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Corrosion inhibition of the API 5L X60 in steel alkaline sour medium by derivative compounds methylimidazole

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ABSTRACT

The electrochemical behavior of API 5L X60 steel in the characteristic medium found inside an FCC (Fluid catalytic cracking) unit was studied as well as the corrosion inhibiting properties of molecules using methyl imidazole as a base molecule. The samples were characterized by infrared spectroscopy (IR).
Based on the electrochemical results, the molecule possessing better inhibitory properties was identified. This is remarkable due to the lack of information regarding the corrosion processes in an alkaline sour medium.

Key words: Inhibitor, FCC, Electrochemical, Methylimidazole and alkaline sour medium

INTRODUCTION

The environment present in the light end recovery units of the Fluid Catalytic Cracking Unit (FCC) is typically called an alkaline sour medium. The water vapor that condenses in the surface of these units carries highly corrosive ions such as HS-, NH_3 and CN- [1].

One of the most recent treatments used to minimize the impact of the corrosion phenomena in the FCC consists of the injection of water used to dissolve the corrosive agents present in the damp parts of the tower, thus maintaining the corrosion kinetic at acceptable levels [2], however this technique produces hydrogen blistering in the FCC steel.

Several media have been proposed to study and control the corrosion phenomena in the FCC tower, Russell C. Strong et. al. [3] evaluated the addition of carbohydrazide as a method for corrosion prevention; on the other hand H.B. Walker et. al. [1] studied the addition of polysulfides in the cleaning water, this prevented hydrogen blistering, however, if the water's pH is greater than 7.8 it tends to produce heavy iron oxidation.

Another one the most effective methods used to prevent this phenomenon is the injection of corrosion inhibitors, most well-known corrosion inhibitors are organic compounds containing polar groups including nitrogen, sulfur, and/or oxygen atoms and heterocyclic compounds with polar functional groups and conjugated double bonds [4], these inhibitors act through adsorption on the metal surface, covering the cathode or the anode, preventing further corrosion. Different studies about imidazole derivatives show the importance of the alkyl chain length in the efficiency of the corrosion inhibitor; that is, the hydrophobic chain serves as a barrier between the water and the corrosive products [5].

Because of these earlier statements, it becomes clear the corrosion phenomena in the FCC unit is extremely complex, this is reflected by the fact that treatments proposed to control them are insufficient, thus new alternative methods to minimize and control corrosion effects in alkaline sour mediums are needed.

EXPERIMENTAL PROCEDURE

Synthesis

The molecular basis use was 1-methyl imidazole, this molecule reacted with 3 primary amines. The chosen ones were: 1- butylamine, 1- decylamine, 1 - octadecylamine.

The substances that where obtained were termed as BMI (1 – methyl imidazole with butylamine), DMI (decylamine whit 1 – methyl imidazole with butylamine) and ODAMI (1 – methyl imidazole with butylamine with octadecylamine).

The infrared Spectroscopy (IR) technique was used, using FTIR spectroscopy nicolet magna 560 model with 4 cm^{-1} resolution, in order to characterize the functional groups present in the reaction product.

Electrochemical studies

An electrolyte comprising 35 000 ppm of NH3 and 250 ppm of CN-, adjusting the pH to 8.5 with H2S, at a temperature of 40° C and dynamic conditions (working electrode rotating at 600 rpm) [6], was used for the study of API 5L X60 steel with the typical characteristics of an FCC unit.

The study was conducted based on an arrangement of a conventional three electrodes cell consisting of a $Hg/HgSO_4(s)/K_2SO_4$ reference electrode (hereafter referenced as SSE) , a platinum wire was use as a counter electrode and steel API 5L X60 as the working electrode, these were arranged in a three-neck reactor, in which nitrogen was also supplied during the test. Electrochemical measurements were made with a galvanostat potentiostat Metrohom Autolab, using the Nova 1.7.8 software.

The steel surface was prepared by grinding with sandpaper metallographic silicon carbide No. 600, the samples were then submerged in an ethanol ultrasonic bath for 30 minutes.

A preliminary cyclic voltamperometry test from the characterization of various corrosive processes that occur in these environments was performed. The scanning started from Ecor, at a scan rate of 1 mV/s, from -0.8V to 0.6V

The Potentiodynamic Polarization curves technique was used to evaluate the inhibitors, by changing the electrode potential from ± 300 mV vs. Ecorr and 1 mV/s scanning rate. The concentrations of each molecule are evaluated at concentrations of 5, 25 and 50 ppm.

RESULTS

Chemical Synthesis and Characterization

The results obtained by Infrared Spectroscopy are presented below, in cm^{-1}.

BMI: 3113 (NH2), 2952 (CH3), 2162 and 1665 (N-N) 7 8 9, 1524 (C-N).

DMI: 3335 (C = N), 2925 (-CH3), 2167 and 1654 (N-N) 7 8 9, 1562 (C-N).

ODAMI: 3335 (C = N), 2925 (-CH3), 2100 and 1572 (N-N) 7 8 9, 1480 (C-N).

In all three cases the typical signs of an N-N [7-9] bond are present, which implies that the binding of these molecules was generated between the amine functional group and one of the nitrogens of imidazole, the latter, in either case, should undergo a deprotonation and generate a distributed charge in the electronic charge density of the ring [10].

Electrochemical studies results

Figure 1 shows a typical cyclic voltammogram for the API 5L X60 steel, where a first oxidation process can be seen (indicated in section 1, figure 1), which may be associated with the iron oxidation contained within the steel in the alkaline sour medium. At more positive values of the potential, passive behavior, which is associated with the formation of a layer of corrosion products, presumably iron sulfides which are lightly conductive, are seen; either subsequently breaking off the passive deposit of iron sulfide or the subsequent oxidation of this deposit was observed, in any case, it is assumed the system underwent a transpassivation process; oxidation continues until the typical behavior of a diffusion controlled process (i.e., oxidation persists independently of the displacement of potential) is reached. In the reverse scan, it is observed that in the transpassive region, the surface was more active than in the direct scanning. Furthermore during the reverse sweep, two reduction processes were observed, which in turn can be attributed to the corrosion products that are found on the metallic surface. Towards more negative potentials, a third reduction process is observed with a current maximum, the former is assigned to the disulfide ion (HS-) and finally , a fourth reduction that because of the electrical potential value at which it occurs can be attributed to hydrogen evolution in water.

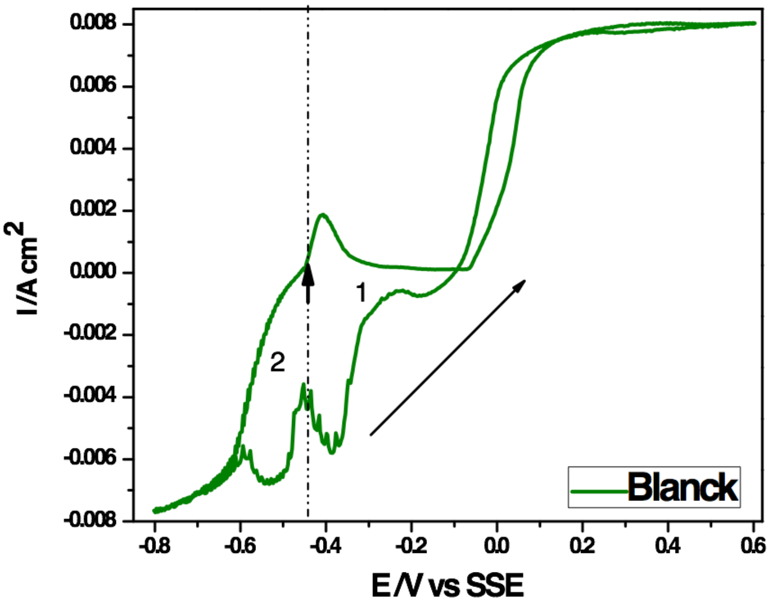

Figure 1: *Voltammetric curve obtained on a typical electrode API 5L X60 steel in a system consisting of:* NH_3*=500 ppm, pH =8.5(adjusted with* H_2S*), CN- =250 ppm, and T=40°C, v = 1 mV/s in a range of potential of -0.8V to 0.6V. The potential scan was initiated in the positive direction from the corrosion potential (Ecorr).*

Because the main oxidation process occurs in a window of a smaller potential than the one initially used, the inhibitory effect of the molecules is comparatively evaluated using a sweep of ± 300 mV from the corrosion potential (Ecorr = -0.44 V) and a scan rate of 1 mV/s using Polarization curves .

The efficiency of each concentration was calculated using the following equation:

$$efficiency = \frac{Icorrbl - icorrinh}{Icorrbl} * 100$$

Where Icorrbl is the blank corrosion current and Icorrinh is the current exhibited by the corrosion inhibitor.

Figure 2 shows the effect of each one of the concentrations of the reaction product of butylamine with 1-methyl imidazole added to the system by their respective Evans-diagrams.

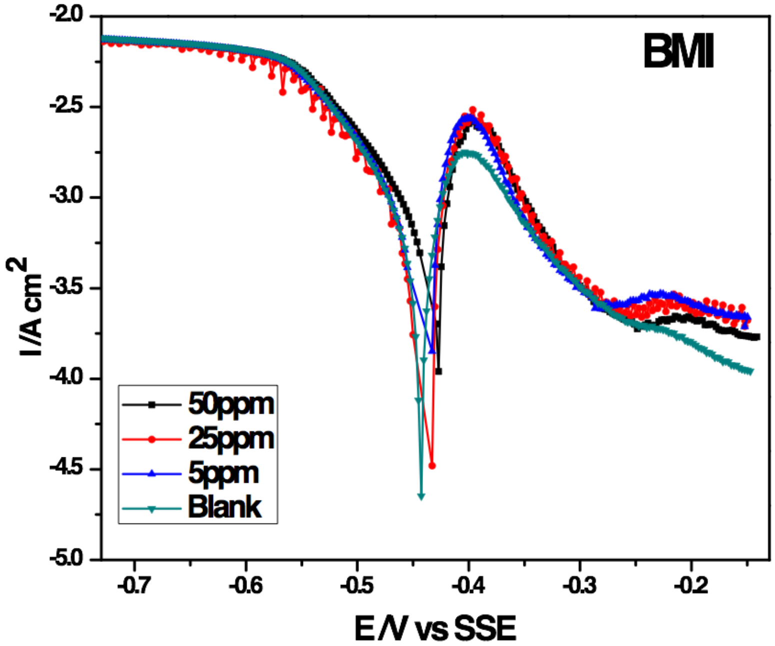

Figure 2: *Potentiodynamic polarization curves for API 5L X60 steel in a system consisting of: NH3=500 ppm, pH =8.5(adjusted with H2S), CN- =250 ppm, and T=40°C, v = 1 mV/s, in the presence and absence of inhibitor BMI.*

When analyzing and comparing the effect of the BMI molecule at different concentrations with the blank, we can see that this influences the current density values, displacing them to positive values without significantly changing the potential. Table 1 shows the analysis of the polarization curves to determine the corrosion kinetics, in every test sample no effect of the molecule is observed, a opposed to the corrosion rate, which saw an increase. Figure 3 shows the electrodes after being subjected to electrochemical analysis, making a comparison between the target and the electrodes subjected to the medium with 5, 25, and 50 ppm of BMI product. All samples show similar damage: a homogeneous oxide layer is formed of presumed iron sulfides and ferrocyanides.

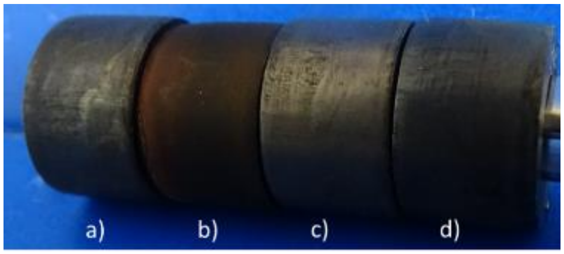

Figure 3: *API 5L X60 iron Working electrodes exposed to a system consisting of: NH3=500 ppm, pH =8.5 (adjusted with H2S), CN- =250 ppm, and T=40°C, v = 1 mV/s a) Blank ,b)5, c) 25, d)50 ppm of inhibitor BMI.*

Table 1. Electrochemical parameters and percentage inhibition efficiency obtained from polarization studies for a typical API 5L X60 steel electrode in the system consisting of: NH3=500 ppm, pH =8.5 (adjusted with H2S), CN- =250 ppm, and T=40°C, v = 1 mV/s in the presence and absence of inhibitor BMI.

Molecule	**ppm**	**Ecorr (V)**	**Log Io (A/dec)**	**Icorr (A)/cm^2**	**Corr rate (mm/year)**	**Corr rate (mpy)**	**% efficiency**
BMI	0	-0.44	-3.21	0.000734466	2.849752036	0.000112195	**------**
	5	-0.44	-3.10	0.000794168	3.081394889	0.000121315	0
	25	0.44	-3.16	0.000787793	3.056661578	0.000120341	0
	50	-0.43	-3.15	0.000806143	3.127860371	0.000123144	0

The potentiodynamic polarization curves for the API 5L X60 steel electrode in the absence and presence of different concentrations of DMI molecule is shown in Figure 4. The concentrations of 5 and 25 ppm the Evans diagram did not show a significant change in potential and current, but at 50 ppm (black curve) the system displaced towards a -2.5 V potential and showed a significant decrease in current, near to 1.7018E-06 A / cm^2 (table 2); these values indicate an important effect in corrosion kinetics.

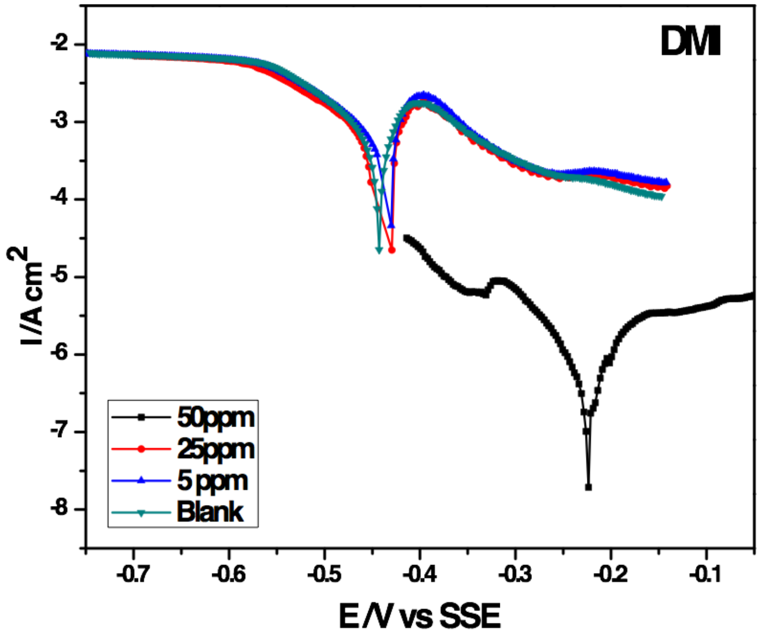

Fig. 4. *Potentiodynamic polarization curves for API 5L X60 steel in a system consisting of: NH3=500 ppm, pH =8.5(adjusted with H2S), CN- =250 ppm, and T=40°C, v = 1 mV/, in the presence and absence of inhibitor DMI.*

The specimen subjected to 50 ppm of this molecule, marked with the letter d), did not have any corrosion products or significant damage, unlike the blank and tests 5 and 25 ppm, having a similar behavior observed in BMI product.

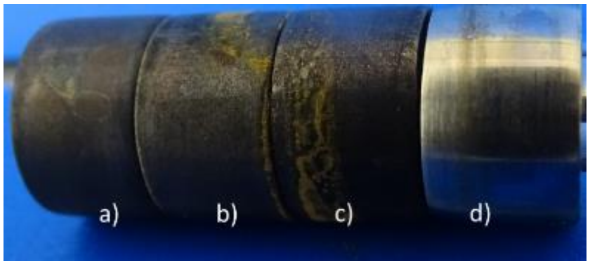

Fig. 5. *API 5L X60 iron Working electrodes exposed to a system consisting of: NH3=500 ppm, pH =8.5 (adjusted with H2S), CN- =250 ppm, and T=40°C, v = 1 mV/s a) Blank ,b)5, c) 25, d)50 ppm of inhibitor DMI.*

With regard to the kinetics (table 2), we obtained zero efficiency for a concentration of 5 and 25ppm, unlike the concentration of 50 ppm was found to be good with 99% efficiency.

Table 2. *Electrochemical parameters and percentage inhibition efficiency obtained from polarization studies for a typical API 5L X60 steel electrode in the system consisting of: NH3=500 ppm, pH =8.5 (adjusted with H2S), CN- =250 ppm, and T=40°C, v = 1 mV/s in the presence and absence of inhibitor DMI.*

Molecule	**ppm**	**Ecorr (V)**	**Log Io (A/dec)**	**Icorr (A)/cm^2**	**Corr rate (mm/year)**	**Corr rate (mpy)**	**% efficiency**
DMI	0	-0.449	-3.21	0.00073446	2.84975203	0.00011219	**---**
	5	-0.43	-3.18	0.00074767	2.90099752	0.00011421	0
	25	-0.422	-3.23	0.00066071	2.56358285	0.00010092	10
	50	-0.26	-5.60	1.7018E-06	0.00660303	2.59962E-07	99

The result of used ODAMI molecule is shown in Figure 6, the concentration of 5ppm in the Evans-diagram did not show a significant change in terms of potential but at 25 and 50 ppm it begins to have a significant impact on the corrosion kinetics (see table 3), showed by the movement of the current and potential towards more passive values.

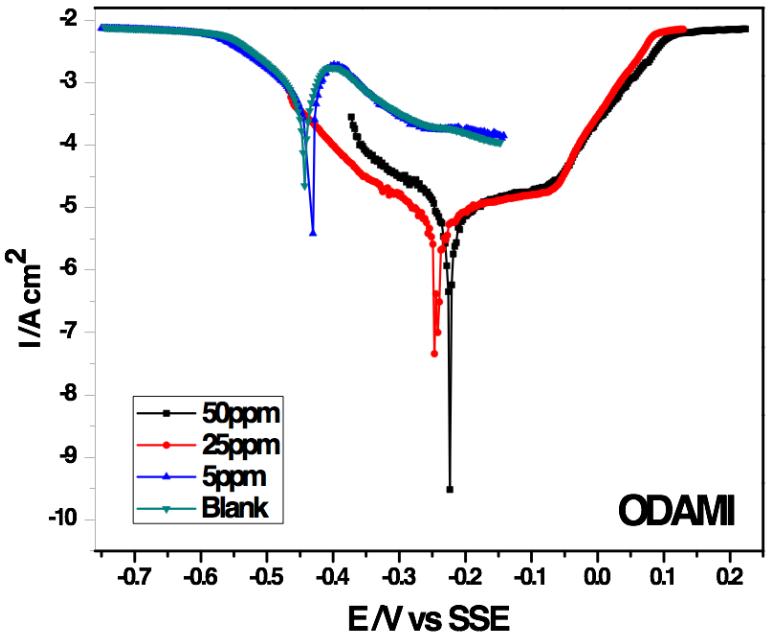

Fig. 6. *Potentiodynamic polarization curves for API 5L X60 steel in a system consisting of: NH3=500 ppm, pH =8.5(adjusted with H2S), CN- =250 ppm, and T=40°C, v = 1 mV/, in the presence and absence of inhibitor ODAMI.*

Contrary to the last two molecules, ODAMI presents significant positive results beginning at 25ppm. It is clear the damage in the figure 7, of the part b) is different to the blank, c) part shows less degradation than d), in which only two separate strips of corrosion products are formed.

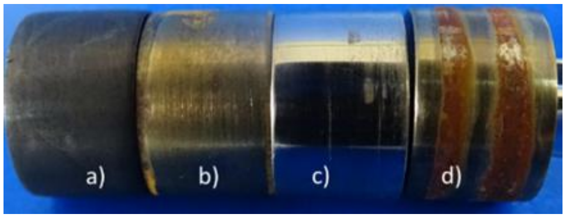

Fig. 7. *API 5L X60 iron Working electrodes exposed to a system consisting of: NH3=500 ppm, pH =8.5 (adjusted with H2S), CN- =250 ppm, and T=40°C, v = 1 mV/s a) Blank ,b)5, c) 25, d)50 ppm of inhibitor ODAMI.*

Perhaps the corrosion products in the presence of this molecule, change with respect to the blank, this is supposed because the color of the oxide of the working electrode with letter b) is different to the blank.

Table 3. *Electrochemical parameters and percentage inhibition efficiency obtained from polarization studies for a typical API 5L X60 steel electrode in the system consisting of: NH3=500 ppm, pH =8.5 (adjusted with H2S), CN- =250 ppm, and T=40°C, v = 1 mV/s in the presence and absence of inhibitor ODAMI.*

Molecule	***ppm***	**Ecorr (V)**	**Log Io (A/dec)**	**Icorr (A/cm^2)**	**Corr rate (mm/year)**	**Corr rate (mpy)**	**% efficiency**
ODAMI	0	-0.44	-3.21	0.00073446	2.8497520	0.00011219	**---**
	5	-0.43	-3.15	0.00080614	3.1278603	0.00012314	0
	25	-0.23	-5.34	4.5228E-06	0.0175487	6.9089E-07	99
	50	-0.22	-4.99	6.1152E-05	0.237272	9.3414E-06	96

The results of 25 ppm of the ODAMI product have higher efficiency than those with 50ppm, this means that decrease in the corrosion rate does not follow a linear relationship with respect to concentration.

CONCLUSIONS

When analyzing the IR signals for the N-N bond, it was found in the three molecules. The further analysis of these is recommended by other spectroscopic techniques in order to propose an accurate atomic distribution.

The product BMI had no favorable performance in these media.

As a corrosion inhibitor DMI at 50 ppm, decreased the corrosion rate from a value of 2.8497520 to 0.00660303 mm/year, with respect to the blank, which, originated an efficiency of about 99%, such behavior was visually evident.

The best result was achieved with the ODAMI product at 25ppm, including being superior to behavior observed in a dose of 50 ppm, which indicates that the behavior of that product should not necessarily be linear under conditions of the alkaline sour medium.

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