Study of efficiency and stability of film forming amines (FFA) for the corrosion protection of the carbon steel in water circuits

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1. Introduction

Metal corrosion in industrial water systems like cooling circuits is a major problem. Excessive corrosion does not only lead to serious damages of installations but also causes significant environmental and economic repercussions. To reduce or eliminate these problems, water used in cooling circuits is usually chemically processed and treated with inhibitive formulations containing corrosion inhibitors.

In the past, efficient protective treatments of carbon steels were based on inorganic inhibitors (e.g. chromates, nitrites) [1] but today their use is restricted due to their high toxicity. Since the 1960’s, other treatments using organic compounds like phosphonates, molybdates and amines have been proposed because of their non-toxic nature. Nevertheless, high concentrations are necessary to obtain good inhibition [2, 3].

For many years, the prevention of corrosion in cooling systems is achieved by film forming amines (FFA) which are often referred to as fatty amines or polyamines [4, 5, 6]. They are able to form a mono-molecular film or layer adsorbed on the metal surfaces, which constitutes a homogeneous protective barrier against corrosion.

Today, due to a lack of knowledge and systematic research about the influence of chemical structure on the anticorrosion properties, especially for FFA, this paper presents the results of studies with new inhibitive formulations based on amines for cooling systems.

Comparative studies have been carried out to evaluate the efficiency of film forming amines (FFA), and to optimize their inhibitive properties against the corrosion of carbon steel.

In this aim, the present work is devoted to study the behavior of the carbon steel, in presence of different inhibitive formulations based of FFA of different structures, by steady-state electrochemical measurements, impedance spectroscopy measurements using a rotating disc electrode and pilot test in laboratory. From the data obtained, it is intended to develop structure/property relations in order to find optimal corrosion inhibitors also taking into account ecological and economical aspects.

2. Experimental procedure

2.1. Materials

The corrosion inhibitor compounds selected for the study are based on 3 different chemical families of fatty amines (FFA), that vary in the number of amino groups and the
aliphatic alkyl group, generally a fatty alkyl chain. The generic structure of these compounds is presented in Figure 1.

\[
R^1\text{-(NH-R^2)}_n\text{-NH}_2
\]

With: \( n \) = number of monomers
\( R^1 \) = alkyl chain: \( \text{CH}_3\text{-(CH}_2)_7\text{-CH=CH-(CH}_2)_8 \)
\( R^2 \) = alkyl group: \( -(\text{CH}_2)_3\text{-} \)

*Figure 1: Generic chemical structure of the different film forming amines*

In our paper, we used four compounds different in the number of amino groups, e.g. \( \text{N}_2 \) indicates a diamine, or the type of alkyl chain \( R \), i.e. saturated or unsaturated, which is indicated by a subscript “s” respectively “u”. As an example, \( \text{R}_\text{uN}_2 \) is an oleylpropylenediamine.

2.2. Electrochemical experiments

Electrochemical measurements are carried out using an Autolab Metrohm frequency response analyser (frequency range of 65 kHz to a few mHz with eight points per decade) with an electrochemical interface. The polarization curves are determined potentiostatically with ohmic drop compensation. They are plotted point by point to ensure quasi steady-state conditions. The anodic and the cathodic parts are obtained independently from the corrosion potential after 2 h of immersion. The electrolytic resistance (Re) is determined from the high-frequency limit of the electrochemical impedance measurements.

The material selected for the study is an XC 35 carbon steel and has the following composition in percentage by weight: C=0.35, Mn=0.65, Si=0.25, P=0.035, S=0.035 and Fe to 100. A rod of 1 cm² cross-sectional area is used as working electrode. For all the experiments, the carbon steel samples are polished with SiC paper down to grade 2400, cleaned in water in an ultrasonic bath then dried in warm air.

The counter-electrode is a platinum grid and a saturated calomel electrode (SCE) is used as reference.

For all the experiments, each compound has been studied at the same concentration of 100 mg L⁻¹. The corrosive medium is a 200 mg L⁻¹ NaCl solution (reagent grade) in contact with air maintained at 25 °C for the experimental experiments.

2.3. Pilot test system

More practice-like but accelerated corrosion tests have been carried out to simulate the conditions of real industrial water circuits. First, a set of experiments was run on the laboratory scale in a circulation device. For this, the steel coupons were mounted in a miniaturized cooling circuit with a test rack according to ASTM 2688 [7]. Water was then circulated from a reservoir at 600 L/h for the predefined exposure time (usually between 1 and 3 days). Various water qualities can be employed, in our study we used decarbonized water with addition of chloride (see Table 1).
Table 1: Chemical composition of the corrosive water used in our pilot test system during the experiments

<table>
<thead>
<tr>
<th>Water quality</th>
<th>Ca$^{2+}$</th>
<th>Mg$^{2+}$</th>
<th>Cl$^{-}$</th>
<th>HCO$_3^-$</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration in mg L$^{-1}$</td>
<td>24</td>
<td>9.7</td>
<td>350</td>
<td>24.4</td>
<td>7.0</td>
</tr>
</tbody>
</table>

Figure 2 shows a schematic representation of the apparatus. Visual inspection and weight loss evaluation (after pickling, rinsing and drying) were then used to evaluate inhibitor performance. The optical appearance of the coupons was graded from -- (severe corrosion) to ++ (no visual corrosion damage), taking into account both planiform and localized corrosion attack. Corrosion protection factors were calculated from the weight loss measurements with untreated water as the reference system.

Second, inhibitor systems which have shown good performance in the laboratory-scale experiments were subsequently tested in an upscaled pilot plant experiment. The pilot plant used is a fully-equipped simulation facility operating under field conditions. A closed primary cooling circuit and an open secondary circuit are combined to form the basic framework. Heat transfer between the circuits is achieved via combination of tube-bundle heat exchanger (HE) and a single tube HE. Back-cooling of the circulation water is effected by a spiral condenser.
Application of treatment chemicals and water exchange in the circuit are implemented such as to closely resemble field conditions. Water qualities of the circulating water used in this pilot were deionized and soft water.

A scheme of the facility is shown in the figure 3. Corrosion rates can be measured both by test coupon analysis (visual inspection & weight loss evaluation) and electrochemical corrosion rates (Corrater® system). A typical testing time in the pilot plant is 14 days.

Figure 3: Picture of the pilot cooling plant

3. Results and discussion

3.1. Electrochemical results

These series of experiments have been done to establish the mode of action of three different FFA compounds used separately, to characterize their behavior and to know if they have an anodic, cathodic or mixed action. Thus, steady-state current–voltage curves and impedance diagrams are obtained in the presence of each compound and compared with the curve obtained in the inhibitor-free solution after 2 hours of immersion.

3.1.1. Steady state polarizations curves obtained in the presence of fatty monoamines, diamines and triamines

Figure 4 shows the current-voltage curves obtained for the solutions containing the different types of FFA and without inhibitor.

First, a slight shift (about 100 mV) of the corrosion potential ($E_{corr}$) towards more anodic potentials is noted when fatty amines are added to the aggressive solution. Initially, the
corrosion potential ($E_{corr}$) of the carbon steel (without inhibitor) measured in our experimental conditions is about -0.45 V/SCE.

In the cathodic range, the curves show an influence of the FFA presence because the cathodic oxygen reduction is modified due to the presence of amines. Precisely, a significant decrease of the cathodic current densities is noted (almost 1 log) for each compound. The strongest reduction is obtained with $R_{UN1}$ and $R_{SN2}$.

In the anodic range, the current densities are significantly lowered in the presence of the monoamine $R_{UN1}$ and the diamines $R_{UN2} / R_{SN2}$. In contrast to this effect of the triamine is less significant.

Around -0.3V vs SCE, a slight passivity plateau appears for these compounds, it demonstrates the protective properties of the film formed by fatty amine. Around 0V vs SCE, an abrupt increase of the anodic current density occurs. This increase is associated with the development of localized corrosion. This behavior is usually observed for anodic inhibitors and is intensified in solutions containing aggressive ions such chloride.

However, in the anodic range, the curve is independent of the presence of $R_{UN3}$ (alkyl triamine).

Thus, except the $R_{UN3}$ compound, these results show that film forming amines act both on the cathodic and anodic partial reactions. A decrease in the cathodic and anodic current densities is observed by comparison with results obtained without inhibitor.

**Figure 4**: Steady-state current-voltage curves obtained after 2 hours of immersion at $E_{corr}$ for different types of FFA (dose=100 mg/L): (...) $R_{UN1}$; (- - -) $R_{UN2}$; (− − −) $R_{SN2}$; (− − −−) $R_{UN3}$; (− −) blank solution.
### 3.1.2. EIS measurements for 3 different families of film forming amines

Figure 5 shows the impedance diagrams obtained for the same four different inhibitive compounds. They are characterized by a single capacitive loop. The distorted shape of the diagrams (especially for RSN2 and RUN3) in the high-frequency part (for y axis < 200 Ω cm² and for x axis < 1000 Ω cm²) can be attributed to the formation of a relatively thick and compact protective film on the metal surface in agreement with the previous work of Duprat et al. [8] (however, an immersion time of 2 h might not be sufficient to show the occurrence of a clear loop in the high-frequency domain).

The polarization resistance values (Rp) obtained from the diagrams can be related to the charge transfer resistance of iron dissolution in the pores of the inhibitive layer [8, 9]. 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 [10, 11]. In fact, higher is the Rp value, better is the anticorrosion efficiency.

The Rp values obtained for each FFA tested are reported in Table 2.

The results presented below, that for all amines tested, the Rp values are significantly higher than that obtained for the blank solution (without inhibitor). It can be pointed out that the highest values have been obtained with RUN2 and then RUN1. The Rp values measured with RSN2 and RUN3 are slightly lower but remained clearly above the value corresponding to the blank. These results are in accordance with the polarization curves (3.1.1.).

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**Figure 5:** Electrochemical impedance diagrams obtained after 2 hours of immersion at $E_{corr}$ for different types of FFA (dose=100 mg/L): (●) RUN1; (♦) RUN2; (○) RSN2; (□) RUN3; (—) blank solution
Table 2: Polarization resistance deduced from the impedance diagrams presented in Figure 5 for carbon steel immersed in NaCl solution containing different film forming amines

<table>
<thead>
<tr>
<th>Film Forming Amines</th>
<th>R_p in [Ω cm²]</th>
</tr>
</thead>
<tbody>
<tr>
<td>RUN1</td>
<td>6800</td>
</tr>
<tr>
<td>RUN2</td>
<td>6500</td>
</tr>
<tr>
<td>RSN2</td>
<td>4100</td>
</tr>
<tr>
<td>RUN3</td>
<td>4000</td>
</tr>
<tr>
<td>Blank (solution without inhibitor)</td>
<td>1600</td>
</tr>
</tbody>
</table>

The inhibitive properties of fatty amines in neutral or alkaline media are frequently attributed to their hydrophobic character [12, 13]. In previous studies [14–15], it was shown that there is a relationship between inhibitory efficiency and the hydrophobic properties. This model is confirmed by the data of polarization resistance, since it is decreasing with the number of amino groups, i.e. the increase of hydrophily.

3.2. Comparative pilot tests

Figure 6 shows the results for the corrosion efficiency, by the corrosion rate measurements, of each FFA compound after 10 days of corrosion testing in the circulation device. These results clearly indicate a significant anticorrosion protection on the carbon steel of the all FFA compared to the blank value (solution without inhibitor). The corrosion rate obtained with RUN1, RUN2, RSN2 were similar and very low, showed an efficient corrosion inhibition above 75 %. But the corrosion rate measured in presence of RUN3 is higher and leaded to a limited anticorrosion efficiency with a corrosion inhibition which is almost 50 %.

![Figure 6: Corrosion inhibition values obtained by the corrosion rate measurements for each FFA tested after 10 days in the lab circulation device](image)
These tendencies confirmed the experimental results presented previously (see § 3.1.1. and 3.1.2.) and were in agreement with the order of anticorrosion efficiency obtained with the electrochemical experiments (Figure 7). Thus, we could establish the following classification of protection efficiency on the carbon steel for the different FFA:

\[
R_{U1}N_1 \geq R_{U1}N_2 > R_{S2}N_2 >> R_{U3}N_3
\]

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**Figure 7:** Comparison between the values of the relative corrosion inhibition obtained with the corrosion rate measurements and the polarization resistance of impedance analysis for each FFA

The experimental results show the influence of the amino groups presence in each compound and more precisely the number of nitrogen atoms. In fact, it seems that the anticorrosion efficiency decreases when the number of N increases. This tendency could be explained by the difficulty to form a homogeneous film on the metal surface when there are several nitrogen atoms because of a possible steric obstruction effect. On the other hand, there is also the possibility of repulsion phenomena between the free electrons pairs of each nitrogen atoms. Thus, it would explain the gap of efficiency between a triamine (\(R_{U3}N_3\)) and diamine or monoamine.

The influence between the amino group presence and the corrosion efficiency for FFA could also be explained by the interaction of the nitrogen atoms and the metallic surface described by several authors who propose a complementary inhibitive mechanism: FFA interact with the metal ions to form a complex of low solubility providing supplementary barrier [12, 16, 17]. Using the hard and soft acids and bases principle, Aramaki *et al.* [19] have found that the nitrogen atom is preferentially combined to \(\text{Fe}^{3+}\).

In contrast to the number of amino groups, there is a limited influence of the alkyl chains tested. The difference in corrosion inhibition between a saturated (\(R_{S2}N_2\)) and unsaturated chain (\(R_{U1}N_2\)) for a same type of amine seems to be not of relevance, but considering the impedance data, the layer formed on the surface is certainly different.
Besides the corrosion inhibition, also the other parameters are of importance for the application in a cooling system. Therefore, the residual free film forming amine content and the concentration of iron has been determined during selecting test trials for the two diamines.

Figure 7 shows the residual amount of FFA (7a) and the iron content (7b) in water during 10 days. Precisely, it can be noted that there is for both amines a strong decrease of free FFA during the first 4 days indicating the film formation on the surface and afterwards, when the film formation is completed, a stable and low content is measured which corresponds to the excess amine in water.

Thus, it is very interesting to observe that the iron content becomes low when the residual content is stable, it means that the corrosion protection is really efficient only when the film is formed. From these results, it can be stated that the type of alkyl chain has no significant impact on the protection of the steel surfaces.

In order to study in more detail possible differences in behavior of the two diamines long term trials have been carried out in pilot cooling plants. Figures 8 and 9 show the dependence of the corrosion rate measured by Corrater® during a test period of 4 weeks with the presence of saturated ($R_5N_2$) and unsaturated chain ($R_7N_2$).

The results presented in these 2 figures show clearly that there is no significant difference for the two parameters considered: the residual amount of amine and the Corrater® measurement showing similar performing of the anticorrosion efficiency during the test period. The results obtained with the presence of a diamine with saturated ($R_5N_2$) and unsaturated chain ($R_7N_2$) are in accordance with the previous conclusion: the type of alkyl chain has no significant impact on the protection of the steel surfaces.
Figure 8: Residual content of R$_{u}$N$_2$ (▲) and corrosion rate measured by corrater (◆) during the experiments with the pilot cooling plan.

Figure 9: Residual content of R$_{u}$N$_2$ (▲) and corrosion rate measured by corrater (◆) during the experiments with the pilot cooling plan.

Figure 10 complete the previous data and confirm that the efficient anticorrosion protection obtained with R$_{s}$N$_2$ and R$_{u}$N$_2$. More precisely, this figure shows some pictures of steel coupons which were included in the coupon test rack of the pilot cooling plant with deionized water and soft water. We can easily note the clean aspect (without picking or damages due to the corrosion) of them with the presence of the 2 families of diamine (saturated and unsaturated chain) after 4 weeks of corrosion testing.
4. Conclusions

Systematic studies on the corrosion inhibition of film forming amines (FFA) applying both electrochemical and weight loss experiments in cooling system simulations have shown a dependence of the corrosion protection on carbon steel on the chemical structure of the inhibitor. According to the results, FFA are efficient corrosion inhibitors on carbon steel.

It could be noted that the number of amino groups influences the anticorrosion efficiency which decreases with increasing number of amino groups. In contrast to this, there is a limited impact of the type of the investigated alkyl chains.

Besides the efficiency data, the formulability and environmental profile must be considered to deliver the optimal solution both from technical and ecological point of view.

For a better understanding of the mode of action of FFA, complementary experiments could provide more deep knowledge on the mechanisms involved in the interactions between FFA and the metal surface.

5. References