

A CORROSION INHIBITION STUDY OF A CARBON STEEL IN A LOW CONDUCTIVITY MEDIUM BY FATTY AMINES/ SULPHONATED POLYACRYLATES ASSOCIATION

M.C. Lafont¹, N. Pébère¹ and F. Moran²

**¹ UPRESA CNRS 5071, Equipe Corrosion et Protection
ENSCT - 118 Route de Narbonne - 31077 Toulouse cedex 4 FRANCE**

**² CONCORDE CHIMIE FRANCE,
118 Avenue du Dr. Rosenfeld - 93230 Romainville FRANCE**

1. INTRODUCTION

Efficient corrosion treatments of carbon steels in cooling water systems were based on inorganic inhibitors such as chromates, nitrites, polyphosphates or zinc salts. Nowadays, the use of chromates and nitrites is submitted to severe restrictions due to their high toxicity. In the case of zinc salts, their rejection in waste water at high level has become unacceptable.

Since the 1960's, more advanced treatments including organic compounds (*i.e.* phosphonates, polyacrylates, amines, phosphonocarboxylic acid) have been proposed to improve corrosion protection; their principal advantage being the absence of toxicity. Nevertheless, high concentrations are necessary to obtain a good inhibition. More recently, molybdate-based treatments are considered as an alternative to chromate-based inhibitors. However these compounds have a poor trading interest because they present the disadvantage of being very expensive. Actually, the prevention of corrosion and scaling in recirculating cooling systems is usually achieved by organic mixtures.

In the present study, we present and discuss the results concerning the corrosion inhibition of a carbon steel in 200 mg l⁻¹ NaCl solution by an original multi-component inhibitor (fatty amines in association with sulphonated polyacrylates).

Steady-state current-voltage curves were combined with electrochemical impedance measurements in order to evaluate the efficiency of this mixture and to show the interest of its use by comparison with a sodium molybdate salt. Electrochemical impedance spectroscopy was used to study the formation of the protective layer either on freshly polished surface and on pre-corroded electrode.

2. EXPERIMENTAL

The carbon steel used in this work was an XC38 type (composition in wt % : C = 0.35 ; Mn = 0.65 ; Si = 0.25 ; P = 0.035 and Fe to 100). For all the experiments, the carbon steel samples were polished with 4000 grade emery paper, cleaned in water in an ultrasonic bath and dried in warm air.

The corrosion medium was a 200 mg l⁻¹ NaCl (reagent grade) solution in contact with air maintained at 25°C. The pH value have been adjusted with sodium hydroxyde.

The products used in this study were a sodium molybdate salt and an inhibitor mixture (fatty amines associated with sulphonated polyacrylates). The formulations tested consist of aqueous solutions supplied by "Concorde Chimie France". The active concentrations were 100 ppm for the molybdate salt and 50 ppm/50ppm for the amines/ polyacrylates mixture.

The working electrode was a rotating disc consisting of a carbon steel rod of 1 cm² cross-sectional area. A saturated calomel electrode (S.C.E.) was used as reference and the auxiliary electrode was a platinum grid.

The ohmic drop in the electrolyte was high (between 400 and 700 Ω.cm²). As a consequence, the polarization curves were obtained with ohmic drop compensation. Electrochemical test were carried out using a Solartron 1250 Frequency Response Analyser with a Solartron 1286 Electrochemical Interface. The data were processed by a HP 9000 computer.

3 - RESULTS AND DISCUSSION

The addition of the inhibitor mixture in the aggressive medium leads to a modification of the pH of the solution. Without inhibitor, the pH is 5.6 and in the presence of the mixture the pH is 11. Fig. 1 represents the potentiostatic curves plotted without inhibitor for two pH values. A clear difference is observed particularly in the anodic range. For the pH = 11, the current densities are low in a large potential domain. This result is attributed to a passivation of the surface. In the cathodic range, the current densities are higher than for pH = 5.6. For this pH value, the oxygen reduction is slow down due to a diffusion barrier effect created by the progressive deposit of insoluble corrosion products [1].

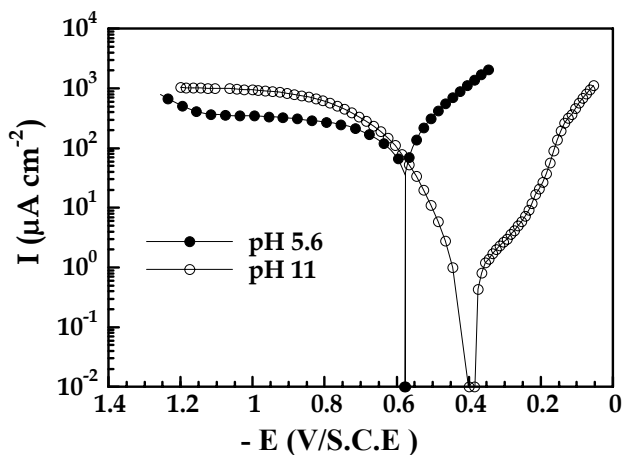


Fig. 1 : Steady-state current-voltage curves obtained without inhibitor for two pH values after 2 h of immersion at E_{corr} Ω = 1000 rpm

The impedance diagrams obtained for the two pH values are given in Fig. 2. In the two cases, a capacitive loop is observed. For pH = 5.6, the loop is more flattened. The polarisation resistance value is low (400 Ω cm²). This result is in agreement with the severe attack of the steel surface. Corrosion products appear all over the surface in the form of hydrodynamic figures. For pH = 11, the polarisation resistance value is around 25 kΩ cm². In this case, the surface is tarnished without corrosion product.

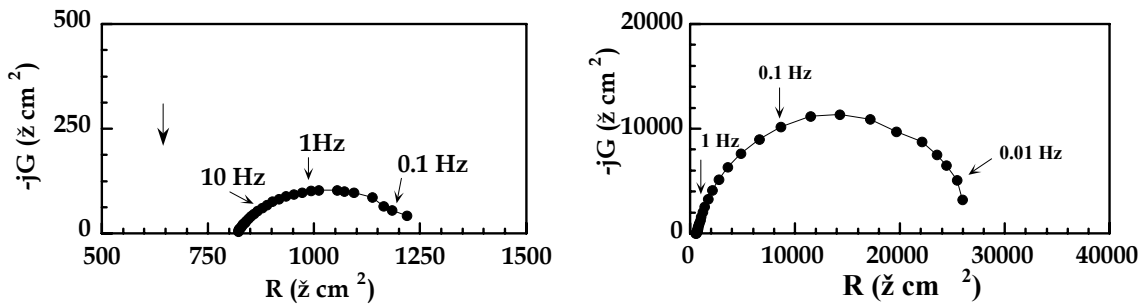


Fig. 2 : Electrochemical impedance diagrams obtained without inhibitor for two pH values after 2 h of immersion at $E_{corr} - \Omega = 1000 \text{ rpm}$ (a) $\text{pH} = 5.6$ and (b) $\text{pH} = 11$

Fig. 3 compares the current-voltage curves in the presence of molybdate salt and the inhibitor mixture. By comparison with the blank solution, the addition of the compounds significantly decreases the anodic current densities and the cathodic current densities around the corrosion potential. The limiting current density (around -1 V) remains identical. These observations suggest that the two inhibitive formulations act only on the anodic sites. For the inhibitive mixture, an anodic current plateau is observed (500nA). The inhibitive action is more marked for the amine/polyacrylate formulation and this result validate the interest of this formulation.

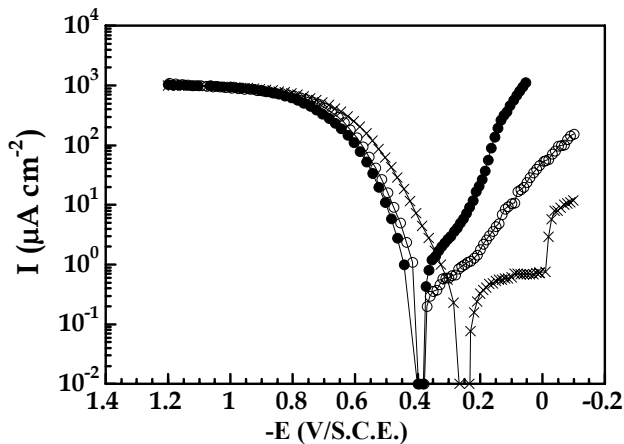


Fig. 3 : Steady-state current-voltage curves obtained after 2 h of immersion at E_{corr} (●) without inhibitor (○) with molybdate salt (+) with amines + polyacrylates $\Omega = 1000 \text{ rpm}$

In the second part of the study, EIS is used to study the mechanism of inhibitor film formation. Fig. 4 gives the impedance spectra in Bode coordinates in the presence of the mixture for a freshly polished surface for different immersion times. After 2 h of immersion, the diagram is characterized by a single time constant. When the immersion time increases a capacitive behaviour is observed with an increase of the low frequency limit of the diagram. Between 21 h and 48 h the diagram is unchanged and is not given on the figure. These results illustrate the formation of a protective layer on the carbon steel surface. A very good inhibition is obtained from the first hours of immersion.

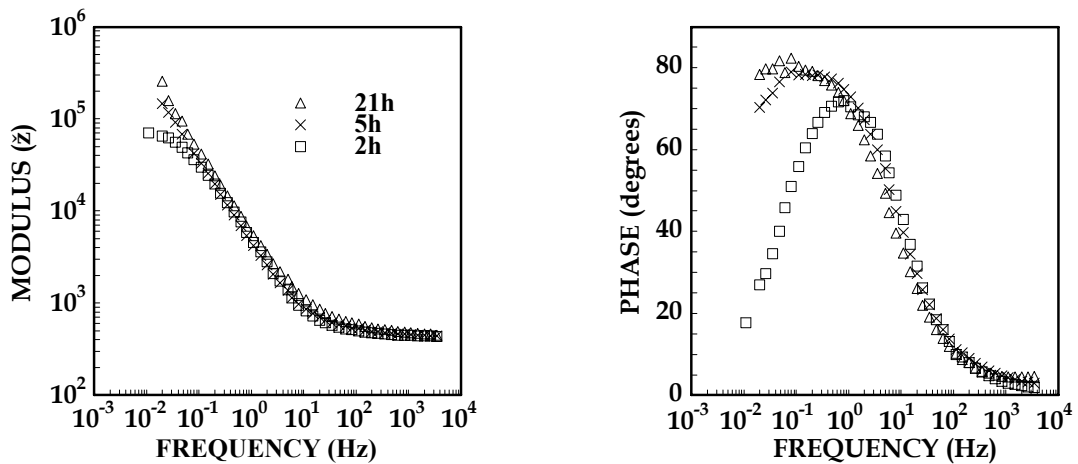


Fig. 4 : Bode plots for a freshly polished carbon steel surface in the presence of the inhibitive mixture as a function of immersion time

Then the formation of the film was analyzed on precorroded surface. First, the electrode was left 2 h in the aggressive solution without inhibitor. Then, the inhibitor mixture was injected in the NaCl solution and the impedance diagrams are plotted for different immersion time (Fig. 5). Whatever the immersion time, a capacitive behaviour is observed. In this case, even if the surface is degraded, the inhibitor can be adsorbed and the protection achieved by the mixture is satisfactory.

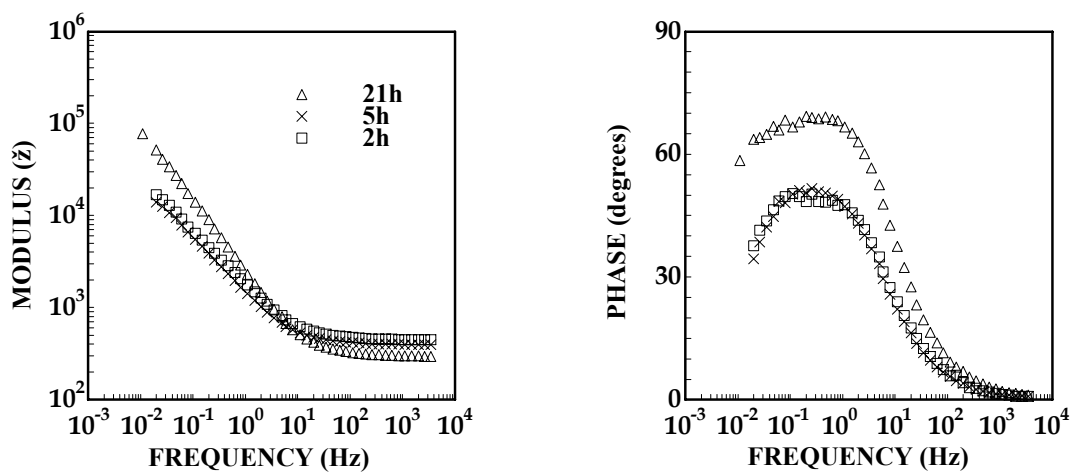


Fig. 5 : Bode plots for a precorroded steel surface (2 h without inhibitor) in the presence of the inhibitive mixture as a function of immersion time