

Inhibition on Carbon Steel Corrosion in Presence of Hydrocarbon

L. D. López León^{1,2}, M. A. Veloz Rodríguez^{1,*}, V. E. Reyes Cruz¹, S. A. Pérez García²,
A.L. López León³

¹ Universidad Autónoma del Estado de Hidalgo, Carr. Pachuca Tulancingo Km 4.5, Col Carboneras, Mineral de la reforma, Hgo. México C.P. 42184

² Centro de Investigación en Materiales Avanzados, Miguel de Cervantes 120, Complejo Industrial Chihuahua, Chihuahua, Chih. México C.P. 31109

³ Universidad Autónoma de Ciudad Juárez, Av. Del Charro 450 Norte, Col. Partido Romero, Ciudad Juárez, Chih. México C.P. 32310

*E-mail: mveloz@uaeh.edu.mx

Received: 9 September 2011 / Accepted: 11 October 2011 / Published: 1 November 2011

In this work the study of electrochemical behaviour of organic compounds as corrosion inhibitors is being done over a carbon steel AISI 1018 immersed in a corrosive synthetic environment (brine type NACE 1D196), in the absence and presence of hydrocarbon. The techniques used were the electrochemical Polarisation curves and electrochemical impedance spectroscopy. In the Polarisation curves, the presence of corrosion inhibitors in the system shows that increasing of the concentration affects both the anodic and the cathodic stages of the corrosion process, showing that the obtained currents are lower by increasing the concentration of the inhibitor. On the other hand the inhibitor efficiency decreases with the presence of hydrocarbon in different systems. Electrochemical impedance spectroscopy shows that steel has high activity in the environments studied, being more remarkable at low frequencies and in the presence of hydrocarbon since the spectra shows flattened semicircles, with low values of real impedance and inductive trends. This establishes that the interaction of ions in the solution with the metal, where adsorption processes are governing the corrosion mechanism, is favoured by the presence of hydrocarbon.

Keywords: Carbon steel, Polarisation curves, Electrochemical Impedance Spectroscopy, Adsorptive processes.

1. INTRODUCTION

The use of corrosion inhibitors has provided, for a long time, a solution to the damage caused by corrosion in the oil industry; however, due to the large number of corrosive environments, the

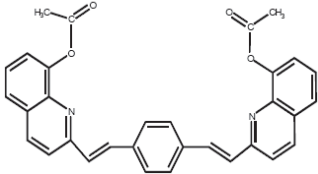
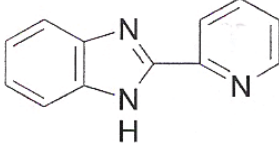
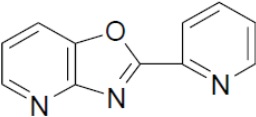
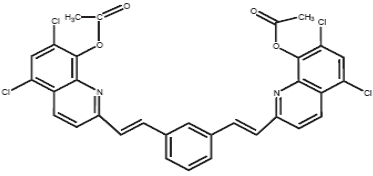
selection of a corrosion inhibitor is a challenging task. The number of different inhibitors available is very large and the selection depends on the metal that has to be protected, also the nature of the corrosive environment and operating conditions to which they are subjected. Currently the field of the development of corrosion inhibitors is in a stage of evaluation for different compounds which have strong characteristics of corrosion inhibition and which promise to be an excellent raw material for the development of effective corrosion inhibitors in various corrosive media [1,2].

Thus, in the corrosion field it is very important to understanding the corrosive characteristics of the environments within the oil industry; since the contact with metal equipment causes serious damages and the economic lost is significant [3,4]. The presence of hydrocarbon on the other hand, it is also a determining factor, due to the conditions acquired by the surface of the metallic material that can cause severe material damages leading to the loss of the entire equipment. This work is an attempt to contribute to the corrosion understanding by evaluating the electrochemical behaviour of the system AISI 1018 carbon steel-hydrocarbon- solution NACE 1D196, in the presence of some organic compounds with corrosion inhibiting properties. This could serve to determine whether the efficiency and mechanism of the corrosion inhibitors is affected (and which way) by the presence of hydrocarbon.

2. EXPERIMENTAL

2.1. Organic Compounds Used

Table I Compounds Tested: Denomination and Chemical Structure in this paper.

Name	Chemical Structure	Denomination
8-hidroxiquinaldina, tereftaldehido		a) Hidro Q
2-piridin-2-yl-1H-benzoimidazol		b) Benzo
2-piridin-2-yl-oxazolo[4,5-b]piridina		c) Piridin
Tereftadehido 5,7-dicloro 2-metil-8-quinolinol		d) Tere

The compounds used are shown in Table I as well as the names that were given for the purposes of this paper. These compounds have been used before to evaluate its inhibition in acidic media without hydrocarbon [5], indicating good inhibition properties.

2.2. Experimental Setup

A typical three-electrode cell setup was used in electrochemical techniques with a Hg/HgCl(s)/KCl(sat) electrode as reference and a graphite bar as counter electrode. As working electrodes, discs of low carbon steel AISI 1018 (C 0.15/0.20%; Mn 0.60/0.90%; Si 0.15/0.30%; P max. 0.04%; S max. 0.05%) were used and coupled to a Teflon support. Prior to each experiment, electrode surface was abraded with 280 SiC emery paper.

The corrosive environment, similar to that used in the document NACE 1D196 [6], has the following composition: 0.0304M Calcium Chloride Dehydrate, 0.0101M Magnesium chloride hexahydrate and 1.824 M Sodium chloride saturated with CO₂ in the absence and presence of hydrocarbon in a ratio 8:2.

The solution was prepared with deionized water, deaerated with high purity nitrogen for 30 min. The following reagents were used (A. R. grade): 99% purity NaCl Baker; 100% purity MgCl₂ hexahydrate Baker, 99% purity CaCl₂ dehydrate Baker and kerosene (hydrocarbon) from Baker. Once the brine is prepared, it is purged with CO₂ (30 minutes per litre of brine). A controlled pressure of 10 lb/in² is used.

All experiments were performed at 49°C and after 10 minutes of immersion of the working steel electrode, allowing the corrosion potential stabilization. The potentiodynamic polarisation curves were registered at a scan rate of 0.1mV/s in a potential range between ± 300 mV (vs. o.c.p.) and each curve was obtained from a freshly abraded steel surface.

The electrochemical impedance spectroscopy (EIS) measurements were carried out with an amplitude of 10 mV (vs. o.c.p.) and in the frequency range of 10 mHz to 10 kHz. A Frequency Response Analyser (FRA) was used, coupled to a Potentiostat-Galvanostat Autolab Mod PGSTAT30 and managed through the software of the same company.

It is important to stress that all electrochemical experiments were carried out under hydrodynamic conditions, using a mechanic stirrer at 2000 rpm in order to achieve a homogeneous emulsion when kerosene was introduced in the model solution.

3. RESULTS AND DISCUSSION

3.1. Polarisation curves without hydrocarbon

Figure 1 shows the potentiodynamic Polarisation curves in the studied system when evaluated in the presence of organic compounds with inhibiting properties in several concentrations and in the absence of hydrocarbon. There is a similar behaviour for each compound evaluated in the system, since the increasing concentration of the inhibitor affects both anodic and cathodic processes, showing that the currents obtained are lower by increasing the concentration of the inhibitor. The

corrosion potential presented by the different systems is $-0.60 \pm 0.01\text{V}$ vs Hg /HgCl (s) / KCl (sat) (SCE), indicating that the initial surface conditions are nearly the same. However, it is important to notice, on the cathodic branch, that all compounds clearly have a diffusion controlled behaviour, which can be seen in the high cathodic slopes. Also it is noteworthy the behaviour that the inhibitor compounds evaluated present at the cathodic reaction, as they show a very significant change as the concentration increases it even more important than the anodic reaction, which indicates that the organic compounds used act mainly as cathodic inhibitors.

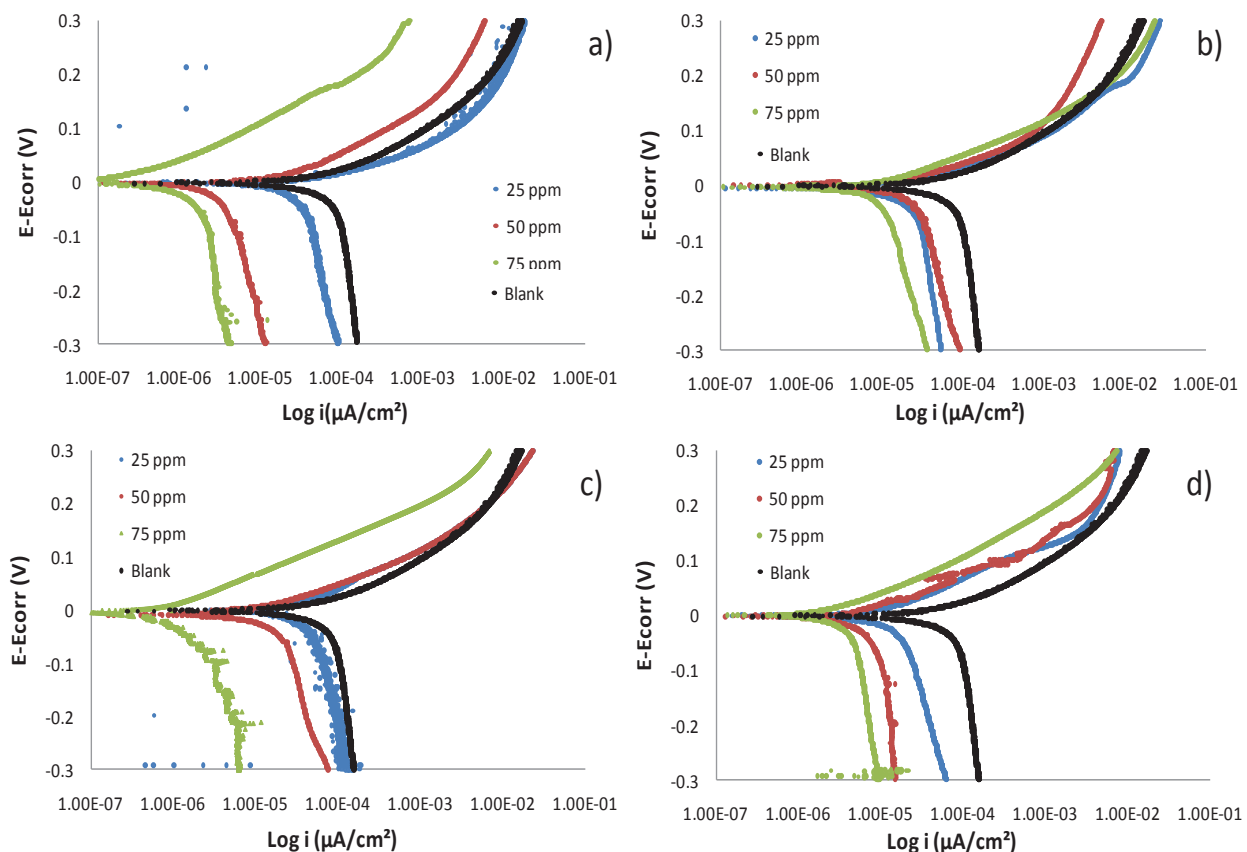


Figure 1. Polarisation curves obtained for a system of carbon steel AISI 1018 immersed in a solution NACE 1D196 and the compounds evaluated a) Hidro Q, b) Benzo, c) Piridin, d) Tere at different concentrations and in absence of hydrocarbon.

3.2. Polarisation curves in the presence of hydrocarbon

Figure 2 shows potentiodynamic Polarisation curves when evaluating the organic compounds at several concentrations and in the presence of hydrocarbon.

It is observed that when increasing the concentration of the compounds, cathodic and anodic reactions of the system are affected, decreasing the currents obtained. The corrosion potential, as in the

case of the absence of hydrocarbon, is $-0.60 \pm 0.01\text{V}$ vs Hg / HgCl (s) / KCl (sat) (SCE), indicating that the initial conditions of the surface are quite similar, even though the presence of hydrocarbon.

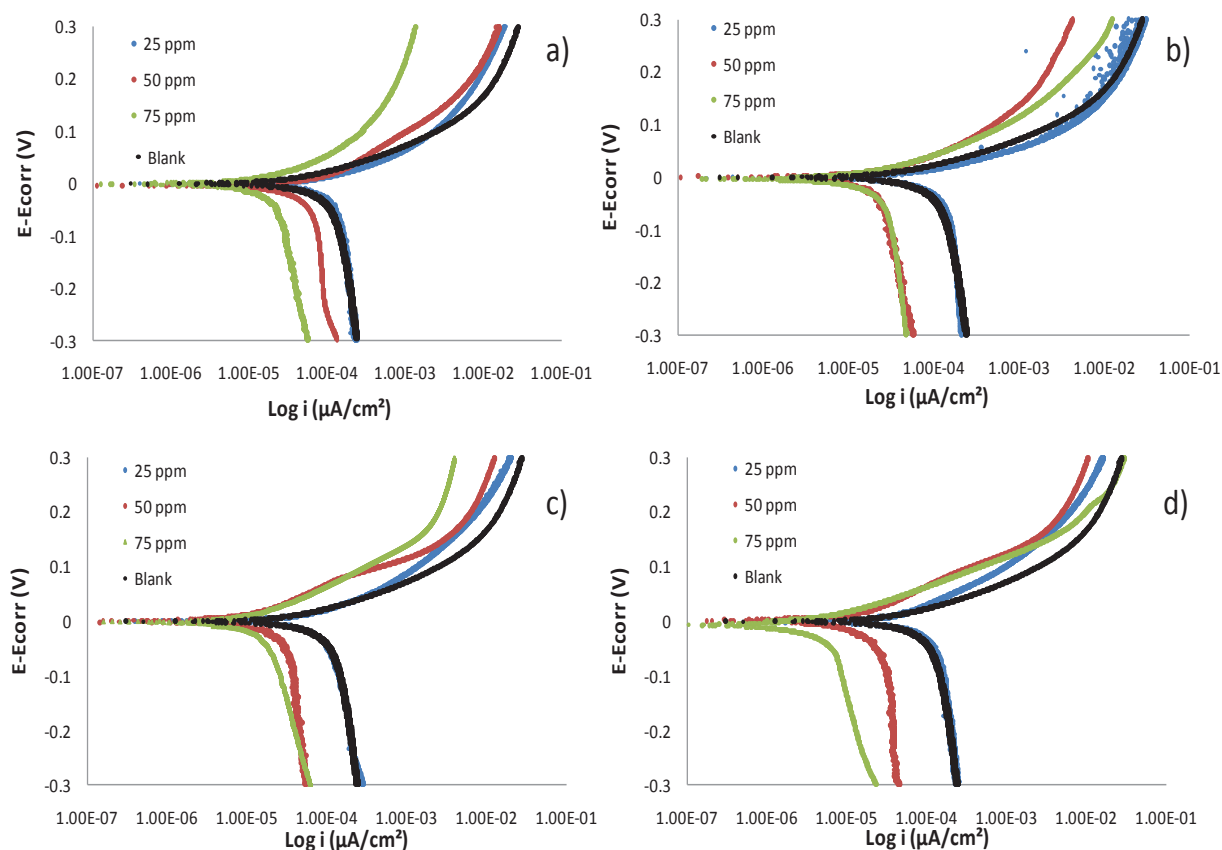


Figure 2. Polarisation curves obtained for a system of carbon steel AISI 1018 immersed in a solution NACE 1D196 and the compounds evaluated a) Hidro Q, b) Benzo, c) Piridin, d) Tere at different concentrations and in presence of hydrocarbon.

It is important to note that the currents shown by the system in the presence of hydrocarbon are higher than that in absence of the latter and the effect of the compound concentration is lower, though in some cases the effect is the same with 50 ppm or 75 ppm of concentration, as in the cases of Benzo and Piridin compounds. Such behaviour could be attributed to the presence of a hydrocarbon film in contact with the metal surface, which is constant and that somehow favours the interaction between the compounds or corrosive species and metal [7, 8].

In order to determine the values of some corrosion parameters such as the corrosion potential and Tafel slopes, an analysis of the polarisation curves was made.

3.3 Corrosion parameters for the system without hydrocarbon

In Table II the corrosion parameters (i.e. corrosion potential, anodic and cathodic slopes and the corrosion current), obtained from the potentiodynamic polarisation curves, are shown. Corrosion

potentials obtained showed a non-significant difference between them and the value of the “blank” system, indicating that the initial energetic conditions are nearly the same.

On the other hand, analysis of the polarisation curves show that the presence of the different organic compounds modifies the diffusive processes [9], since the values of anodic and cathodic slopes increase rapidly in the various systems showing non-Tafel behaviour. So, the values of the cathodic and anodic slopes were calculated, taking into account the diffusion processes, in the range of $E_{corr} \pm 60\text{mV}$, where the transfer control is assumed.

Table II. Corrosion parameters of different systems without hydrocarbon

Organic Composed		E_{corr} (V)	b_a (V/dec)	b_c (V/dec)
	Blank	-0.61	0.0635	-0.2174
Hidro Q	25 ppm	-0.60	0.0380	-0.2904
	50 ppm	-0.61	0.0672	-0.2220
	75 ppm	-0.61	0.0613	-0.2704
Benzo	25 ppm	-0.60	0.0679	-0.2904
	50 ppm	-0.59	0.0363	-0.2223
	75 ppm	-0.60	0.0445	-0.2705
Piridin	25 ppm	-0.61	0.0641	-0.1250
	50 ppm	-0.61	0.0406	-0.1538
	75 ppm	-0.60	0.0339	-0.1228
Tere	25 ppm	-0.60	0.0405	-0.0579
	50 ppm	-0.60	0.0342	-0.0513
	75 ppm	-0.61	0.0396	-0.0630

Values of the anodic slopes indicate that the transfer mechanism is being modified by the presence of the organic compounds, depending on the concentration. This effect is more evident for the Tere compound, where both slopes are indicative of a more active reaction [10,11], while Hidro Q presented anodic slopes similar to the blank at higher concentrations. This effect could be associated with the initial interaction of the organic compounds with the metallic surface, and could be modified through the immersion time. However this will be corroborated in posterior works.

Lorenz and Mansfeld [12] classified the modes of inhibition effect of interface inhibitors into that caused by the blocking effect of adsorbed inhibitive species on the metal surface and the electrocatalytic effect of the inhibitor or its reaction products. It has been discussed [13] in the case of the geometric blocking mode the inhibition effect comes from the reduction of the reaction area on the surface of the corroding metal, whereas for the electrocatalytic effect the inhibition properties are due to the changes in the average activation energy barriers of the anodic and cathodic reactions of the corrosion process. Thus, the electrochemical behaviour and the interpretation of the measured electrochemical data will not be the same for all modes. There are many factors affecting the inhibition efficiency of the organic compounds in acidic media [14].

According to Hackerman [15], the inhibiting properties of many compounds are determined by the electron density at the reaction center. With an increase in the electron density at the reaction center, the chemisorption bonds between the inhibitor and the metal are strengthened. Hackerman established the protective properties of pyridine and its derivatives and he found that, the ability of these compounds to reduce corrosion, are actually enhanced at higher electron densities around the nitrogen atom, according to the sequence: pyridine < 3-picoline < 2-picoline < 4- picoline. It is assumed that for organic compounds during the first ionization of the unshared pair electrons is detached, then the ionization potential can serves as a measure of the electron density at the nitrogen atom [14]. So, in the case of the compounds used in this work it is very probable that they are acting through their pairs of electrons unshared interacting with the metal surface, changing its energy barriers and affecting the corrosion mechanism which provokes corrosion products that in some cases could be insoluble and soluble in other.

3.4. Corrosion parameters for the system with hydrocarbon

As in the case of the system without hydrocarbon, the corrosion parameters for the system with hydrocarbon were calculated from the polarisation curves. These curves indicate that the presence of hydrocarbon favours diffusive processes, showing non-Tafel behaviour, that is why the calculation of slopes is also considered within the potential range of $E_{corr} \pm 60$ mV obtaining the corrosion parameters shown in Table III.

In the table it is observed that the corrosion potential remains almost unchanged, which is indicative of the same energetic conditions at the very beginning of the experiment. On the other hand, anodic slopes show high discrepancies between the increasing concentrations of each compound. However, the values of the anodic slopes are suggesting high surface activity and the control of the charge transfer process. In the case of the cathodic slopes, it is worth to mention that the values obtained in the presence of the organic compounds indicate that the diffusion processes diminished respect to the blank system, which also points toward the favouring effect to the corrosion process with the presence of hydrocarbon in the system.

Table III. Corrosion parameters of the different systems with hydrocarbon

Organic Composed		Ecorr (V)	ba (V/dec)	bc (V/dec)
	Blank	-0.60	0.0635	-0.2174
Hidro Q	25 ppm	-0.61	0.0530	-0.1287
	50 ppm	-0.61	0.0438	-0.1483
	75 ppm	-0.61	0.0576	-0.1803
Benzo	25 ppm	-0.60	0.0452	-0.1240
	50 ppm	-0.61	0.0344	-0.1302
	75 ppm	-0.60	0.0584	-0.1488
Piridin	25 ppm	-0.61	0.0688	-0.1299
	50 ppm	-0.61	0.0431	-0.1138
	75 ppm	-0.60	0.0582	-0.1575
Tere	25 ppm	-0.60	0.0679	-0.1227
	50 ppm	-0.61	0.0363	-0.1238
	75 ppm	-0.61	0.0445	-0.1229

In order to determine in a precise mane the effect of the presence of hydrocarbon on the corrosion inhibition with the compounds tested, Electrochemical Impedance measurements were performed, without and with hydrocarbon and different concentrations of the compounds.

3.5. Electrochemical Impedance behaviour of the system without hydrocarbon

Figure 3 shows the Nyquist diagrams as a result of the electrochemical impedance spectroscopy measurements for the system evaluating the different organic compounds (Hidro Q, Benzo, Piridin and Tere, incises a, b, c and d respectively) and in absence of hydrocarbon. They display in general, open semicircles indicating the presence of diffusive processes and increasing real and imaginary impedance values as the concentration of the organic compounds increases. However, it is worth to note that the presence of the organic compounds has a similar behaviour at high frequencies and they differ at the lower ones.

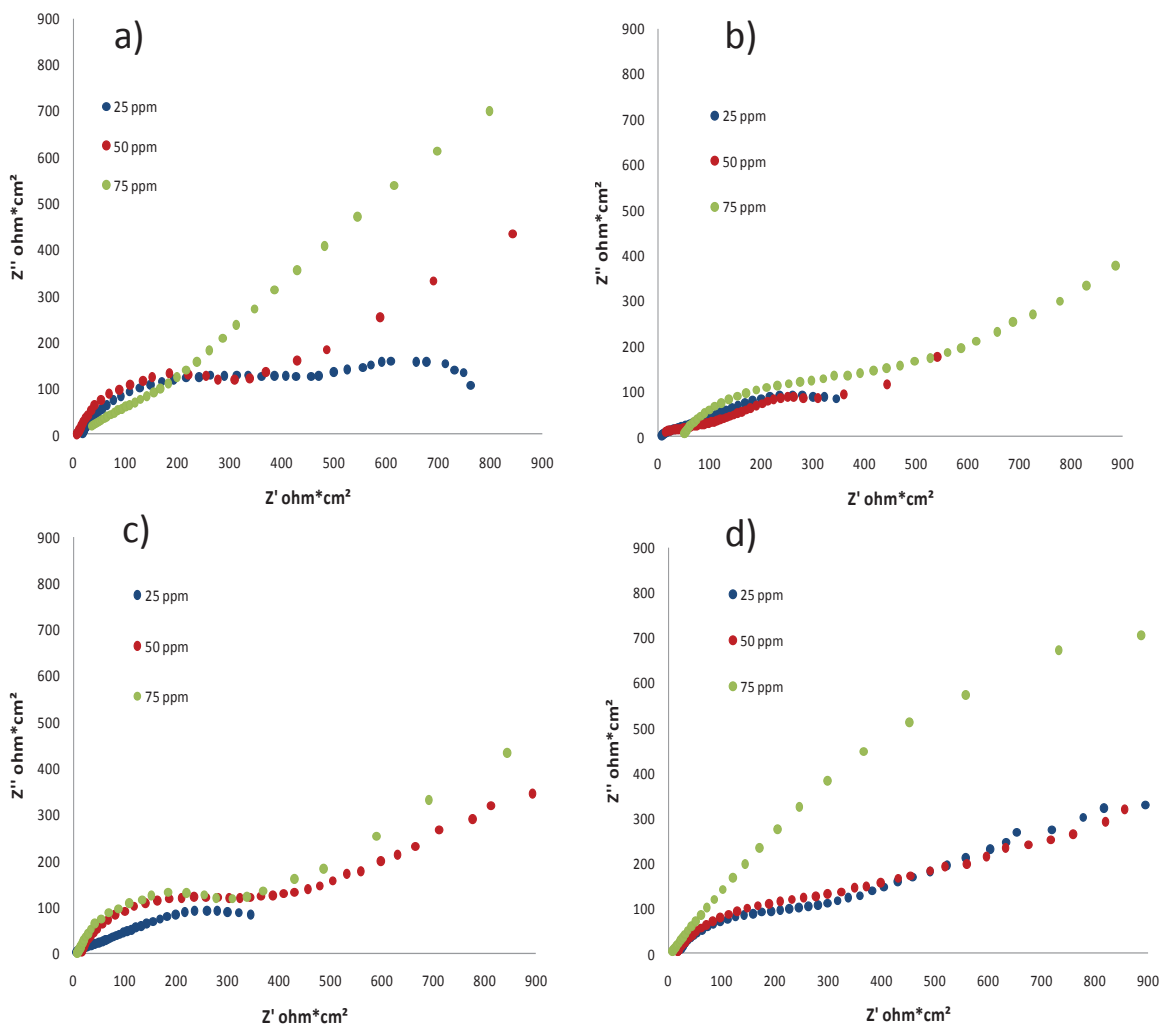


Figure 3. Nyquist diagrams for the system of carbon steel AISI 1018 immersed in a solution NACE 1D196 evaluating the compounds a) Hidro Q, b) Benzo, c) Piridin and d) Tere in the absence of hydrocarbon

Similar to the behaviour observed in the Polarisation curves, it appears that diffusive processes are very important [16,17,18], since all the compounds showed open semicircles with linear trend toward lower frequencies. This can be attributed primarily to the charge transfer and subsequent to the dissemination of either corrosion products into the solution or corrosive species into the surface [7,19,20,21].

3.6. Electrochemical Impedance behaviour of the system with hydrocarbon

Figure 4 shows the Nyquist diagrams of the system studied in the presence of the organic compounds used in this work (Hidro Q, Benzo, Piridin and Tere; incises a, b, c and d respectively) with the presence of hydrocarbon. Here is observed that the form of the semicircles changes respect to the system without hydrocarbon, becoming flattened semicircles with an adsorptive tendency, which

have been attributed to adsorption or dissolution processes [7,22,24]. The impedance values also diminished in comparison with the systems without hydrocarbon indicating higher corrosion rates. It could point to the increasing relationship between the steel surface and the concentration of the organic compounds in the neighbourhood which is increased by the presence of hydrocarbon, favouring the adsorption processes, which is corroborated because the behaviour at low frequencies is completely changed respect to the system without hydrocarbon [24,25,26]. Thus, it highlights the importance of the study because of the presence of hydrocarbon in a corrosion system can promote the adsorption of corrosive species but also the corrosion inhibiting compounds.

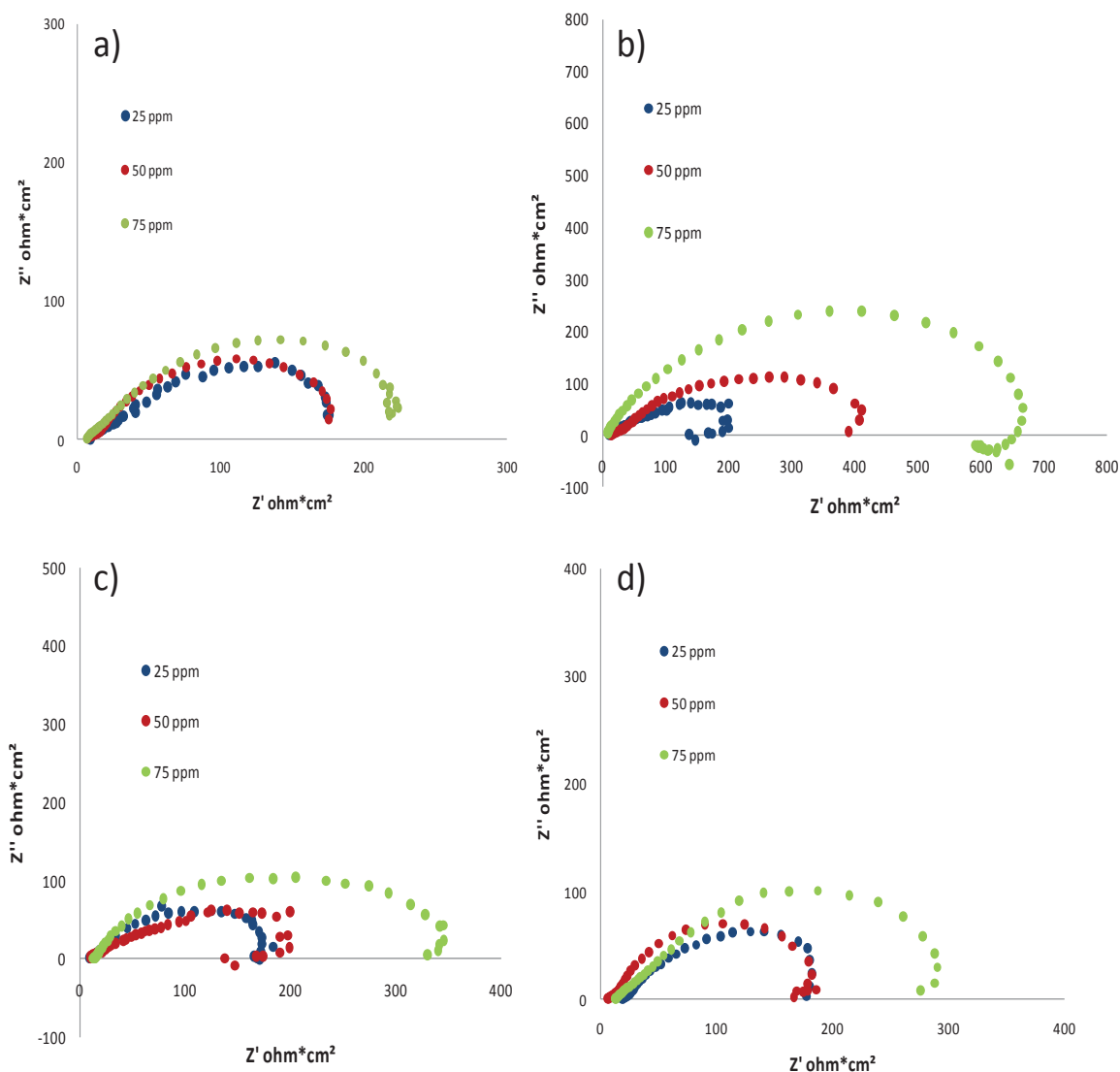


Figure 4. Nyquist diagrams for the system of carbon steel AISI 1018 immersed in a solution NACE 1D196 evaluating the compounds a) Hidro Q, b) Benzo, c) Piridin and d) Tere in the presence of hydrocarbon.

4. CONCLUSIONS

In the potentiodynamic Polarisation curves, the presence of the organic compounds in the system studied show that increasing its concentration have an effect on both, the anodic and cathodic, reaction rates, showing corrosion inhibition since the currents obtained are lower by increasing the concentration of the compound. The inhibition efficiency decreases with the presence of hydrocarbon in the system showing an increase in currents. However, the diffusive processes are still present in the system.

The use of the electrochemical impedance spectroscopy technique allowed us to demonstrate that the interaction of hydrocarbon with different organic compounds modifies the corrosion process and to observe that the presence of hydrocarbon favours the adsorptive processes and the arrival of the corrosive agents to the metal surface by generating corrosion products soluble in some cases or insoluble in other.

ACKNOWLEDGMENTS

To PROMEP by the project UAEHGO-PTC-293 and CONACYT for Basic Science project 00023889, these provided financial resources to acquire the infrastructure used in this work.

References

1. Z.A. Foroulis, "Role of solution pH on wet H₂S cracking in hydrocarbon production", Corrosion Prevention & Control, (1993) 84.
2. B. R. Álvarez, S. G. Negrón, Q. M. Abreu, H.H. Herrera, M. Romero, A. Cuán., P. M. Palomar., *Electrochimica Acta*, 54, (2009) 5393.
3. M.A. Veloz, I. Gonzalez, *Electrochim. Acta*, 48 (2002) 135.
4. I. V. Sieber, H. Hildebrand, S. Virtanen, P. Schmuki., *Corros Sci* 48 (2006) 3472.
5. Method NACE 1D196 "Laboratory Test Methods for Evaluating Oilfield Corrosion Inhibitors", NACE, (1996).
6. B. Esparza Zúñiga, Tesis UAEH, Pachuca, Hgo., México, 2007.
7. Kedam M., Mattos O. R., Takenouti H., *J. Electrochem. Soc*, 128 (1981) 257K. Magne, *J. of Disp. Sci. and Tech*, 27 (2006) 587.
8. M. M. Singh, A. Gupta, *Corrosion*, 56 (2000) 371.
9. H. Ma, X. Cheng, G. Li, S. Chen, Z. Quan, S. Zhao, L. Niu, *Corros. Sci.*, 42 (2000) 1669.
10. M.G. Hosseine, M. Ehteshamzadeh and T. Shahrabi : *Electrochim. Acta*, 25 (2007)3680.
11. H.E. El Ashry, A. El Nemr, S.A. Esawy, S. Ragab, *Electrochimica Acta* 51 (2006) 3957.
12. W.J. Lorenz, F.Mansfeld., in: proceeding of the 6th Symposium on European Inhibition of Corrosion, University of Ferrara, Ferrara, 1985, p. 23.
13. C. Cao, *Corros. Sci.*, 38 (1996) 2073.
14. S.A.Abd El-Maksoud, *Int. J. Electrochem. Sci.*, 3 (2008) 528-555
15. R.R. Annand, R.M. Hurd, N. Hackerman, *J.Electrochem. Soc.*, 112 (1965) 1968
16. H. Nord, G. Bech-Nielsen, *Electrochim. Acta*, 16 (1971) 849.
17. C. Azevedo, P. S. A. Bezerra, F. Esteves, C. J. B. M. Joia, O. R. Mattos, *Electrochim. Acta*, 44 (1999) 4431.
18. D. Wang, S. Li, M. Wang, H. Xiao, Z. Chen, *Corros. Sci.*, 41 (1999) 1911.
19. H Ashassi, T.A Aliyev, S Nasiri, R Zareipoor, *Electrochimica Acta*, 52 (2007) 5238.
20. Lj. Vracar, D. M. Drazic, *J. Electroanal. Chem.*, 339 (1992) 269.

21. A. Benmoussat, M. Hadjel, *Journal of Corrosion Science and Engineering*, 7 (2005)14.
22. D. M. Drazic, *Modern Aspects of Electrochemistry*, Plenum Press, New York. (1990).
23. Liu, C., Bi, Q.; Leyland, A. Matthews A., *Corr. Sci.*, 45 (2003) 1243.
24. G.Z. Meng, et al, *Corros. Sci.*, 50 (2008) 3116.
25. J.K. Heuer, J.F. Stubbings, *Corrosion*, 54 (1998) 566.
26. A.M. Alsabagh, M.A. Migahed , and H.S. Awadi., *Corros. Sci.*, 48 (2006)813.