Corrosion inhibition of carbon steel in hydrochloric acid 0.5 M by Hexa methylene diamine tetra methyl-phosphonic acid

My R. LAAMARI[a*], J. BENZAKOUR[a], F. BERREKHIS[b], A. ABOUELFIDA[a], A. DERJA[a], D. VILLEMIN[c].

[a] Laboratoire d'Electrochimie et de Chimie Analytique, Université Cadi Ayyad,

Faculté des Sciences Semlalia, BP 2390, Marrakech, Maroc

[b] Laboratoire de Chimie Physique, Ecole Normale Supérieure, BP 2400   , Marrakech, Maroc.

[c] École Nationale Supérieure d'Ingénieurs de Caen UMR 6507 CNRS,

Bd Maréchal Juin 14050 Caen Cedex, France

Abstract

The efficiency of Hexa methylene diamine tetra methyl-phosphonic acid (HMDTMP), as corrosion inhibitor for carbon steel in 0.5 M HCl, has been determined by gravimetric and electrochemical measurements. Polarization curves indicate that the compound is mixed inhibitor, affecting both cathodic and anodic corrosion currents. Adsorption of HMDTMP derivatives on the carbon steel surface is in agreement with the Langmuir adsorption isotherm model, and the calculated Gibbs free energy value confirms the chemical nature of the adsorption. EIS results show that the charge in the impedance parameters (R_t and C_{dl}) with concentrations of HMDTMP is indicative. The adsorption of this molecule leads to the formation of a protective layer on carbon steel surface. The electrochemical results have also been supplemented by surface morphological studies.

Keywords: Corrosion; Inhibition; impedance; Adsorption; Phosphonic acid

* Corresponding author: Fax: (+212) 5 24 62 70 26   E-mail: r.laamari@ucam.ac.ma

1. Introduction

Acid solutions are widely used in industry, chemical cleaning, descaling and pickling, which lead to corrosive attack. Therefore, the consumption of inhibitors to reduce corrosion has

increased in recent years. The corrosion control by inhibitors is one of the most common, effective and economic methods to protect metals in acid media [1,2]. The majority of the well-known inhibitors are organic compounds containing heteroatoms, such as oxygen, nitrogen or sulphur, and multiple bonds, which allow an adsorption on the metal surface [3,4]. It has been observed that the adsorption of these inhibitors depends on the physico-chemical properties of the functional groups and the electron density at the donor atom. The adsorption occurs due to the interaction of the lone pair and/or π-orbitals of inhibitor with d-orbitals of the metal surface atoms, which evokes a greater adsorption of the inhibitor molecules onto the surface, leading to the formation of a corrosion protection film [5–7]. The adsorption is also influenced by the structure and the charge of metal surface, and the type of testing electrolyte [8–12]. A large number of organic compounds were studied as corrosion inhibitors for iron and low alloyed steels [13–15]. Most of them are toxic in nature. This has led to the development of non-toxic corrosion inhibitors such as Tryptamine [16], Cefazolin [17], Mebendazole [18], and Cefatrexyl [19], Tryptamine [20], Cefotaxime [21], sulfa drugs [22], 2.3-diphenylbenzoquinoxaline [23].

Phosphonates, which were originally introduced as scale inhibitors in water treatment, were later proved to be good corrosion inhibitors also [24]. Their impact on environment was reported to be negligible at the concentration levels used for corrosion inhibition [25-26]. There are excellent sequestering agents for electroplating, chemical plating, degreasing and cleaning [27]. The use of phosphonic acids for the protection of carbon steel from corrosion in different media has been the subject of works reported by several researchers [28-33].

The objective of the present work is to investigate the inhibitor effects of Hexa methylene diamine tetra methyl-phosphonic acid (HMDTMP) on carbon steel corrosion in 0.5 M hydrochloric acid (HCl) using weight loss, potentiodynamic polarization, Electrochemical impedance spectroscopy (EIS), and scanning electronic microscope (SEM).

2. Experimental

2.1. *Materials and solutions*

The corrosion inhibitor studied Hexa methylene diamine tetra methyl-phosphonic acid (HMDTMP) was synthesized by the micro-wave technique. The obtained product is purified and characterized by ^{1}H-NMR, ^{13}C-NMR, ^{31}P-NMR and IR spectroscopic methods. The molecular structure is shown in fig. 1.
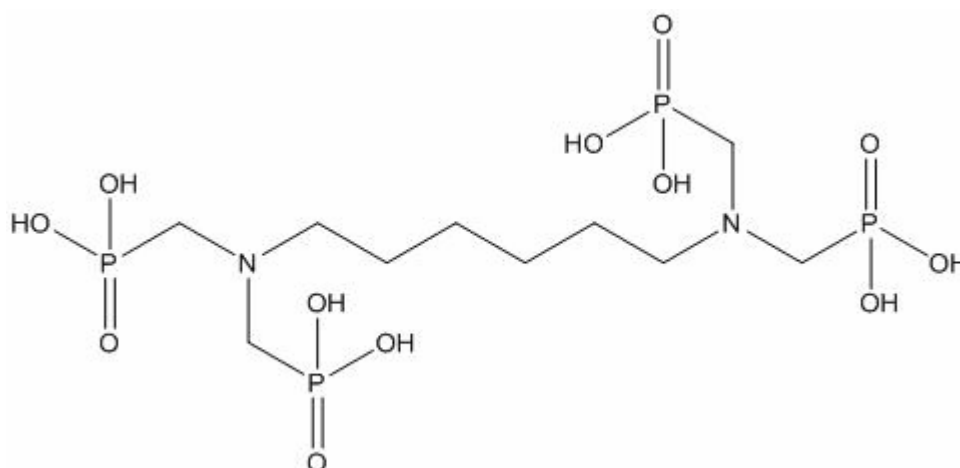

Fig. 1. Structure of Hexamethylene diamine tetramethyl-phosphonic acid (HMDTMP).

The aggressive solutions made of AR grade 37% HCl. Appropriate concentrations of acid were prepared using double distilled water. The inhibitors were added to freshly prepared 0.5 M HCl in the concentration range of 5.10^{-4} to 4.10^{-3} M.

Electrochemical experiments were performed using a conventional three electrode cell assembly. The working electrode is a carbon steel rotating disk with surface area of 1 cm^{2}. The electrode pre-treatment was carried out by polishing mechanically with silicon carbide abrasive paper up to 1200 grade. Then, it was rinsed with acetone and finally washed thoroughly with distilled water. A saturated calomel electrode (SCE) was used as the reference electrode. All the measured potentials presented in this paper are referred to this electrode.

The counter electrode was a platinum plate with a surface area of 2 cm^{2}.

2.2. Methods

2.2.1. Gravimetric measurements

The tests were carried out in a glass vessel containing 250 mL of 0.5 M HCl with and without addition of different concentrations of inhibitor at room temperature (25 °C). After immersion times (24 h), the specimens were withdrawn, rinsed with doubly distilled water, washed with acetone, dried and weighted.

2.2.2. Electrochemical measurements

Two electrochemical techniques, namely DC-Tafel slope and AC-electrochemical impedance spectroscopy (EIS), were used to study the corrosion behaviour. All experiments were performed in one-compartment cell with three electrodes connected to voltalab 10 (Tacussel-Radiometer PGZ 100) system controlled by the Tacussel Volta master 4 corrosion analysis software model.

Polarisation curves were obtained by changing the electrode potential automatically from -800 to $+200$ mV versus open circuit potential (E_{ocp}) at a scan rate of 1 mVs^{-1}.

EIS measurements were carried out under potentiostatic conditions in a frequency range from 100 kHz to 0.1 Hz, with amplitude of 10 mV peak-to-peak, using AC signal at open circuit potential (OCP) E_{ocp}. All experiments were measured after immersion for 60 min in 0.5 M HCl with and without addition of inhibitor.

2.2.3. Surface morphology

For morphological study, surface features (0.9 x 0.8 x 0.2 cm) of carbon steel were examined after exposure to 0.5 M HCl solutions after one day with and without inhibitor. JEOL JSM-5500 scanning electron microscope was used for this investigation.

3. Results and discussions

3.1. Weight loss studies

The weight loss results regarding the corrosion parameters for carbon steel in 0.5 M HCl solution in the absence and presence of different concentrations of the inhibitor are summarized in Table 1.

Table 1 Weight loss data of mild steel in 0.5 M HCl for various concentrations of HMDTMP.

HMDTMP Concentration (mol.dm^{-3})	w (mg.cm^{-2}.h^{-1})	IE (%)
blank	0.34	-
5×10^{-4}	0.13	62
10^{-3}	0.07	79
2×10^{-3}	0.03	91
4×10^{-3}	0.01	97

The inhibition efficiency (IE %) was determined by using the following equation:

$$IE\% = \frac{W_0 - W}{W_0} \times 100 \qquad (1)$$

Where W and W_0 are the corrosion rates of carbon steel with and without the inhibitor respectively.

It can be seen that corrosion rate values in 0.5 M HCl solution containing HMDTMP, decreased as the concentration of inhibitor increased. Maximum inhibition efficiency was shown at 10^{-3} M of HMDTMP. This result reveals that the compound under investigation is fairly efficient inhibitor for carbon steel dissolution in 0.5 M HCl solution. The inhibition of corrosion of carbon steel by HMDTMP can be explained in terms of adsorption on the metal surface [17-21]. This compound can be adsorbed on the carbon steel surface by the interaction between lone pairs of electrons of nitrogen, oxygen and phosphorus atoms of the inhibitor and the metal surface. This process is facilitated by the presence of vacant orbital of low energy in iron atom, as observed in the transition group elements [34,35].

3.2. Polarisation measurements

Fig. 2 shows the influence of HMDTMP on the cathodic and anodic potentiodynamic polarization curves of carbon steel in 0.5 M HCl. Electrochemical corrosion parameters such

as corrosion potential E_{corr}, cathodic and anodic Tafel slops b_a, b_c and corrosion current density i_{corr}, obtained by extrapolation of Tafel lines, are collected in Table 2. The inhibition efficiency is calculated by the following expression:

$$IE\% = \frac{i_{corr}^{0} - i_{corr}}{i_{corr}^{0}} \qquad (2)$$

Where i_{corr}^{0} and i_{corr} are the corrosion current density values without and with inhibitor, respectively.
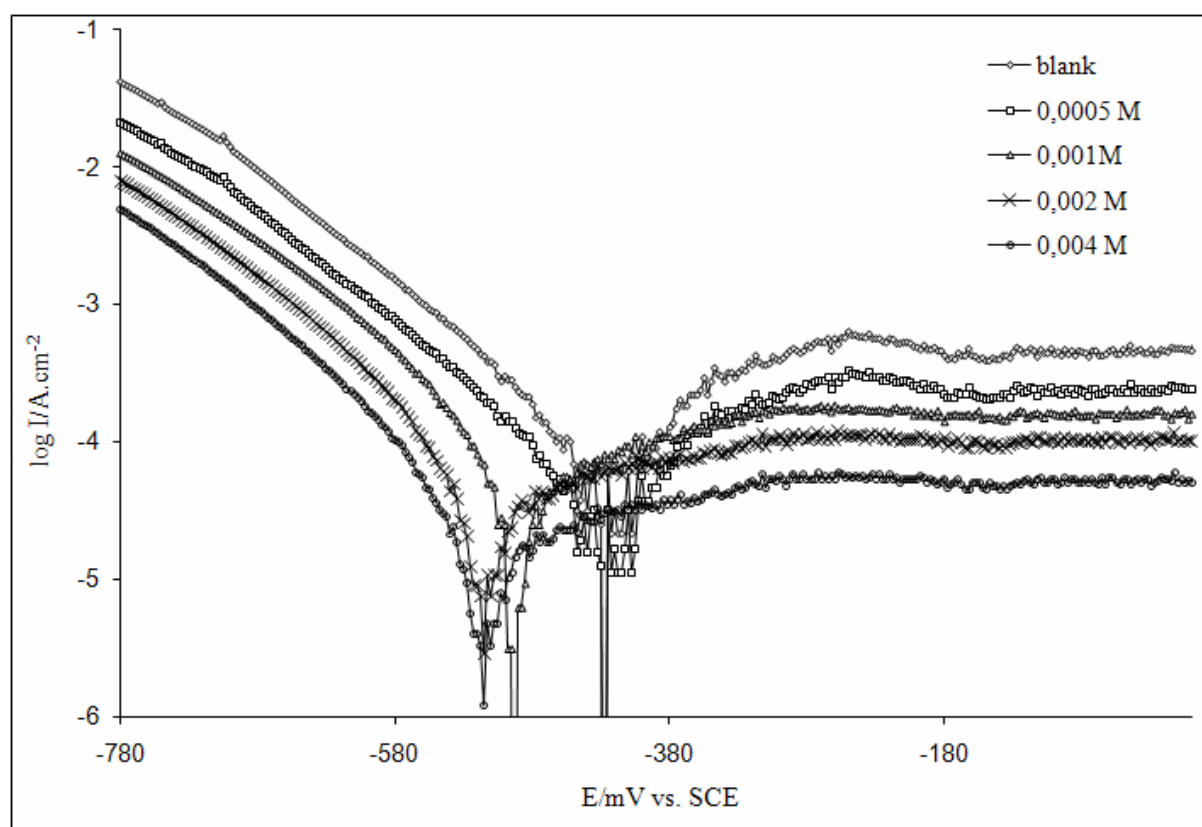

Fig. 2. Potentiodynamic polarization curves for mild steel in 0.5 M HCl containing different concentrations of HMDTMP.

Table 2 Potentiodynamic polarization parameters of mild steel in 0.5 M HCl for various concentrations of HMDTMP.

C (mol.dm^{-3})	E$_{corr}$ mV/SCE	I$_{corr}$ (μA.cm^{-2})	b$_a$ (mV.dec^{-1})	b$_c$ (mV.dec^{-1})	IE (%)
blank	-426	641	36	-100	-
5×10^{-4}	-449	197	35	-96	69
10^{-3}	-493	100	32	-95	84
2×10^{-3}	-507	52	33	-92	91
4×10^{-3}	-514	25	32	-95	96

The obtained results indicate that the cathodic and anodic curves exhibit Tafel-type behaviour. Additionally, the form of these curves is very similar either in the cathodic or in the anodic side, which indicates that the mechanisms of carbon steel dissolution and hydrogen reduction apparently remain unaltered in the presence of the inhibitor [34-36]. The addition of HMDTMP compound decreased both the cathodic and anodic current densities and acts as a mixed-type inhibitor in 0.5 M HCl with overall shift of E$_{corr}$ to more negative values with respect to the open circuit potential. The corrosion current value I_{corr} is decreased from 641 μA.cm^{-2} of the blank to 25 μA.cm^{-2} corresponding to the addition of 4.10^{-3} M inhibitor. Furthermore, we notice that the inhibition efficiency increased with inhibitor concentration reaching a maximum value of 96 % at 4.10^{-3} M HMDTMP. The results also show that the slopes of anodic and cathodic Tafel lines b$_a$ and b$_c$ were slightly changed on increasing the concentration of the tested compound. This indicates that there is no change of the mechanism of inhibition in the presence and absence of inhibitors. We noted also that the results found from the weight loss are in good agreement with the polarization curves.

3.3. Adsorption isotherm

Basic information on the interaction between the inhibitor and the carbon steel can be provided by the adsorption isotherm. Two main types of interaction can describe the adsorption of the organic compound: physical adsorption and chemisorption. These are

influenced by the chemical structure of the inhibitor, the type of the electrolyte, the charge and nature of the metal.
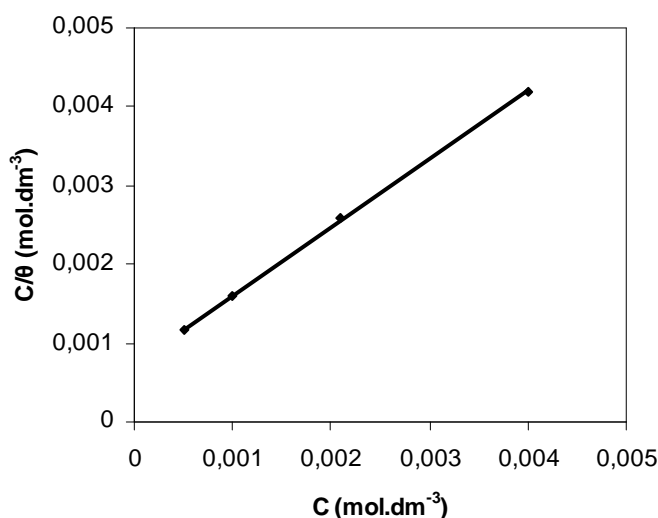

Fig. 3. Langmuir adsorption isotherm model of HMDTMP on the carbon steel surface at 298 K.

The plots of $\dfrac{C_{inh}}{\theta}$ against C_{inh} for the inhibitor at 298 K were straight lines (Fig.3) indicating that the inhibitor obeys Langmuir adsorption isotherm given by the equation:

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh} \qquad (3)$$

Where C is the molar concentration of inhibitor, K_{ads} is the equilibrium constant of the adsorption process and θ is the degree of coverage by inhibitor molecules on the metal surface, calculated from the relationship:

$$\theta = \frac{w_0 - w}{w_0} \qquad (4)$$

Adsorption equilibrium constant (K_{ads}) and free energy of adsorption (ΔG°_{ads}) were calculated using equation (3) and the relationships [21]:

$$\Delta G^{\circ}_{ads} = -2.303RT \log(55.5 K_{ads}) \qquad (6)$$

The value of 55.5 is the concentration of water in solution expressed in mol dm^{-3}.

It generally accepted that the values of (ΔG°_{ads}) up to -20 kJ mol^{-1}, the types of adsorption were regarded as physisorption, the inhibition acts due to the electrostatic interaction between the charged molecules and the charged metal, while the values around -40 kJ mol^{-1} or smaller, were seen as chemisorption, which is due to the charge sharing or a transfer from the inhibitor molecules to the metal surface to form covalent bond [34-38]. In this study, the free energy of adsorption (ΔG°_{ads}) and adsorption equilibrium constant (K_{ads}) are found to be -28.107 KJ mol^{-1} and $1.42.10^3$ mol dm^{-3}, respectively. The higher value of (K_{ads}) and the negative and low value of ΔG°_{ads} indicate the spontaneous adsorption of the inhibitor and are strong interaction with the metal surface [39-41]. It suggested that the adsorption mechanism of the HMDTMP on carbon steel in 0.5 M HCl solution was typical of chemisorptions.

3.4. Electrochemical impedances spectroscopy

Electrochemical impedance spectroscopy (EIS) is a well-established and powerful tool in the study of corrosion. Surface properties, electrode kinetics and mechanistic information can be obtained from the impedance diagrams [42]. Fig. 4 shows the Nyquist plot obtained at the open-circuit potential after immersion for 1h. Table 3 summarizes the impedance data extracted from EIS experiments carried out both in the absence and presence of increasing concentrations of HMDTMP.

The inhibition efficiency got from the charge transfer resistance is calculated by the following expression

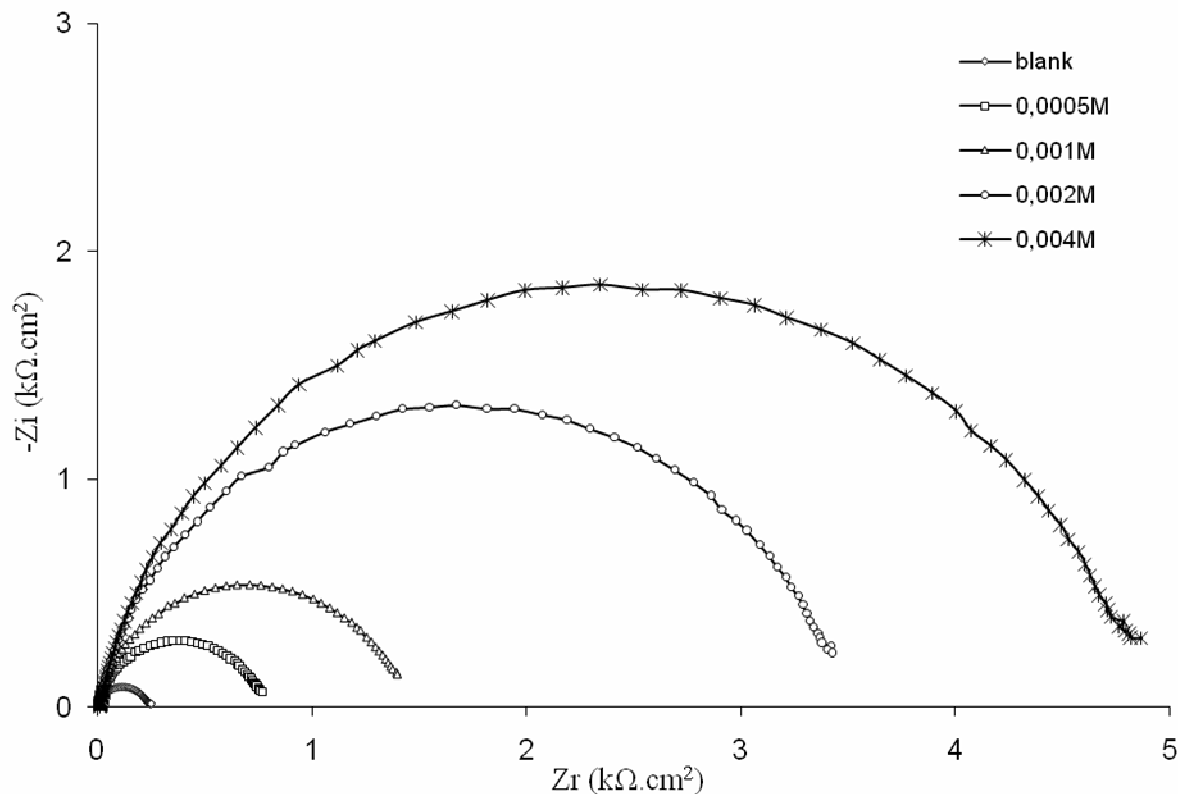$$IE\% = \frac{R_t - R_t^o}{R_t^o} \times 100 \quad (7)$$

Fig. 4. Nyquist plot for MS in 0.5 M HCl in the presence and absence of different concentrations of HMDTMP.

Table 3 Impedance measurements and inhibition efficiency for carbon steel in 0.5 M HCl containing different concentrations of HMDTMP.

C (mol.dm^{-3})	R$_s$ (Ω.cm^2)	C$_{dl}$ (μF/cm^2)	R$_p$ (Ω.cm^2)	IE (%)
blank	1	423	240	-
5×10^{-4}	1.6	130.8	768.7	69
10^{-3}	1.3	70.1	1434	83
2×10^{-3}	3.7	25.6	3480	93
4×10^{-3}	2.3	18.3	4872	95

R_t and R_t^o are the charge transfer resistance values with and without inhibitor, respectively.

The semi circular appearance of Nyquist plot shows that the charge transfer process takes place during dissolution [43]. From the curves it is clear that the impedance response for carbon steel in uninhibited acid solution has significantly changed after the addition of inhibitor. The simplest fitting is represented by Rundles equivalent circuit (Fig. 5), which is a

parallel combination of the charge-transfer resistance (R_t) and double layer capacitance C_{dl}, both in series with the solution resistance (R_s).
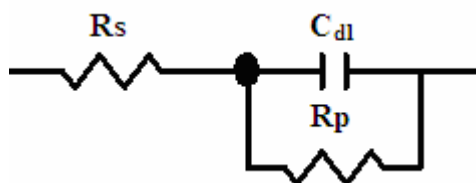

Fig. 5. Equivalent circuit used to fit the EIS data of carbon steel in 0.5 M HCl in the presence and absence of HMDTMP .

The fact that impedance diagrams have an approximately semicircular appearance shows that the corrosion of carbon steel in 0.5 M HCl is controlled by a charge-transfer process.

Data in Table 4 show that the R_s values are very small compared to the R_t values. By increasing the inhibitor concentrations, the R_t values increase and the C_{dl} values decrease, which causes an increase of inhibition efficiency. The most pronounced effect and the highest R_t is obtained by concentration 4.10^{-3} M of inhibitor.

The decrease in C_{dl} can result from the decrease of the local dielectric constant and/or from the increase of thickness of the electrical double layer, which suggests an adsorption of the inhibitor molecules on the carbon steel surface [17]. The thickness of the protective layer δ, is related to C_{dl} by the following equation [44]:

$$\delta = \frac{\varepsilon_0 \times \varepsilon_r}{C_{dl}} \qquad (8)$$

Where ε_0 is the dielectric constant and ε_r is the relative dielectric constant. McCafferty and al. [45] attributed the change in C_{dl} values to the gradual replacement of water molecules by the adsorption of the organic molecules on the metal surface, decreasing the extent of metal dissolution. The impedance data confirm the inhibition behaviour of the inhibitor with that obtained from other techniques. It can be concluded that the inhibition efficiency found from weight loss, polarization curves, and electrochemical impedance spectroscopy measurements are in good agreement.
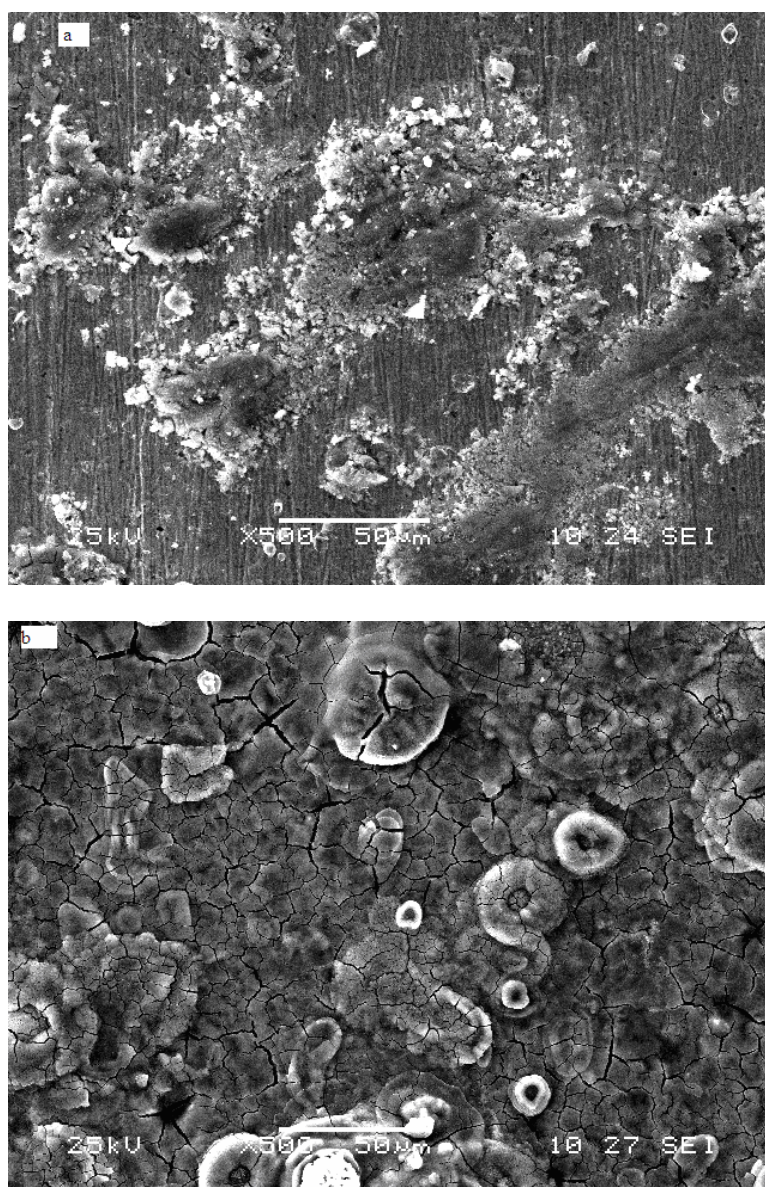
Fig. 6. SEM micrographs of samples after immersion in 0.5 M HCl (a) without (b) with

4×10^{-3} M HMDTMP.

Fig. 6 shows the results of the SEM analysis on the topography of the samples examined.

Fig. 6a presents the micrograph obtained of the carbon steel sample after exposure to the

corrosive environment, and Fig. 6b reveals the surface on the carbon steel after exposure to

the 0.5 M HCl solution containing the inhibitor HMDTMP at 4.10^{-3} M concentration. It is

important to stress out that when the compound is present in the solution, the morphology of

the carbon steel surface are quite different from the previous one. We noted the formation of a

film, which is distributed in a random way on the whole surface of the metal. This may be interpreted as due to the adsorption of the inhibitor on the metal surface incorporating into the passive film in order to block the active site present on the carbon steel surface.

4. Mechanism of inhibition

A clarification of mechanism of inhibition requires full knowledge of the interaction between the protective compound and the metal surface. Many of the organic corrosion inhibitors have at least one polar unit with atoms of nitrogen, sulphur, oxygen and phosphorous. It has been reported that the inhibition efficiency decreases in the order to $O < N < S < P$. Also, iron is well known for its co-ordination affinity to heteroatom bearing ligands [46]. From the previous results of various experimental techniques used, it was concluded that Hexamethylene diamine tetramethyl-phosphonic acid inhibit the corrosion of carbon steel in 0.5 M HCl by adsorption at the metal/solution interface.

In hydrochloric acid medium, inhibitor molecules exist as protonated species and it is assumed that Cl^{-} ions are first adsorbed on the metal surface and the net positive charge on the metal surface enhances the specific adsorption of chloride ions [47]. The adsorption of the cationic forms of inhibitor would be limited by the concentration of the anions on the metal surface. The Hexamethylene diamine tetramethyl-phosphonic acid molecules may also be adsorbed via donor–acceptor interactions between the unshared electrons pairs of the heteroatoms (P, N, O) to form a bond with the vacant d orbitals of the iron atom on the metal surface, which act as a Lewis acid, leading to the formation of a protective chemisorbed film [18].

5. Conclusion

1. All measurements showed that the Hexa methylene diamine tetra methyl-phosphonic acid has excellent inhibition properties for the corrosion of carbon steel in 0.5 M HCl solution. The

weight loss measurements show that the inhibition efficiency increases with HMDTMP concentration and reaches its highest value (97 %) at 4.10^{-3} M concentration.

2. Potentiodynamic polarization measurements showed that the HMDTMP acts as mixed type inhibitor. EIS measurements also indicate that the inhibitor increases the charge transfer resistance and show that the inhibitive performance depends on adsorption of the molecules on the metal surface.

3. The inhibition efficiencies determined by weight loss, potentiodynamic polarization and EIS techniques are in reasonably good agreement.

4. The adsorption model obeys the Langmuir isotherm at 298 K. The negative value of ΔG°_{ads} indicate that the adsorption of the inhibitor molecule is a spontaneous process and an adsorption mechanism is typical of chemisorption.

6. References

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