



The synergistic effect between phosphonocarboxylic acid salts and fatty amines for the corrosion protection of a carbon steel

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Abstract

This work was carried out to have a better understanding of the synergistic effect between phosphonocarboxylic acid salts (PCAS) and fatty amines (FA) for the corrosion protection of a carbon steel in a 200 mg l⁻¹ NaCl solution. These compounds, combined with a biocide at low dosage, are used for water treatment in cooling circuits. First, electrochemical impedance measurements were performed to verify the inhibitive properties of the mixtures. Among the different concentrations tested, maximum efficiency was reached for the mixture containing 200 mg l⁻¹ PCAS + 50 mg l⁻¹ FA. Then, electrochemical measurements (current–voltage curves and impedance diagrams) were combined with surface analysis (X-ray photoelectron spectroscopy) for each compound at the optimized concentrations and for the mixture. In the presence of amines, the iron oxide/hydroxide layer remained porous and the inhibition efficiency was relatively low. The FA acted by repelling the water molecules from the interface. PCAS sealed the pores of the oxide layer by forming a chelate. Thus, the growth of the inhibitive layer was limited but the efficiency was higher than for the FA alone. For the optimized mixture, the formation of the chelate was enhanced and the protective properties of the layer improved. A competitive adsorption mechanism was proposed to account for the synergistic effect observed in the presence of both compounds.

1. Introduction

In a previous paper [1], the corrosion inhibition of a carbon steel in an aerated 200 mg l⁻¹ NaCl solution by a nontoxic multicomponent inhibitor used for water treatment in cooling circuits was studied. The inhibitive formulation was composed of fatty amines (FA) associated with phosphonocarboxylic acid salts (PCAS) and a biocide at low dosage [2]. The biocide was a quaternary ammonium salt (QAS). Steady-state current–voltage curves were combined with electrochemical impedance measurements to characterize the inhibitive properties of each compound and to optimize their concentrations in the mixture. It was found that PCAS act as anodic inhibitors whereas FA and QAS act as mixed inhibitors. The polarization resistance (R_p) measured from impedance diagrams was strongly dependent on the PCAS concentration. A slight increase of the R_p value was observed when the FA were incorporated to the PCAS-containing solutions. The mixture containing 200 mg l⁻¹ PCAS and 50 mg l⁻¹ FA led to the highest efficiency. It was assumed that a cooperative

adsorption mechanism occurred between the compounds.

XPS analysis carried out on the steel surface after immersion in the optimized inhibitive solution revealed the presence of a thin inner iron oxide layer covering the steel surface and an outer iron oxide/hydroxide mixture above it. The functional groups of the inhibitive molecules were identified: the P 2p and the N 1s peaks showed that the PCAS, FA and biocide are present and distributed throughout the oxide/hydroxide layers. Nevertheless, these results do not clearly explain the increase of the inhibitive properties observed by electrochemical measurements. The aim of the present paper is to have a better understanding of the adsorption mechanism between PCAS and FA removing the biocide from the inhibitive mixture. As in the previous study, steady-state current–voltage curves and electrochemical impedance measurements were carried out in 200 mg l⁻¹ NaCl solutions. The electrochemical measurements were also completed by XPS analysis to compare the chemical composition of the inhibitive film formed in the presence of the mixture to that obtained for each compound.

2. Experimental details

2.1. Materials

Oleylaminopropylene amine and phosphonocarboxylic acid salts were used as corrosion inhibitors. The structures of the compounds are presented in Figure 1. The corrosive medium was a 200 mg l⁻¹ NaCl solution (reagent grade) in contact with air maintained at 25 °C. Depending on the concentration of the compounds, the pH of the inhibitive solutions varied between 8 and 10. In the inhibitor-free solution, the pH was adjusted to 10 by NaOH. A rod of the XC 35 carbon steel of 1 cm² cross-sectional area was used as working electrode. Its composition in percentage by weight was: C = 0.35, Mn = 0.65, Si = 0.25, P = 0.035, S = 0.035 and Fe to 100. The carbon steel samples were polished with SiC paper down to grade 2400, cleaned in water in an ultrasonic bath and then dried in warm air.

2.2. Electrochemical experiments

A Solartron 1286 potentiostat linked to a Solartron 1250 frequency response analyser was used for the electrochemical measurements. The working electrode was a rotating disc to ensure a uniform thickness of the diffusion layer at the electrode surface. A heat-shrinkable sheath left only the tip of the cylinder in contact with the solution. The rotation rate was fixed at 1000 rpm. A saturated calomel electrode (SCE) was used as reference and a platinum grid was used as counter electrode. Polarization curves were plotted under potentiostatic regulation corrected for the ohmic drop, determined by electrochemical impedance measurements. They were plotted point by point to ensure quasi steady-state conditions (20 mV/2 min). The anodic and the cathodic parts were obtained independently from the corrosion potential after 2 h of immersion. The impedance diagrams were plotted at the corrosion potential after 2 h of immersion in a frequency range of 65 kHz to a few mHz with eight points per decade. The electrochemical results were obtained from at least three experiments to ensure reproducibility. The carbon steel/solution interface was mathematically described in terms of an electric equivalent circuit consisting of a resistance electrolyte in series with a parallel constant phase element (CPE)/resistor combination. The semicir-

cular shape of the impedance diagrams led us to choose this equivalent circuit to obtain the characteristic parameters: R_p , polarization resistance and C , double layer capacitance. The CPE is generally attributed to the roughness of the surface or to a nonuniform distribution of the current density on the electrode undergoing corrosion [3–5].

2.3. X-ray photoelectron spectroscopy

The carbon steel electrode was immersed in the aerated 200 mg l⁻¹ NaCl solution with inhibitors. The samples were prepared by the same procedure as for the electrochemical experiments: 2 h of immersion at the corrosion potential in the inhibitor-containing solutions. Then immediately, the electrode was removed from the solution, dried in warm air and placed in a vacuum chamber. The specimens were irradiated with a MgK_α ray source. The X-ray power was 300 W. The experimental resolution of the binding energy was 1 eV. After background noise subtraction, peak deconvolution was performed using a least squares fit routine. P 2p, N 1s and O 1s peaks were recorded to monitor the adsorption of the inhibitors on the metal surface. The oxidation state of the iron was followed using the Fe 2p signal. The binding energies were corrected for charging effects by referencing C 1s to the peak at 284.5 eV.

3. Results and discussion

3.1. Electrochemical results

The electrochemical measurements were carried out to confirm the properties of mixtures of PCAS + FA for the corrosion inhibition of a carbon steel in a 200 mg l⁻¹ NaCl solution in the absence of biocide. To have a better understanding of the PCAS and FA effect, impedance diagrams and current–voltage curves were obtained for each inhibitor at the optimized concentration in the corrosive solution. Thus, electrochemical parameters were compared with those obtained in the presence of the mixture.

3.1.1. EIS measurements for different inhibitive mixtures

Figure 2 shows the impedance diagrams obtained for different inhibitive mixtures. They are characterized by a single capacitive loop. The Polarization resistance values (R_p) obtained from the diagrams can be related to the charge transfer resistance of iron dissolution in the pores of the inhibitive layer [6, 7]. Assuming that electrochemical processes are taking place only at the pores, the change of the polarization resistance value gives direct information on the quality of the protective layer [8, 9]. The fitted parameters obtained from the impedance data are reported in Table 1. The R_p value obtained for the mixture containing 100 mg l⁻¹ PCAS + 75 mg l⁻¹ FA was the lowest. The value was approximately the same as that obtained in the presence of biocide [1]. The

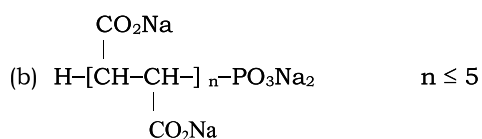
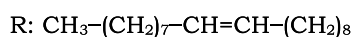
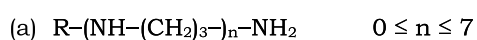


Fig. 1. Chemical structure of the inhibitors: (a) oleylaminopropylene amine (fatty amines); (b) phosphonocarboxylic acid salts.

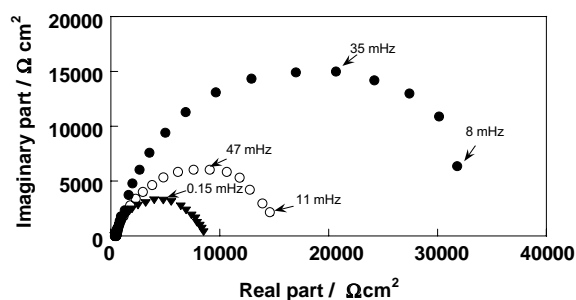


Fig. 2. Electrochemical impedance diagrams obtained for carbon steel at E_{corr} after 2 h of immersion in different inhibitive mixtures: (▼) 100 mg l⁻¹ PCAS + 75 mg l⁻¹ FA; (●) 200 mg l⁻¹ PCAS + 50 mg l⁻¹ FA; (○) 300 mg l⁻¹ PCAS + 25 mg l⁻¹ FA.

Table 1. Parameters deduced from the impedance diagrams presented in Figure 2 for carbon steel immersed in different inhibitive mixtures composed of PCAS and FA

Inhibitive mixture	R_p / Ω cm ²	C / μF cm ⁻²	α
100 mg l ⁻¹ PCAS + 75 mg l ⁻¹ FA	8200	153	0.85
200 mg l ⁻¹ PCAS + 50 mg l ⁻¹ FA	36100	94	0.89
300 mg l ⁻¹ PCAS + 25 mg l ⁻¹ FA	15700	47	0.83

mixture containing 200 mg l⁻¹ PCAS + 50 mg l⁻¹ FA reached the highest polarization resistance value, as in the presence of biocide [1] although this value was twice as high here, in the absence of biocide. The R_p value obtained for the mixture containing 300 mg l⁻¹ PCAS + 25 mg l⁻¹ FA was intermediate.

In the previous work [1], an increase of the loop size was observed when the salt concentration increased for the solutions containing only PCAS. Kuznetsov et al. [10] observed that the introduction of surfactants of cationic type like amines increased the adsorption ability of carboxylates. Thus, an increase of the R_p value was expected when FA was added to the PCAS-containing solution but it was not so. For this mixture, the R_p value was approximately the same as that obtained with 300 mg l⁻¹ PCAS alone [2]. Kern and Landolt [11, 12], using a rotating electrochemical quartz crystal microbalance, observed a decrease in the adsorption of a carboxylic acid on passive iron beyond certain acid concentrations but this behaviour was not well explained. In our case, it can be assumed that for the mixture 300 mg l⁻¹ PCAS + 25 mg l⁻¹ FA, the action of the amine is negligible and the action of PCAS alone is observed. To study the FA concentration effect, a variable quantity of FA was added to the solution containing 200 mg l⁻¹ PCAS (Figure 3). The fitted parameters obtained from the impedance results are given in Table 2. The mixture containing 200 mg l⁻¹ PCAS + 50 mg l⁻¹ FA again showed the best efficiency. It can be pointed out that, whatever the FA concentration, the R_p values were higher than that obtained for the solution containing only 200 mg l⁻¹ PCAS [2]. From Table 2, an increase of the R_p value was observed when the FA concentration increased from 25

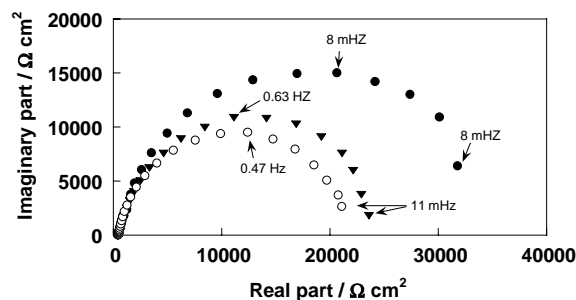


Fig. 3. Electrochemical impedance diagrams obtained at E_{corr} for carbon steel after 2 h of immersion in the solutions containing 200 mg l⁻¹ PCAS and different FA concentrations: (▼) 25, (●) 50 and (○) 75 mg l⁻¹.

Table 2. Parameters deduced from the impedance diagrams presented in Figure 3 for carbon steel immersed in the solution containing 200 mg l⁻¹ PCAS and FA variable

Inhibitive mixture	R_p / Ω cm ²	C / μF cm ⁻²	α
200 mg l ⁻¹ PCAS + 25 mg l ⁻¹ FA	24900	109	0.89
200 mg l ⁻¹ PCAS + 50 mg l ⁻¹ FA	36100	94	0.89
200 mg l ⁻¹ PCAS + 75 mg l ⁻¹ FA	21500	96	0.91

to 50 mg l⁻¹ but a decrease was observed when the FA concentration increased to 75 mg l⁻¹. This behaviour was also observed by Wieczorec et al. [13] studying the synergistic effect between a carboxylic acid and an amine on steel corrosion inhibition in 0.5 M sulfuric acid solution. The authors showed that for a given carboxylic acid concentration, there exists a specific amine concentration to obtain the maximum synergistic effect: the higher the carboxylic acid concentration, the smaller the concentration of amine. In our case, regarding the concentration of 300 mg l⁻¹ PCAS + 25 mg l⁻¹ FA (Table 1), it can be assumed that the amine concentration is not high enough to observe a synergistic effect.

Concerning the interfacial capacitance, the values obtained correspond to those expected for double layer capacitance of a rough surface [7, 12, 14]. In Table 1, a decrease of the capacitance value is observed when the total inhibitor concentration increases, as expected for the adsorption of organic molecules [12–15]. However, the capacitance value remained relatively constant when the PCAS concentration was fixed at 200 mg l⁻¹ (Table 2). These results essentially indicate that the capacitance values are strongly influenced by the PCAS concentration in the mixture.

In acid solutions, variations of the interfacial capacitance values are commonly used to estimate the coverage of the adsorbed inhibitive species on the metal surface [14–17] but this approach is not valid in neutral/alkaline solutions due the formation of oxide layers on the metal surface. In this case, the capacitance values are directly related to the thickness of the iron oxide layer because it is regarded as a dielectric film [18]. In the presence of inhibitors, the incorporation of the organic molecules throughout the oxide layers modifies their

electrical properties and therefore the interfacial capacitance values are altered. The inhibition efficiency in neutral-alkaline medium depends strongly on the properties of the layer formed: the inhibitor molecules block the active sites for cathodic oxygen reduction or/and drastically decrease the pore density [6, 17]. Thus, the capacitance values may be interpreted as a permeability factor of the active species through the inhibitive layer. Monticelli et al. [19] pointed out that a porous layer induces an increase of the interfacial capacitance. In our case, the fact that the capacitance value increased when the total inhibitor concentration decreased could be related to an insufficient quantity of inhibitor adsorbed on the metal surface.

3.1.2. Synergistic effect of FA and PCAS mixture

Figures 4 and 5 show the current–voltage curves and the impedance diagrams respectively obtained for the solutions containing PCAS, FA and both compounds at the optimized concentrations. Results obtained without inhibitor are also reported. Figure 4 shows that cathodic oxygen reduction was slightly modified in the presence of the mixture and not modified in the presence of the

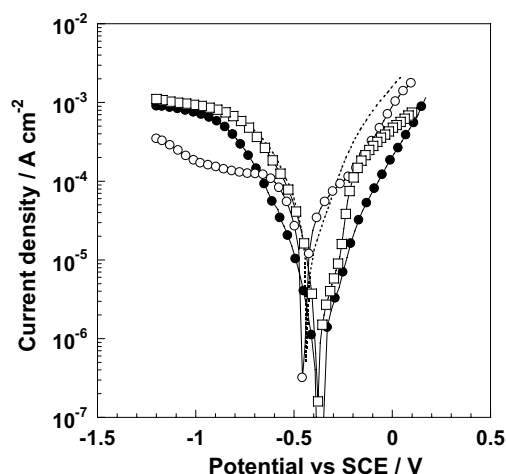


Fig. 4. Steady-state current–voltage curves obtained for carbon steel after 2 h of immersion in the solutions: (---) without inhibitor and with (○) 50 mg l⁻¹ FA; (□) 200 mg l⁻¹ PCAS; (●) 200 mg l⁻¹ PCAS + 50 mg l⁻¹ FA.

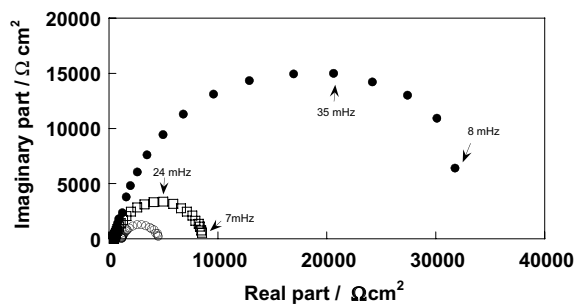


Fig. 5. Electrochemical impedance diagrams obtained at E_{corr} for the carbon steel after 2 h of immersion in the solutions: (○) 50 mg l⁻¹ FA; (□) 200 mg l⁻¹ PCAS and (●) 200 mg l⁻¹ PCAS + 50 mg l⁻¹ FA.

Table 3. Parameters deduced from the impedance diagrams presented in Figure 4 for carbon steel immersed in the solution containing PCAS and FA at the optimised concentrations

Inhibitive mixture	R_p / Ω cm ²	C / μ F cm ⁻²	α
without inhibitor	2460	158	0.79
50 mg l ⁻¹ FA	4400	155	0.80
200 mg l ⁻¹ PCAS	8500	57	0.80

PCAS alone by comparison with the curve obtained in the absence of inhibitor. In contrast, for the solution containing 50 mg l⁻¹ FA, a significant decrease of the cathodic current densities was noted. The anodic current densities decreased in the presence of each compound tested separately but were further decreased in the presence of the inhibitive mixture. From the polarization curves, the inhibition mechanism for the mixture does not seem to combine the cathodic and the anodic effects of both compounds. A simple summation of the effectiveness of the role of each inhibitor is not obvious since the cathodic action of FA is hidden. The results rather suggest that the presence of FA promotes the adsorption of PCAS on the anodic sites [10,13,20]. Figure 5 shows the impedance diagrams obtained in the same conditions. The R_p value determined for the inhibitive mixture was higher than those obtained in the presence of each inhibitor tested separately in agreement with the steady state results. This clearly shows the synergistic effect between the two compounds. Table 3 gives the capacitance values obtained for the solution containing each inhibitor at the optimized concentration for comparison with the value obtained in the absence of inhibitor. The capacitance value obtained in the presence of 200 mg l⁻¹ PCAS was lower than that obtained in the presence of 50 mg l⁻¹ FA. Because the capacitance value obtained for the solution containing 50 mg l⁻¹ FA was of the same order as that obtained for the blank solution, the strong dependence of this value on the PCAS concentration was corroborated. It can be recalled that the value obtained for the solution containing the mixture was intermediate.

3.2. Surface analysis

Figure 6 shows a comparison of the X-ray photoelectron spectra of Fe 2p, O 1s, N 1s and P 2p for the carbon steel surface after 2 h of immersion in the 200 mg l⁻¹ NaCl solution containing PCAS, FA and both compounds. The Fe 2p spectra, obtained for the three solutions, was essentially composed of a broad peak at 711 eV attributed to an iron oxide/hydroxide mixture. At 707 eV, a shoulder of varying intensity, depending on the system investigated, was observed. This is attributable to the metallic iron under the oxide film [21, 22]. Several authors have mentioned that the presence of the metal substrate signal reveals the thinness of the inhibitive film estimated to be about 2 nm [21, 22]. According to the height of the peak it can be observed

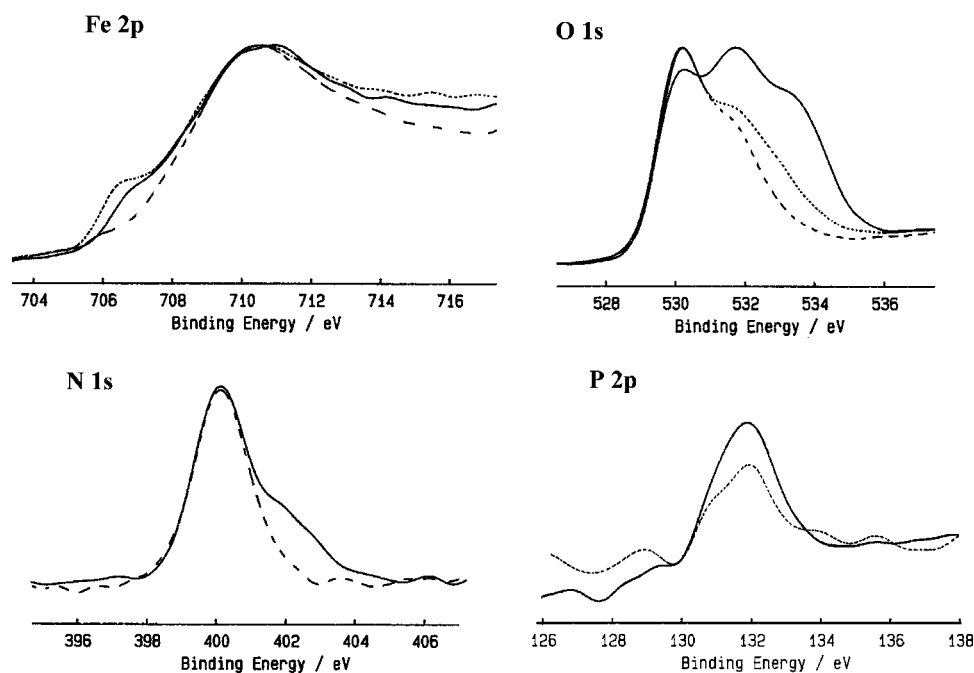


Fig. 6. Comparison of the XPS spectra of Fe 2p, O 1s, N 1s, P 2p regions obtained for carbon steel surface after 2 h of immersion in the solutions containing (---) 50 mg l⁻¹ FA; (- - -) 200 mg l⁻¹ PCAS; (—) 200 mg l⁻¹ PCAS + 50 mg l⁻¹ FA.

that qualitatively the film thickness decreases in the order FA > mixture > PCAS.

For the O 1s spectra, the presence of the two peaks at 530 and 531.5 eV are in agreement with the analysis of the Fe 2p peak. The former is related to the O²⁻ ion and the second is attributed to the OH⁻ ion corroborating the fact that the inhibitive film is mainly composed of an iron oxide/hydroxide mixture. A third peak at 533 eV is clearly observed on the O 1s spectrum obtained in the presence of the PCAS/FA mixture. For studies concerning passive films, this peak is frequently attributed to water physically adsorbed on the oxide/hydroxide layers. Nevertheless, it also corresponds to the binding energy of the carbonyl which is a functional group present in the PCAS molecule. This peak was also observed by Alexander et al. [23] studying the interaction between carboxylic acids and the oxyhydroxide surface of aluminium. Figure 7 shows the deconvolution of the different O 1s spectra. It can be observed for the mixture, that the peak at 533 eV becomes significant to the detriment of the two other peaks. Suzuki et al. [24] have also observed this peak studying the inhibition mechanism of a mixture composed of a carboxylate and an amine. They attributed the presence of this signal to a chelate formed between the carboxylate and the Fe³⁺ ions. Their observations by electron-probe microanalysis revealed that this chelate is preferentially formed at the defect, repairing the protective layer. In the present case, the formation of the chelate was more favoured in the presence of the mixture than with the PCAS alone.

Returning back to Figure 6, the N 1s spectra show a peak at 400 eV for the solutions containing FA and the mixture. This is related to the presence of amine (R-

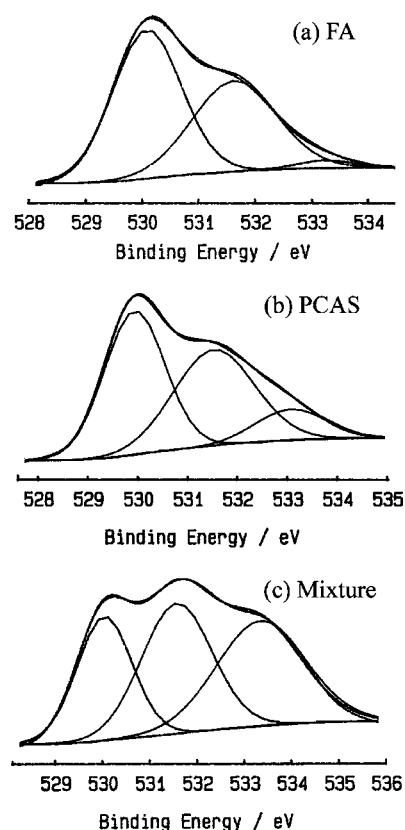


Fig. 7. XPS spectra of the O 1s region for the carbon steel surface after 2 h of immersion in the solutions containing (a) 50 mg l⁻¹ FA; (b) 200 mg l⁻¹ PCAS; (c) 200 mg l⁻¹ PCAS + 50 mg l⁻¹ FA.

NH₂ or R-NH-R) adsorbed on the metal surface. It can be observed that the spectrum obtained in the presence of the mixture revealed a broad shoulder at higher

energies. Tsuji et al. [25] have pointed out that the signal at 399.0 eV is related to the adsorption of a N atom within the film and that obtained at 401.9 eV indicates the presence of NH^+ at the outermost part of the film. Welle et al. [26] underlined that the nitrogen signals found at binding energies above 402 eV correspond to the protonated and oxidised nitrogen species and are associated with an increase in the film thickness. In the presence of biocide [1], this signal was clearly defined and was associated with the adsorption of QAS on the iron oxide/hydroxide layer. In the absence of biocide, according to O'Shea et al. [27], the presence of this shoulder may be related to hydrogen bonding between the hydroxyl ions and the amino group. The presence of an analogous zwitterionic species ($\text{NH}_3^+\text{RCOO}^-$), resulting from the reaction between the carboxylic acid and the amine base [28], could occur when both compounds are adsorbed on the oxide layer. The P 2p spectra were obtained for the solutions containing PCAS and the mixture. They are mainly composed of a peak at 132.5 eV which corresponds to the binding energy of the PO_3^{2-} ion present in the PCAS molecule. For the solution containing only PCAS, a shoulder is observed at 131 eV but this peak is not clear for the solution containing the mixture. It is frequently attributed to the PCAS bonded to the iron oxide substrate [29].

From XPS spectra, it can be concluded that in the presence of the mixture both inhibitors were adsorbed throughout the iron oxide/hydroxide layers. The quantity of PCAS in the layer was higher in the presence of the optimized mixture than that obtained with PCAS alone. Our results are in agreement with the previous data published by Kuznetsov [10], Landolt [11] and Wiczorek [13].

3.3. General discussion

The main inhibitive properties of FA and PCAS tested separately can be summarized as follows: for FA, the low cathodic current densities observed can be explained by their hydrophobicity which expels water molecules from the interface [11, 30]. The low R_p value and the high capacitance measured suggest the existence of a porous inhibitive layer which allows the transport of electroactive species. Their adsorption is not enough to cover the oxide film explaining the rather low protection level reached. For PCAS, a decrease of the anodic current densities and an increase of the R_p value were observed by comparison with FA alone. This is attributed to chelate formation between the iron hydroxide and the carboxylic group in agreement with the anodic action of PCAS. It can be recalled that the anodic effect was improved when the PCAS concentration increased [1]. The low capacitance measured could be explained by the sealing of the oxide/hydroxide layer by the chelate. The layer was thin and protective. In addition, the capacitance value was strongly decreased though the cathodic process was not inhibited.

In the presence of the optimized mixture, electrochemical results and XPS analysis revealed the joint adsorption of both inhibitors. Aramaki [14–16] has proposed two kinds of joint adsorption to explain the synergistic action observed between an anion and a cation. For competitive adsorption, the anion and cation are adsorbed at different sites on the electrode surface. For cooperative adsorption, the anion is chemisorbed on the surface and the cation is adsorbed on the layer of the anions [16]. The two types of adsorption can be characterised by a synergistic factor 's' [14–16, 31] calculated according to Equation 1:

$$s = \frac{1 - E_{1+2}}{1 - E'_{1+2}} \quad (1)$$

where E_{1+2} and E'_{1+2} are the calculated and measured inhibition efficiencies for the mixture, respectively. The former is obtained from Equation 2 and the latter is obtained from Equation 3 using the R_p value measured in the presence of the mixture. R_{p0} is the polarization resistance measured in the absence of inhibitor.

$$E_{1+2} = E_1 + E_2 - \frac{E_1 E_2}{100} \quad (2)$$

$$E'_{1+2} = 1 - \frac{1/R_{p(1+2)}}{1/R_{p0}} \quad (3)$$

For Equation 2, E_1 and E_2 represent the individual efficiency of each inhibitor calculated on the basis of Equation 3 but by using R_{p1} and R_{p2} measured in the presence of each compound. The 's'-factor obtained for the optimized mixture (200 mg l⁻¹ PCAS + 50 mg l⁻¹ FA) was 0.998. According to Aramaki criteria, if $s < 1$, a competitive adsorption mechanism occurs. In our case, 's' is near 1 due to the fact that the R_{p1} and R_{p2} values are of the same order of magnitude (Table 3). In so far as the efficiency of the compounds tested separately is significantly different, the synergistic factor will be higher than 1. The competitive adsorption can be explained by the fact that the amine is more rapidly adsorbed on the surface whereas PCAS is more strongly adsorbed [16, 31, 32]. In the presence of the mixture, the fact that the measured capacitance and the estimated layer thickness were intermediate by comparison with those obtained in the presence of each compound is in agreement with the competitive adsorption mechanism. In addition, this mechanism explains why, for a high FA concentration in the mixture, the efficiency decreased. As a matter of fact, in this case, the fast adsorption of amine impedes PCAS adsorption.

4. Conclusion

The corrosion inhibition of a carbon steel by a mixture composed of phosphonocarboxylic acid salts and fatty amines in a 200 mg l⁻¹ NaCl solution, was studied. The following points can be emphasised:

- (i) The synergistic effect observed for the mixture containing 200 mg l⁻¹ PCAS + 50 mg l⁻¹ FA was explained by the joint adsorption of the compounds throughout the iron oxide/hydroxide layers and more particularly by an enhancement of the formation of a chelate between the iron hydroxide and the PCAS molecules. In spite of the presence of FA in the inhibitive layer, the cathodic process was slightly inhibited.
- (ii) The protection level was dependent on the FA/PCAS ratio. Indeed, the synergistic effect will be observed only for a specific FA concentration at a given PCAS concentration. A competitive adsorption mechanism enabled us to explain this behaviour. Our results were in agreement with those already found in acid solution. Thus, in spite of the formation of oxide layers on the metal surface, the same phenomenology was observed in neutral/alkaline solutions. This suggests that the mechanism of inhibition for mixtures composed of amines and carboxylic acid is independent of the solution pH.

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