

Corrosion of carbon steel in a buffered solution like NACE TM 0177 in the presence of hydrocarbon

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Abstract

In this work, the study of the behavior of carbon steel AISI 1018 in a buffered solution of acetic acid and chlorides (electrolyte equivalent to the used in NACE TM 0177 method) with and without hydrocarbon is presented. The study took as starting point the results reported in literature about the corrosion mechanism in such system [1].

The electrochemical techniques used in this work were polarization curves and electrochemical impedance spectroscopy (EIS). The polarization curves obtained indicated that the anodic Tafel slopes do not suffer a significant change with the addition of hydrocarbon, while the cathodic ones suffered a slight change indicating the acceleration of the reduction reaction by the presence of the hydrocarbon.

Electrochemical impedance spectroscopy shows that steel has a high activity in the solution studied which is most noticeable in low frequencies. This establishes that the interaction of acetic acid, acetate and chlorides with the metal is enhanced by the presence of hydrocarbon, where the adsorption processes are those that govern the corrosion mechanism. The adsorptions of corrosive agents prevent the formation and growth of a passive layer of corrosion products, even in the presence of hydrocarbon, so the corrosion rates obtained are high.

1. Introduction

One of the methods used for evaluation of metallic materials subject to stress and / or blistering in the oil industry is the NACE TM 0177 [2]. This method uses a highly corrosive in contact with the materials to be evaluated. The high aggressiveness of the means of assessment is adequate for reliable results in a very short time, it also has a high concentration of hydrogen, low pH, which is commonly found in primary distillation plants. On the other hand, the presence of organic acids and chloride causes corrosion becomes a more complex phenomenon.

In this work is studying the behavior of SAE 1018 carbon steel in a buffered solution of acetic acid and chloride (electrolytes equivalent to the method used in NACE TM 0177) with and without hydrocarbon and used as a starting point work reported in the literature about the mechanism of corrosion in such systems can be used later to establish whether the interaction of acetic

acid, acetate and chlorides with the metal [1], is augmented by the presence of hydrocarbon, where the adsorption processes are those that govern the process of corrosion. To determine how it affects the assessed hydrocarbon material, through the description of the effect of the compound, the mechanism of corrosion.

2. Experimental

For electrochemical techniques used in a typical three-electrode cell setup was used with a Hg/HgSO₄(s)/KSO₄(sat) electrode as reference and a graphite bar as counter electrode. As working electrodes were used discs of carbon steel SAE 1018, coupled to a Teflon support. Prior to each experiment, electrode surface was polished with 280 SiC emery paper.

The corrosive environment equivalent to the method used in NACE TM 0177 [1], has the following composition: 0.04M CH₃COOH / NaCOOCH₃, pH = 3.5, 30172 ppm Cl⁻ as NaCl (0.52 M Cl⁻) in the absence and

presence of hydrocarbon (20% v). Buffered solution is used to avoid to the greatest degree possible, the change in pH and the consequent change of experimental conditions.

To prepare the solution were used corrosive analytical grade reagents and deionized water. The latter is placed in the reactor with stirring and bubbling with nitrogen gas for half an hour.

After this is added salt and acetic acid to bring the solution to a pH of 3.5. All

experiments were performed at 25 ° C and after 10 minutes of immersion of the electrode.

Electrochemical techniques to be used the following experimental parameters (Table 2.1), these were the same as those used in reported work [1] that is the best compromise between performance and time to be well enough to achieve reproducibility and reliability in the results.

Table 2.1 Parameters used in experimental electrochemical techniques.

Potentiodynamic polarization	Electrochemical impedance spectroscopy
Time of 10 min immersion of the electrode	Time of 10 min immersion of the electrode
Scan rate 0.1 mV/s	Amplitude of 10mV
In a interval of potential $E_{corr} \pm 300\text{mV}$	Interval of frequencies 0.01Hz to 10,000Hz

The Potentiodynamics polarization curves were drawn a scan rate of 0.1mV/s, we used the reference electrode in a separate compartment and in contact via a Luggin capillary and a clean steel surface (freshly polished).

For the electrochemical impedance technique, measurements were carried out with amplitude of 10 mV, with reference to the corrosion potential and the frequency interval of 10 mHz to 10 kHz. It employed a Frequency Response Analyzer (FRA) coupled to a Potentiostatic-Galvanostatic Autolab Mod PGSTAT30.

3. Results

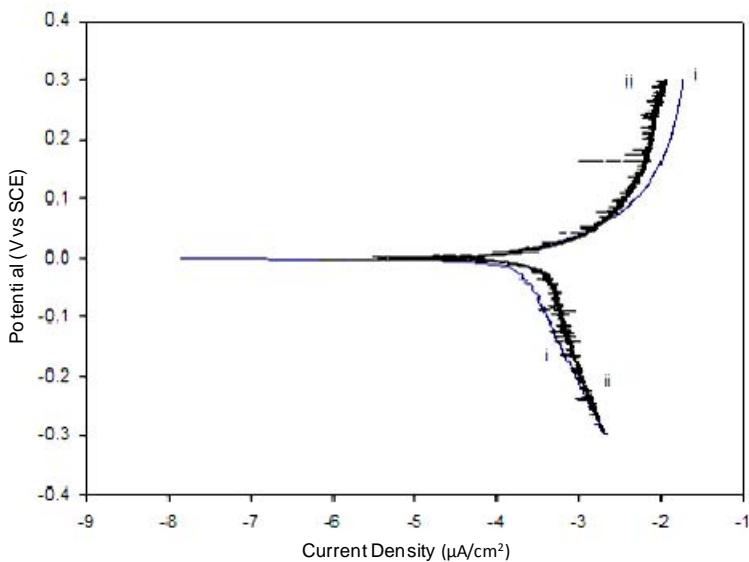
3.1 Polarization curves

The graph 3.1 shows the Potentiodynamics polarization curves for the system under study, function in the absence (curve i) and presence of hydrocarbon (curve ii). For the solution with hydrocarbon, shows that it affects the presence of both the anode and the cathode, showed a greater effect on the oxidation and provides protection apparently because the currents are lower than those obtained with hydrocarbon. Furthermore, the reduction reaction, a slight activation process in the presence of hydrocarbon.

It was the analysis of polarization curves, by determining the values of R_p and the resistance obtained for the system in the presence of hydrocarbon shows a value greater than the system free of hydrocarbon.

This value indicates an effect of inhibition by either the presence in this area because it is a non-conductive compound, or an increase in competition with the adsorption of corrosive agents. Moreover, the anodic Tafel slope for the hydrocarbon system show an increase of approximately 20 mV/decade, with the system without hydrocarbon, while for the cathodic Tafel slope is seen a major change with regard to the system without hydrocarbon (about 100 mV/decade), indicating that the process is mostly concerned with the presence of hydrocarbon is reduced.

The specific adsorption of acetate ions and Cl^- , appears to be modified by the hydrocarbon favoring its arrival at the metal surface which is shown in the increase of the cathodes currents. However, there are also diffusive processes to become more important with the presence of hydrocarbon, which is manifested in a greater increase in the Tafel slope.



Graph 3.1 Potentiodynamics polarization curves obtained with a scan rate of 0.1 mV/s, on SAE 1018 carbon steel in a buffered solution of Ac/Ac⁻ pH 3.5, 30,172 ppm Cl⁻ in presence and absence of hydrocarbon (marked, respectively, in figure) i) without hydrocarbon ii) with hydrocarbon.

In table 3.1, are observed corrosion parameters obtained for the different systems reported in the literature and the system under study (acetic acid, NaCl and hydrocarbon).

The analysis of the values of I_{corr} (current density), shows that the presence of hydrocarbon significantly increases the current density and hence the corrosion

rate in comparison to the system acetic acid and NaCl. Compared to the system with acetic acid, NaCl and H₂S current density is lower but not significantly because they have a similar order of magnitude. This is important because the presence of hydrocarbon makes the specific adsorption of ions acetate and Cl⁻, is amended by the hydrocarbon favoring his arrival at the metal surface.

Table 3.1 Corrosion parameters obtained for the different systems reported in the literature and the system under study (acetic acid, NaCl and hydrocarbon).

Solution	I_{corr} (A/cm ²)
*Acetic acid, NaCl	1.62E-07
*Acetic acid, NaCl and H ₂ S	7.54E-04
Acetic acid, NaCl and Hydrocarbon	3.05E-04

*Veloz M.A. (2003), Ph. D. Thesis, UAMI, México.

3.2 Electrochemical Impedance Spectroscopy

In order to establish easier, the number of stages involved both in the anodic process in the cathodic, was tested with the technique of electrochemical impedance spectroscopy. This technique is used by exploiting the characteristics of the same order to separate the contributions of

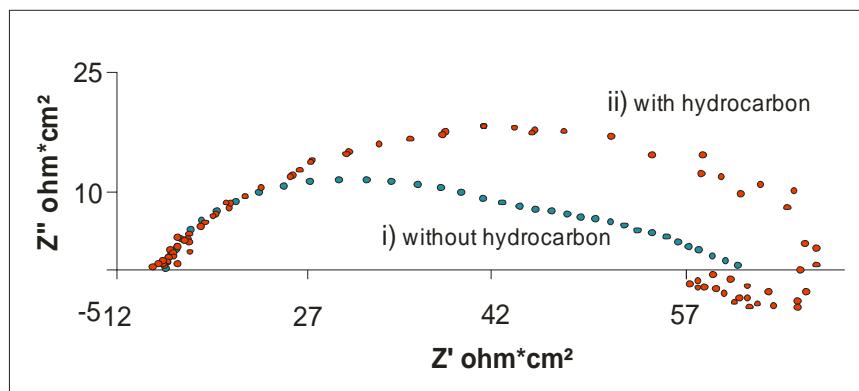
different phenomena, according to the relaxation time of each.

The results of the technique of electrochemical impedance spectroscopy showed that the steel surface is active (see Graph 3.2), since the values of impedance real and imaginary is low compared with work reported in the literature [1].

The spectra obtained are deformed and show the presence of a flattened semicircle.

The presence of hydrocarbon in the solution, modifying the process which is observed on increasing the values of the impedances and exhibited an inductive loop

at low frequencies, which has been attributed to species adsorbed or dissolution processes.



Graph 3.2 Nyquist diagrams for the hydrocarbon system without and with hydrocarbon (marked, respectively, in the figure) i) without hydrocarbon ii) with hydrocarbon to the system of carbon steel in a solution 0.04M HAc / Ac, pH = 3.5, 30,172 ppm Cl-, determined at a frequency of 10 mHz to 10 KHz.

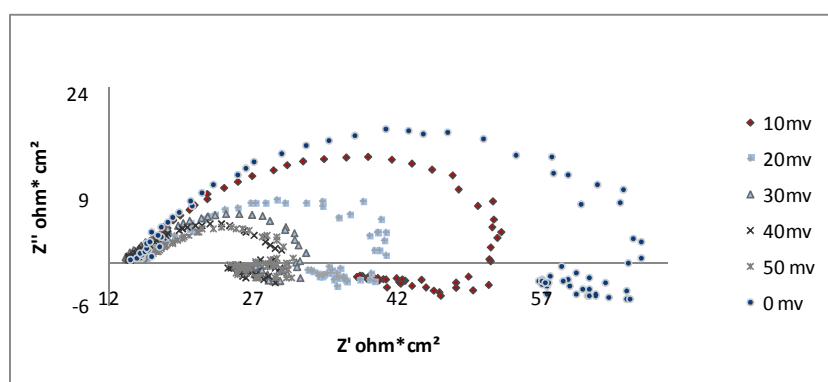
3.2.1 Electrochemical impedance with imposed potential

Graphs 3.3 and 3.4 present the Nyquist diagrams obtained for the solution in the presence of hydrocarbon through the imposition of different potentials anodic and cathodic, respectively.

In experiments with imposed potential, it was observed that the imposition of potential causes an immediate change in the shape of the inductive loop system for the presence of hydrocarbon which is

observed on increasing the values of the impedances and performs this loop at low frequencies, which has been attributed to species adsorbed or dissolution processes [3].

Nyquist diagrams obtained by imposing over potentials anodic have similar behavior at high frequencies, but as the imposed potential increases are observed only a decrease in magnitudes of the impedances total, indicating a decrease in resistance polarization.



Graph 3.3 Typical Nyquist diagrams obtained for the carbon steel in a solution 0.04M HAc / Ac, pH = 3.5, 30,172 ppm Cl-, varying the amplitude of 10mV, 20mV, 30mV, 40mV and 50mV on the corrosion potential in a frequency range of 10 mHz - 10 kHz.

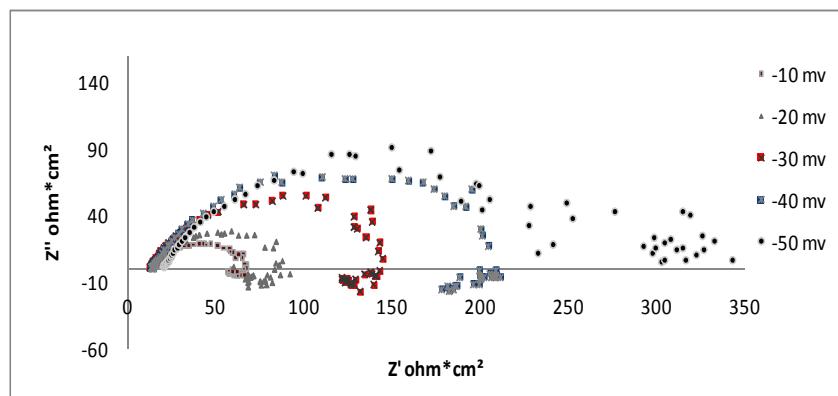
Nyquist diagrams obtained (Figure 3.3) exhibit an inductive loop at low frequencies, indicating the adsorption and desorption of species on the electrode surface. Kedam and colleagues [3] found this type of inductive loops in the anodic dissolution of iron in acid environment, attributed mainly to the number of adsorbed species and the process of relaxation, where the potential is imposed.

Moreover, for over potential negative (Figure 3.4) is observed in the Nyquist diagram again change the shape of the inductive loop, greatly increasing the total impedance and showing great similarity in behavior at high frequencies.

The series of points that appear at low frequencies, different from that seen in the over potential anode, may indicate a competition in the adsorption of species, or that the inductive effect is becoming less important. Here, it was felt that these points

could be associated with diffusive processes and the electrode is in an emulsion is agitated at high speeds resulting in a stable layer near the electrode surface.

When increasing the potential difference imposed the values of real and imaginary impedance increase, unlike what was observed when faced with potentially more positive. This indicates that the process cathodic generates products which slow down the charge transfer, and that is associated to a competitive adsorption between HAc and Cl^- .



Graph 3.4 Typical Nyquist diagrams obtained for the carbon steel in a solution 0.04M HAc / Ac, pH = 3.5, 30,172 ppm Cl^- , varying the amplitude of -10mV, -20mV, -30mV, -40mV and -50mV on the corrosion potential in a frequency range of 10 mHz - 10 kHz.

4. Discussion of Experimental Results of Impedance

To perform a quantitative analysis of the results of impedance spectra obtained for both solutions were simulated with the equivalent circuit shown in Figure 4.1. Some authors [4,5] have used a circuit similar to Figure 4.1, to discuss the process of corrosion in acid environment in the presence of H_2S , allowing them to consider not only the inductive part of the spectra EIS.

In this part of the work is the interpretation of some parameters obtained by adjusting the spectra using the program Zview2, and using the physical interpretation proposed by other authors [4,5], the elements of the proposed equivalent circuit. The circuit (Figure 4.1) allows to identify both the solution resistance (R_s) and the charge transfer resistance (R_1), but the double layer capacitance is affected by imperfections in the surface, which is simulated using a constant phase element (CPE1) [4,5].

Elements are also obtained for the adsorptive characteristics of the system (CPE2 and R2). It is worth mentioning that

these are the best fit to the experimental results, and yet not achieved a complete reproduction of the same, as to frequencies below 0.1 Hz are very high deviation.

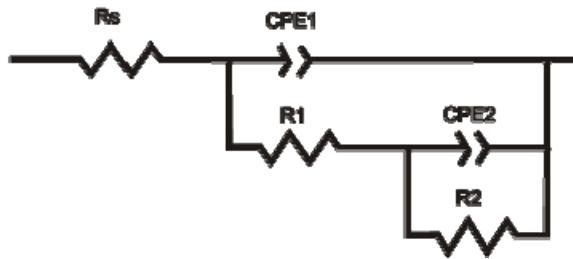


Figure 4.1 Equivalent circuit used to simulate impedance diagrams obtained for a system carbon steel SAE 1018 (rotation speed 2000 rpm) in a 0.04M HAc/Ac- solution, pH = 3.5, 30,172 ppm Cl- in the presence of hydrocarbon.

Table 4.1 shows the representative values for the resistances (solution resistance; R_s , the resistance associated with adsorptive processes, R_1 and R_2) obtained from the fit to the experimental data using the circuit in Figure 4.1.

The resistances for the resolution (R_s in table), presentations much uniformity, there is a slight change, especially towards positive overpotentials, indicating only slight variations in the adjustment of the impedance spectra.

In the case of R_1 and R_2 (in Table 4.1) obtained for different values of corrosion potential for the solution generally show an increase compared to that for E_{corr} .

When imposing more negative potential than E_{corr} , there is a tendency of R_1 and R_2 to increase imposed as the potential becomes more negative, whereas towards more positive potential E_{corr} , R_1 and R_2 decreases. Thus, one might propose that the predominant phase in the corrosion process, seem to be a stage associated with the process of oxidation. Moreover, the positive overpotentials, see that R_1 and R_2 have a value greater than the corrosion potential, but they diminished with increasing potential difference of the potential for corrosion. Toward negative overpotentials has practically the same behavior, suggesting that the potential imposed causes a reduction of the adsorbed species. However it is necessary to the analysis of constant phase elements associated these resistances in arrangements R_1 and R_2 -CPE1-CPE2.

Table 4.1 Resistances and constant phase elements for the data calculated EIE through the best fit of experimental data to the equivalent circuit in Figure 3.2.

E- Ecorr (mV)	Resistances (Ω)			CPE1		CPE2	
	Rs	R1	R2	Y_0 ($\Omega^{-1}s^n$)	n_1 (0 – 1)	Y_0 ($\Omega^{-1}s^n$)	n_2 (0 – 1)
50	14.62	11.26	25.02	0.00062	0.76333	0.10231	-0.43111
40	14.22	12.12	28.01	0.00056	0.77327	0.08961	-0.42336
30	14.97	14.96	33.4	0.00052	0.77835	0.098599	-0.62544
20	15.47	16.12	42.85	0.000779	0.6878	0.10266	-0.59256
10	14.5	21.76	53.05	0.00077	0.64	0.1112	-0.41148
0	14.97	35.12	65.41	0.000533	0.72846	0.0952	-0.52131
-10	14.61	51.43	83.01	0.000705	0.66498	0.083776	-0.60702
-20	14.87	66.4	130.12	0.000368	0.79429	0.086713	-0.52155
-30	14.07	78.1	150.23	0.000328	0.77707	0.1333	-0.41223
-40	14.23	90.05	170.21	0.000546	0.73011	0.09891	-0.45332
-50	15.01	105.1	185.86	0.000423	0.7011	0.1163	-0.5231

Table 4.1 shows the values of the constant phase elements obtained for best fit of experimental data, the equivalent circuit in Figure 4.1. It is observed that the values of n_1 , for the CPE1 obtained at different potentials imposed, are very similar (about 0.65-0.75) and can be attributed mainly to the roughness of the electrode surface, while values of Y_0 have high similarity indicating the modification of the interface steel - electrolytic environment. In the case of CPE2, it is important to note that all calculated n are similar in magnitude, validating the assumption that these elements are associated to the adsorption of species and the negative of these is attributed to the CPE2 is a inductor and not a capacitor, which is consistent with the physical interpretation given to adsorptive processes.

In studies of systems containing HAc/Ac-[6,7,8] has been proposed that the corrosion mechanism occurs through adsorption of HAc in the metal surface, but the values of the slopes anodic informed in this work are affected by both the conductivity of the solution, and the presence of other ions and in general by other the experimental conditions. For example, Christiansen et al. [6]. Anodic Tafel slopes are 106 mV/decade and attribute the difference in slopes found by other studies (29 mV/decade) [9,10], the

treatment provided to the electrodes before performing the experiments, which would change the mechanism.

On the other part, the slopes of anodic polarization curves obtained are similar to those obtained by Nord and Bech-Nielsen [7] where it is proposed that, given the initial presence of a layer of ferric ions on the surface of metal and since the coordination number of these, the number of Ac-ions adsorbed on an iron atom in its active state, should not be more than two, thus obtaining a slope of 90 mV/decade.

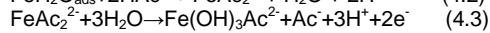
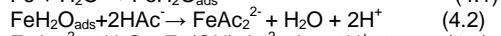
This agrees with that observed anodic slope values very similar to those obtained by Nord and Bech-Nielsen, and with the anodic behavior of the impedance diagrams, the difference is observed only in the adsorptive.

Some authors agree that the output of a proton from the adsorbed acetic acid governs the rate of corrosion and, since the chloride adsorption on the metal surface is slower than that of acetate ions [11,12] is feasible to think that in anodic conditions, the mechanism is by adsorption of the latter.

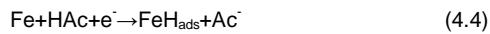
The role of chlorides in the system can be through two mechanisms: the promotion of corrosion or inhibition [13,14], implying that

the chloride in the solution have an important role in the dissolution process, however in this work is not appreciated their effect on the mechanism of chloride, so that would recommend a study to verify this effect.

Thus, one can establish that the general mechanism of anodic process for the system under study is similar to that proposed by Nord and Bech-Nielsen [7], where metal dissolution occurs primarily by adsorption without charge transfer of ions Ac^- , which is further emphasized by the presence of hydrocarbon.



For the cathodic process, Singh and Gupta [8] found slopes cathodic more than 300mV/decade, reporting that the behavior of polarization curves in a system HAc/Ac- indicate that the cathodic reaction and its mechanism are themselves for what they propose the following:



Thus the overall mechanism involves the HAC diffusion through the film of hydrocarbon, the adsorption of HAc, acetate production and evolution of H_2 which is confirmed experimentally in the curves of cathodic polarization whose slopes have very high values and the impedance spectra showing the predominance both of adsorptive processes and diffusive by showing flattened shape.

5 Conclusions

The analysis of the values of I_{corr} showed that the presence of hydrocarbon significantly increases the current density and hence the corrosion rate compared to the system of acetic acid and NaCl. The presence of hydrocarbon makes the specific adsorption of acetate ions and Cl^- , is amended by the hydrocarbon promoting their arrival to the metal surface. Using the technique of electrochemical impedance spectroscopy (EIS) in combination with the results obtained by analyzing the polarization curves, it was possible to propose a mechanism to represent the corrosion of carbon steel SAE 1018 in an environment of acetic acid, chlorides and hydrocarbon. In the proposed mechanism,

the adsorption of acetic acid remains decisive for the process. The chlorides, for its part, appear to act only in secondary reactions or corrosion products. The interaction of acetic acid, acetate and chlorides with the metal is increased by the presence of hydrocarbon substantially modify the corrosion rate of the system where adsorption processes are the rulers and leading to corrosion rates very similar to system in the presence of H_2S . The adsorption of corrosive agents prevents the formation and growth of a passive layer of corrosion products thus obtained corrosion rates are high.

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