

**INFLUENCE OF FLOW ON THE CORROSION INHIBITION OF
CARBON STEEL BY FATTY AMINES IN ASSOCIATION WITH
PHOSPHONOCARBOXYLIC ACID SALTS**

Nathalie Ochoa¹, Francis Moran², Nadine Pébère^{1*}, Bernard Tribollet³

¹Centre Interuniversitaire de Recherche et d'Ingénierie des Matériaux,

UMR CNRS 5085

ENSIACET, 118 Route de Narbonne, 31077 Toulouse cedex 4, France

²Concorde Chimie, 118 Avenue du Docteur Rosenfeld

93230 Romainville, France

³UPR 15 CNRS, 4, Place Jussieu

75252 Paris cedex 05, France

*Corresponding author

Fax: 00-33-5-62-88-56-63

Mail: Nadine.Pebere@ensiacet.fr

Abstract

This work was carried out to study the inhibition mechanism of a carbon steel in a 200 mg l⁻¹ NaCl solution by a non-toxic multicomponent inhibitor used for water treatment in cooling circuits. The inhibitive formulation was composed of 50 mg l⁻¹ fatty amines associated with 200 mg l⁻¹ phosphonocarboxylic acid salts. Steady-state current-voltage curves, obtained with a rotating disc electrode, revealed that the properties of the protective layer were dependent on the electrode rotation rate and on the immersion time. The cathodic process of oxygen reduction was not modified in the presence of the inhibitive mixture. As expected, the current densities increased when the rotation rate was increased. In the anodic range, original behaviour was observed: the current densities decreased when the electrode rotation rate increased. The morphology and the chemical composition of the inhibitive layers allowed the electrochemical results to be explained. Two distinct surface areas were visualised on the metal surface and the ratio between the two zones was dependent on the flow conditions. This behaviour was attributed to a mechanical effect linked to centrifugal force. XPS analysis revealed that the formation of a chelate between the phosphonocarboxylic acid salt molecules and the iron oxide/hydroxide was enhanced by the increase of the electrode rotation rate.

1. Introduction

Cooling water circuits can present several problems. Corrosion, formation of salt deposits and fouling by micro-organisms can appear when natural waters are used as thermal fluid. These problems can occur jointly, reducing the thermal efficiency of the circuit with significant economic repercussions. To reduce or eliminate these problems, waters used in cooling circuits are treated with inhibitive formulations composed of corrosion inhibitors associated with chemical reagents used to limit the scaling and fouling phenomena. Today, due to new restrictive laws concerning the environment, these compounds must be non-toxic and biodegradable.

In previous studies [1, 2], the corrosion inhibition of a carbon steel in a 200 mg l^{-1} NaCl solution by an original multi-component inhibitor used for water treatment in cooling circuits was investigated. The inhibitive formulation was composed of fatty amines (FA) in association with phosphonocarboxylic acid salts (PCAS) [3]. It was shown that PCAS acted as an anodic inhibitor whereas mixed action was seen for FA. A synergistic effect was observed for the mixture containing 200 mg l^{-1} PCAS + 50 mg l^{-1} FA [1]. X-ray photoelectron spectroscopy showed that the inhibitive film was composed of an iron oxide/hydroxide mixture incorporating the organic compounds. A competitive adsorption mechanism was proposed to account for the synergistic effect observed [2].

The present work was designed to gain further understanding of the inhibition mechanism of the mixture. Particular attention was paid to the effects of flow on the formation of the inhibitive film. The behaviour of the carbon steel in the presence of the inhibitive formulation was investigated by steady-state electrochemical measurements using a rotating disc electrode. Local electrochemical impedance spectroscopy (LEIS) was used in mapping mode to characterize the protective layers. Photographs of the electrode surface were taken to

observe the layers formed for different electrode rotation rates. In addition, XPS analyses were performed to compare the chemical composition of the inhibitive film formed under different hydrodynamic conditions.

2. Experimental

2.1. Materials

Fatty amines and phosphonocarboxylic acid salts were used as corrosion inhibitors. The compounds are presented in Figure 1. They are current commercial products. Only the mixture with optimized concentrations (200 mg l⁻¹ PCAS + 50 mg l⁻¹ FA) was studied. The inhibitive formulation has been patented [3]. The corrosive medium was a 200 mg l⁻¹ NaCl solution (reagent grade) in contact with air maintained at 25 °C. The choice of this medium was based upon the following criteria [4]: (i) its low electrical conductivity is close to that encountered in natural waters, (ii) its corrosivity is fairly high and (iii) it is an easily reproducible baseline solution. The pH of the solution containing the inhibitive mixture was 10. For comparison, in the inhibitor-free solution, the pH was adjusted to 10 by NaOH.

A rod of XC 35 carbon steel of 1cm² 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 microstructure corresponded to fine perlite with some inclusions of MnS. A heat-shrinkable sheath left only the tip of the carbon steel cylinder in contact with the solution. For all the experiments, 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. The counter-electrode was a platinum grid. A saturated calomel electrode (SCE) was used as reference.

2.2. Electrochemical experiments

Electrochemical measurements were carried out under potentiostatic regulation using a Solartron 1286 electrochemical interface. The polarization curves were obtained for different immersion times and different electrode rotation rates (Ω). The anodic and the cathodic parts were obtained independently from the corrosion potential. They were plotted point by point in steps of 20 mV every 2 min to ensure quasi steady-state conditions. They were corrected for the ohmic drop, previously determined by electrochemical impedance measurements. The correction level was 80 % of the ohmic drop measured at the corrosion potential. Localized Electrochemical Impedance Spectroscopy (LEIS) was carried out with a Solartron 1275 in mapping mode. The method and the experimental set-up were presented in detail elsewhere [5]. The excitation frequency was fixed at 5 kHz. During the LEIS measurement, the electrode was static but the inhibitive films were formed using the rotating disc electrode. The electrochemical results were obtained from at least three experiments to ensure reproducibility.

2.3. X-ray photoelectron spectroscopy

The carbon steel electrode was immersed in the 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 for different electrode rotation rates. Then, 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 1eV. The oxidation state of the iron was followed using the Fe 2p signal. The binding energies were corrected for charge effects by referencing C 1s to the peak at 284.5 eV. The adsorption of the inhibitive mixture on the steel surface was monitored using the characteristic P 2p, N 1s and O 1s peaks.

3. Experimental results

Fig. 2 shows the polarization curves obtained for two electrode rotation rates (100 rpm and 2000 rpm) and after two immersion times at the corrosion potential (2 h and 24 h). The results obtained without inhibitor are also reported for each rotation rate after 2 h of immersion. In the cathodic range, the oxygen reduction reaction was not modified in the presence of the compounds for either of the rotation rates. In addition, the height of the current plateau was the same independently of the immersion time. On the contrary, in the anodic range, the current densities were significantly lowered in the presence of the inhibitive mixture. Thus, the formulation acted only on the anodic reaction. A shift of the corrosion potential of about 100 mV towards more positive values was noted when the electrode rotation rate increased. The polarization curves obtained at 100 rpm were strongly modified between 2 h and 24 h of immersion whereas the curves obtained at 2000 rpm were relatively close particularly at low anodic overvoltages. These results revealed that the formation of the inhibitive layer is significantly dependent on the electrode rotation rate and its development with time is also determined by the hydrodynamic conditions.

In the absence of inhibitor, the cathodic curves are mass transport controlled [6, 7]. Thus, the corrosion rate increases with the flow velocity. Nevertheless, Uchida et al. [8] mentioned that in some cases, a remarkable reduction of corrosion rates occurs at high velocity. Streicher [9] attributed this drop to an improvement of the passivation by an increase of the oxygen supply. In our case, it can be observed that, in the vicinity of the corrosion potential, the anodic current densities were lower for the highest rotation rate. This phenomenon seems to be enhanced in the presence of the inhibitive mixture.

To have a better understanding of the influence of flow on the electrode kinetics in the presence of the inhibitive mixture, the plots I vs $\Omega^{1/2}$ were performed over the cathodic and anodic domains. Fig. 3 shows the plots I vs $\Omega^{1/2}$ obtained on the cathodic plateau ($E = -950$ mV). Two experimental protocols were used. Curve (a) was obtained after a preliminary hold time of 2 h at E_{corr} for $\Omega = 100$ rpm and for curve (b) the electrode was maintained 2 h at E_{corr} for $\Omega = 2000$ rpm. Then, the cathodic potential was applied and the rotation rate was varied in the ascending or descending sense. For each rotation rate, the current density was collected after 30 minutes of stabilization. For both protocols, the same behaviour was observed: the current densities increased with the square root of the rotation rate. This is explained by an increase of the oxygen supply on the metal surface. The curves are differentiated by the greater curvature of curve (b). This is due to the contribution of a non-diffusional current to the total current measured. Indeed in Fig. 2, it can be seen that at 2000 rpm, the mixed kinetics domain was enlarged and the current plateau was less well-defined. A modification of the oxygen reduction kinetics on the electrode surface probably occurred during the hold time at the corrosion potential. In the absence of inhibitor, for either of the protocols, the curve was superimposable on curve (b) and therefore, was not reported here.

From Fig. 3, it can be considered that the cathodic current followed the relationship [10, 11]:

$$\frac{1}{I} = \frac{1}{I_K} + \frac{1}{I_L} \quad (1)$$

where I_K is the kinetic current and represents the current in the absence of any mass transfer effect and I_L the diffusion current which follows the Levich relationship [11]:

$$I_L = 0.620 n F S D_{O_2}^{2/3} \nu^{-1/6} C_{O_2} \Omega^{1/2} \quad (2)$$

where n is the number of electrons transferred taken as 4, F the Faraday constant, S the electrode surface area (1 cm^2), D_{O_2} the oxygen diffusion coefficient, ν the kinematic viscosity

$(0.82 \times 10^{-6} \text{ m}^2 \text{ s}^{-1})$ and C_{O_2} , the oxygen concentration in the bulk, which is usually taken as 0.2 mol m^{-3} [4]. From the slope of the plot $(I-I_K)^{-1}$ vs $\Omega^{-1/2}$ ($1.9 \text{ A}^{-1} \text{ m}^{-2} \text{ rad}^{1/2} \text{ s}^{-1/2}$), the diffusion coefficient of oxygen was calculated and was found equal to $1.1 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$. This value agrees with that reported by Deslouis et al. [7] and You et al. [12].

Fig. 4 reports the plots I vs $\Omega^{1/2}$ obtained for an anodic overvoltage of 140 mV with respect to the corrosion potential. The two protocols used in the cathodic range (Fig. 3) were also applied after a preliminary hold time of 2 h at the corrosion potential. Unlike the results obtained in the cathodic range, a monotonous decrease of the anodic current densities was observed whatever the conditions of formation of the inhibitive layer. The same behaviour was obtained after 24 h of immersion at the corrosion potential. This unusual result will be discussed later considering complementary experiments.

XPS analyses were carried out on the carbon steel surface after 2 h of immersion in the NaCl solution containing the inhibitive mixture. The films formed at 100 rpm and 2000 rpm were analysed. Argon sputtering was performed to qualitatively evaluate the thickness of the inhibitive layer. Fig. 5 shows the general spectra obtained for the films formed at 100 rpm and 2000 rpm with and without sputtering. The metallic peak of iron appears after 20 min of sputtering for the film formed at 100 rpm whereas it was observed after 5 min for the film formed at 2000 rpm. From this result, it can be concluded that the film formed at 2000 rpm is thinner than that formed at 100 rpm. This conclusion can be explained by comparing the N 1s and O 1s spectra obtained for the films formed for the two rotation rates (Fig. 6). For 100 rpm, a double peak was observed on the N 1s spectrum. The signal at 400 eV is related to the amine adsorbed and that obtained at 402 eV to positively charged nitrogen species [13, 14]. The presence of the peak at 402 eV is associated with an increase in the film thickness [2, 14].

Conversely, for 2000 rpm, the N 1s region is composed of a single peak at 400 eV. For 100 rpm, the O 1s spectrum is composed of at least two peaks: one at 530 eV related to the O²⁻ ion and a second at 531.5 eV attributed to the OH⁻ ion. For 2000 rpm, a third peak at 533 eV is clearly observed. In our previous study, we concluded that this peak corresponds to the binding energy of the carbonyl group present in the PCAS molecule [2]. It is attributed to a chelate formed between the carboxylate and the Fe³⁺ ions, preferentially formed at the defect repairing the protective layer [15]. From XPS results it can be concluded that the formation of the chelate is favoured by the increase of the electrode rotation rate explaining the thinness of the protective film.

Photographs of the electrode surface were taken for different rotation rates after 24 h of immersion in the solution containing the inhibitive mixture (Fig. 7). According to the rotation rate, two zones can be observed on the metal surface. For 100 rpm, a whitish layer covered the whole electrode surface. By touch, the layer was found to be oily. For the three other rotation rates, the surface area covered by the whitish layer decreased as the rotation rate increased. For 2000 rpm, only a small circular spot is observed. On the edge, the electrode surface appears bright. It must be underlined that after 2 h of immersion, the electrode surface appeared bright, irrespective of the electrode rotation rate. To have a better knowledge of the origin of this behaviour, observations were made on an electrode of twice the radius. The same phenomenology was observed: the surface area covered by the whitish layer decreased as the electrode rotation rate increased. In addition, the size of the spot was independent of the electrode radius. Thus, this behaviour was attributed to a mechanical effect due to the centrifugal force and flow conditions and not to a current or a potential distribution. To characterise the protective properties of these two layers, local electrochemical impedance mapping was performed above an electrode surface containing the two zones (Fig. 8).

Admittance values were reported because it was seen that the resolution was higher when plotting admittance rather than impedance. The mapping clearly revealed the two surface areas. It can be seen that the middle zone presented a higher admittance and thus, a lower impedance than the rest of the electrode. This shows that the layer formed on the centre is less protective than that formed on the edge of the electrode. In agreement with XPS results, it can be inferred that the formation of the chelate was favoured at the edge of the electrode improving the protective properties of the layer.

4. Discussion

The electrochemical results revealed specific behaviour as illustrated by the plots I vs $\Omega^{1/2}$ in the anodic range (Fig. 4). The photographs reported in Fig. 7 clearly showed the existence of two zones on the electrode surface. A change of the ratio between the two surface areas was observed on varying the electrode rotation rate. A model can be proposed to explain the above results.

At the corrosion potential:

$$I_{\text{measured}} = I_a - I_c = 0 \quad (3)$$

$$I_a = i_{a1}\Theta + i_{a2}(1-\Theta) \quad (4)$$

i_{a1} and i_{a2} are the anodic current densities at the centre and at the edge respectively. Θ represents the surface covered by the whitish layer.

From LEIM it was shown that:

$$i_{a1} > i_{a2} \quad (5)$$

thus,

$$I_{\text{measured}} = (i_{a1} - i_{a2})\Theta + i_{a2} - I_c = 0 \quad (6)$$

In the cathodic range, the anodic current can be neglected and thus:

$$I_{\text{measured}} = I_c \quad (7)$$

From the I vs $\Omega^{1/2}$ plots (Fig. 3), it can be seen that an increase of the electrode rotation rate resulted in an increase of the cathodic current densities. Thus, the observed behaviour is linked to the increase of oxygen reduction reaction in a classical manner.

In the anodic range, the cathodic current can be neglected and thus:

$$I_{\text{measured}} = (i_{a1} - i_{a2})\Theta + i_{a2} \quad (8)$$

In Fig. 7 it was observed that when the rotation rate increased, Θ decreased. Thus, according to eq. (8), the decrease of the anodic current densities with the electrode rotation rate (Fig. 4) can be attributed to a decrease of Θ .

Fig. 9 summarises, in a schematic representation, the influence of the electrode rotation rates on the polarisation curves. In agreement with the experimental results, the cathodic current densities increased, the anodic densities decreased and the corrosion potential shifted in the anodic direction as the electrode rotation rate increased. From this schema, it can be observed that, for a given rotation rate, an overvoltage of 140 mV with respect to the corrosion potential corresponds to an applied anodic potential (E_{applied}). Thus, when the electrode rotation rate was varied, the anodic overvoltage increased or decreased because the applied potential was fixed and the corrosion potential changed. More precisely, for protocol (a) (Fig. 4), the current densities fell close to zero as the rotation rate was increased because the corrosion potential draws near the anodic applied potential. Finally, Fig. 9 explains why the anodic current densities measured were dependent on the protocol used.

It must be underlined that a global current density was used for ohmic drop correction because the currents for each surface area cannot be measured. However, in the potential domain studied, the experimental error introduced by this simplification is negligible since the current densities are low. Moreover, the electrochemical results were interpreted qualitatively.

5. Conclusion

The influence of flow on the corrosion inhibition of carbon steel by a mixture composed of phosphonocarboxylic acid salts (PCAS) and fatty amines (FA) in a 200 mg l⁻¹ NaCl solution was studied. The formation and the development of the inhibitive layer were dependent on the electrode rotation rate. It was demonstrated that the cathodic process was not modified in the presence of the inhibitive mixture and was classically controlled by oxygen diffusion. In the anodic range, original behaviour was observed: the current density decreased as the electrode rotation rate increased. Two zones were observed on the electrode surface. At the centre, the surface area covered by the less protective layer decreased when the electrode rotation rate increased. The change of the ratio between the two zones allowed the anodic behaviour to be analysed. In addition, the formation of a chelate between the PCAS and the iron oxide/hydroxide layer was favoured at higher rotation rates and the protection afforded by the inhibitive layer was improved. This supports the model proposed. The study will be completed by electrochemical and electrohydrodynamical impedance measurements.

Acknowledgements

The authors wish to express their gratitude to Jean-Baptiste Jorcin for help with LEIS measurements.

References

- [1] N. Ochoa, G. Baril, F. Moran and N. Pébère, *J. Appl. Electrochem.* **32** (2002) 497.
- [2] N. Ochoa, F. Moran and N. Pébère, *J. Appl. Electrochem.* To be published.
- [3] International patent N° PCT/FR99/01408.
- [4] M. Duprat, M.C. Lafont, F. Moran and F. Dabosi, *Electrochim. Acta* **30** (1985) 353.
- [5] G. Baril, C. Blanc, M. Keddam, N. Pébère, *J. Electrochem. Soc.* **151** (2003) B488.
- [6] A. Bonnel, F. Dabosi, C. Deslouis, M. Duprat, M. Keddam, B. Tribollet, *J. Electrochem. Soc.* **130** (1983) 753.
- [7] C. Deslouis, M.C. Lafont, N. Pébère, D. You, *Corros. Sci.* **34** (1993) 1567.
- [8] T. Uchida, T. Nishiyama, T. Kawamura, *Proc. of 7th European Symposium on Corrosion Inhibitors (7 SEIC)*, Ann. Univ. Ferrara, N. S., Sez. V. Suppl. N.9 (1990) 471.
- [9] L. Streicher, *J. Am. Wat. Wks. Ass.*, **48** (1956) 219.
- [10] A.J. Bard, L.R. Faulkner, *Electrochemical Methods*. John Wiley and sons (1980).
- [11] G. Levich, *Physicochemical Hydrodynamics*. Prentice Hall, Englewood Cliffs, New Jersey (1962).
- [12] D. You, N. Pébère, F. Dabosi, *Corros. Sci.* **34** (1993) 5.
- [13] N. Tsuji, K. Nozawa, K. Aramaki, *Corros. Sci.* **42** (2000) 1523.
- [14] A. Welle, J. D. Liao, K. Kaiser, M. Grunze, U. Mäder, N. Blank, *Appl. Surf. Sci.* **119** (1997) 185.
- [15] T. Suzuki, H. Nishihara, K. Aramaki, *Corros. Sci.* **38** (1996) 1223.

CAPTION OF FIGURES

Figure 1: Chemical structure of the inhibitors:

(a) Fatty amines.

(b) Phosphonocarboxylic acid salts.

Figure 2: Steady-state current-voltage curves obtained for the carbon steel electrode for two rotation rates after (●) 2 h and (○) 24 h of immersion at E_{corr} in the 200 mg l⁻¹ NaCl solution containing the inhibitive mixture (200 mg l⁻¹ PCAS + 50 mg l⁻¹ FA). (a) 100 rpm, (b) 2000 rpm, (----) without inhibitor for each rotation rate after 2 h of immersion.

Figure 3: I versus $\Omega^{1/2}$ obtained in the cathodic range ($E = -950$ mV/SCE). Curve (a): the electrode rotation rate was varied in the ascending sense after a preliminary hold time of 2 h at E_{corr} at 100 rpm, Curve (b): the electrode rotation rate was varied in the descending sense after a preliminary hold time of 2 h at E_{corr} at 2000 rpm.

Figure 4: I versus $\Omega^{1/2}$ obtained in the anodic range ($\Delta V = 140$ mV). Curve (a): the electrode rotation rate was varied in the ascending sense after a preliminary hold time of 2 h at E_{corr} at 100 rpm, Curve (b): the electrode rotation rate was varied in the descending sense after a preliminary hold time of 2 h at E_{corr} at 2000 rpm.

Figure 5: XPS general spectra of the carbon steel surface after 2 h of immersion in the 200 mg l⁻¹ NaCl solution containing the inhibitive mixture. (a) 100 rpm: (—) surface and (----) 20 min of sputtering; (b) 2000 rpm: (—) surface and (----) 5 min of sputtering.

Figure 6: XPS spectra of the N 1s and the O 1s regions for the carbon steel surface after 2 h of immersion in the 200 mg l⁻¹ NaCl solution containing the inhibitive mixture. (a) 100 rpm; (b) 2000 rpm.

Figure 7: Photographs of the electrode surface obtained after 24 h of immersion in the 200 mg l⁻¹ NaCl solution containing the inhibitive mixture for different electrode rotation rates.

Figure 8: (a) Photograph of the electrode surface after 24 h of immersion in the 200 mg l⁻¹ NaCl solution containing the inhibitive mixture for 1000 rpm. (b) Local electrochemical admittance mapping corresponding to the photograph.

Figure 9: Schematic representation of the influence of the electrode rotation rate on the polarization curves with $\Omega_1 < \Omega_2 < \Omega_3$. For protocol (a): $E^1_{\text{applied}} = E^1_{\text{corr}} + 140 \text{ mV}$ and the rotation rate varied from Ω_1 to Ω_3 . For protocol (b): $E^2_{\text{applied}} = E^2_{\text{corr}} + 140 \text{ mV}$ and the rotation rate varied from Ω_3 to Ω_1 .