Electrochemical Impedance Spectroscopy (EIS) Study of the Film Formation of 2-imidazoline Derivatives on Carbon Steel in Acid Solution

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In this work, EIS has been used to study the film formation of 2-methyl-2-imidazoline (MI), and N-methyl-2-methyl-2-imidazoline (MMI) on carbon steel 1018 in hydrochloric acid 0.5 M. EIS experiments were recorded at 0, 100, 200, 300, 400, and 500 min at 1, 5 and 12.5 mM. EIS data were used to calculate corrosion related electrochemical parameters, and this technique was shown to be a very useful tool for studying corrosion inhibitors. The results showed an increment in the charge transfer resistant values (R_{ct}), and a decrease in the double layer electrochemical capacitance values (C_{dl}) when concentration of the imidazoline compound is increasing, suggesting that the pendant group significantly affects the electrochemical behavior of 2-imidazoline derivatives against corrosion.
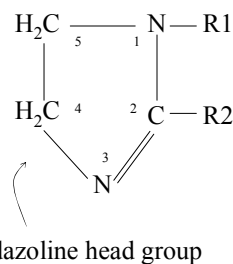*Keywords*: corrosion inhibition, imidazoline, electrochemical impedance spectroscopy (EIS).

INTRODUCTION

Electrochemical impedance spectroscopy (EIS) is an electrochemical technique which has already been successfully used in various corrosion and protection fields such as organic coating studies [1], passive layer analysis [2 – 4] and water treatment corrosion inhibitor evaluation [5]. This technique can provide information on the corrosion and protection mechanisms as for example, when an adsorbed film or an applied organic coating is present [6]. The study of the persistency of an inhibitor film is an important aspect because when a corrosion inhibitor is added to an oil and gas wells and flowlines, one of the most important concerns is to make sure that an inhibitor film is formed with the anticipated film persistency [4]. Here, imidazoline corrosion inhibitors has been used to protect oil wells, gas wells or pipelines from CO_2 and H_2S corrosion although little has been reported about the corrosion protection mechanism and film properties: the performance of the imidazoline molecule is still not understood [7 – 8]. As shown in Figure 1, the typical imidazoline molecule consists of the following: (i) an imidazoline head group, (ii) a long hydrocarbon tail group, and (iii) a short pendant group.

Each part of the molecule can contribute in different ways to the corrosion inhibition process, and the presence of the pendant group in MMI must have some advantages compared with MI where pendant group is not present. Experimental evidence in support of specific mechanisms has been difficult to obtain due to the low concentrations at which the inhibitors are used (10 ppm – 20 ppm in the petroleum industry), the complexity of the environments surrounding the inhibitor under real conditions (as high temperatures, high pressures) and, the difficulty in experimentally obtaining information about the metal-solution interface: EIS data can be used to calculate corrosion related electrochemical parameters to understand the performance of imidazoline corrosion inhibitors.

Fig. 1. Typical imidazoline molecule

The aim of this study is to investigate the behavior of MI and MMI molecules as corrosion inhibitors on carbon steel 1018 in hydrochloric acid 0.5 M when these compounds are used as corrosion inhibitors.

EXPERIMENTAL PROCEDURE

The imidazoline compounds were obtained in the laboratory as follows:

Synthesis of 2-methyl-2-imidazoline (*MI*). Acetic anhydride (15 ml, 0.15 mol) was slowly added to ethylenediamine (13 ml, 0.10 mol), the resulting mixture solution was refluxed for 2.0 hours. A colorless liquid was collected when the mixture was distilled at 170 °C – 175 °C and that liquid becomes colorless solid at room temperature (*sym*-diacetylethylenediamine). M.P: 174.5 °C ±0.5 °C [9]. The mixture of *sym*-diacetylethylenediamine (25.8 g, 0.18 mol) and magnesium powder (2.2 g, 0.09 mole) was heated in a metal bath at 310 °C – 315 °C and 2-methyl-2-imidazoline distilled as a nearly colorless liquid which crystallized in the receiver. The distillate was

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crystallized from dry benzene (25.0 ml) to give a colorless crystalline compound (14.2 g, 94 % yield); m.p. 85 °C [10].

Synthesis of N-methyl-2-methyl-2-imidazoline (MMI). Methyl iodide (14.2 g, 0.10 mol) was added dropwise to the solution of 2-methyl-2-imidazoline (4.2 g, 0.05 mole) in benzene (15.0 ml). The mixture was refluxed on the steam-cone for two hours, then the solvent was evaporated under vacuum and the residue was washed two times with ethanol (40.0 ml) and ethyl acetate (3.0 ml) was added to incipient cloudiness. After the solution was chilled, N-methyl-2-methyl-2-imidazoline was obtained and kept under vacuum. The spectral data obtained for this compound were found to coincide with the reported results [10].

The reagents were used as received: acetic anhydride (Fluka), ethylenediamine, benzene, magnesium powder, ethyl acetate, methyl iodide (Aldrich).

EIS technique – EIS studies were carried out with an interface Solartron 1287 connected to a Frequency Response Analyzer (FRA) Solartron 1260, which was controlled by a CorrWare and Zplot software. A standard cell (1.0 L) of PARC (Princeton Applied Research) was used. The cell assembly consisted of carbon steel working electrode (WE), a graphite counter electrode (CE), and a saturated calomel electrode (SCE) as the reference electrode. The test material was carbon steel (composition, wt %: 0.18 C, 0.35 Mn, 0.17 Si, 0.025 S, 0.03 P and Fe, with 1.0 cm^2 surface). Before to introduce the carbon steel to the solution it was polished with 600-grit silicon carbide (SiC) paper wetted with de-ionized water, then polished with 600-grit SiC paper wetted with ethanol and then rinsed with ethanol. Doubly distilled water and analytical grade hydrochloric acid, 0.5 M HCl, were used to prepare the test solutions, which was de-aerated by means of nitrogen during a period of 45 min. Tests were done at room temperature and under static conditions.

RESULTS AND DISCUSSIONS

In Fig. 2 the Nyquist plots after 500 min of exhibition to the corrosive medium, without imidazolines, with MI 12.5 mM, and with MMI 12.5 mM are shown. The EIS data show that the presence of a pendant group with the methyl radical increase the values of R_{ct}. Different concentrations of inhibitor were used, and R_{ct} increases when the inhibitor concentration increase as is shown in Fig. 3 and Fig. 4. The biggest increment in R_{ct} is observed for MMI.

The EIS results are interpreted in terms of an equivalent circuit, which is shown in Fig. 5. From this figure, a Constant-Phase Element (CPE) is introduced because the semicircles in the Nyquist plots are depressed due to surface roughness, heterogeneity of the surface, or other effects that causes uneven current distributions on the electrode surface [11]. In this case, the impedance of a CPE is given by [12 – 13]:

$$\frac{1}{Z_{(CPE)}} = Q \cdot (j\omega)^n ,$$

where $Z_{(CPE)}$ is the impedance of CPE, Q is a proportional factor, ω is the angular frequency, and n is a factor which takes values between 0 and 1 (if n is equal to 1 then we

have an ideal capacitor). Then values obtained for the zero concentration of inhibitor are 0.74 – 0.76, while the systems with inhibitor show n values in the range of 0.78 – 0.9. The increase in the n parameter indicates that inhibitor adsorption brings about a decrease in surface heterogeneity. The increase in n may be attributed to a non
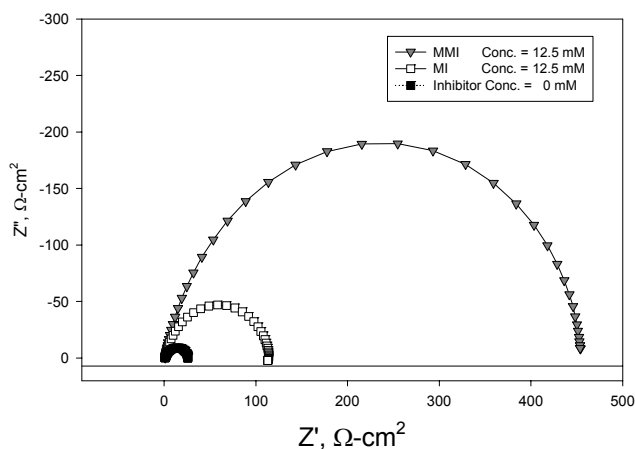

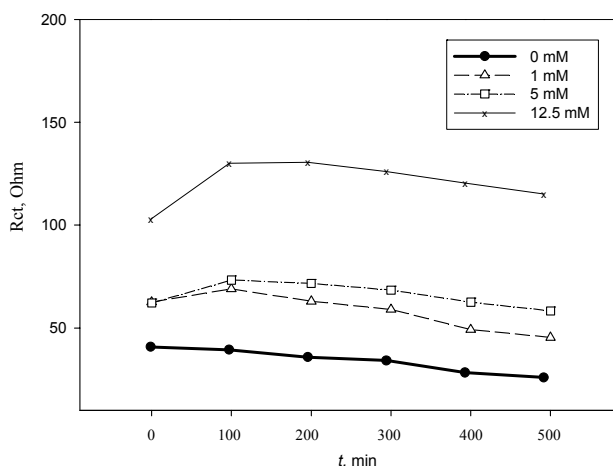**Fig. 2.** Nyquist plots for carbon steel in 0.5 M HCL containing MI or MMI at 500 min

Fig. 3. The R_{ct} against time for carbon steel in 0.5 M HCl at different concentrations of MI
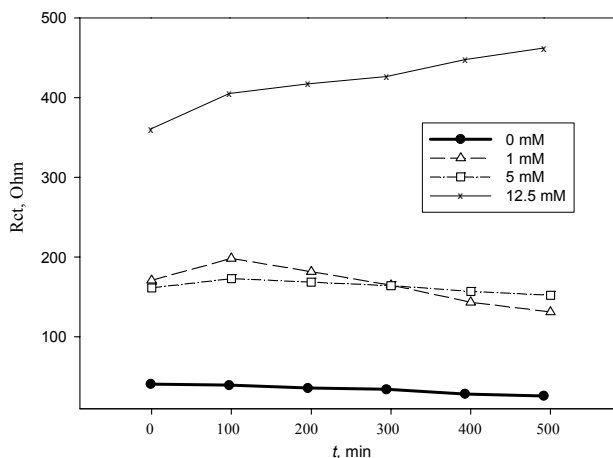

Fig. 4. The R_{ct} against time for carbon steel in 0.5 M HCl at different concentrations of MMI
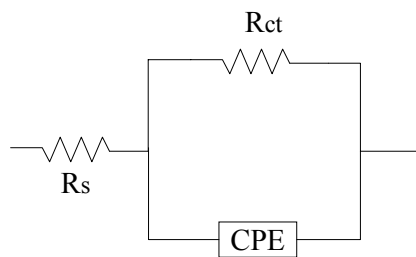
Fig. 5. Equivalent circuit model with a CPE

uniform adsorption. Based on this equivalent circuit, the C_{dl} values were determined, and related as [14 – 15]:

$$C_{dl} = \left(Q \cdot R_{ct}^{1-n} r \right)^{1/n} .$$

In Figs. 6 and 7 the values of C_{dl} as a function of time are presented at different concentrations of inhibitor. From these figures, high C_{dl} values were obtained at 0 mM, but when the concentration of MI increases then the values of C_{dl} decrease. In these figures MI shows a C_{dl} of 216.97 $\mu F/cm^2$ at 500 min, but a lower capacitance value is recorded for MMI, showing 118.17 $\mu F/cm^2$ at the same time.

The time constant of the CPE can be calculated by the following equation [14]:

$$Q = \frac{\tau^n}{R_{ct}} .$$

The time constant gives information about the charge and discharge of the double electrochemical layer in the metal–solution interface. In Figs. 8 and 9 are reported the changes that are experienced by the time constant (τ) of the capacitor at different concentrations. The results show that the lowest values are obtained at the concentration 0 mM. When the concentration of MI is increased the τ values are low at the beginning of the experiment, but at the end it is possible to observe an increment of τ with an increase in concentration. Figure 9 shows clearly that MMI behaves in different way: the time required for the charge and discharged of the time constant value is high even at the beginning of the experiment.
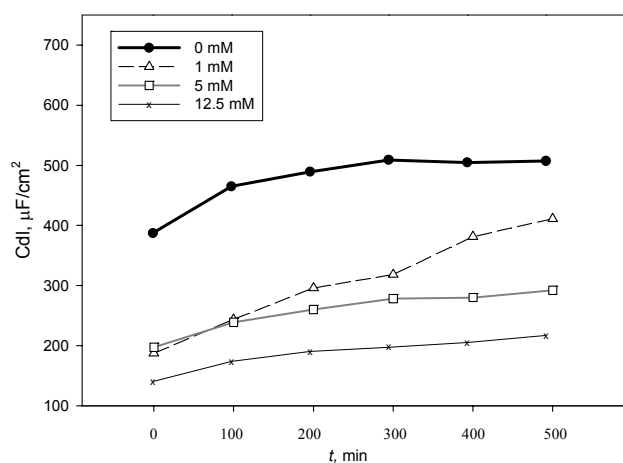

Fig. 6. The C_{dl} against time for carbon steel in 0.5 M HCl at different concentrations of MI
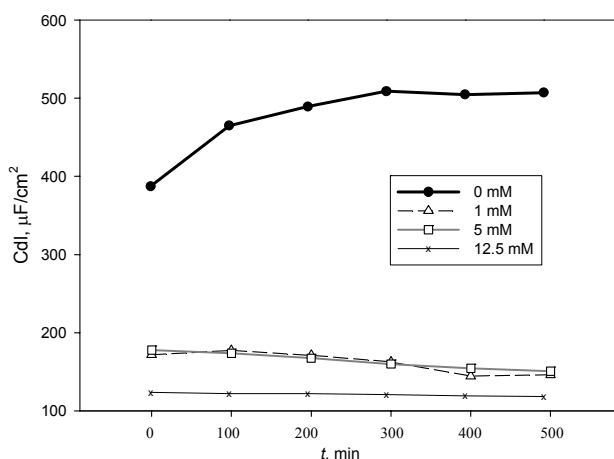

Fig. 7. The C_{dl} against time for carbon steel in 0.5 M HCl at different concentrations of MMI
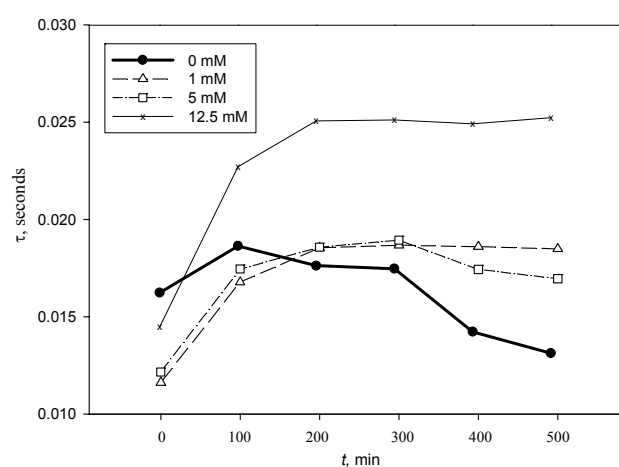

Fig. 8. The time constant against time for carbon steel in 0.5 M HCl at different concentrations of MI
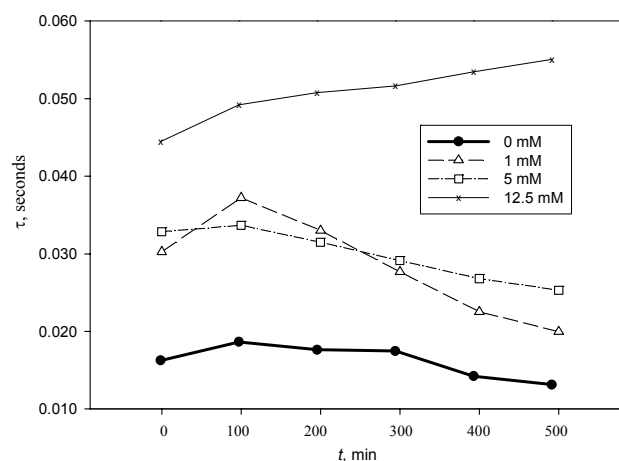

Fig. 9. The time constant against time for carbon steel in 0.5 M HCl at different concentrations of MMI

If the capacitance of the associated capacitor is a measure of its capacity to store charge, the time constant informs about the velocity that the charge stores. When MI shows a decrement in C_{dl} at high concentrations the time constant values are still low, it means that the interactions

with the metallic surface are unstable, and under this situation the development and stability of a protective film is difficult. In comparison, MMI exhibit low C_{dl} values at any concentration, and the time constant values increase with an increase of concentration as high as 0.055 seconds for the highest concentration, while MI shows 0.025 seconds in Fig. 8. The behavior of MMI is much better than MI where the difference is that MI does not contain a pendant group.

CONCLUSIONS

EIS can be used to measure corrosion related electrochemical parameters such as charge transfer resistance and double layer capacitance. In this paper we show that the C_{dl} values decrease with an increase in concentration. MMI showed lower values than MI suggesting that the pendant group significantly affects the electrochemical behavior of 2-imidazoline derivatives against corrosion. The time constant values increase with an increase of the inhibitor concentration as is evident for MMI, by this way, MMI shows again the effect of the pendant group.

Acknowledgments

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