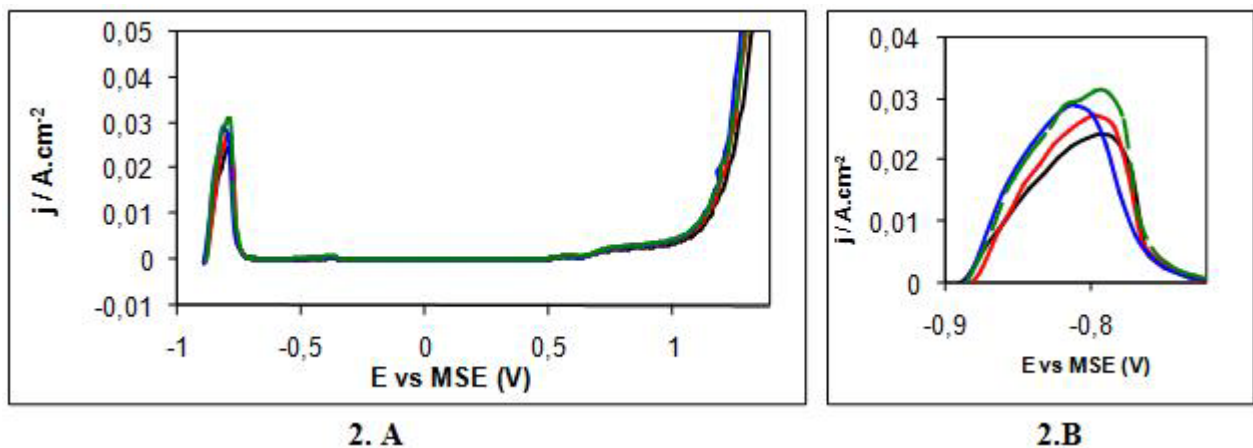


Figure 2 - Potentiodynamic anodic polarization curves of 430 stainless steel in $1 \text{ mol L}^{-1} \text{H}_2\text{SO}_4$ media in the absence (—) and presence of indole concentrations (—) 1×10^{-3} , (—) 5×10^{-4} and (—) $1 \times 10^{-4} \text{ mol L}^{-1}$ in the following regions: (2.A) active-passive-transpassive and (2.B) active.

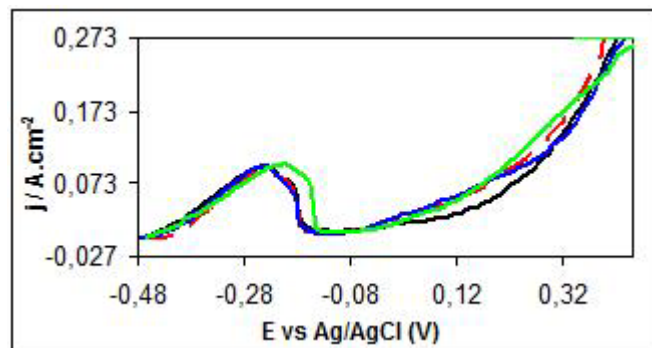


Figure 3 - Potentiodynamic anodic polarization curves of 430 SS in HCl media in the absence (—) and presence of indole in the following concentrations (—) 1×10^{-3} , (—) 5×10^{-4} e (—) $1 \times 10^{-4} \text{ mol.L}^{-1}$.

In Figure 4 the potentiodynamic cathodic polarization curves for 430 SS are shown in the absence and presence of Indole at different concentrations in 1 mol L⁻¹ H₂SO₄ and 1 mol L⁻¹ HCl media.

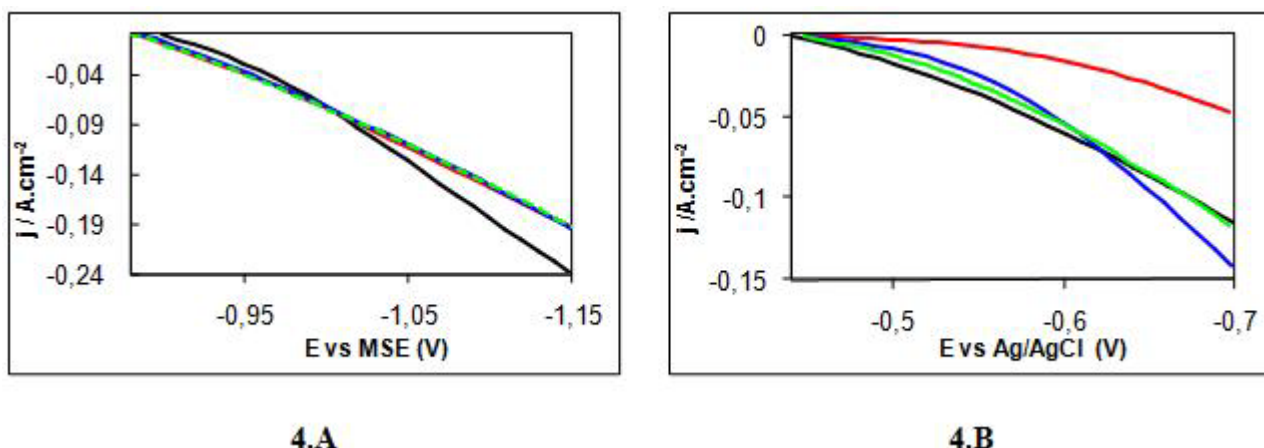


Figure 4: Cathodic potentiodynamic polarization curves of 430 SS in the (4.A) H₂SO₄ and (4.B) HCl media in the absence (—) and presence of Indole in the following concentrations: (—) 1x10⁻³, (—) 5x10⁻⁴ e (—) 1x10⁻⁴ mol L⁻¹.

Tables 2 and 3 show the coverage degrees (θ) in the media of 1 mol L⁻¹ HCl and 1 mol L⁻¹ H₂SO₄ in the presence of Indole. These values of θ were calculated at different voltages from the equation I (TUSSOLINI, 2007):

$$\theta = \left(j_{s/i} - j_{c/i} \right) / j_{s/i} \text{ (Equation I)}$$

Where:

$j_{c/i}$ = current density in the presence of indole.

$j_{s/i}$ = current density in the absence of indole.

Table 2 - The inhibiting action of Indole in 1 mol L⁻¹ H₂SO₄ media in 430 SS oxidation at different anodic and cathodic overvoltage.

| η / mV | +70 | -70 | +100 | -100 | +160 | -160 | +200 | -200 |
|-----------------------------|----------|----------|----------|----------|----------|----------|----------|----------|
| [Indol] mol L ⁻¹ | θ | θ | θ | θ | θ | θ | θ | θ |
| 1x10 ⁻⁴ | -23±7 | 7±5 | -2±7 | 14±5 | 33±7 | 24±5 | 27±7 | 26±5 |
| 5x10 ⁻⁴ | -38±8 | 8±6 | 7±8 | 15±6 | 21±8 | 22±6 | 28±8 | 24±6 |
| 1x10 ⁻³ | -23±9 | 9±6 | -27±9 | 17±6 | -7±9 | 23±6 | 16±9 | 25±6 |

Table 3 - The inhibiting action of Indole in 1 mol L⁻¹ or HCl media in 430 SS oxidation at different anodic and cathodic overvoltage.

| η / mV | +70 | -70 | +100 | -100 | +160 | -160 | +200 | -200 |
|-----------------------------|----------|----------|----------|----------|----------|----------|----------|----------|
| [Indol] mol L ⁻¹ | θ | θ | θ | θ | θ | θ | θ | θ |
| 1x10 ⁻⁴ | 7±5 | 13±6 | 8±5 | 9±6 | 11±5 | 1±6 | 9±5 | -2±6 |
| 5x10 ⁻⁴ | 37±5 | 38±5 | 10±5 | 25±5 | 7±5 | 1±5 | 2±5 | -14±5 |
| 1x10 ⁻³ | 65±6 | 83±6 | 78±6 | 80±6 | 7±6 | 71±6 | 4±6 | 64±6 |

The EIS measurements were carried out in the corrosion potential in 1 mol L⁻¹ H₂SO₄ and 1 mol.L⁻¹ HCl media in the presence and absence of Indole 1x10⁻³ mol L⁻¹, the curves are presented in figure 5.

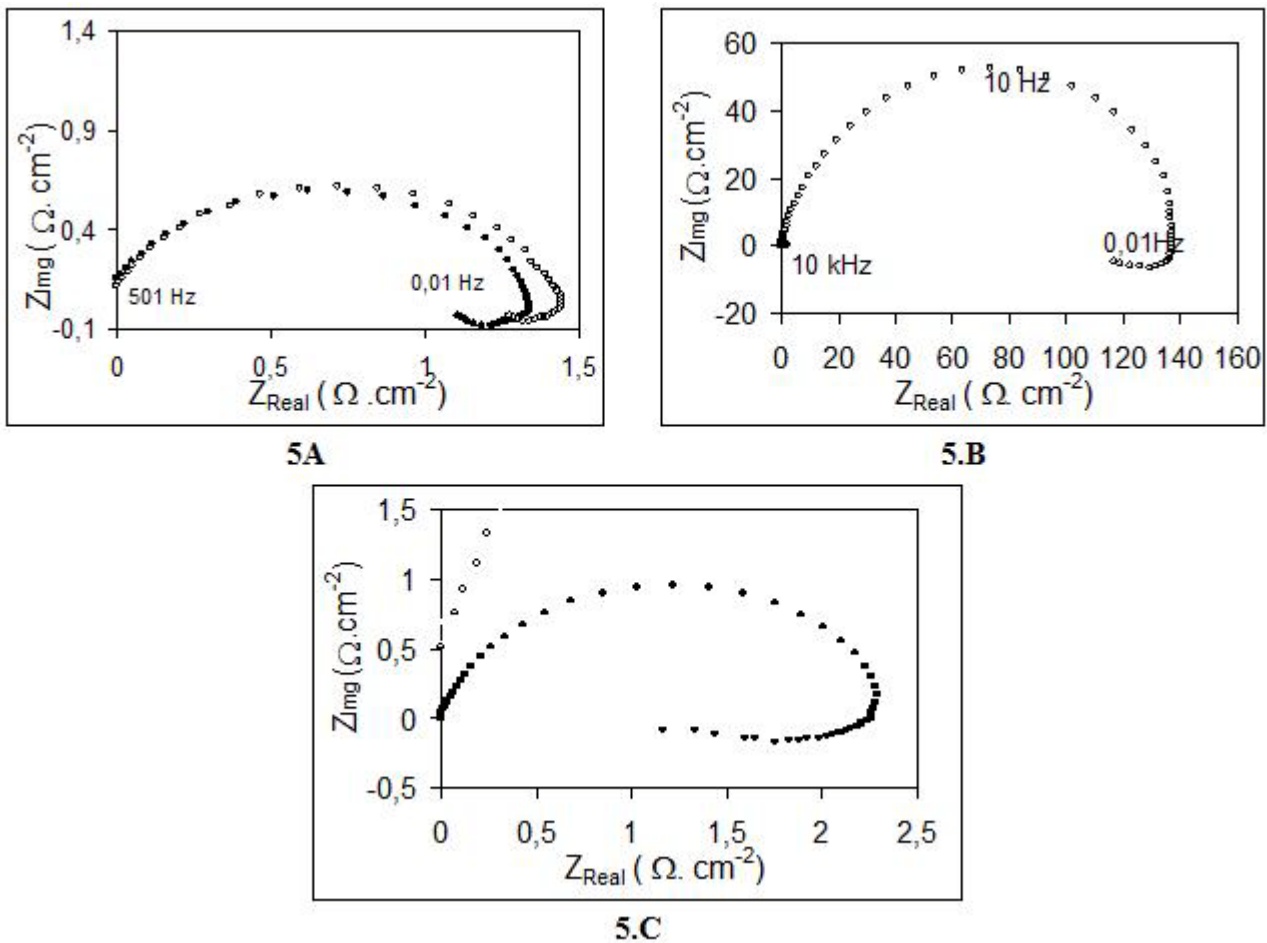


Figure 5: EIS Diagram for 430 SS in (5.A) 1 mol L⁻¹ H₂SO₄ and (5.B) 1 mol L⁻¹ HCl in the absence (●) and presence (◊) of indole at a 1x10⁻³ mol L⁻¹ concentration. EIS carried out in E_{corr} and E_{perturbation} = ± 10 mV vs. MSE. In (5.C) the expansion of (5.B) is shown for better visualization of the curve in the absence of Indoles in 1 mol L⁻¹ HCl.

Figure 6 presents the scanning electron microscopy for 430 SS in the presence and absence of indole in 1 mol L⁻¹ HCl and 1 mol L⁻¹ H₂SO₄ media.

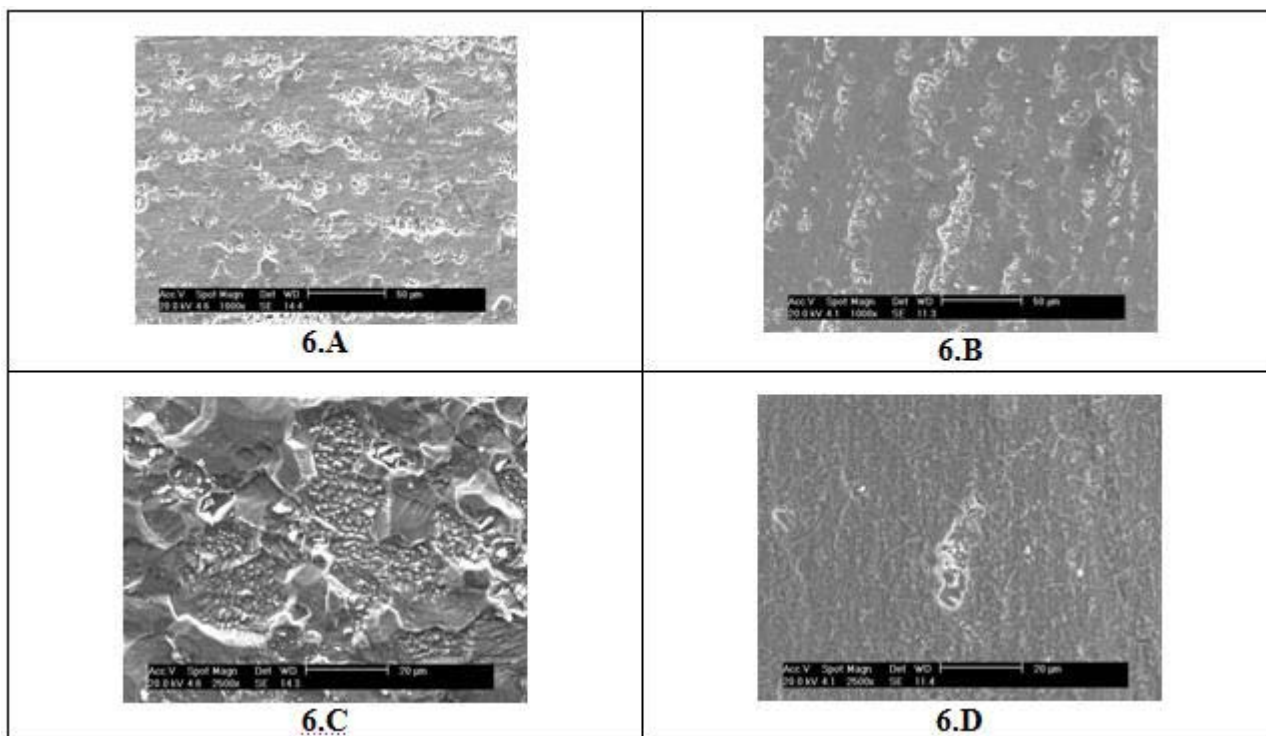


Figure 6 - Scanning Electron Microscope (SEM) of 430 stainless steel ABNT in: (A) $1 \text{ mol L}^{-1} \text{H}_2\text{SO}_4$ in the absence of indole, (B) $1 \text{ mol L}^{-1} \text{H}_2\text{SO}_4$ in the presence of indole, (C) $1 \text{ mol L}^{-1} \text{HCl}$ in the absence of indole and (D) $1 \text{ mol L}^{-1} \text{HCl}$ in the presence of indole.

Discussion

Figures 1.A and 1.B show that in the presence of Indole in the first few minutes, the potential decreases, after that time, more positive values are reached where it stabilizes. This behavior is probably due to rupture of the pre-existing oxide layer before immersion in the metal, which accelerates the process of hydrogen evolution and after these initial minutes the potential tends to rise due to the generation of new oxide layer in the presence of the corresponding indole .

Table 1 shows that the addition of Indole to the two media studied did not promote significant change in the E_{corr} values, suggesting that the inhibitory action of azoles in relation to the oxidation of 430 SS in both media studies is mixed.

Figure 2 reveals that the addition of indole to the concentrations studied increases the current density (j) in the region of the anodic curve studied, suggesting the indole action as a catalyst of corrosion in the active region and transpassive for 430 SS in $1 \text{ mol L}^{-1} \text{H}_2\text{SO}_4$ media. Figure 3 shows that the Indole concentration is the highest when more negative potentials decreased (j). And for the lowest concentration at lower potentials there was no change, yet at potentials above -0.26 V increases occurred (j). There is a breakdown of passive film, probably by the presence of Cl^- .

In Figure 4.A, it can be observed that indole has a double behavior at lower potentials. In potentials lower than -1V an increase occurs in the current density and when potentials are increased the current density decreases, sometimes acting either as a catalyst or as an inhibitor.

It is observed in Figure 4.B that the indole in the highest concentration reduces the current density in the region studied. While lower concentrations in greater $E \geq -0.62 \text{ V/SME}$ there is some increase in (j), suggesting a dual effect for these concentrations, catalyst and inhibitor, probably because at low concentrations there are more exposed active sites catalyzing the reaction rate of hydrogen detachment.

The indole in sulfuric acid media had an inhibitory effect for the cathodic overvoltage, while the anodic region to the inhibitory effect is only relevant at high voltages, as shown in table 2, where $\eta \geq 200 \text{ mV}$. In Table 3 it is possible to see the indole in the cathodic and low anodic overvoltage, the highest concentration showed a highly efficient inhibitor.

In figure 5.A it is possible to observe that the impedance in the presence of indole is slightly larger than for the system with only $1 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$. The presence of an arc can be noticed: capacitive in high frequency and inductive in low frequency. In the first arc, the capacitor can be attributed to faradaic processes and the second inductive due to the indole presence.

Figure 5.B reveals that in $1 \text{ mol L}^{-1} \text{ HCl}$ the impedance in the presence of indole is significantly greater than in its absence. Featuring two arcs and the inductive arc is due to the adsorption of indole.

"Holes" characteristic of generalized attacks can be seen in figure 6.A, probably due to dissolution around the inclusions, the remaining area suggested generalized corrosion of 430 stainless steel in $1 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$. In the presence of Indole in figure 6.B, corrosion is lower than that observed for the system in its absence.

Figure 6.C shows that the corrosion is localized for 430 stainless steel type in the $1 \text{ mol L}^{-1} \text{ HCl}$ media. In figure 6.D a minimization of corrosion of 430 SS in the presence of indole in HCl media is observed when compared to figure 6.C.

Comparing tables 2 and 3, the results in hydrochloric acid 1 mol L^{-1} media, the inhibitory efficiency in the presence of indole in the $1 \times 10^{-3} \text{ mol L}^{-1}$ concentration is considerably higher when compared with the same concentration for the sulfuric acid media. This increase can be attributed to the fact that the nitrogen atom provides electrons to the aromatic ring, thus catalyzing the protonation process in hydrochloric acid media, which follows the mechanism suggested in Figure 7. It is suggested that the indole in protonated form can adsorb on electrode surface by simple electrostatic attraction of positively charged molecule, due to the chloride ions adsorbed in that metal surface.

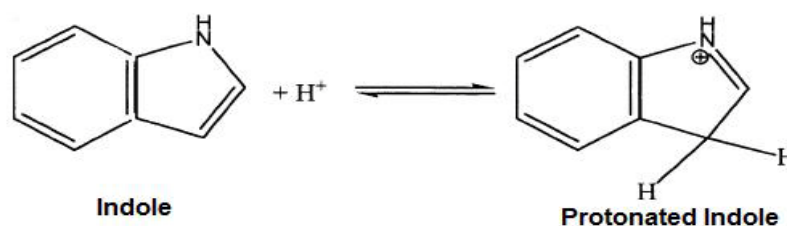


Figure 7 – Mechanism proposition of protonation to Indole in media of HCl.

Conclusions

The corrosion of 430 SS in sulfuric acid media is typically generalized, while in the hydrochloric acid media the attack is very aggressive. A considerable reduction of the localized corrosion was observed in the presence of indole.

EIS diagrams showed that for the H_2SO_4 and $1 \text{ mol L}^{-1} \text{ HCl}$ media, the highest impedances were found in the presence of indole, being higher for the hydrochloric acid medium.

The potentiodynamic polarization showed that in the two media studied the presence of indole had no significant inhibitory effect in the anodic region. However, in the cathodic region, the highest concentration studied for the $1 \text{ mol L}^{-1} \text{ HCl}$ media presented high inhibitory effect. It can be suggested that this behavior is due to the fact that the indole in this medium is protonated, which would facilitate the adsorption on metallic substrate in the presence of Cl^- .

Acknowledgments

CNPq, CAPES, FINEP and Araucaria Foundation.

References

ANUNZIATO, P; TUSSOLINI, M; CAPARICA, R; FURSTENBERGER, C. B; RODRIGUES, P. R. P. A influência do Thiobacillus Thiooxidans na corrosão do aço inoxidável 430 em H_2SO_4 1 mol L^{-1} . *REM- Revista Escola de Minas*, v. 63, n. 1, p. 97-102, 2010.

DÜDÜKCÜ, M; YAZICI, B; ERBIL, M. The effect of indole on the corrosion behaviour of stainless steel. *Materials Chemistry and Physics*, v. 87, p.138-141, 2004.

GENTIL, V. *Corrosão*. 4ª Edição. Rio de Janeiro: LTC, 1987;

KHAMIS, E. - "The effect of temperature on the acid dissolution of steel in the presence of inhibitors", *Corrosion*, v.46, n°. 6,1990.

MAZURKIEWICZ, B., et. Al.; - "Anodic passivity of iron in Sulphuric acid", *Electrochim. Acta*, v. 38, n°. 4, p.495-502, 1993

MORAES, J. E; SPAGNOL, C.; TUSSOLINI, M.; RODRIGUES, P. R. P.; FURSTENBERGER, C. B; Corrosão microbiológica do aço inoxidável austenítico 316 em Na_2SO_4 0,5 mol L^{-1} na ausência e presença de Escherichia coli. *REM- Revista Escola de Minas*, v. 63, n. 1, p. 111-115, 2010.

RAMANATHAN, L. V. , *Corrosão e seu controle*, 1ª ed., Hemus Editora Ltda, São Paulo, 1990.

RODRIGUES, P. R. P; ANDRADE, A. H. P.; AGOSTINHO, S. M. L. Benzotriazole as corrosion inhibitor for type 304 stainless steel in water-ethanol media containig 2M H_2SO_4 . *British Corrosion Journal, Inglaterra*, v.33, n.3, p. 211-213, 1998.

POPOVA, A; CHRISTOV, M; ZWETANOVA, A. Effect of the molecular structure on the inhibitor properties of azoles on mild steel corrosion in 1M hydrochloric acid. *Corrosion Science*, v.49, n.5, p. 2131-2143, 2006.

RODRIGUES, P. R. P. *O Benzotriazol como inibidor de corrosão para ferro e ligas ferrosas em meios de ácido sulfúrico*. 1997. Tese de doutorado - Instituto de Química da USP-SP.

TUSSOLINI, M; SPAGNOL, C; ALVES, G. J. T; CUNHA, M. T; RODRIGUES, P. R. P. Estudo do comportamento eletroquímico de azóis para o aço inoxidável AISI 430 em H_2SO_4 1 mol L^{-1} . *REM- Revista Escola de Minas*, v. 63, n. 1, p. 103-109, 2010.

Correspondng author: Paulo Rogério Pinto Rodrigues (prprodrigues@unicentro.br)