# **Carbon Dioxide Corrosion Inhibition of Carbon Steels Through Bis-imidazoline and Imidazoline Compounds Studied by EIS**

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The performance of (1-(2-hidroxyethyl)-2(heptadec-8-enyl)-imidazoline and 1-(2-aminoethyl)-2(heptadec-8-enyl)-bis-imidazoline has been studied by Electrochemical Impedance Spectroscopy (EIS) and Linear Polarization Resistance (LPR). A rotating cylinder electrode (RCE) was used for simulating turbulent conditions in a 3 wt. % NaCl solution saturated with CO<sub>2</sub> at 80 °C, pH 4. EIS helped in the characterization of the inhibitor film at different concentrations and its respective evolution with time. It was found that 1-(2-aminoethyl)-2(heptadec-8-enyl)-bis-imidazoline formed a more compact inhibitor layer and therefore the corrosion protection was enhanced. The molecular structure of this inhibitor allows the usage of lower concentration (10 ppm) without loss of efficiency.

Keywords: CO<sub>2</sub> corrosion, imidazoline, EIS, steel.

# **1. INTRODUCTION**

Carbon dioxide (CO<sub>2</sub>) corrosion of carbon steel pipelines and equipment in the oil and gas industry has been given much attention in recent years because of an increased tendency to inject CO<sub>2</sub> into oil wells to reduce the viscosity of oil and increase the its production [1,2]. An important fact is that when CO<sub>2</sub> dissolves in water, carbonic acid (H<sub>2</sub>CO<sub>3</sub>) is produced with the characteristic that is more aggressive than hydrochloric acid at the same pH [3]. Despite the fact that carbon steel has low resistance to CO<sub>2</sub> environments, it is widely used in the petroleum industry mainly due to economical reasons [2]. What makes feasible the use of carbon steels is the natural precipitation of protective iron carbonate (FeCO<sub>3</sub>) [4,5]. However, when there are not favorable conditions for its precipitation, the use of corrosion inhibitors is very important in the protection of carbon steels [6]. Some of the most effective corrosion inhibitors used for oil field applications are imidazolines (IM) compounds (e.g. oleic imidazoline) [7-9]. They have been widely used when carbon steels are exposed to CO<sub>2</sub> environments. A typical imidazoline molecule can be divided into three different substructures [7,10]: a nitrogen-containing five member ring, a pendant side chain with a hydrophilic active functional group (R1) and a long hydrophobic hydrocarbon chain (R2). Some researchers have investigated the effect of R1 and R2 in the corrosion efficiency of IM. X. Liu *et al.* [10] investigated the inhibition performance of four imidazoline inhibitors with different hydrophilic groups. It was found that the presence of the hydrophilic group improved the corrosion inhibition performance. In contrast, Jovancicevic *et al.* [11] performed a detailed study of the effects of hydrocarbon chain length (R2), finding that the R2 length has a key role in the inhibitive behavior of IM. Owing to the fact that IM inhibitors are extensively used in the petroleum industry, it is mandatory to understand their mechanism and propose new molecular structures.

EIS has shown to be a powerful technique to understand the interfacial process happening during the inhibitor adsorption on steels corroding in CO<sub>2</sub> environments [12-14]. In the present research, EIS and d.c. techniques (LPR and  $E_{corr}$ ) were used to study the inhibition performance of two imidazolines derivatives: (1-(2-hidroxyethyl)-2(heptadec-8-enyl)-imidazoline and 1-(2-aminoethyl)-2(heptadec-8-enyl)-bis-imidazoline. The experimental research was performed using a carbon steel API 5L X65 exposed to a 3 wt. % NaCl solution saturated with CO<sub>2</sub>, at 80 °C, pH 4 and under turbulent conditions. In addition, scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) were used to analyze the metal surface with and without inhibitor.

## 2. EXPERIMENTAL PROCEDURE

### 2.1. Imidazoline compounds

Oleic acid, 2-(2-aminoethylamnino)ethanol and triethylenetetramine (TETA), obtained from Aldrich, were used as-received for the synthesis of the two inhibitors tested in the present work. In order to corroborate that the objective compounds had been synthesized, <sup>1</sup>H and <sup>13</sup>C NMR spectra were obtained. However, the synthesis procedure and characterization of the inhibitors are beyond the scope of this research. The structures of the two imidazolines (IM) derivatives are shown in Figure 1. Figure 1a shows the molecular structure of (1-(2-hidroxyethyl)-2(heptadec-8-enyl)-imidazoline (IM-HOL) with a pendant group R1=OH. This oleic imidazoline has shown to be good a corrosion inhibitor for CO<sub>2</sub> corrosion [10,15]. Figure 1b depicts the molecular structure of 1-(2-aminoethyl)-2(heptadec-8-enyl)-bis-imidazoline (BIM-NH). For both IM-HOL and BIM-NH the hydrophobic tail was R2=C<sub>17</sub>H<sub>33</sub>.





Figure 1. Molecular structure of (a) IM-HOL and (b) BIM-NH.

## 2.2. Experimental setup

All the experiments were performed at atmospheric pressure in a 2 liters glass cell. A schematic representation of the experimental setup is shown in Figure 2. It consisted of a typical three electrode configuration where an X65 steel-made cylinder was used as working electrode (WE), a concentric platinum wire was used as a counter electrode and a Ag/AgCl<sub>sat</sub> electrode served as reference. The glass cell was filled with 2 liters of a 3 wt. % NaCl solution that was purged with CO<sub>2</sub> during 2 h prior the immersion of the metal coupons. Chemet<sup>®</sup> ampoules were used for measuring the oxygen concentration. After 2 h the oxygen concentration was measured to be less than 10 ppb and the pH was constant (4.18  $\pm$  0.5) meaning that the system was in equilibrium and saturated with CO<sub>2</sub>. It is important to point out that the CO<sub>2</sub> injection was maintained during the test with the aim of avoiding any oxygen contamination. Along with the purging process the temperature was set at 80  $\pm$  2 °C. The pH of the test solution was adjusted to the desired pH by adding deoxygenated hydrochloric acid solution (HCl).

The WE had a 5.3  $\text{cm}^2$  exposed area and chemical composition (wt.%): C 0.08, Cr 0.03, Cu 0.10, Mn 1.47, Mo 0.002, Ni 0.10, P 0.016, S 0.004, Si 0.32, V 0.08 and Fe balance. It was polished by silicon carbide sand paper to a 600 grit surface finish, cleaned in an ultrasonic bath, rinsed with isopropyl alcohol and immersed into the glass cell. The experimental conditions are summarized in Table 1.

## 2.3. Electrochemical measurements

Electrochemical measurements were performed using a Solartron SI 1287 electrochemical interface and a SI 1255 frequency response analyzer. The software ZView 3.1 (Scribner Associates) was used for analyzing the EIS results. The LPR results were obtained by polarizing the working electrode  $\pm 5$  mV versus the open circuit potential at a scan rate of 0.125 mV s<sup>-1</sup>. A "B" constant value of 20 mV was used to calculate the change in corrosion rate with time [16,17]. EIS was measured under a sinusoidal excitation potential of 10 mV (rms) with a frequency range of 10 kHz to 10 mHz with eight points per decade.



**Figure 2**. Experimental Set up: 1.- Reference electrode, 2. Luggin capillary, 3.- Platinum ring, 4.-Thermo probe, 5.- pH probe, 6.- Gas bubbler, 7.- Working electrode, 8.- Magnetic stirrer bar, 9.- Hotplate.

**Table 1.** Experimental conditions and electrochemical measurements.

Parameters	Conditions
Total Pressure	1 bar
$pCO_2$	0.54 bar
Temperature	$80 \pm 2 \ ^{\circ}\text{C}$
Rotation rate	1000 rpm
Solution	3 wt.% NaCl
рН	$4 \pm 0.05$
Material	X65 steel
Inhibitor concentration	5, 10, 25, 50 ppm
Electrochemical measurements	
Linear polarization resistance (LPR)	$\pm 5 \text{ mV}$ polarization, 0.125 mV s <sup>-1</sup>
Electrochemical Impedance Spectroscopy (EIS)	10 mV amplitude (rms), 10 kHz – 10 mHz

## 2.4. Surface characterization

SEM analyses were performed on a JOEL JSM-6390LV instrument. Superficial observations were carried out using an accelerating voltage of 25 kV in the image mode of secondary electrons. Chemical composition of the corrosion product was recorded by an EDS detector that is coupled to the SEM at 10 kV accelerating voltage.

## **3. RESULTS AND DISCUSSIONS**

## 3.1. Effect of inhibitor concentration

#### 3.1.1 LPR corrosion rate and corrosion potential

The change in CR with time at different inhibitor concentrations is shown in Figure 3. The inhibitor was added after 0.5 h of exposure because at this time the corrosion potential got stable, allowing the measurement of the CR prior the injection of the inhibitor. The initial CR, without inhibitor, was measured to be between 4.5 and 5.1 mm y<sup>-1</sup>. It can be observed from Figure 3 (a-b) that the CR, in the absent of inhibitor, tends to increase with time. The increase in CR has been attributed to the galvanic effect between the ferrite phase and cementite (Fe<sub>3</sub>C) which is part of the carbon steel [18]. Fe<sub>3</sub>C is known to be less active than the ferrite phase. Therefore, there is a preferential dissolution of ferrite over cementite, working the former as the anode and latter as the cathode, favoring the hydrogen evolved reaction (HER) during the corrosion process [19,20].



Figure 3. Variation of the CR with time at different inhibitor concentrations, (a) IM-HOL, (b) BIM-NH : □ Blank, ○ 5 ppm △ 10 ppm, ■ 25 ppm, ▶ 50 ppm.

Variation of the CR for IM-HOL at different concentrations is presented in Figure 3a. In the case of this inhibitor, the CR decreases as the inhibitor concentration increases, getting maximum inhibition efficiency of 98.90 % at 50 ppm after 24 h of exposure (Table 2). Figure 3b shows the change in CR for BIM-NH. In contrast to IM-HOL, the highest inhibitor efficiency was measured to be 99.51 % (Table 2), obtained after 24 h of exposure, at a concentration of 10 ppm and decreased at higher concentrations. Similar results have been observed for other kind of inhibitors by different authors [21,22]. The inhibition efficiency ( $\eta$ ) was calculated according to the following equation:

$$\eta = \left[ (CR_o - CR_i) / CR_o \right] \quad x \quad 100 \tag{1}$$

where  $CR_o$  is the corrosion rate without inhibitor and  $CR_i$  the corrosion rate when inhibitor is present.

Inhibitor	Concentration (ppm)	$CR (mm y^{-1})$	η(%)
IM-HOL	Blank	5.46	
	5	0.48	91.21
	10	0.11	97.99
	25	0.07	98.72
	50	0.06	98.90
BIM-NH	5	0.30	94.51
	10	0.04	99.51
	25	0.31	94.32
	50	0.51	90.66

**Table 2.** Corrosion inhibition efficiency ( $\eta$ ) at different inhibitor concentrations.

Figure 4 shows the change in corrosion potential ( $E_{corr}$ ) with time after adding the corrosion inhibitor. It can be observed, for both inhibitors, an anodic shift in  $E_{corr}$  that is characteristic of anodic and anodic/cathodic inhibitor [11,12]. Cao [23] studied the different modes of the inhibition. It was explained that this shift in  $E_{corr}$  is due to active sites blocking effect that occurs when an inhibitor is added. In the case of CO<sub>2</sub> corrosion the anodic a cathodic reactions are the oxidation of iron and the reduction of hydrogen, respectively [24]. If it is considered that the active sites on the metal surface are the same for both reactions before adding the inhibitor, it is logical the change in  $E_{corr}$  when the inhibitor is present because its adsorption change those active sites and therefore the anodic and cathodic reaction rates. Another important aspect is that the change in  $E_{corr}$  is proportional to the inhibitor efficiency (Figure 3, Table 2). Higher efficiencies were observed when the change in  $E_{corr}$  was toward more noble values.



Figure 4. Change in corrosion potential at different inhibitor concentrations, (a) IM-HOL, (b) BIM-NH : □ Blank, 0 5 ppm △ 10 ppm, ■ 25 ppm, ▶ 50 ppm.

# 3.1.2. EIS results

The EIS results obtained after 24 h of exposure for IM-HOL are shown in Figure **5**. The Nyquist representation (

Figure 5a) depicts a depressed semicircle at high frequencies (HF), with the center under the real axis. This behavior is typical for solid metal electrodes that show frequency dispersion of the impedance data [25]. At low frequencies (LF) and inductive loop was observed in the absent of inhibitor and with 5 ppm. For the rest of inhibitor concentrations the inductive loop disappeared. The capacitive loop (semicircle) arises from the time constant of the electric double layer and the charge transfer resistance and the inductive loop at LF values was originated from the adsorption of intermediates and inhibitor molecules that cover the metal surface [21,26]. The magnitude of the impedance observed in

Figure 5a and its respective modulus (

**Figure 5**b) increased with inhibitor concentration. This suggests an increment of the inhibitor adsorption and an enhancement of the corrosion protection. The EIS results for IM-HOL at different concentrations are in good agreement with the efficiencies reported in Table 2.



Figure 5. Variation of the EIS response at different concentrations of IM-HOL: □ Blank, ○ 5 ppm, △ 10 ppm, ■ 25 ppm, ▶ 50 ppm: Nyquist (a) and Bode (b) plots representation.

Figure 6 shows the EIS results for IM\_HOL. In contrast to IM-HOL, the highest capacitive loop, that is directly proportional to the inhibition efficiency, was observed at 10 ppm and decreased with inhibitor concentration. It has been demonstrated that greater molecular structures made lower concentrations possible without a loss of efficiency (Figure 1b) [27]. Jiang et al. [21,22] reported similar results. They attributed the loss of inhibition efficiency, with the inhibitor concentration, to the tendency of inhibitor molecules to repel each other. When the inhibitor concentration was greater than 10 ppm, the inhibitor molecules tended to perpendicularly adsorb on the metal surface due to a repellent function. As a consequence, instead of adsorbing paralleled to the metal surface, decreasing the active sites, the inhibitor molecules would cover a smaller metal surface area, which resulted in a less corrosion efficiency.



Figure 6. Variation of the EIS response at different concentrations of BIM-NH: □ Blank, ○ 5 ppm △ 10 ppm, ■ 25 ppm, ▶ 50 ppm: Nyquist (a) and Bode (b) plots representation.

In order to investigate the inhibition performance for both IM-HOL and BIM-MH, the evolution of the EIS results with time, for the highest efficiencies, is analyzed in this section.

## 3.2.1. IM-HOL at 50 ppm

The EIS data for IM-HOL at a concentration of 50 ppm is shown in Figure 7. Two time constants are clearly observed in the Nyquist representation (Figure 7a). A capacitive loop at HF and an inductive loop at LF. The capacitive loop characterizes the active surface state and increased with time as a consequence of the protection offered by the inhibitor. The inductive loop appears in the absent of inhibitor and after 3 h of inhibitor addition. Then, it disappeared suggesting a change in the corrosion mechanism with time. It is common to observe this inductive behavior when carbon steels are exposed to  $CO_2$  environments [28]. Several authors have attributed the appearance of the inductive loop, in the absent of inhibitor, to the adsorption of an intermediate product on the metal surface according to the following reactions [4,26].

$Fe + H_2O \leftrightarrow FeOH_{ads} + H^+ + e^-$	(2)
$\text{FeOH}_{\text{ads}} \rightarrow \text{FeOH}_{\text{sol}}^+ + e^-$	(3)

$$FeOH_{sol}^{+} + H^{+} \leftrightarrow Fe_{sol}^{2+} + H_{2}O$$
(4)

These reactions represent the active dissolution of the metal surface that follows the adsorption of an intermediate product FeOH<sub>ads</sub>. When inhibitor is present, the inductive loop appears due to the adsorption and desorption process of the inhibitor [21,22]. It has been explained [25,29] that the adsorption of the inhibitor molecules in the solution can be regarded as a quasi-substitution process between the organic compounds in the solution, ( $Org_{(sol)}$ ), and water molecules adsorbed on the metal surface, ( $H_2O_{(ads)}$ ). Therefore, the water molecule replaced by one organic absorbate (IM-HOL) would be:

$$IM - HOL_{(sol)} + H_2O_{(ads)} \leftrightarrow IM - HOL_{(ads)} + H_2O_{(sol)}$$
(5)

When no inhibitor molecules are present the adsorption process of intermediate products controls the interfacial process as represented in expression (3). After the inhibitor addition the inductive loop appeared at 3 h of exposure because, according to expression (5), the replacement of water molecules by inhibitor molecules is the controlling process. After 6 h the adsorption of inhibitor on the metal surface is high enough and no longer the control mechanism. This statement is supported by the disappearance of the inductive loop. The phase angle (Figure 7b) increased to a more capacitive behavior due to continuous inhibitor adsorption. The evidence of an inhibitor film appeared after 6 h when a non-well defined second time constant evolved at HF in the Bode representation (Figure 7b).

The Bode plot of phase angle vs. frequency shows two peaks after 6 h. One at around 100 Hz and the other one at 4 Hz. The former has been related to the film on the metal surface due to the presence of inhibitor and the latter to the active metal surface [3]. The Bode plot of modulus of impedance (|Z|) vs. frequency shows the presence of two plateaus: one at HF related to the solution resistance of the system and one at LF associated to the charge transfer resistance [31]. Two negative slopes were also observed due to the two time constants previously mentioned [32].



**Figure 7.** Variation of the EIS response with time for IM-HOL:  $\Box$  blank,  $\bigcirc 3$  h,  $\triangle 6$  h,  $\blacksquare 11$  h,  $\triangleright 14$  h,  $\cancel{11}$  h,  $\bullet 20$  h,  $\bigstar 23$  h: Nyquist (a) and Bode (b) plots representation.

The evolution of the metal/inhibitor interface with time was characterized by the equivalent circuits shown in Figure 8. Where  $R_s$  is the electrolyte resistance,  $Q_{dl}$  and  $Q_{inh}$  are constant phase elements (CPE) representing the double–charge layer capacitance and the inhibitor film respectively. CPE is used in order to compensate for the non-homogeneity of the electrode surface [25].  $R_{ct}$  is the charge transfer resistance,  $R_{inh}$  is pore resistance of the inhibitor film,  $R_L$  is the adsorption resistance and L is the adsorption induction. The CPE impedance (Z<sub>CPE</sub>) is described by equation (6) as follows:

$$Z_{CPE} = 1/(Qj\omega)^n$$
(6)

Where  $Z_{CPE}$  is the impedance of CPE, Q is a proportional factor (CPE), "j" is  $\sqrt{-1}$ , is  $2\pi f$ , and n is a factor which takes values between 0 and 1. The equivalent circuit (EC) shown in Figure 8a has been used for modeling the steel-CO<sub>2</sub> interface involving an adsorbed intermediate product [3,4] and the inhibitor adsorption [21]. When an inhibitor film is present, the EC shown in Figure 8b has been employed [3].



Figure 8. Equivalent circuits used for fitting the experimental EIS results.

The impedance parameters obtained following the fitting of the EIS experimental results by using the EC displayed in Figure 8(a-b) are listed in Table 3. These parameters support the evolution of the inhibitor adsorption with time and the modification of the active surface by the inhibitor. The data obtained with the proposed equivalent circuits showed good agreement with the experimental results as seen in Figure 9.  $Q_{dl}$  and  $R_{ct}$  showed opposite trend as the immersion time increases.  $Q_{dl}$  decreased from 469.58 to 26.61 uF cm<sup>-2</sup> s<sup>n-1</sup> due to the continuous inhibitor adsorption on the metal surface. The behavior of  $Q_{dl}$  can be explained by the following expression [33]:

$$Q_{dl} = \varepsilon \varepsilon_0 A / \delta \tag{7}$$

where is  $\varepsilon$  the dielectric constant of the medium,  $\varepsilon_0$  is the vacuum permittivity, *A* is the surface area and  $\delta$  is the thickness of the electrical double layer. As more inhibitor is adsorbed, the active metal surface (*A*) is reduced. According to equation (7) this area is proportional to  $Q_{dl}$  which explains its reduction with time.  $R_{ct}$  increased from 48.46 to 4197 (Ohm cm<sup>2</sup>).  $R_{ct}$  is inversely proportional to charge transfer area available for the corrosion process. The increase of the  $R_{ct}$  values may be due to the gradual substitution of water molecules by the adsorption of the inhibitors molecules (reaction 5) on the metal surface, decreasing the extent of dissolution reaction.  $Q_{inh}$  and  $n_{inh}$  remained to some extent constant suggesting that a homogenous inhibitor film has been formed [25].  $R_{inh}$  ranged between 2.85 and 8.13 (Ohm cm<sup>2</sup>), indicating that a more compact inhibitor film is forming as immersion time increased [12].



**Figure 9**. Nyquist (a) and Bode (b) plots, a comparison of the experimental data at 23 h with the fitted results using the EC shown in Fig 8(b).

The adsorption of imidazoline inhibitors on the metal surface has been studied recently by Zhang *et al.* [34] by molecular modeling. This kind of inhibitor molecules had larger adsorption energy than the water molecule. This means that the inhibitor molecules adsorb preferentially on the metal surface in aqueous medium, justifying the rapid decrease CR when the inhibitor is added (Figure 3a), high  $R_{ct}$  values and a considerable diminishment of  $C_{dl}$  (Table 3). It was also pointed out that the reactive sites of imidazoline molecules are located at the imidazoline ring which favors the preferential adsorption of the imidazoline ring on the metal surface by forming coordinate and back-donating bonds with atoms on the metal surface.

Time	$Q_{inh}$		$R_{ m inh}$	$Q_{dl}$		$R_{ m ct}$	$R_L$
(h)	$(uF cm^{-2} s^{n-1})$	n <sub>inh</sub>	$(Ohm cm^2)$	$(uF cm^{-2} s^{n-1})$	n <sub>dl</sub>	$(Ohm cm^2)$	$(Ohm cm^2)$
Blank				469.58	0.87	48.46	135.4
3				74.08	0.80	1057	4357
5	38.40	0.93	2.85	37.23	0.82	1982	
6	40.24	0.91	3.99	34.20	0.84	2380	
11	40.41	0.90	7.46	29.48	0.86	3333	
14	38.84	0.90	7.79	29.01	0.87	3556	
17	36.38	0.90	7.64	28.26	0.87	3785	
20	34.29	0.89	8.02	27.32	0.87	4048	
23	32.61	0.89	8.13	26.61	0.87	4197	

**Table 3.** Parameters obtained by fitting the experimental results using the EC shown in Fig. 8 (a-b) for IM\_HOL.

#### 3.2.2. BIM-NH at 10 ppm

The EIS data for BIM-NH at a concentration of 10 ppm is shown in Figure 10. From 3 to 11 h the Nyquist plot (Figure 10a) shows two time constants. At HF a capacitive loop that increases with time due to the inhibitor adsorption on the metal surface. This capacitive loop represents the active state of the metal surface. At LF the adsorption of the inhibitor molecules is manifested by the appearance of an inductive loop by the mechanism described in section 3.2.1. After 14 h of exposure the adsorption of the inhibitor molecules is no longer the controlling process and a charge transfer control process took over. A more capacitive behavior is observed by an increase in the phase angle shown in Figure 10b, suggesting the continuous formation of an inhibitor film. A non-well defined second time constant evolved at HF after 14 h, attributed to the inhibitor film. The Bode plot of phase angle vs. frequency shows a slight asymmetry that implies a second time constant [15]. The presence of an inhibitor film was also supported by the two negative slopes observed in the Bode plot of modulus of impedance (|Z|) vs. frequency [32].

The evolution of the metal/inhibitor interface with time for BIM-NH was characterized by the equivalent circuits used for inhibitor IM-HOL (Figure 8). The impedance parameters obtained following the fitting of the EIS experimental results by using the EC displayed in Figure 8(a-b) are listed in Table 4. These parameters support the evolution of the inhibitor adsorption with time, the formation of an inhibitor film and the modification of the active metal surface by the inhibitor.  $Q_{dl}$  decreased sharply as soon as the inhibitor is added. According to expression (7),  $Q_{dl}$  is proportional to the area available for the reduction of hydrogen ions. The continuous inhibitor adsorption on the metals surface blocks the active surface decreasing  $Q_{dl}$  and increasing  $R_{ct}$  from 48.46 to 6680 (Ohm cm<sup>2</sup>).  $R_L$  is the adsorption resistance of the inhibitor which increases as more inhibitor molecules reach the metal surface.  $Q_{inh}$  and  $n_{inh}$  remained almost constant suggesting the formation of a homogenous inhibitor film [25].  $R_{inh}$  can be associated with the pore sized of the inhibitor film [12]. The increase of  $R_{inh}$  could be related to the formation of a more compact film. The more densely the film packs, the

larger the diameter of the semicircle is (Figure 10a). Therefore, there is a higher resistance to corrosion which results in higher  $R_{ct}$  values.



**Figure 10.** Variation of the EIS response with time for BIM-NH:  $\Box$  blank,  $\bigcirc 3$  h,  $\triangle 6$  h,  $\blacksquare 11$  h,  $\blacktriangleright 14$  h,  $\cancel{17}$  h,  $\bullet 20$  h,  $\bigstar 23$  h: Nyquist (a) and Bode (b) plots representation.

If the performance of BIM-NH and IM-HOL is analyzed, it is found that BIM-NH has the highest  $R_{inh}$  value and therefore a bigger charge transfer resistance. This suggests that the BIM-NH forms a more compact layer and therefore offers better corrosion protection. The presence of two imidazoline rings could have enhanced the inhibitor adsorption since there are more active sites that

react with the metal surface [34]. Besides, there are two extra electrons in the NH group that might be interacting with the metal surface as well. It is important to mention that this kind of inhibitor has not been reported in the literature up to know.

Time	$Q_{inh}$		$R_{ m inh}$	$Q_{dl}$		$R_{\rm ct}$	$R_L$
(h)	$(uF cm^{-2} s^{n-1})$	n <sub>c</sub>	$(Ohm cm^2)$	$(uF cm^{-2} s^{n-1})$	n <sub>dl</sub>	$(Ohm cm^2)$	$(Ohm cm^2)$
Blank				469.58	0.87	48.46	135.4
3				72.00	0.77	253.8	562.6
6				52.76	0.77	719.2	2078
11				42.25	0.77	1813	6691
14	21.06	0.83	13.74	29.04	0.84	2703	
17	19.17	0.83	18.57	27.96	0.85	4976	
20	17.92	0.83	22.99	28.55	0.86	6463	
23	17.23	0.83	23.15	29.27	0.86	6680	

**Table 4.** Parameters obtained by fitting the experimental results using the EC shown in Fig. 8 (a-b) for BIM-NH.

# 3.3. SEM and EDS characterization

SEM pictures were taken and EDS analysis were performed in the absence and presence of 50 ppm of IM-HOL and 10 ppm of BIM-NH. Figure 11a shows a SEM image and its respective chemical analysis from the surface after 24 h of being exposed to a 3 %wt. NaCl solution saturated with CO<sub>2</sub>, pH 4, 1000 rpm and without inhibitor. It is clear that a porous-liked surface has been formed as a consequence of the corrosion process. Besides, the appearance of the corrosion film was gray to black, typical of Fe<sub>3</sub>C films [35]. The chemical analysis revealed the presence of some alloying elements; say Cu, Ni, Mn and V. Considering that this surface has been formed after the preferential dissolution of the ferrite phase over cementite, the presence of alloying elements should be expected on the porous carbide layer. Other authors have also found similar results [18,36]. In the presence of 50 ppm of IM-HOL (Figure 11b) and 10 ppm of BIM-NH (Figure 11c), respectively, the rough surface is visibly reduced indicating the formation of a film on the metal surface. Besides, the EDS analysis showed the presence of nitrogen on the metal surface, corroborating the existence of the inhibitor film. A less damaged metal surface was found for BIM-NH (Figure 11c). This is in good agreement with the electrochemical results.



Figure 11. SEM pictures and its corresponding EDS analysis for the metal surface after 24 h of exposure: (a) Blank, (b) 50 ppm of IM-HOL, (c) 10 ppm of BIM-NH.

# 4. CONCLUSIONS

The CO<sub>2</sub> corrosion inhibition of X65 carbon steel through (1-(2-hidroxyethyl)-2(heptadec-8-enyl)-imidazoline and 1-(2-aminoethyl)-2(heptadec-8-enyl)-bis-imidazoline has been studied in a 3 wt.% NaCl at 80 °C, pH 4 and under turbulent conditions. The information obtained by

electrochemical impedance helped in the characterization of the inhibitor films at different concentrations and its evolution with time. By means of EIS analysis and surface observations, it was found that 1-(2-aminoethyl)-2(heptadec-8-enyl)-bis-imidazoline formed a more compact inhibitor layer and therefore the corrosion protection was enhanced. The molecular structure of this inhibitor allows the usage of lower concentration without a loss of efficiency. That feature is economically important. Further studies focusing on the persistency of the inhibitor film should be considered.

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