

# Corrosion inhibition of pipeline steel grade API 5L X52 immersed in a 1 M H<sub>2</sub>SO<sub>4</sub> aqueous solution using heterocyclic organic molecules

P. Morales-Gil<sup>a,c</sup>, G. Negrón-Silva<sup>b</sup>, M. Romero-Romo<sup>a</sup>,  
C. Ángeles-Chávez<sup>c</sup>, M. Palomar-Pardavé<sup>a,\*</sup>

<sup>a</sup>Departamento de Materiales, Universidad Autónoma Metropolitana-Azcapotzalco, Av. San Pablo 180, Código Postal 02200, México City, DF, México

<sup>b</sup>Departamento de Ciencias Básicas, Universidad Autónoma Metropolitana-Azcapotzalco, Av. San Pablo 180, CP 02200, México City, DF, México

<sup>c</sup>Instituto Mexicano del Petróleo, Programa de Investigación y Desarrollo de Ductos, Eje Central Lázaro Cárdenas 152, CP 07730, DF, México

Received 14 January 2004; received in revised form 26 April 2004; accepted 20 May 2004

Available online 25 June 2004

## Abstract

The effect of the concentration of four types of inhibiting heterocyclic molecules on the corrosion susceptibility of steel pipeline samples grade API 5L X52 in 1 M H<sub>2</sub>SO<sub>4</sub> was studied by electrochemical testing and SEM analysis. The compounds used were: 2-mercapto-benzimidazole (MBI), 5-mercapto-1-tetrazoleacetic sodium salt (MTAc), 1-hydroxybenzotriazole (HBT) and benzimidazole (BIA). The results showed that there was an optimum inhibitor concentration at which the maximum inhibiting efficiency, IE, was reached. Further, the MBI displayed the best inhibiting characteristics for this system, with a maximum IE of approximately 99% having added only 25 ppm. It is shown that this compound can affect both the anodic and cathodic processes, thus it can be classified as a mixed-type inhibitor for API 5L X52 steel corrosion in sulphuric acid. Moreover, this compound follows an adsorption mechanism, which can be adequately described by the Langmuir isotherm with an adsorption standard free energy difference ( $\Delta G^\circ$ ) of  $-28.5 \text{ kJ mol}^{-1}$ .

© 2004 Elsevier Ltd. All rights reserved.

**Keywords:** Steel; Corrosion inhibition; Sulphuric acid; Benzimidazole; Adsorption

## 1. Introduction

Heterocyclic compounds are widely used in diverse industries for preventing corrosion of different metallic materials, for example carbon steel, in rather a wide variety of environments. An assortment of organic compounds having two or more heteroatoms such as O, N, S and multiple bonds in their molecular structure, are of particular interest because of their better inhibition efficiency as compared to those containing N or S alone [1]. The corrosion inhibiting properties of these compounds are empirically attributed to their molecular structure. Rather, the planarity of the molecule ( $\pi$ -bonds) and the delocalised electron pair present on the heteroatoms, are the salient structural features that determine the adsorption of these

molecules onto metal surfaces [2]. The effect of the molecular structure on chemical activity has been the subject of intense interest in every discipline in chemistry [3]. The selection of these inhibitors is based on their mechanism of action, for example their ability to donate electrons [4].

The use of inhibitors added in the liquid phase constitutes one of the most cost-effective methods to control steel corrosion in many industrial systems. It has been known for some time now, that inhibitor treatment programs for pipeline systems transporting hydrocarbons and other diverse fluids associated to operations of the petroleum extraction and refining enterprises, enable considerable savings to the oil industry. The efficiency of such large scale inhibitor-treatment programs mainly results from consideration of two aspects: first, the capability of the inhibiting compounds to provide continuous control on low corrosion rates of the systems involved, and second, their compliance with increasing standards of industrial security

\* Corresponding author. Tel.: +52 5 553189472; fax: +52 5 553189087.  
E-mail address: [mepp@correo.azc.uam.mx](mailto:mepp@correo.azc.uam.mx) (M. Palomar-Pardavé).

and stringent environmental protection standards. Presently, there is a variety of organic compounds that are used widely in industry for corrosion abatement and control in environmentally acid or basic conditions of operation.

A corrosion inhibitor is a substance, which lowers the corrosion rate after it has been added to a given stream of interest, within a system, which is presumed to be working under a set of corrosive conditions. Thus, additions of a substance in appropriately small concentrations that subsequently bring about a controllable reduction of the rate of measurable chemical wastage, without effecting reductions to the concentration of the corrosive species present, represent a fundamental aspect of a highly desirable, safe and economic kind of operation. Therefore, an inhibitor is considered to be effective when it reduces the corrosion rate present in low concentrations, such as those of the parts per million ranges.

The inhibiting mechanism has been attributed to the existence of a basic polar group of the molecule, which is adsorbed over the anodic/cathodic sites of the steel surface immersed in the corrosive environment. It would seem that when the hydrophobic molecular segments, or as it were the tails, of the adsorbed molecules extend into the bulk of the solution, there forms a relatively dense, self-arrangement of projecting tails that remain head-anchored onto the metal surface, which due to their overall polarity, are capable of constituting a corrosive species-repellent layer that affords protection; thus, this is assumed as a form of protective coating that lowers the rate of at least one of the reactions responsible of corrosion [5]. Hence, the inhibitor functions usually as a producer of a protective monomolecular coating of adsorbed inhibitor, which in order to be considered technologically fulfilling, it should display two desirable features: a prolonged durability under hydrodynamic conditions of flow, and a significant imperviousness toward hydrogen-bearing compounds, to aid preventing its diffusion and subsequent adsorption onto the metal surface, thus avoiding metal hydrogen damage.

Another alternative is that the protective coating is formed due to chemical reactions between the metal and the inhibitor, possibly when assorted corrosion products are involved. Other possibility is that a thin coating (>100 nm) of inhibitor is formed, over the metal surface. The steps building up the mechanism of corrosion inhibition suggested here are still unknown, although it has been proposed that changing the polar group of these molecules produce their attachment to anodic/cathodic sites on the corroding steel surface. The hydrophobic part of the molecules extends into solution where oil can be coadsorbed, producing a protective film/barrier that retards corrosion of the steel.

The inhibitors are classified as anodic, cathodic or mixed, depending on which reactions become inhibited during the corrosion process. A mixed inhibitor influences both the anodic and cathodic processes likely to be taking place; many inhibitors belong to this sort. The benzotriazole can be considered an example of the latter. The character of the

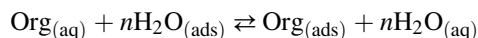
inhibitor depends on environmental factors, such as the pH and the redox potential, so they may be anodic or cathodic under certain conditions.

The selection of inhibitors is obviously related to their mechanism of action, and to other more fundamental characteristics such as their electron-donating ability [4]. In the present investigation, we report on the effect of the inhibitor concentration of four types of heterocyclic molecules in 1 M sulphuric acid on the corrosion rate of pipeline steel samples grade API 5L X52, being the objective to determine the corrosion inhibition efficiency of organic compounds containing N and S, and N and O. The inhibiting heterocycles tested were 2-mercaptobenzoimidazole (MBI), 5-mercapto-1-tetrazoleacetic sodium salt (MTAc), 1-hydroxybenzotriazole (HBT) and benzimidazole (BIA). The electrochemical testing procedure performed to conduct adsorption measurements that are related to the standard free energy of adsorption was the linear polarization method.

## 2. Inhibition mechanism

Corrosion inhibition features of several substances are directly associated to adsorption phenomena, which can follow different types of isotherms such as those of Temkin, Langmuir, Freundlich and Frumkin that have been employed to rate adsorption phenomena over steel electrodes [6,7].

The adsorption of organic inhibitors at an electrode/electrolyte interface may take place through displacement of adsorbed water molecules at the inner Helmholtz plane of the electrode, likely in agreement with the following reaction scheme [6]:



If it is assumed that the steel electrode is corroding uniformly, then the corrosion rate in the absence of inhibitors is representative of the total number of corroding sites. Consequently, the corrosion rate in the presence of inhibitors may be assumed to represent the number of potentially corroding sites that remain after blockage due to inhibitor adsorption [7].

The fractional surface coverage ( $\theta$ ) is represented by the following equation:

$$\theta = \frac{i_{\text{corr}}(\text{blank}) - i_{\text{corr}}(\text{inhibited})}{i_{\text{corr}}(\text{blank})} \quad (1)$$

where  $i_{\text{corr}}(\text{blank})$  is the corrosion rate of the steel without inhibitor addition and  $i_{\text{corr}}(\text{inhibited})$  is the corrosion rate in the presence of the inhibitor [8]. As mentioned before, four isotherm adsorption models can be employed to determine empirically which adsorption isotherm fits best the surface coverage data. The equations pertaining to the adsorption models cited are:

Temkin's model:

$$K_{ad}C = e^{f\theta} \quad (2)$$

Langmuir's model:

$$K_{ad}C = \frac{\theta}{1-\theta} \quad (3)$$

Freundlich's model:

$$K_{ad}C^{1/n} = \theta \quad (4)$$

Frumkin's model:

$$K_{ad}C = \left( \frac{\theta}{1-\theta} \right) e^{f\theta} \quad (5)$$

where  $K_{ad}$  is the adsorption equilibrium constant,  $C$  the concentration, and  $f$  is the molecular interaction constant.

Once a suitable adsorption isotherm has been selected, the corrosion rate measurements can be used to calculate the thermodynamic data pertaining to adsorption of the inhibitors tested. The standard free energy of adsorption ( $\Delta G_{ad}^\circ$ ) can be evaluated with the following expression:

$$\Delta G_{ad}^\circ = -RT \ln(K_{ad}) \quad (6)$$

### 2.1. Evaluation

It is relevant to point out that many substances had been introduced purportedly to work like inhibitors, of which quite a few have shown little promise. Therefore, it is indeed important to evaluate the inhibitor candidates and to determine the conditions of their effectivity. The inhibiting efficiency (IE), can be expressed with the following equation [9]:

$$IE = \frac{i_{corr}(\text{blank}) - i_{corr}(\text{inhibited})}{i_{corr}(\text{blank})} \times 100 \quad (7)$$

## 3. Experimental

In the present work, the commercially available inhibitors (without any further preparation) were dissolved, in a simple mixture of solvents, to produce solutions with adequate concentrations to be added into the experimental electrochemical cell containing the electrolyte. The molecular structure of the used inhibitors is shown in Fig. 1.

All reagents were purchased from Aldrich as reagent grade materials; the organic solutions from the MBI, MTAc, HBT and BIA, tested as corrosion inhibitors, were dissolved in ethanol/water 1:1 to make 0.01 M solutions. Thereafter solutions containing (5–1000 ppm) of each inhibitor were prepared by dissolving them in an aqueous 1 M  $H_2SO_4$  solution. A three-electrode electrochemical cell was used. The working electrode was made from API 5L X52 steel pipeline samples in such a form that a disc of 0.82 cm<sup>2</sup> area was exposed to the electrolyte; the surface was polished with

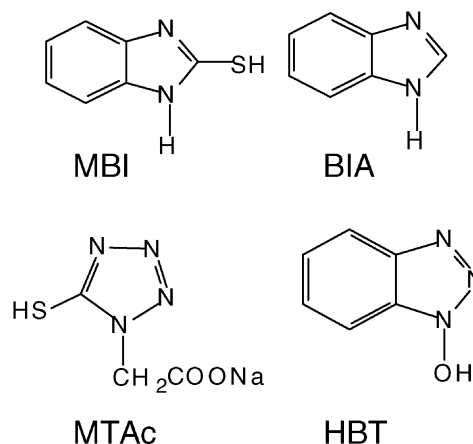


Fig. 1. Molecular structure of the heterocyclic compounds tested as corrosion inhibitors of API X52 pipeline steel samples immersed in 1 M sulphuric acid aqueous solutions.

different grades of alumina down to 0.3  $\mu\text{m}$  and ultrasonically cleaned before the experiments. A saturated calomel electrode (SCE) was used as reference along with a graphite rod as auxiliary electrode for all electrochemical measurements. The electrochemical cell was connected to a computer-controlled potentiostat–galvanostat (ZRA PC3 GAMRY) with the CMS100 and CMS105 softwares to exert control of the imposed conditions and to acquire data. Linear polarization (LP) measurements were conducted in the potential range  $[-20 \text{ mV} \leq E_{ocp} \leq 20 \text{ mV}]$  with a scan rate of  $0.125 \text{ mV s}^{-1}$ .  $E_{ocp}$  represent the open circuit potential of the cell. From these experiments, the polarisation resistance ( $R_p$ ) of each system was obtained. After the electrochemical corrosion testing the corroded samples were characterized by means of scanning electron microscopy, SEM, ESEM XL 30, using an accelerating voltage in the 20–25 kV range and secondary electrons imaging. Compositional results were obtained using the EDX module attached to the microscope.

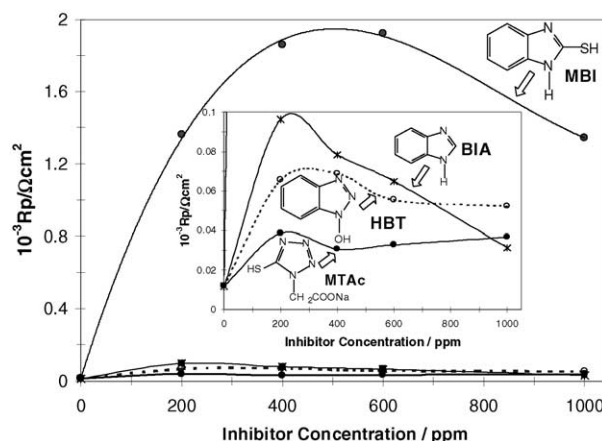


Fig. 2. Variation of the polarization resistance of API 5L X52 pipeline steel sample immersed in  $H_2SO_4$ , as a function of the concentration of the different organic compounds tested, as shown in the figure. Inset shows the same graph but for a smaller  $R_p$  range.

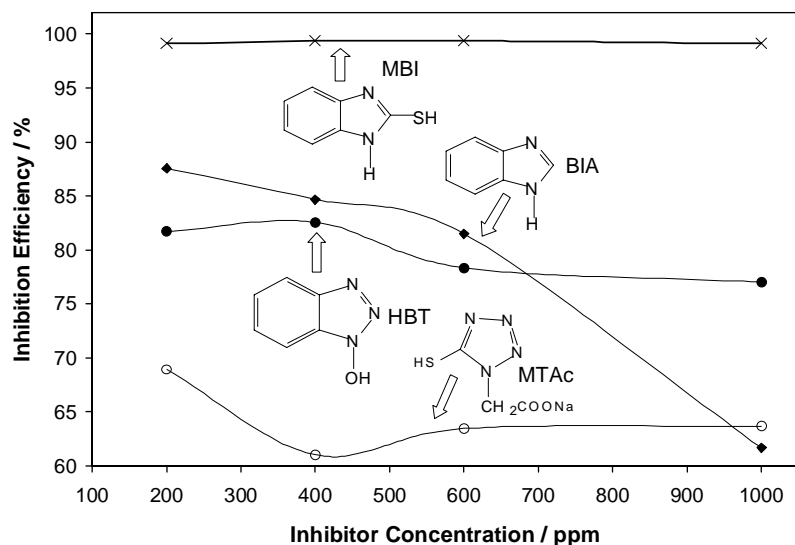


Fig. 3. Variation of the inhibition efficiency of the MBI, BIA, HBT and MTAc inhibitors as a function of their concentration/ppm.

#### 4. Results and discussion

Fig. 2 shows the variation of the polarisation resistance of an API 5L X52 steel sample exposed to  $H_2SO_4$ , containing different concentrations of the organic compounds tested. From the results, it becomes noticeable that the MBI is the compound exhibiting the best characteristics as corrosion inhibitor, as it may be deduced from the fact that the greater the polarisation resistance, the lower the corrosion current associated to a proportionally small rate of electrochemical metal dissolution.

##### 4.1. Inhibiting efficiency

Fig. 3 shows the inhibition efficiency of the four types of inhibiting molecules selected in this work as a function of

the inhibitor concentration, as evaluated with the Eq. (7). It becomes evident that the MBI molecule displayed the best inhibiting characteristics in this acid medium. When the concentration added was 200 ppm it reached 99% inhibition efficiency meanwhile, for the same amount of the other molecules, the IE was only 87.5, 82 and 68% for BIA, HBT and MTAc, respectively.

It is important to mention that recently, Quraishi and Sharma [2] have studied the applicability of 4-amino-3-butyl-5-mercapto-1,2,4-triazole as a new corrosion inhibitor for mild steel in sulfuric acid. The authors showed that IE for the compound reached only 60% when 200 ppm were added and that it was required to add 5 times that amount to attain 90% IE. In that same respect, Khaled [4] has studied benzimidazole derivatives as corrosion inhibitors of iron in 1 M HCl solutions and found that the 2-aminobenzimidazole

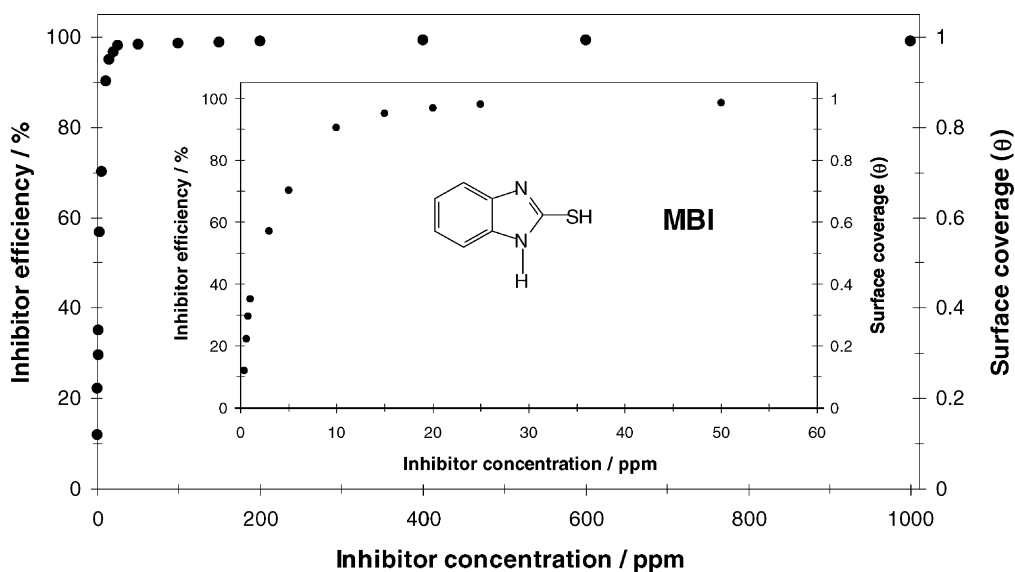


Fig. 4. Variation of the inhibitor efficiency (IE%), principal Y-axis, and surface coverage ( $\theta$ ), secondary Y-axis, as a function of the concentration evaluated in the system API 5L X52 steel/1 M  $H_2SO_4$ , x ppm MBI. Inset shows the same graph but for a smaller range of the inhibitor concentration.

exhibited the best IE percentages, namely 70.6–78.2, in this system. However the amounts required were in the range of 1000–6000 ppm approximately.

The adsorption of these molecules depends mainly on certain physicochemical properties such as the chemical nature of the functional groups, steric factors, aromaticity, electron density of the donor atoms, the  $\pi$  orbital character of the donating electrons [9–13], and the electronic structure of the molecules [14,15], to name but the most important ones. Presently, from a comparison of the molecular structure and the respective IE of both MBI and BIA compounds,

it becomes possible to advert the influence of the presence of S in the molecular structure; in the MBI inhibitor the delocalised electron pair present in the sulphur atom is an important structural feature that determines the adsorption of this molecule onto the metal surface.

It is relevant to note that although the polarization resistance appears to diminish slightly in the case of the MBI inhibitor when the concentration reached 1000 ppm, this fact has very little significance upon the efficiency of the inhibitor and therefore on the degree of coverage as can be noted also in Figs. 3 and 4.

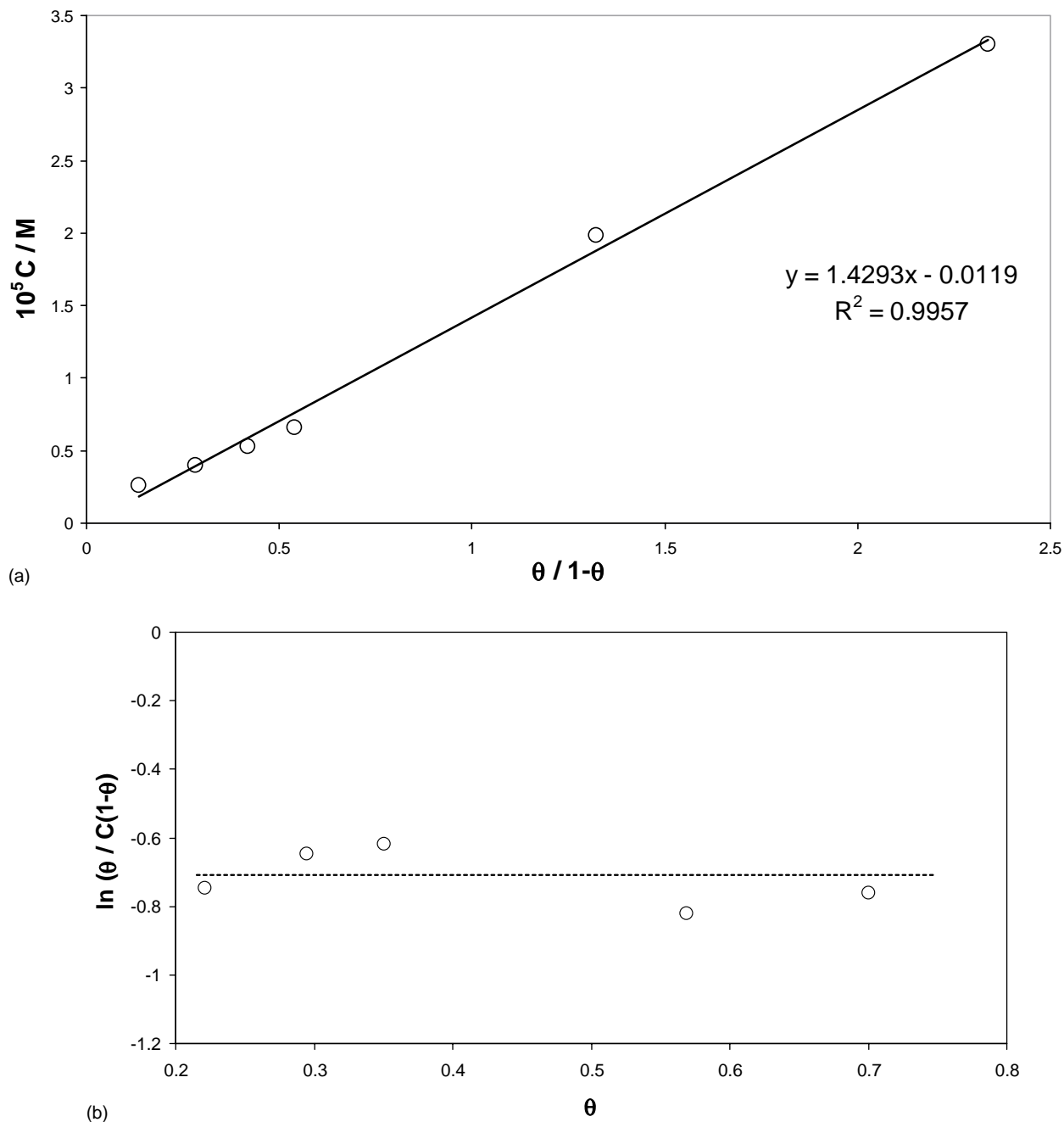


Fig. 5. (a) Comparison between the experimental adsorption isotherm (○) for the MBI inhibitor in the system API 5L X52 steel/1 M  $H_2SO_4$ , x ppm MBI, and the theoretical model (—) proposed by Langmuir, Eq. (3). (b) Same experimental data plotted as a linearized form of the Frumkin isotherm, Eq. (5).

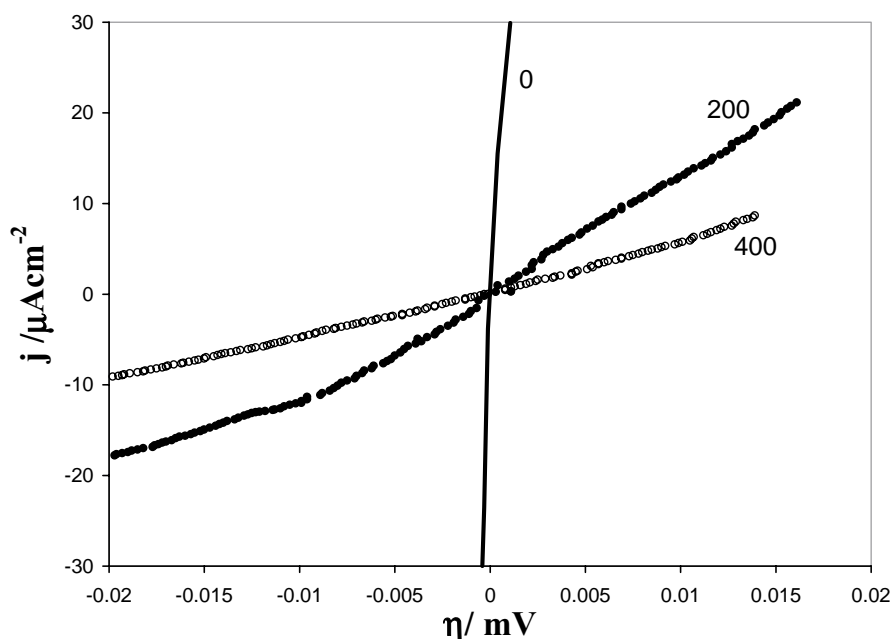


Fig. 6. Experimental linear sweep polarization curves recorded in the system API 5L X52 steel/1 M H<sub>2</sub>SO<sub>4</sub> with different MBI concentrations as shown in the picture, in ppm.

However, in the case of the BIA inhibitor it is possible to observe a large drop in both: polarization resistance (see Fig. 2) and inhibiting efficiency (see Fig. 3). A similar behaviour has been reported by Abdennabi et al. [3], who reported a drop in the inhibition efficiency as result of increasing the concentration of the compound used, 1-(4-bromobenzyl)-1-H-4,5-dibenzoyl-1,2,3-triazole (BBDBT), allegedly due to a decrease in solubility of the inhibitor in the hydrochloric acid testing media. It is our belief that the reason adduced by Abdennabi et al., does not fully explain the drop in inhibiting efficiency. The decrease in solubility of the BBDBT would only give a plausible explanation as to why the efficiency did not increase, but it cannot explain the efficiency decrease. The efficiency decreased because the inhibitor is desorbing from the substrate surface due to interactions among the inhibiting molecules already adsorbed and those present in the solution. A likely explanation for this to occur is that the attached molecules interact with other incoming molecules to form some sort of soluble oligomers which cause secondary desorption, thus the efficiency decreases. The said interaction becomes stronger as the concentration of the inhibitor raises in solution, which would appear to be consistent with our own findings.

#### 4.2. MBI inhibitor characterization

As it is possible to note from Fig. 4, the highest IE for the MBI molecule can be reached with as small a quantity as 25 ppm, and that it remains constant with further additions. The latter remark underlines the economic viability of the MBI as candidate inhibitor for large-scale treatment programs, where the cost-effectiveness must be based, per

necessity, on the amount added to very large volumes of process fluids streams.

The experimental corrosion current values and Eq. (1) served to obtain the fractional surface coverage ( $\theta$ ) due to the presence of the inhibitor molecules as a function of their concentration. With this information and the adsorption models represented by Eqs. (2)–(5), it was possible to determine which of the adsorption models would better explain the behaviour associated to the experimental results. It turned out to be that the Langmuir model represented by Eq. (3) permitted to fit best the experimental results obtained with the MBI inhibitor (see Fig. 5a). It is important to note that the Langmuir model is a particular case of the more general model described by the Frumkin isotherm (Eq. (5) and that both models should coincide when the interaction parameter ( $f$ ) is zero. Thus to verify that no lateral interactions are involved and to be able to reject the Frumkin isotherm, we plotted the experimental data in the form:  $\ln[\theta/C(1 - \theta)] = f(\theta)$ , which corresponds to the linearization of Eq. (5), see Fig. 5b. It is clear from the figure that, in this case, the  $f$  parameter is practically zero.

Table 1, summarizes the MBI adsorption parameters, as obtained from the fitting procedure of Eq. (3) to the experimental data shown in Fig. 5a. It is relevant to mention that when the 4-amino-3-butyl-5-mercapto-1,2,4-triazole

Table 1

Estimation of the adsorption constant ( $K_{ad}$ ) and the standard free energy of adsorption ( $\Delta G_{ads}^\circ$ ) of the MBI inhibitor in the system API 5L X52 steel in 1 M H<sub>2</sub>SO<sub>4</sub>; the experimental isotherm was fitted with the Langmuir model

Substrate	API 5L X52
Corrosion inhibitor	MBI
$\Delta G_{ads}^\circ$ (kJ mol <sup>-1</sup> )	-28.5
$\ln(K_{ad})$	11.51

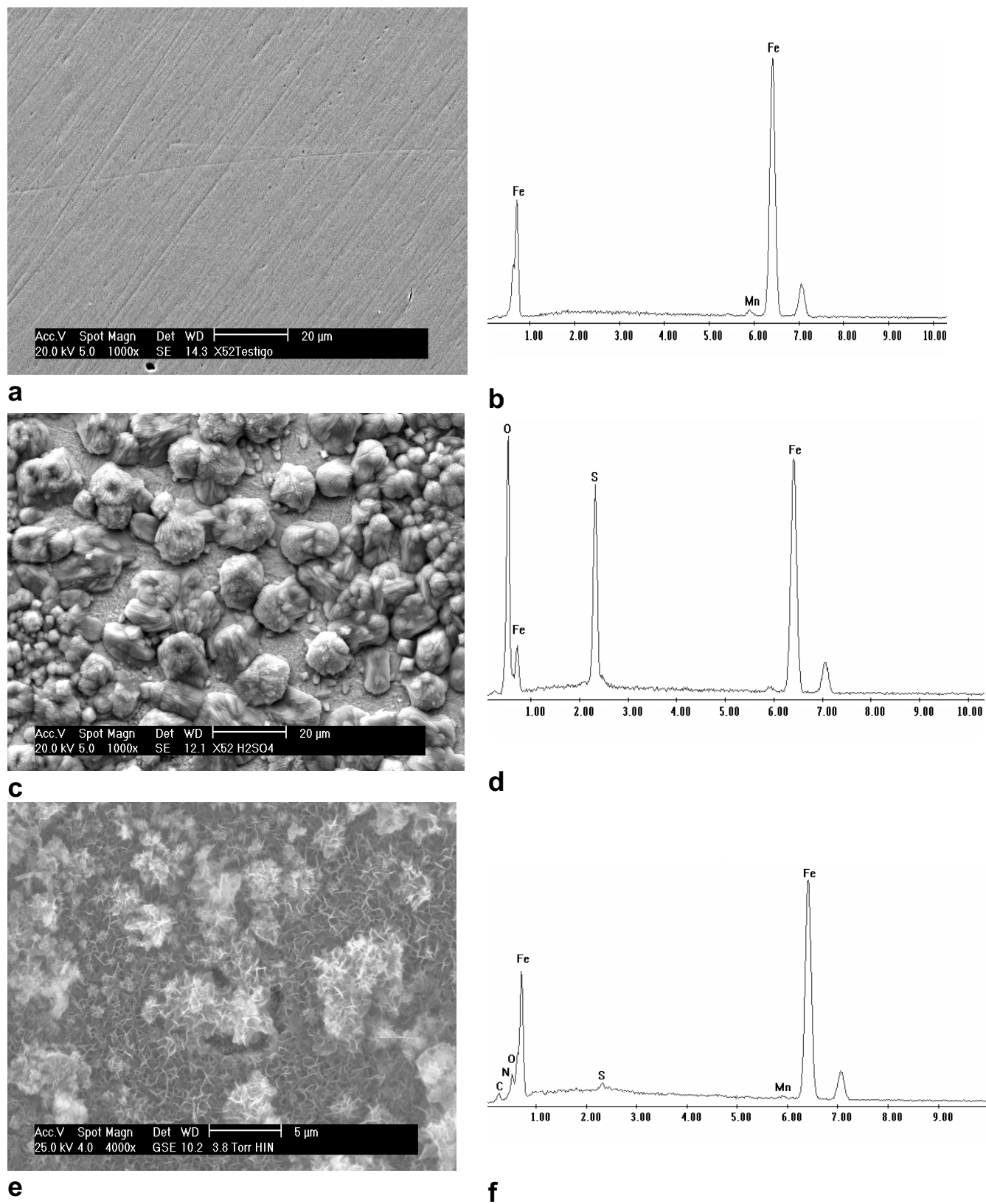


Fig. 7. Secondary electron images and their corresponding EDX analyses, of the API 5L X52 surface: (a–b) prior to exposure to the medium, (c–d) after immersion in the aqueous solution containing 1 M  $\text{H}_2\text{SO}_4$ , and (e–f) exposure in the said medium plus 600 ppm addition of the MBI inhibitor.

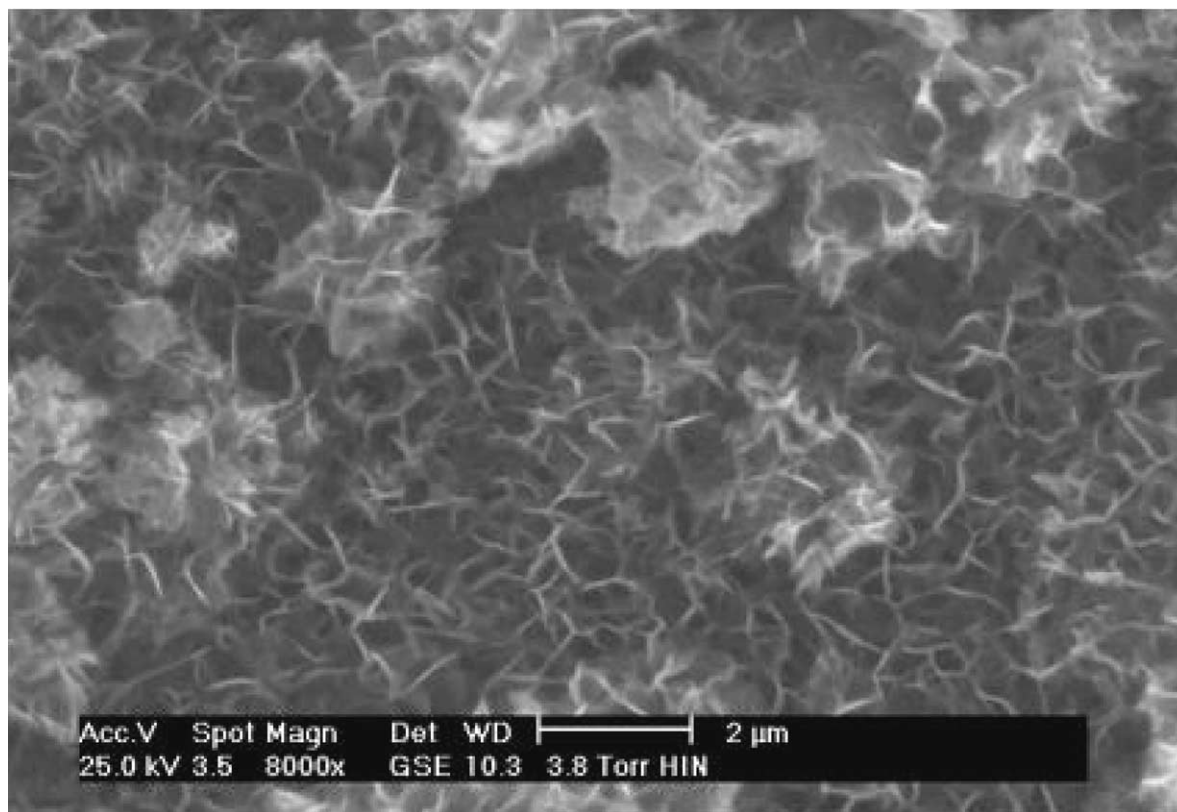


Fig. 8. Secondary electron image of the steel surface: details of the surface that resulted after treatment in the system API 5L X52/1 M  $\text{H}_2\text{SO}_4$  containing 600 ppm of the MBI inhibitor.

molecule was tested as a corrosion inhibitor of mild steel in  $\text{H}_2\text{SO}_4$  [2], it was found that the Temkin model described better its adsorption behaviour with an adsorption free energy of about  $-11.34 \text{ kJ mol}^{-1}$ .

From Fig. 6 it is possible to note that the MBI molecules can affect both the anodic and cathodic process, thus it can be classified as a mixed-type inhibitor for API 5L X52 steel corrosion in sulphuric acid.

Fig. 7 shows the results of the SEM analysis on the topography of the samples examined. Fig. 7a reveals some of relevant surface characteristics of the steel before exposure to the corrosive environment, while Fig. 7b presents the microanalysis that resulted from energy dispersive analysis, EDX, it becomes clear that it corresponds to the basic elemental composition of the steel. Fig. 7c presents the micrograph obtained after the steel sample was immersed in the 1 M  $\text{H}_2\text{SO}_4$ , and Fig. 7d shows the corresponding elemental microanalysis, from these results it is straightforward that in this case, nodular corrosion products having a sulfate-rich composition were formed. Fig. 7e reveals the surface of the steel sample after exposure to the 1 M  $\text{H}_2\text{SO}_4$  containing the MBI inhibitor at the concentration that represented the highest polarization resistance value and the greatest inhibition efficiency and Fig. 7f shows the corresponding EDX microanalysis. It is important to stress out that when the MBI compound was present in the solution, the morphology of the steel surface is quite different from both the previous ones

and that the MBI molecules are still present on the substrate surface possibly forming some kind of complex with iron. Furthermore, corrosion products having a sulfate-rich composition were not formed.

Fig. 8 shows the details at a greater magnification of the API 5L X52 surface after exposure to the medium containing the MBI inhibitor. It becomes plain the presence of a corrugated surface topography mainly due to formation of a complex morphology resembling a cellular distribution of flakes, some of them gathered in more dense formations, which covered the steel.

## 5. Conclusions

The results proved that the 2-Mercaptobenzoimidazole (MBI) compound displayed noticeable corrosion inhibition features for pipeline steel grade API 5L X52 samples immersed in 1 M  $\text{H}_2\text{SO}_4$ . The corrosion inhibition efficiency of the molecule can reach high values, greater than 98% with very small additions of MBI, namely 25 ppm. From the electrochemical evaluation of these systems it was found that the MBI adsorbs on the steel surface following the Langmuir isotherm model and that it can affect both anodic and cathodic processes during the corrosion course. From SEM and EDX analysis of the steel surface in the absence and presence of MBI it was possible to note that MBI



molecules remained in the surface after exposure to the acid medium preventing the formation of sulphate-containing corrosion products.

### Acknowledgements

The authors wish to express their gratitude to Departamento de Materiales of the DCBI-UAMA for the support given through projects 2260220 and 2260225, and to the IMP for project 0041. PMG would like to thank CONACYT for the studentship to carry out her postgraduate studies and to the IMP for the complementary grant received through project 0041. GNS, MRR and MPP gratefully acknowledge the SNI for the distinction of their membership and the stipend received.

### References

- [1] G. Schmitt, Br. Corros. J. 19 (1984) 165.
- [2] M.A. Quraishi, H.K. Sharma, Mater. Chem. Phys. 78 (2002) 18.
- [3] A.M.S. Abdennabi, A.I. Abdulhadi, S. Abu-Orabi, Anti-Corros. Met. Mater. 45 (1998) 103.
- [4] K.F. Khaled, Electrochim. Acta 48 (2003) 2493.
- [5] S. Vasseghi, K. Nobe, Corrosion 35 (1979) 300.
- [6] E. Schaschl, in: C.C. Nathan (Ed.), Corrosion Inhibitors, National Association of Corrosion Engineers, Houston, TX, 1981, p. 28.
- [7] J.L. Dawson, A.N. Rothwell, T.G. Walsh, K. Lowson, T.W. Palmer, in: Proceeding of the 48th Annual NACE Corrosion 93, Paper No. 108, 1993.
- [8] W. Durnie, R. De Marco, A. Jefferson, B. Kinsella, J. Electrochem. Soc. 146 (1999) 1751.
- [9] B.B. Damaskin, O.A. Petrii, V.V. Batrakov, Adsorption of Organic Compounds on Electrodes, Plenum Press, New York, 1971.
- [10] E. Mattson, Basic Corrosion Technology for Scientists and Engineers, second ed., The Institute of Materials, London, 1996.
- [11] F.B. Growcok, W.W. Frenier, P.A. Andrezzi, Corrosion 45 (1989) 1007.
- [12] I. Lukovits, E. Kalman, G. Palinkas, Corrosion 51 (1995) 201.
- [13] F. Bentiss, M. Lagrennee, M. Traisnel, B. Mernari, H. El Attari, J. Heterocycl. Chem. 36 (1999) 149.
- [14] F. Bentiss, M. Lagrennee, M. Traisnel, J.C. Hornez, Corros. Sci. 41 (1999) 789.
- [15] E. McCafferty, V. Pravdic, A.C. Zettlemoyer, Trans. Faraday Soc. 66 (1999) 237.