LABORATORY INVESTIGATIONS FOR THE REPLACEMENT OF CYCLOHEXYLAMINE BY 2-(DIETHYLAMINO)ETHANOL IN FILM FORMING AMINE PRODUCT FORMULATIONS

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ABSTRACT

A decade ago, the ammonia/morpholine treated 125 bar steam system of one of SABIC’s naphtha crackers in Geleen, Netherlands, was successfully converted to a film forming amine (FFA) program. An essential constituent of many FFA formulations currently used is cyclohexylamine (CHA). This volatile neutralizing amine, however, now is characterized by hazard phrase 361f, i.e. it is suspected of damaging fertility. In the steam generation community this situation has prompted the search for suitable alternatives.

The research presented in this paper has been carried out to investigate the possibility to replace CHA by 2-(diethylamino)ethanol (DEAE) in the Kurita Cetamine® products employed in SABIC’s cracker. For this, the following suite of techniques has been used to expand on previous electrochemical impedance spectroscopy work conducted by Kurita:

- additional electrochemical impedance spectroscopy measurements
- contact angle measurements
- quartz crystal microbalance with dissipation monitoring experiments

The results show that DEAE is a viable substitute of CHA.

Keywords: steam system, corrosion, inhibitor, amine, films, electrochemical impedance spectroscopy, quartz crystal microbalance with dissipation monitoring, contact angle.
1 INTRODUCTION

Film forming amines (FFAs) are widely used to inhibit corrosion in industrial water cycle applications, because they form films which act as a hydrophobic barrier against corrosive species (Betova, et al., 2014) (Forêt, et al., 2013) (Hater, et al., 2014).

For over 10 years, FFAs have successfully been employed at one of SABIC’s naphtha crackers in Geleen, Netherlands, to treat the 125 bar steam system of the olefins plant. The FFA treatment program has replaced the historical ammonia/morpholine program of the plant’s water/steam cycle at the end of 2005. Although application of FFA chemistry does not come without challenges, experience in Geleen generally has been positive. For instance, during the last cracker turnaround steam turbines were found to be mechanically sound and exceptionally clean (van Lier, et al., 2015). FFA formulations typically contain neutralizing amines to control the pH (Betova, et al., 2014). Examples of common neutralizing amines are cyclohexylamine, methoxypropylamine, ethylamine, ethanolamine, morpholine and dimethylaminoethanol. Some of these amines, and specifically cyclohexylamine (CHA), can provide the required volatility for alkalization of the steam/condensate part of the steam cycle, and stabilize filming amine based formulations (Betova, et al., 2014) by increasing their solubility in the product blend.

Although CHA has been effectively used in many FFA formulations, it is now characterized by hazard phrase 361f, i.e. it is suspected of damaging fertility, thus begging the search for substitutes. Kurita has selected 2-(diethylamino)ethanol (DEAE) as the alternative to CHA.

The transition of CHA to DEAE has already been practiced in the industry at boiler pressure and superheat temperatures similar to those of SABIC’s naphtha cracker, for instance at the Polish Adamów power plant (Sylwestrzak, et al., 2016). The joint research presented in this paper is aimed at providing scientific support to the use of DEAE as a substitute to CHA. To achieve this, the following suite of techniques has been used to expand on previous electrochemical impedance spectroscopy (EIS) work carried out by Kurita:

- additional electrochemical impedance spectroscopy measurements
- contact angle measurements
- quartz crystal microbalance with dissipation monitoring experiments

2 MATERIALS AND METHODS

2.1 Corrosion inhibitors

Two proprietary FFA inhibitor formulations provided by Kurita were used in this study: Cetamine® V211 and G811, which contain CHA and DEAE, respectively. Both contain ca. 2% of N-oleyl-1,3-propanediamine as the filming compound.

2.2 Corrosion coupons

Two types of AISI certified coupons were employed for contact angle measurements: C1010 (plain carbon steel) and 316L (austenitic stainless steel) coupons. All coupons were cleaned with ethanol and milli-Q water and dried with nitrogen prior to each test.

2.3 Electrochemical Impedance Spectroscopy measurements

EIS measurements were performed to study the formation of passivating films on carbon steel surfaces upon addition of Cetamine® V211 (CHA-based) and G811 (DEAE-based), using a Metrohm Autolab frequency response analyzer with an electrochemical interface.
EIS measurements were performed at room temperature and atmospheric pressure using demineralized water, to which NaCl was added at a concentration of 200 ppm (mass based), and the pH of which was adjusted to 9.0 using HCl or NaOH. The dosage of the formulated products was 200 ppm, volume based. The working electrode was a rotating carbon steel disc having a surface area of approx. 0.2 cm². All experiments were carried out at a stirring rate of 500 rpm. A saturated calomel electrode (SCE) was used as reference and a platinum grid as the counter-electrode. The systems were mathematically described in terms of electric equivalent circuits comprised of resistances and constant phase elements (CPE). The resistances in the electrical equivalent circuit are as follows: a polarization resistance $R_p$, a resistance $R_f$ representing the resistance of the ion conducting paths in the passivating films, and a resistance $R_s$ representing the resistance of the electrode. CPEs model the behavior of a double layer formed in the proximity of the metal surface immersed in liquid. Such elements are described by two parameters: the capacity $Y_0$ and an exponent $n$, which is correlated to the roughness and inhomogeneity of the surface and/or to a non-uniform distribution of the current density on the electrode undergoing corrosion.

2.4 Contact angle measurements

Contact angle measurements were performed to analyze the hydrophobicity of films formed by the amines present in the Cetamine® V211 and G811 on C1010 and 316L coupons, because such films can repel water and inhibit corrosion. All measurements were conducted using a ThetaLite optical tensiometer (Biolin Scientific) in combination with OneAttension software (Biolin Scientific). Coupons were cleaned with ethanol and milli-Q water, and blow-dried with nitrogen prior to each test. The coupons were then immersed in PTFE containers at room temperature and atmospheric pressure. PTFE tape was used to freely suspend the coupons in solution. Adsorption of amines onto PTFE is negligible (Hater, et al., 2014), and this material was thus selected for containers and the tape used.

Blank samples were obtained by immersing the coupons in ultra-pure water with a resistivity of 18 MΩ·cm (milli-Q water) buffered to pH 9.0 with NaOH, without amine formulations added. The contact angles for the blank samples were compared with those measured for coupons soaked in milli-Q water at pH 9.0 with amine formulations added at 200 ppm dosage (volume based). All coupons were rinsed with milli-Q after soaking, to probe the properties of films irreversibly adsorbed at the coupon surface. At least twenty droplets were analyzed for each system considered, and all measurements were done at room temperature and ambient pressure. Additionally, visual observations for qualitative assessment of corrosion were done after 17 and 24 hours.

2.5 Film forming amine concentration measurements

The Bengal Rose photometric method was utilized to determine the concentration of FFAs in bulk solutions. This method uses pink Bengal Rose dye to form complexes with the amines, and an acid buffer solution to lower the pH, at which the Bengal Rose-amine complexes are soluble in water. Details of the method can be found elsewhere (Stiller, et al., 2011). All measurements were conducted at a wavelength of 560 nm using a portable DR 900 colorimeter (Hach).
2.6 Quartz Crystal Microbalance with Dissipation monitoring

Adsorption of Cetamine® V211 and G811 to stainless steel was investigated with a QCM-D system (Q-Sense, Biolin Scientific). A detailed description of this technique can be found elsewhere (Halthur, et al., 2010) (Pensini, et al., 2013) (Rodahl, et al., 1996). Briefly, the QCM-D system is equipped with a flow cell, at the bottom of which a piezoelectric crystal sputter coated with the material of interest (AISI type 316 stainless steel in the tests described in the present paper) is mounted. The sensor is intermittently oscillated at the fundamental resonance frequency as well as at its overtones, the changes of which are related to the mass adsorbed onto the sensor. The crystal’s oscillation is intermittent and the waves propagating through it decay (evanescent waves) in a way that depends on the visco-elastic properties of the films adsorbed onto the sensor. The rate of the wave’s decay is correlated to the dissipation factor as follows:

$$D_i = \frac{1}{\pi \cdot f_{\text{diff},i} \tau_i} \quad \text{Eq. 1}$$

where $i$ denotes the overtone considered, $D_i$ is the dissipation parameter for each overtone - a function of time $t$, $f_{\text{diff},i} = f_i - f_{o,i}$, $f_i$ is the current frequency of the overtone, $f_{o,i}$ is the frequency of the overtone measured during calibration, and $\tau_i$ is the time decay constant.

In the case of rigid films the mass adsorbed on the sensor surface ($\Delta M$) can be estimated using Sauerbrey’s equation:

$$\Delta M = -C \frac{\Delta f_n}{n} \quad \text{Eq. 2}$$

where $n$ is the number of the overtone, $\Delta f_n$ is the shift in the $n^{th}$ overtone, and $C$ is a constant equal to 17.7 $\text{ng} \cdot \text{Hz}^{-1} \cdot \text{cm}^2$ for 5 MHz AT cut crystals. It must be noted that the Sauerbrey model was developed under the following assumptions: 1) The oscillation of the crystal is in air; 2) Films are rigid; 3) Adsorbed mass is uniformly distributed onto the crystal. Due to the assumptions underlying the model, the mass adsorbed as estimated using this method must be considered approximate and interpreted as merely indicative. The Sauerbrey equation has however been suggested to be a good approximation when the change in dissipation is less than $10^{-6}$ per 5 Hz of $\Delta f$ (Höök, et al, 2001).

QCM-D experiments were conducted to study the adsorption of FFA onto the sensor surface. For this, a dosage of 25 ppm (volume based) FFA formulation was dissolved in milli-Q water. All experiments were conducted at room temperature and ambient pressure. The instrument was equipped with a syringe pump yielding a constant flowrate of 0.04 mL/min and the flow regime was laminar in all tests conducted.

3 RESULTS AND DISCUSSION

3.1 Electrochemical Impedance Spectroscopy measurements

EIS measurements were conducted to quantitate the effectiveness of Cetamine® V211 and G811 in inhibiting corrosion of carbon steel in saline solutions at pH 9.0.

The comparison of the time evolution of the polarization resistances of the blank and the samples exposed to the amine formulations shows significant differences between the two systems. The polarization resistance increased with time in the presence of amines, whereas for the blank it decreased from 9.8 kΩ·cm² after 20 min to 4.2 kΩ·cm² after 100 min (Figure 1). The decrease in the polarization resistance of the blank at pH 9.0 is not visible in the plot due to the scale used. These data suggest that the carbon steel surface became progressively less susceptible to corrosion in the presence of a passivating amine film, whereas it became more prone to corrosion with time in the absence of FFAs.
The polarization resistance measured in this study at pH 9.0 is significantly higher than the one measured in a previous study conducted at pH 8.2 with the same FFA formulations (Hater, et al., 2015). These results indicate that alkaline pH values and filming amines acted synergistically in providing optimal corrosion protection for the system. The polarization resistance was comparable for both formulations (G811 and V211), suggesting that the performance of the formulations was similar, in agreement with the visual observations of coupons soaked in the respective aqueous solutions.

![Figure 1](image)

**Figure 1** Comparison of the polarization resistance derived from spectra fitting of different test solutions at pH 9.0. The observed decrease in the polarization resistance of the blank is not visible due to the large scale used.

### 3.4 Adsorption experiments using Quartz Crystal Microbalance with Dissipation monitoring and film forming amine concentration measurements

QCM-D experiments and Bengal Rose tests were conducted to probe the kinetics of films adsorption and to compare the surface coverage obtained with V211 and G811. QCM-D data reveal that the kinetics of adsorption were very slow (equilibrium was not reached even after 24 hours) and similar for either G811 or V211 (data not shown). After rinsing with milli-Q water the overtones and dissipation factors remained markedly different from the ones measured before V211 or G811 were injected in the cell, indicating irreversible adsorption of FFAs on the stainless steel surface.

QCM-D data further suggest that the films formed by FFAs on sensors coated with stainless steel were rigid, since the ratio of the change in the overtone relative to the dissipation factor was small (data not shown). Since films were rigid, the Sauerbrey model was used to estimate the mass adsorbed at the sensor surface (Table 1). Using this model, the irreversible mass adsorbed onto the stainless steel sensors after rinsing was estimated to be approximately 0.004 g/m² with either V211 or G811, in agreement with data reported by (Bohnsack, 1997), and closely resembling results for lipid bilayers (Richter et al., 2005).

The adsorbed coverage of FFAs calculated on the basis of Bengal Rose analyses of bulk test solution samples was of the order of 0.1 g/m² on either stainless steel (316L) or carbon steel (C1010) coupons, with either V211 or G811 (Table 1). This mass was estimated based on the surface area estimated from the geometry of the coupons and the changes of the FFA concentration before and after soaking the coupons in solution for 12 hours.
Table 1 Mass adsorbed onto either stainless steel or carbon steel coupons, as determined via the Bengal Rose test, and irreversible mass adsorbed onto stainless steel sensors in QCM-D experiments, as estimated using the Sauerbrey model.

<table>
<thead>
<tr>
<th>Method</th>
<th>Coverage (g/m²)</th>
<th>Reference values (g/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bengal Rose</td>
<td>~0.1</td>
<td>0.0005 to 0.002 (Bohnsack, 1997); 0.1-0.3 (Hater, et al., 2014); 0.023 (Jack, et al., 2015)</td>
</tr>
<tr>
<td>QCM-D</td>
<td>~0.004</td>
<td></td>
</tr>
</tbody>
</table>

The observed changes in the bulk FFA concentration are shown in Table 2. It is noted that the concentration of FFA in the blank measured with the Bengal Rose test (2.5 ppm) differed considerably from the expected FFA concentration based on the concentration of filming amine in the formulation (4.0 ppm). This discrepancy is likely due to the fact that FFAs can form micelles in the concentrated formulation, possibly leading to statistical inhomogeneities of the FFA concentration in samples of microliter volume. However, because the comparison between the blank and the solution in which coupons were soaked was done with the same solution, the observed changes in FFA concentration with time are related to the FFA adsorption onto the metal coupons.

Table 2 FFA concentration in the blank (no coupons immersed) and in test solutions into which stainless steel (316L) and carbon steel (C1010) coupons had been immersed.

<table>
<thead>
<tr>
<th>FFA concentration in the bulk (ppm)</th>
<th>V211</th>
<th>G811</th>
</tr>
</thead>
<tbody>
<tr>
<td>blank</td>
<td>2.5</td>
<td>2.4</td>
</tr>
<tr>
<td>316L</td>
<td>2.2</td>
<td>1.9</td>
</tr>
<tr>
<td>C1010</td>
<td>2.1</td>
<td>1.8</td>
</tr>
</tbody>
</table>

The results confirm that the surface coverage obtained with either V211 or G811 is comparable, as shown by QCM-D data. The coverage computed using the Bengal Rose test results is in agreement with previous studies (Hater, et al., 2014) (Jack, et al., 2015), and yet orders of magnitude different from the one determined using the QCM-D method. Reasons for this discrepancy will be elaborated as part of future studies.

Regardless of the dissimilarity between the absolute value of the coverage obtained via QCM-D and Bengal Rose experiments, the important conclusion the data lead to is that the films formed with V211 and G811 are comparable, thus substantiating the use of DEAE-based formulation G811 as an environmentally friendlier alternative to CHA-containing V211, in agreement with EIS results and the visual observations of coupons soaked in solution for up to 24 hours.

3.5 Contact angle measurements

The hydrophobicity of the amine films plays a role in their effectiveness in inhibiting corrosion by protecting the metal from corrosive species dissolved in water. Contact angle measurements were conducted to quantify the degree of hydrophobicity of the amine films formed on the stainless steel and carbon steel coupons.

The contact angles before immersion in solution were approximately 40° and 57° for the 316L and C1010 coupons, respectively.

As expected, 316L coupons did not corrode in milli-Q water at pH 9.0, with or without amines added. However, the contact angles measured for 316L coupons were dependent on the water chemistry. At pH 9.0, when amines were not added to milli-Q water the contact angles decreased with time, whereas when amines were added the contact angles of stainless steel (316L) coupons increased to 79° and
74° after 18 hours, with G811 and V211, respectively. These results indicate that the FFAs had irreversibly adsorbed onto the coupon surface and formed hydrophobic films with either G811 or V211.

Similar trends were observed with the carbon steel (C1010) coupons. After 18 hours water spread perfectly on C1010 coupons without amines added, whereas the contact angles increased from 57° to 60° and 59° after 18 hours, with G811 and V211 added, respectively. The data show a correlation between contact angles and the degree of corrosion of C1010 coupons, with the lowest contact angles measured for the most corroded metal surfaces. The data indicate that both G811 and V211 were able to form hydrophobic films onto either stainless steel (316L) or carbon steel (C1010) surfaces, inhibiting corrosion. The film’s hydrophobicity was comparable with either G811 or V211, indicating that the DEAE-based FFA (G811) can be a suitable substitute for the CHA-based formulation (V211), in agreement with the EIS and QCM-D data discussed before.

4 CONCLUSIONS

The study described in this paper demonstrates that FFA formulations whether based on DEAE or CHA can form hydrophobic films strongly adsorbed to metal surfaces, as shown by adsorption experiments (QCM-D, Bengal Rose analyses) and contact angle measurements. EIS measurements using coupons immersed in water at alkaline pH in saline environments (supported by visual observations) showed that both types of FFA formulations are equally effective in inhibiting corrosion. Therefore, DEAE-based formulation is a viable alternative to CHA-based formulations, which have proven effectiveness but are suspected of being harmful to human health.

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REFERENCES


Forêt, C. et al., 2013. Film forming amines for closed cooling/heating water systems. Uncasville (CT), AWT.


