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Study of corrosion inhibitors and synergisms for 304 stainless steel in 0.2% peracetic acid media

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Abstract

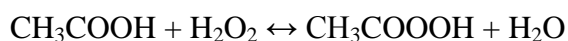
The peracetic acid is a sterilizing compound able to clean very effectively the microbiological life forms on the surface where it is applied. Due to its oxidative characteristic, corrosion studies and inhibitors applications become necessary. The aim of this work is to study corrosion inhibitors for 304 stainless steel in peracetic acid medium. The efficiency of tungstate, molybdate, hexametaphosphate ions, and benzotriazole (BTAH), and the synergism between BTAH and sodium dodecil sulfate (SDS) were evaluated using electrochemical techniques. The BTAH presented the highest efficiency, equal to 46%, and the best synergism was obtained for BTAH+SDS mixture, with 70% efficiency.

Keywords: corrosion, peracetic acid, 304 stainless steel, inhibitors, benzotriazole, sodium dodecil sulfate.

Introduction

There is a large class of compounds used in sterilizing process: alcohols, ammonium compounds, aldehydes, phenolic compounds, chlorinated compounds and peroxides. Among these agents, just a few are really able to perform a full sterilizing process: aldehydes (formaldehyde and glutaraldehyde) and peroxides (hydrogen peroxide and peracetic acid). The hydrogen peroxide is not an efficient sporicidal, on the other hand, the aldehydes are classified as toxic or carcinogenic agents. The peracetic acid presents the highest collection of good properties: it is an efficient sterilizing agent, capable of acting over any microbial life, even spores; it has a very low toxicity; and its decomposition process results in environmental friendly compounds. This is the reason why the use of peracetic acid is growing in hospital and dentistry environment.

The peracetic acid is an artificial compound, synthesized by the mixture of acetic acid and hydrogen peroxide, usually with sulfuric acid as catalyze and stabilizer. Its synthesis corresponds to the equilibrium:



Peracetic acid can cause the corrosion process of metallic materials due to its high oxidant action.

The present paper has the objective to present the effect of corrosion inhibitors and the synergism between them on the electrochemical behavior of 304 stainless steel in peracetic acid medium.

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Methodology

It was used a conventional electrochemical cell with three electrodes: 304 stainless steel (304 SS) as work electrode; saturated Ag/AgCl electrode as reference electrode; 254 stainless steel as auxiliary electrode. The work electrode was polished with 320 to 2000 mesh silicium carbide emery paper.

Commercial 0,2% peracetic acid solution was employed as electrolyte.

The inhibitors studied were: benzotriazole ($2 \times 10^{-2} \text{ mol.L}^{-1}$), sodium hexametaphosphate $[(\text{NaPO}_3)_6]$ ($2 \times 10^{-3} \text{ mol.L}^{-1}$), sodium tungstate ($2 \times 10^{-3} \text{ mol.L}^{-1}$), sodium molibdate ($2 \times 10^{-3} \text{ mol.L}^{-1}$), sodium dodecil sulfate (SDS) ($2 \times 10^{-4} \text{ mol.L}^{-1}$), and their binary mixtures.

All measurements were performed using an Autolab PGSTAT 30 potentiostat/galvanostat and a frequency analyzer Autolab FRA 32.

The experiments were performed at room temperature, (25 ± 1) °C

The present work made use of three electrochemical techniques: open circuit potential (OCP), potentiostatic polarization curves and electrochemical impedance spectroscopy (EIS).

Open circuit potential was performed until the change of potential became 1 mV per 10 min. The quasi stationary value obtained was considered the corrosion potential, named E_{corr} .

Electrochemical impedance spectroscopy was performed through the application of a constant potential with 10 mV sinusoidal amplitude wave, with frequency range between 100 kHz and 10 mHz.

Result and discussion

An example of OCP curves is presented in figure 1a, for 304 SS in 0.2% peracetic acid media in absence of corrosion inhibitors.

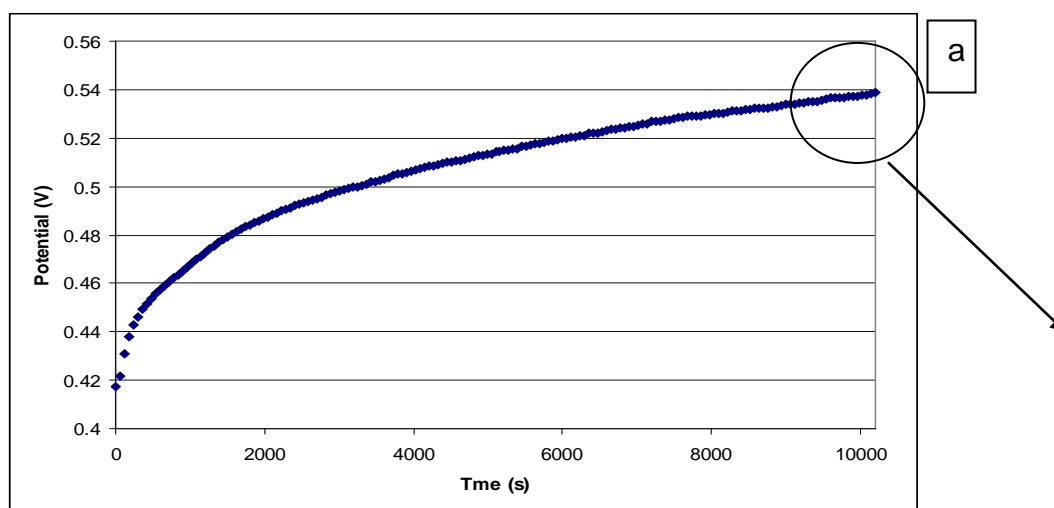


Figure 1 – Time function OCP, measured for 304 stainless steel in 0.2% peracetic acid media in absence of corrosion inhibitors.

It can be seen, from figure 1b, the quasi constant potential value, in the last 10 minutes of the experiment.

Similar treatment was applied to the media in the presence of corrosion inhibitors and their mixtures.

Table 1 presents the average values of E_{corr} for the 304 SS in peracetic acid media, in the absence and presence of corrosion inhibitors and their mixtures.

Table 1 – Average corrosion potential (E_{corr}) for 304 SS in 0.2% peracetic acid media.

Media	E_{corr} (V)
Blank	0.54 ± 0.02
BTAH	0.59 ± 0.01
$(\text{NaPO}_3)_6$	0.60 ± 0.02
SDS	0.59 ± 0.01
Molibdate	0.60 ± 0.01
Tungstate	0.61 ± 0.01
BTAH + $(\text{NaPO}_3)_6$	0.53 ± 0.03
BTAH + SDS	0.59 ± 0.01
BTAH + Tungstate	0.60 ± 0.01
BTAH + Molibdate	0.61 ± 0.01

It is possible to observe that the presence of corrosion inhibitors changes the E_{corr} to more positives values, in most of cases. These results suggest that these inhibitors act as anodic inhibitors.

It can be seen from figure 2 the polarization curves for three of the interfaces studied, in the absence of corrosion inhibitors, in the presence of BTAH and in the presence of BTAH+SDS. It can be seen the inhibitory action as anodic and as cathodic inhibitors, but the effect is more pronounced at anodic polarizations. BTAH is a better inhibitor then the mixture BTAH+SDS at high anodic overvoltages.

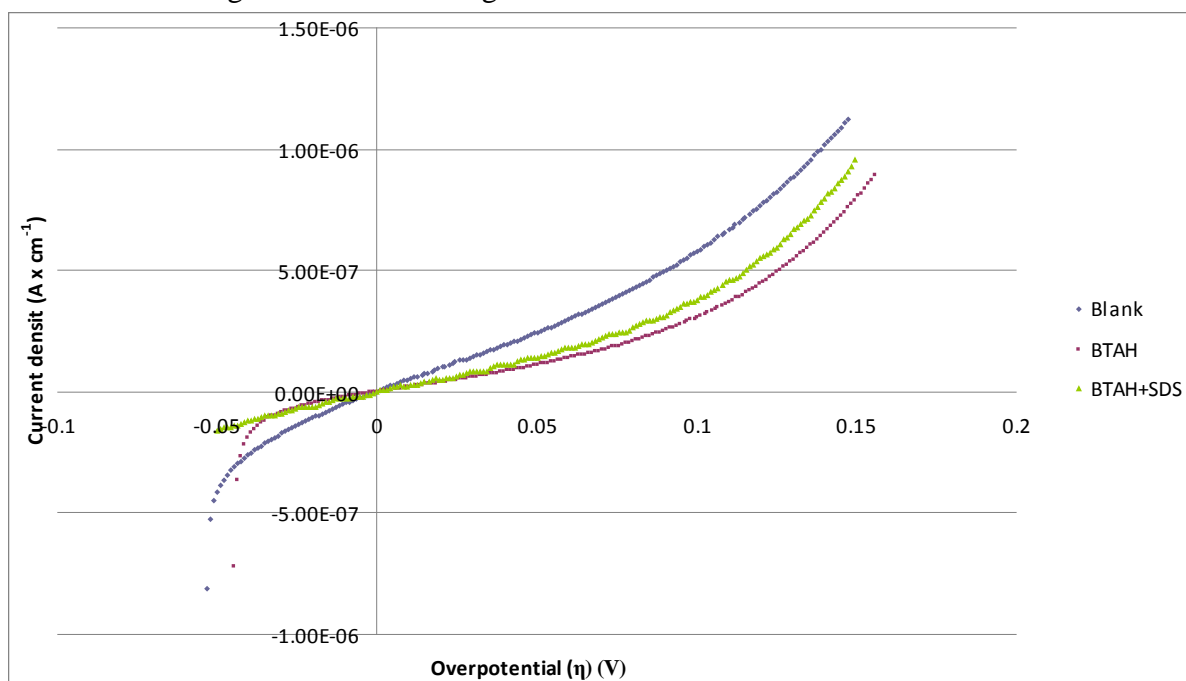


Figure 2 – polarization curves for 304 SS in 0.2%peracetic acid media in absence of corrosion inhibitor, and in presence of BTAH and BTAH+SDS.

Figure 3 corresponds to linear polarization using 10 mV overpotential on the anodic and cathodic branches from E_{corr} .

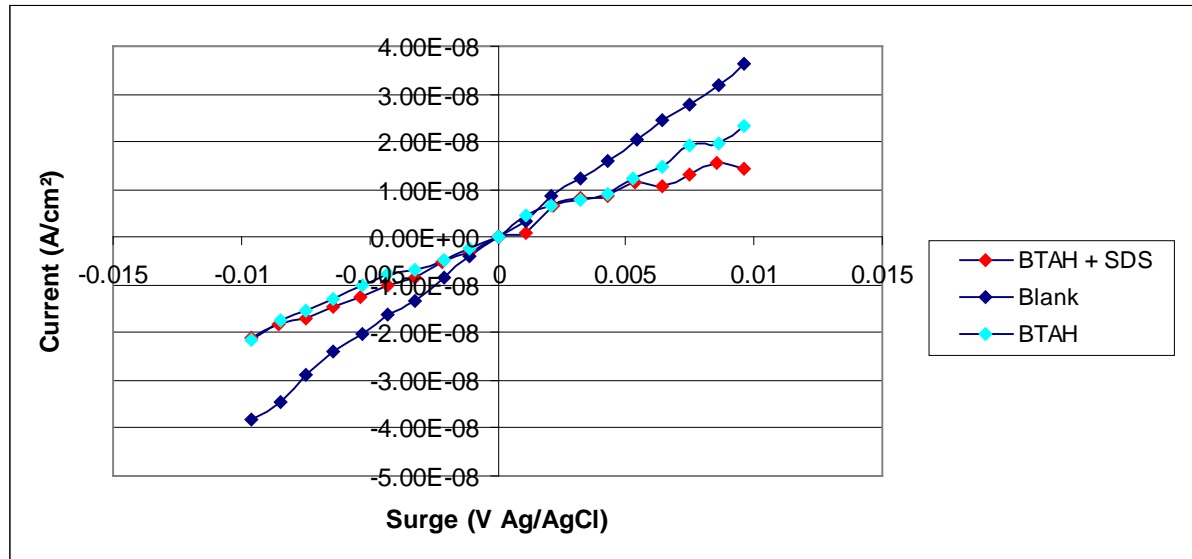


Figure 3 – Linear polarization curves near E_{corr} for 304 stainless steel in 0.2% peracetic acid media in presence and absence of corrosion inhibitors.

It is possible to notice that at low overpotentials the BTAH+SDS mixture is a better corrosion inhibitor than BTAH alone.

Through the inverse of angular coefficient it is possible to calculate the polarization resistance (R_p) in the absence and presence of corrosion inhibitors and the mixtures of them. From the R_p values it is possible to calculate the efficiency (Θ) of the inhibitors, using the equation:

$$\Theta = (R_{pi} - R_{po})/R_{pi}$$

Where R_{po} and R_{pi} are the polarization resistance in the absence and presence of the inhibitor, respectively.

It can be shown from table 2 the Θ values obtained for the studied inhibitors and their mixtures.

Table 2 – Inhibitor efficiency for the corrosion inhibitor and mixtures over 304 stainless steel in 0.2% peracetic acid media.

Inhibitor	Efficiency (Θ)
BTAH	(46 ± 3) %
(NaPO_3) ₆	(24 ± 1) %
Molibdate	(22 ± 2) %
Tungstate	(13 ± 1) %
BTAH + SDS	(70 ± 40)%
BTAH + Molibdate	(15 ± 6) %
BTAH + Tungstate	(23 ± 9) %
BTAH + (NaPO_3) ₆	(30 ± 10)%

It is possible to see that the BTAH+SDS mixture presents the higher efficiency, followed by the BTAH itself but the percentual error is higher in the presence of SDS, suggesting changes in the film performance.

The EIS technique was applied in order to confirm the greater effectiveness of the BTAH+SDS mixture.

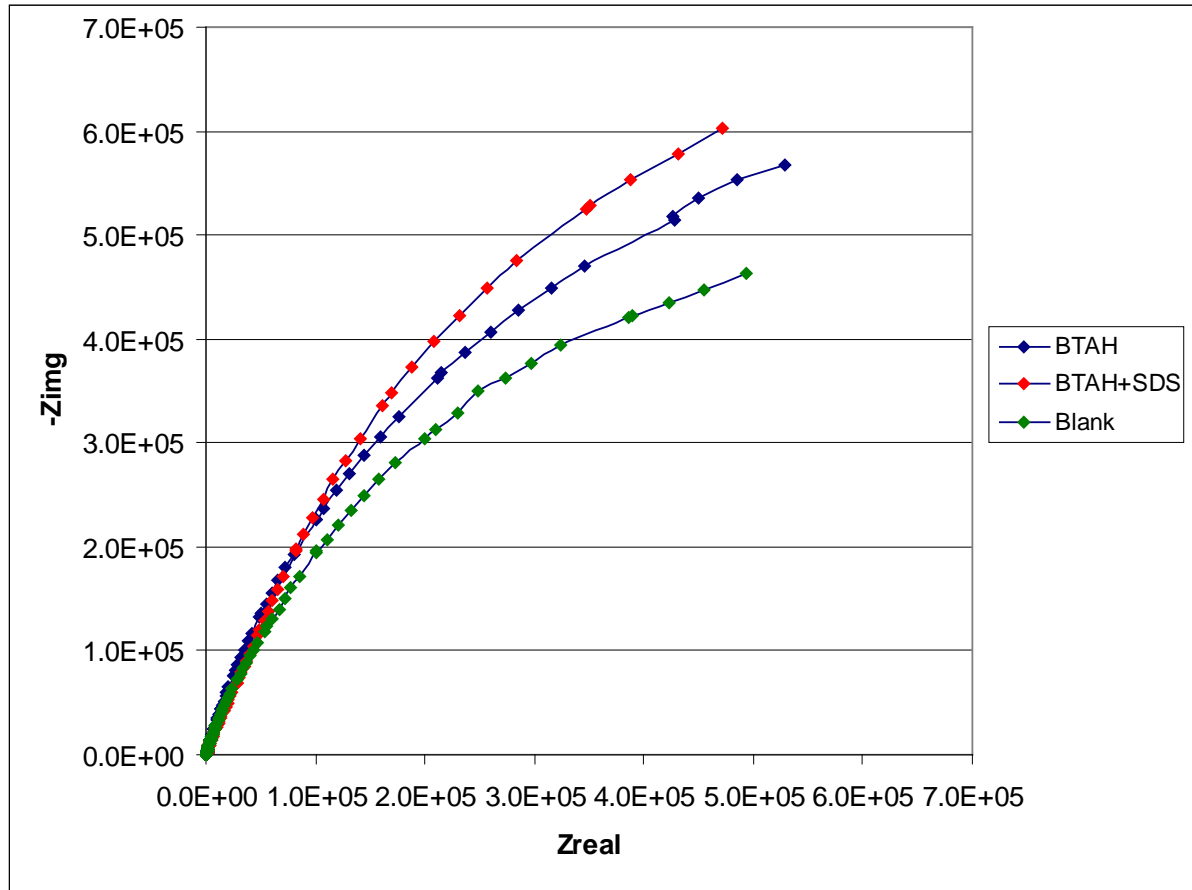


Figure 4 – Nyquist diagram for 304 stainless steel in 0.2% peracetic acid in presence and absence of corrosion inhibitors.

Figure 4 presents the Nyquist diagram for 304 SS in 0.2% peracetic acid in the absence and presence of BTAH and BTAH+SDS, at E_{corr} .

The most closed capacitive arc, correspond to the peracetic solution without inhibitors (blank) and the most opened to the BTAH+SDS mixture. These results are an indicative that the polarization resistance, which would obtain at the limit of zero frequency is higher for the inhibitors mixture and are according to the polarization results.

The table 3 gives the value of Z_{img} at a high frequency, 50 kHz, for comparison.

Table 3 – Z_{img} values for 304 stainless steel in 0.2% peracetic acid media in absence and presence of corrosion inhibitors.

Media	Z_{img} ($\Omega \cdot \text{cm}^2$)
Blank	8 ± 2
BTAH	12.0 ± 0.5
BTAH + SDS	11 ± 2

These results are an indication that the inhibitors are present at the surface at high frequencies, which correspond to the charge of the double electrical layer.

Conclusion

- The 304 stainless steel presents a passive behavior in 0,2% peracetic acid media, but its resistance can be improved by the presence of corrosion inhibitors;
- The BTAH had its effect reduced by the presence of some others inhibitors studied;
- The SDS presented synergism with the BTAH for 304 stainless steel in 0.2% peracetic acid media, almost duplicating its inhibitor efficiency, but the huge uncertainty of the measurement indicates a low quality film.
- The inhibitors acting by fast adsorption.

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