Electrochemical Impedance Spectroscopy Analysis of 2-Mercaptobenzimidazole (2MBI) as Corrosion Inhibitor in HCl 1M

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This work presents the results concerning the effect of different concentrations of an organic heterocyclic compound that displays corrosion inhibiting properties, known as 2-mercaptobenzimidazole, 2MBI, in a system comprising samples of the steel type API 5L X52 exposed to HCl 1M. The impedance spectra revealed that there was a continuous increase of |Z| as a function of increasing inhibitor concentrations in the electrolyte. A 200 ppm 2MBI was tested also, however, the greatest corrosion inhibiting efficiency was attained 99%, IE, with much smaller concentrations of the compound. This is sufficient reason to consider it a good corrosion inhibitor in HCl, just as it was effective for H_2SO_4. Furthermore, the inhibition kinetics study undertaken indicated that the 2MBI added in a fairly large concentration of 200 ppm in 1M HCl maintains its effectivity up to 32 immersion days. Also, it was observed that the corrosion potential, E_{corr}, became more negative as the 2MBI organic molecules concentration increased in the system, which suggests that this inhibitor may be acting on the cathodic and anodic sites, thus being considered a mixed type inhibitor, in agreement with the corrosion mixed potential theory.

Introduction

The oil industry in Mexico uses API standarized tubular oil country goods for the specific purpose of owning, building, operating and maintaining a relatively wide variety of pipelines, purchasing mostly API 5L X52-type steels for hydrocarbons or natural gas transport (1). Most of the lines are buried, whereby the national network extends over quite large distances, traversing varied terrains some with rivers, others with salt-laden marshes, and urban zones alike; the ambient temperatures for the pipelines network vary widely, to put it simply. Man-made attempts have been known to steal the hydrocarbons, though this necessarily means a disruption of their integrity. All this gives as result a complex service milieu that can be termed critical. It has become part of the operators' reality to contend with several corrosion problems that, in spite of many varied published proposals, do not seem to be effectively reduced in magnitude. Therefore, all persisting corrosion problems relate directly to ever-present economical and production losses as well as environment affectations, though human losses also happen (2).

The literature confirms (3) that as part of the normal operating conditions during crude oil transportation, the API 5L X52-type steels, have to face the presence of difficult-to-measure volumes of CO_2-saturated water having also H_2S. Pipeline steel corrosion does not only depend on the factors stated but on fluid dynamic conditions and non-equilibrium physico-chemical conditions, such as acidity variations, conductivity and diversity of ionic species dissolved. Other factors that can adversely affect have to do with pipeline fabrication, final laying out and effectiveness of surface protection methods implemented prior to commissioning the lines into service (4).

Internal corrosion problems may be reduced by providing effective inhibiting substances that are added to processing fluids: there is a wide variety of organic substances known to act as corrosion inhibitors. Recent studies have demonstrated that small inhibitor quantities can be added to the media to diminish its inherent aggressiveness toward the steel surfaces (5). Efficient inhibitors reported in the literature, have been functionalized organic compounds having various heteroatoms like sulphur, nitrogen and oxygen, and a relatively long hydrocarbon chain, also bearing conjugated π-type bonds and aromatic rings in their structure (6). Oil production employs traditionally several organic nitrogen-bearing compounds, usually as amines, imidazolines or ammonium quaternary salts that become adsorbed on the steels surface forming a film that interferes with the electrochemical reactions related with the corrosion process (7). Corrosion inhibitive properties of these compounds are attributed to their molecular structure. Planarity, the π electrons pair and the quantity of O, N and S heteroatoms used to be considered relatively important features thought to determine adsorptive strength for the inhibitor's molecules, capable of forming a physical protective barrier between the metal and the variety of fluids transported. The 2-mercaptobenzimidazole (2MBI) is a heterocyclic molecule that can act as organic inhibitor, which has a benzene ring and π orbitals plus a pentagonal nitrogenated ring. This compound is water insoluble and much used as antioxidant: it has also considerable stability at relatively high temperatures (8,9). Figure 1 shows the chemical structure of the 2MBI.
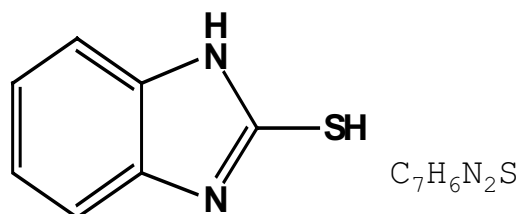

Figure 1. Molecular structure of the 2MBI used in this work as corrosion inhibitor.

The 2MBI has been electrochemically characterized previously by our research group (10) to study its corrosion inhibitive capability testing API 5L X52 pipeline steel samples immersed in 1M H_2SO_4, demonstrating that it needed only 25 ppm 2MBI to attain 99% inhibiting efficiency IE. However, it is our belief that its effectivity has not been tested in the presence of similar hydrochloric acid concentrations. The manner in which we will assess the IE of the 2MBI is by using the following expression (11):

$$IE = \frac{i_{corr}(blank) - i_{corr}(inhibitor)}{i_{corr}(blank)} \times 100 \qquad [1]$$

Where:

i_{corr} (blank) corresponds to the corrosion rate of the steel sample without inhibitor.

i_{corr} (inhibitor) is corrosion rate of the steel sample with inhibitor.

Thus, the purpose of the present work is to evaluate the inhibiting efficiency of 2MBI in 1M HCl aqueous solutions at different inhibitor´s concentrations aided by a small three-electrode electrochemical cell, modified to enable the use of fairly large, unembeded API 5L X52 specimens, to simplify metallographic manipulation and lessen electrolyte´s volumes during testing, employing electrochemical impedance spectroscopy, EIS.

Experimental

A 0.01M 2MBI solution was prepared from analytical grade reagent, mixing water and ethanol 1:1; aliquots were prepared containing 5, 15, 20, 50, 80 and 200 ppm and added to the testing electrolyte 1M HCl. The electrochemical study was done at room temperature aided by a IM6-Zahner frequency response analyzer applying a 10 mV sinusoidal perturbation within the 100KHz to 0.1 Hz frequency range. An Ag/AgCl mini-electrode was used as reference, with a graphite bar as counter electrode, while the working electrode was a sample of API 5L X52 having approximately 1 cm^2 exposed area, that was lightly polished with 0.3 µm alumina. The inhibiting efficiency was evaluated implementing the electrochemical EIS testing in 1 M HCl + inhibitor systems. The 2MBI inhibiting kinetics was evaluated to fairly long times, by exposing the surface of testing samples to the 1M HCl with added 200 ppm during 36 days at room temperature.

Results and discussion

Figure 2 shows the EIS results through BODE plots; it can be clearly noted from Figure 2a, that one time constant operated in the system at high frequency, which indicates that adsorption of the inhibitor took place on the metal surface. It becomes evident that testing with the largest 2MBI concentration, namely 200 ppm, there began to appear two time constants, which suggests that two different processes are involved during the perturbation. One is related to a molecular adsorption mechanism of the organic compound over the polished metal surface, thus giving rise to multilayers, while the second constant is related to infiltration of the corrosive species through assorted passages formed during self-assembly and rearrangement of the organic molecules, very probably due to the diversity of interactive forces operating on the electrodic system. This second time constant that operates at intermediate frequencies can be interpreted as a resistance to charge transfer.
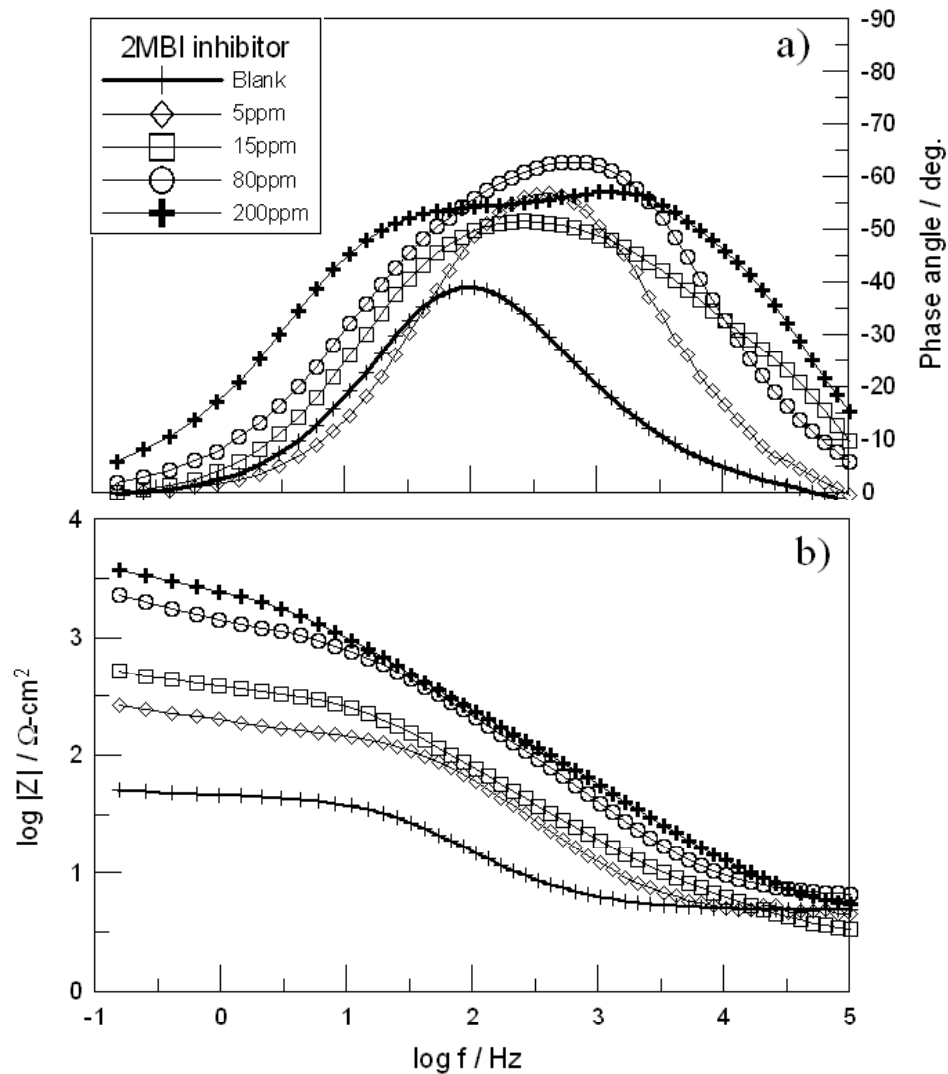
Figure 2. EIS-Bode plots obtained from the pipeline steel API 5L X52 samples immersed in 1M HCl as a function of the 2MBI concentration.

The plot of log Z vs log f, shown in Figure 2b, reveals that as the inhibitor concentration increases, so does the impedance, which is also related to the charge transfer resistance, Rct. This value was obtained through fitting a RC electrical circuit to the experimental data. The Z increment is explained by the excess inhibitor's molecules in the solution, which on being bipolar tend to adhere to the metal surface, also interacting among them thus forming a multilayered assembly, capable of blocking the charge transfer, refer to Figure 3, to appreciate more clearly the said Z increase.
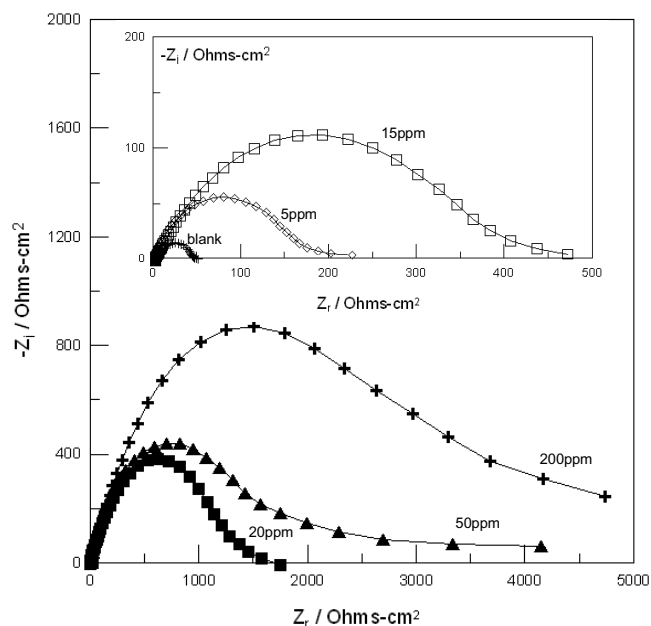
Figure 3. Impedance diagrams for the pipeline steel API 5L X52 samples immersed in 1M HCl as a function of the 2MBI concentration. The graph inset shows the impedance response for the blank.

The inset in Figure 3 shows, for the sake of comparison, the impedance diagram (real component, Z' vs. imaginary component, Z") without inhibitor, displaying a well defined loop that reached less than 50 Ω-cm^2. Also note that this value increases successively to 200, 500, 2000 and to 5000 Ω-cm^2 with increasing inhibitor concentration. In order to appreciate more clearly the data implications and to report on the inhibiting efficiency is necessary to obtain the value of the charge transfer resistance Rct, which is inversely related to the corrosion current, i, as in (1/Rct) (usually expressing the corrosion rate). From fitting the proposed electrical circuit to the experimental data, as shown in Figure 4, one obtains the parameters proper of the electrical circuit. The circuit "A" was used to characterize the system that contained from 5 to 80 ppm 2MBI or without inhibitor. A more complex electrical circuit like that shown in "B" "R(Q(R(QR)))", is used for the system containing 200 ppm de 2MBI. Figure 5 shows an example of the fitting procedure to the experimental data using the equivalent circuit "A", which is considered good because both plots match well.
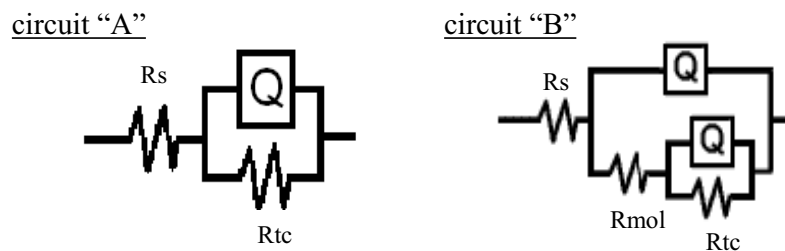

Figure 4. Electrical equivalent circuits used to describe the experimental EIS diagrams: Rs solution resistance, Q constant phase element, Rmol organic molecules resistance, and Rct charge transfer resistance.
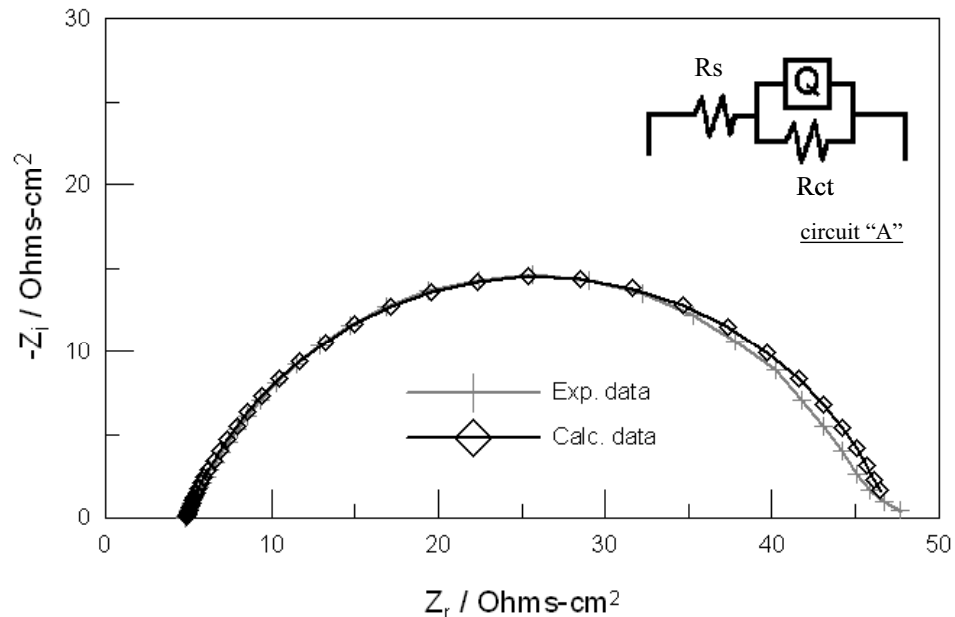
Figure 5. Simulation of the impedance diagram for the pipeline steel API 5L X52 samples immersed in 1M HCl without inhibitor, using the simple equivalent circuit "R(RQ)".

Table I shows the impedance data obtained for the blank (no inhibitor) and for the different 2MBI concentrations added to the 1M HCl. The electrochemical double layer capacitance (Cdl) and the inhibiting efficiency (IE %) can be calculated from the following relationships (10,11):

$$C_{dl} = Q^o \left(\omega_{max}\right)^{n-1} \qquad [2]$$

$$IE,\% = \frac{R_{ct} - R_{ct}^o}{R_{ct}} \times 100 \qquad [3]$$

TABLE I. Impedance parameters for the pipeline steel API 5L X52 samples immersed in1M HCl as a function of the inhibitor concentration.

IMPEDANCE PARAMETER	BLANK	5PPM	15PPM	20PPM	50PPM	80PPM	200PPM
Ecorr [mV]	-457	-471	-488	-490	-475	-480	-461
Rs [Ω]	4.85	4.63	3.98	3.4	4.12	4.4	4.6
CPE [sec/Ω]	5.23E-04	1.44E-04	6.08E-05	4.69E-05	4.33E-05	3.68E-05	2.25E-05
n	0.8	0.83	0.67	0.7	0.7	0.78	0.75
Rct [Ω-cm^2]	43	150	410	1170	1085	1350	2932
Cdl [μF/cm^2]	274.25	87.22	17.7	22.86	21.08	21.71	17.06
EI [%]	-	71.3	89.5	96.3	96	96.8	98.5

 From Eq. [2] Q^o is the constant phase element and ω_{max} represents the frequency at which the imaginary component Z" reaches its maximum value in the Nyquist diagram. As indicated by Eq. [3] Rct^o and Rct are the resistance to the charge transfer in the absence and presence of the inhibitor, respectively, which is similar to the Eq. [1]. As can be observed in Table I, the value of Rct increases continuously with increasing inhibitor concentration, though for the case of the Cdl value, a diminution was observed. This is associated to the decrease of the local dielectric constant or because of the thickness increase of the electrical double layer, which suggests that the 2MBI acts via adsorption at the metal/solution interphase. Therefore, it can be safely assumed that the Cdl value decreases because of the gradual displacement of the water molecules due to 2MBI molecules' adsorption over the surface of the steel API 5L X52, which impedes its dissolution. While, Rs does not change significantly when the inhibitor concentration increases, which indicates that the test solution 1M HCl + x[2MBI] has a good conductivity. Also, it can be observed from Table I that as the 2MBI concentration increases the corrosion potential E_{corr} becomes more negative, which suggests that the 2MBI inhibitor acts as a mixed inhibitor, thus implying that its molecules affect both the anodic and the cathodic processes.

2MBI´s Inhibition Efficiency

    Figure 6 shows the variation of the inhibiting efficiency as a function of its concentration evaluated in accordance with Eq. [3]. It can be observed that from 20 ppm the efficiency attained was excellent, reaching approximately 96%.
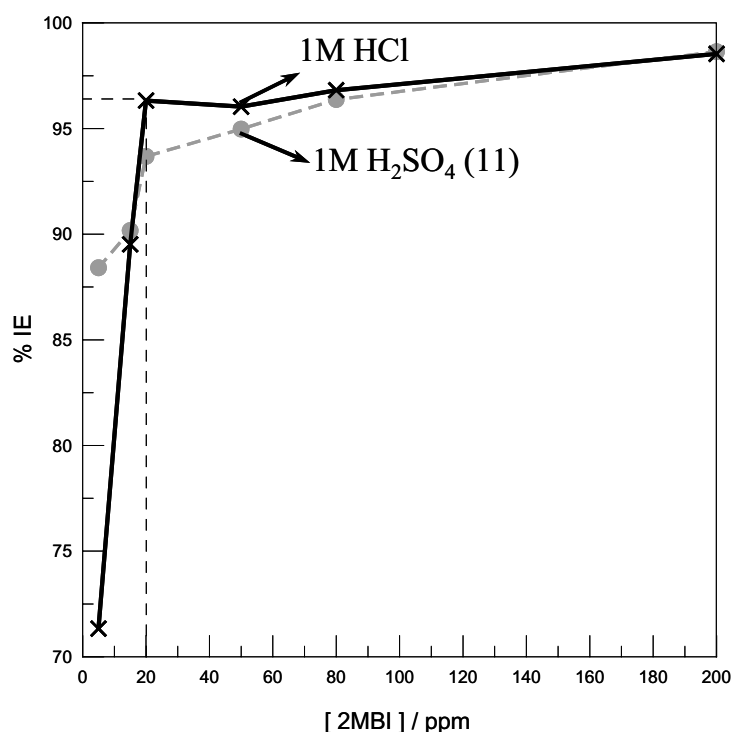

Figure 6. Variation of the inhibiting efficiency (IE%) as a function of 2MBI concentration obtained in the system API 5L X52 / 1.0 M HCl, x[2MBI].

2MBI Inhibition Kinetics

Figure 7 shows the impedance diagram for a 200 ppm 2MBI concentration in 1M HCl exposed for 32 days (768 h); the results indicate the presence of two time constants right from the first immersion hours: one constant at high frequency indicates the formation of a surface barrier between the metal and the corrosive medium, due to accumulation of the 2MBI molecules present in the acid, whereas the one at low frequency, that becomes even more evident as the timepasses, indicates that charge transfer processes between the molecular layer on the steel surface and the aqueous medium. Further, Figure 7b shows an increase of half an order of magnitude for the impedance |Z| after the first 48 h (2 days) immersion; when the exposure period reaches 768 h a decrement of |Z| was observed, of almost to its initial values. This behavior can be generally described by using an equivalent circuit like that in "B", shown in Figure 4. The results obtained by fitting the equivalent circuit to experimental data are listed in Table II, as a function of the immersion time in 1M HCl + 200 ppm 2MBI.
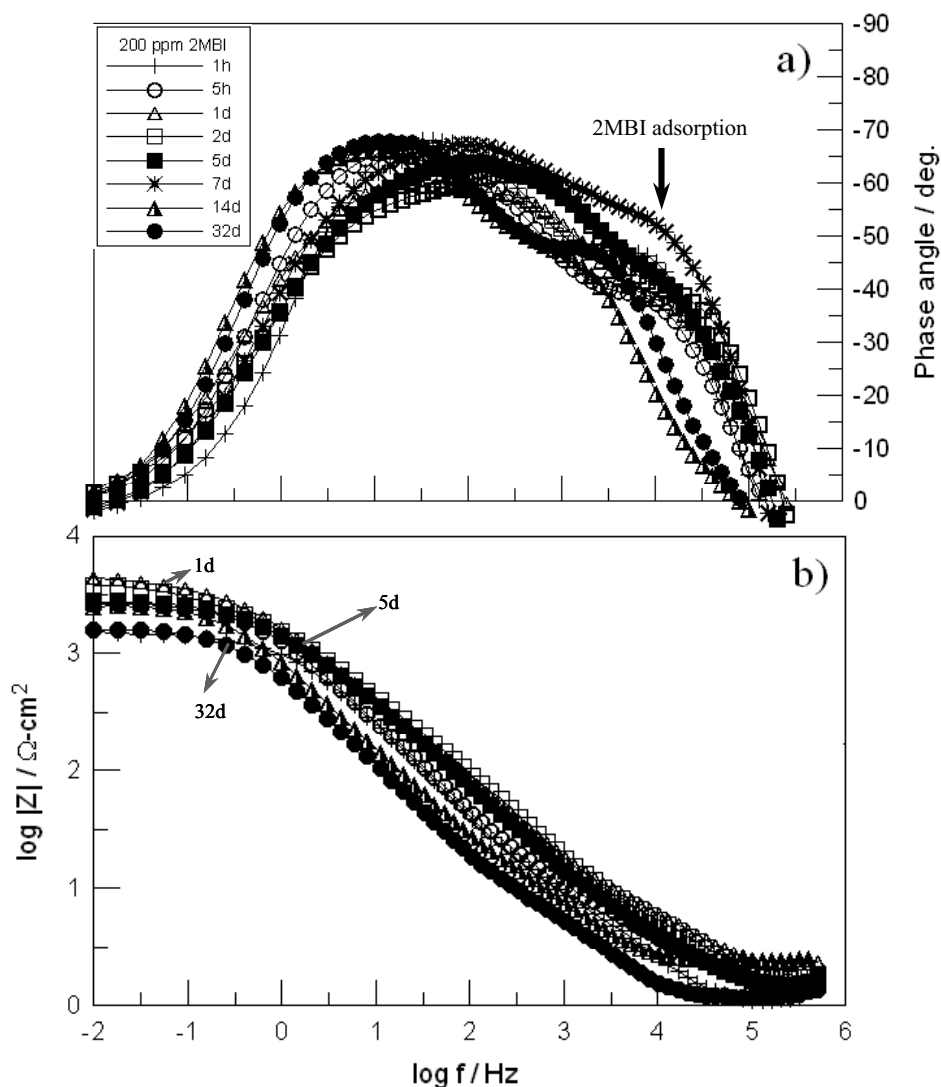

Figure 7. Impedance diagrams for the pipeline steel API 5L X52 samples immersed during 32 days in 1M HCl + 200 ppm 2MBI as a function of the immersion time.

TABLE II. Impedance parameters for the pipeline steel API 5L X52 samples immersed during 32 days in 1M HCl + 200 ppm 2MBI as a function of the immersion time.

IMPEDANCE PARAMETER	1h	3h	5h	24h	48h	120h	168h	336h	768h
Ecorr [mV]	-421	-401	-411	-414	-408	-392	-403	-416	-424
Cdl [$\mu F/cm^2$]	38.76	31.45	36.55	12.46	13.24	33.52	57.12	61.65	64.18
Rct [Ω-cm^2]	1456	3754	2695	4384	3626	2768	2515	2650	1645
IE [%]	96.5	98.7	98.1	98.9	98.6	98.1	98.0	98.1	96.9

The results in Figure 8 and Table II show that the charge transfer resistance increases from 1456 up to 4384 Ω-cm^2 during the first 24 h immersion due to an adsorption effect of the 2MBI molecules on the surface of the steel. This represents an inhibiting efficiency of 98.8% in agreement with the plot shown in Figure 8. From this time a slight drop begins to take place of the charge transfer resistance, Rct, as a function of elapsing immersion time. This way, after 32 days or 768h a Rct = 1645 Ω-cm^2 was obtained, which is similar to the Rct at the beginning of the test (1h immersion). This value is compared with that of the blank, no inhibitor for which Rct = 50 Ω-cm^2, means that the inhibiting efficiency reached, 96.9%, after 32 h immersion was greater by several orders of magnitude.
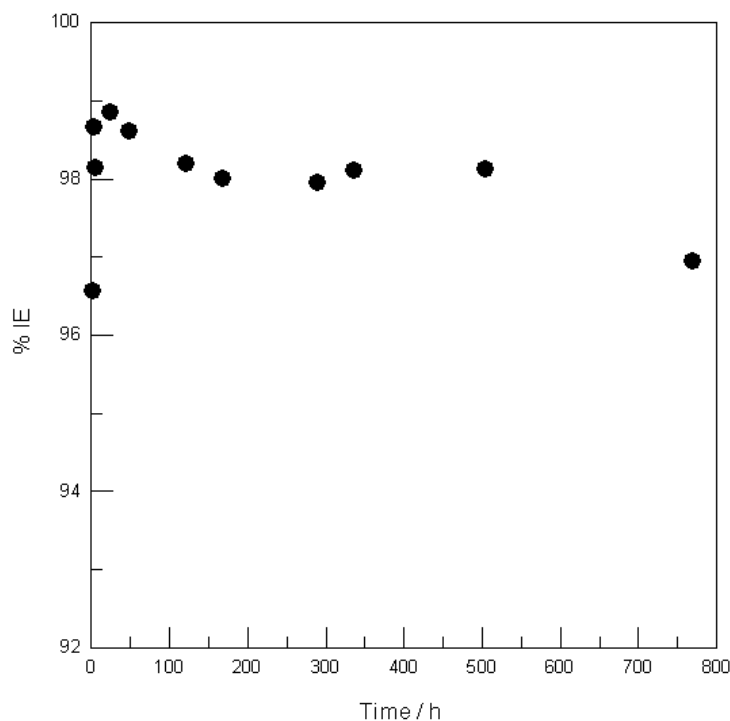

Figure 8. Variation of the inhibiting efficiency (IE%) as a function of immersion time for the pipeline steel API 5L X52 immersed in 200 ppm 2MBI + 1.0 M HCl.

Conclusions

The 2MBI inhibitor gave inhibiting efficiencies over 96% after adding only 20 ppm covering the metal surface exposed to the acid medium 1M HCl. Therefore, the heterocyclic organic molecule 2MBI was an efficient inhibitor also in hydrochloric media, just as it was in sulphuric acid at 25 ppm.

From the kinetic results after prolonged times the presence of 200 ppm 2MBI in HCl, gave a good inhibition efficiency, IE, which was maintained at 96% during nearly 32 days immersion in the acid media. This leads to conclude safely that the 2MBI was efficient to preclude corrosion in 1M HCl for long exposure periods.

The inhibitor acted on both the anodic and cathodic sites as related to the corrosion potential variation when the inhibitor concentration increased.

EIS permitted to pursue a thorough characterization of the 2MBI as efficient corrosion inhibitor in HCl media giving also additional information on the actual adsorption mechanism that controlled the corrosion reaction rate of the surface of the steel. In agreement with other results published (5), the EIS method gives better advantages over the Tafel technique.

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