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Enhanced corrosion resistance properties of carbon steel in hydrochloric acid medium by aminotris-(methylenephosphonic): Surface characterizations

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Abstract

In this work, the surface morphology and chemical analysis of carbon steel substrates after weight loss measurements in 1 M HCl media in the absence and the presence of aminotris-(methylenephosphonic) acid (ATMP) were studied using a scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). X-ray photoelectron spectroscopy was coupled to these characterizations to qualify corrosion layers and morphologies. The solution of immersion was analyzed by inductively coupled plasma. Results indicate that the addition of ATMP reduces the rate of metal attack. EDX, SEM and X-ray photoelectron spectroscopy observations of the electrode surface confirmed existence of a protective adsorbed film of the inhibitor on the electrode surface.

Keywords: Aminotris-**(**methylenephosphonic**)** acid; Carbon steel; Hydrochloric acid; Corrosion inhibition; Surface characterization

1. Introduction

The use of inhibitors is one of the most practical methods for protection metal against corrosion, especially in acidic media [1]. As acidic media, hydrochloric acid (HCl) is often used as industrial acid cleaners and pickling acids. Many organic compounds containing heteroatoms like N, O, P, S, have been reported to be effective inhibitors for the corrosion of steel in acid media by several authors [2-15]. Generally, organic inhibitor molecules might physically or chemically adsorb on a corroding metal. The inhibition efficiency has found to be closely related to inhibitor adsorption abilities and molecular properties for different kinds of organic compounds [16-19].

The use of organic phosphonic acids to protect carbon steel against corrosion has been the subject of various work [20-24]. In this field, we have been studied the corrosion inhibition property and the antibacterial activity of the aminotris-(methylenephosphonic) acid (ATMP) [25]. The ATMP has been investigated as a corrosion inhibitor for carbon steel in 1 M HCl solution using weight loss, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) techniques. The results show that ATMP is effective inhibitor for the carbon steel corrosion in 1 M HCl solutions. The adsorption of ATMP fits a Langmuir isotherm model. Based on the literature [26], the obtained ΔG^0_{ads} indicates that the adsorption mechanism of ATMP on carbon steel surface involves two types of interactions, predominant physisorption (ionic) and weak chemisorption (molecular). In order to gain better understanding of the beneficial effect of ATMP to improve the corrosion resistance of carbon steel in 1 M HCl medium, ICP, SEM, EDX and XPS have been applied to study the mechanism of steel corrosion inhibition of this organic compound in acidic medium.

2. Experimental method

2.1. Material

The molecular structure of the ATMP is shown in Figure 1. The tested compound, namely aminotris-(methylenephosphonic) acid ($N[CH_2P(O)(OH)_2]_3$), (ATMP), obtained from Sigma–Aldrich (50 wt.% in H_2O), was tested without further purification. The material used in this study was a carbon steel with chemical composition (in wt.%) of 0.370% C, 0.230% Si, 0.680% Mn, 0.016% S, 0.077% Cr, 0.011% Ti, 0.059% Ni, 0.009% Co, 0.160% Cu and the remainder iron (Fe). For all the experiments, the surface pre-treatment was carried out by grinding with emery paper SiC (grades 120, 600 and 1200), rinsed with distilled water, degreased in acetone in an ultrasonic bath immersion for 5min and then dried at room temperature before use. The acid solutions (1 M HCl) were prepared by dilution of an analytical reagent grade 37% HCl with doubly distilled water.

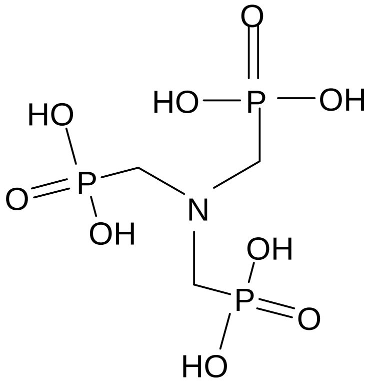


Fig.1. Molecular structure of the aminotris-(methylenephosphonic) acid (ATMP).

2.2. Weight loss tests

Weight loss measurements were performed on rectangular iron specimens of size (length=2cm, width=1cm, thickness= 0.2 cm). After polishing, the samples were immersed for 24 hours in 100 ml of 1 M HCl solution with and without addition of the different concentrations of ATMP at room temperature in non-de-aerated solutions. At the end of the tests, the specimens were carefully washed in acetone under ultrasound and then weighed. Duplicate experiments were performed in each case and the mean value of the weight loss is reported. Weight loss allowed calculation of the mean corrosion rate in mg cm^{-2} h^{-1}.

2.3. Inductively coupled plasma

Spectroscopy induction coupled plasma (ICP) was used to analyze the gravimetric solution**.** The calibration is made in the studied solution in order to eliminate the effect of matrix. After the immersion of the samples for 24 hours in 100 mL of 1 M HCl without and with addition of 5×10^{-3} M of ATMP, the iron and phosphore in the solution was measured using ICP.

2.4. Scanning electron microscopy (SEM)

The carbon steel specimens before and after immersion were investigated by using a Quanta 200 FEI Company scanning electron microscope. The energy of the acceleration beam employed was 20 kV. The group is equipped with a system complete of microanalyse X (detector EDX-EDAX) and with a detector of back-scattered electrons. This SEM allows to give the chemical composition of the sample with a limit of detection going up to the Boron. The analyzed volume is of the order of μm^3.

2.5. X-ray photoelectron spectroscopy

The steel disk was immersed in the 1 M HCl containing 10^{-1} M of ATMP at 30 °C for 24 h without bubbling. After removal from the glass cell the disk was rinsed with ethanol and dried in air at room temperature. Surface analyses were performed with an ESCALAB 220 XL spectrometer from vacuum Generators. The monochromatised Al Kα X-ray source (1486.6 eV) was operated in the CAE (constant analyser energy) mode (CAE=150 eV for survey spectra and CAE=30 eV for high resolution spectra), using the electromagnetic lens mode. A flood gun source (6 eV) was applied to the polymeric samples to compensate the sample charging effect. The binding energy scale was initially calibrated using the $Cu2p_{3/2}$ (932.7 eV), $Ag3d_{5/2}$ (368.2 eV) and $Au4f_{7/2}$ (84 eV) peak positions and internal calibration was referenced to the C1s energy at 285 eV for aliphatic species. Quantification of outer layers atomic composition and spectral simulation of the experimental peaks were achieved using the software provided by VG Scientific.

3. Results and discussion

3.1. Weight loss measurements

The effect of addition of ATMP tested at different concentrations on the corrosion of carbon steel in 1 M HCl solution has been studied by weight loss measurements at 30 °C after 24 h of immersion period [25]. For every concentration the mean value of the corrosion rate *W* (mg cm^{-2} h^{-1}) and *E*(%) were calculated using as described elsewhere [27]. The values of percentage inhibition efficiency, *E*(%), and corrosion rate (*W*) obtained from weight loss method at different concentrations of ATMP are summarized in Table 1. These gravimetric results were described in our previously work [25]. It is very clear that the ATMP inhibits the corrosion of carbon steel in 1 M HCl solution at all concentrations, while the corrosion rate (*W*) decreases continuously with increasing additive concentration at 30°C; the maximum *E*(%) of 96.710 % is achieved at 0.5 M.

Table 1. Corrosion parameters obtained from weight loss measurements of carbon steel in 1 M HCl containing various concentrations of ATMP at 30°C.

Inhibitor	Concentration (M)	Corrosion rate (mg cm^{-2} h^{-1})	*E* (%)
Blank	—	4.56	—
ATMP	5×10^{-5}	3.81	16.44
	1×10^{-4}	3.26	28.51
	5×10^{-4}	2.77	39.25
	1×10^{-3}	2.20	51.75
	5×10^{-3}	1.03	77.41
	1×10^{-2}	0.71	84.43
	5×10^{-2}	0.25	94.52
	1×10^{-1}	0.18	96.05
	5×10^{-1}	0.15	96.71

3.2. I.C.P. analysis

The corrosive solution without and with ATMP was analyzed using ICP technique after 24 h of steel immersion at 30°C. Inspection of obtained results, given in Table 2, clearly shows that the concentration of iron in the solution without ATMP was very high, the presence of the ATMP was limited the passage of the iron in solution. So, we deducted the inhibition efficiency, *E*(%), using the ICP result. Indeed, the obtained value of *E*(%) (Table 2) is in good agreement with that obtained using weight loss measurements at 5 ×10^{-3} M of ATMP (Table 1). The decrease of the phosphor concentration in the corrosive solution (Table 2) after the immersion period can be explained by the adsorption of the ATMP on the carbon steel surface. This behaviour is in good agreement with the probe microanalysis (EPMA) result, described in our previously work [25].

3.3. Scanning electron microscopy (SEM)

The SEM is used here for the observation, in imaging by secondary electrons, of the topography of the sample. The elementary analysis is obtained by coupling the system with a dispersive analysis in energy (EDX). Our observations in the SEM concerned samples of carbon steel after 24 hours of immersion in 30°C in only 1 M HCl (Fig. 2), and with addition of 10^{-1} M of the ATMP (Fig. 3). We observed on the surface the black spots corresponding to the stings of corrosion, as well as grey and white zones which they, correspond to the dandruff of iron oxides (Table 3). Figure 3 shows the morphology of layer formed after 24 hours of immersion in the solution 1 M HCl containing 10^{-1}M of the ATMP.

The analysis EDX of the surface reveals the presence of oxygen and iron, suggesting therefore the presence of iron oxide / hydroxide (Fig. 3). On the three zones analyzed (A, B and C), the presence of the peaks of carbon, nitrogen, and phosphor is explained by the adsorption of the ATMP on the products of corrosion of the steel (Table 4). No shape of corrosion is detected on the surface.

Table 2. The analysis results of the solution immersion by ICP.

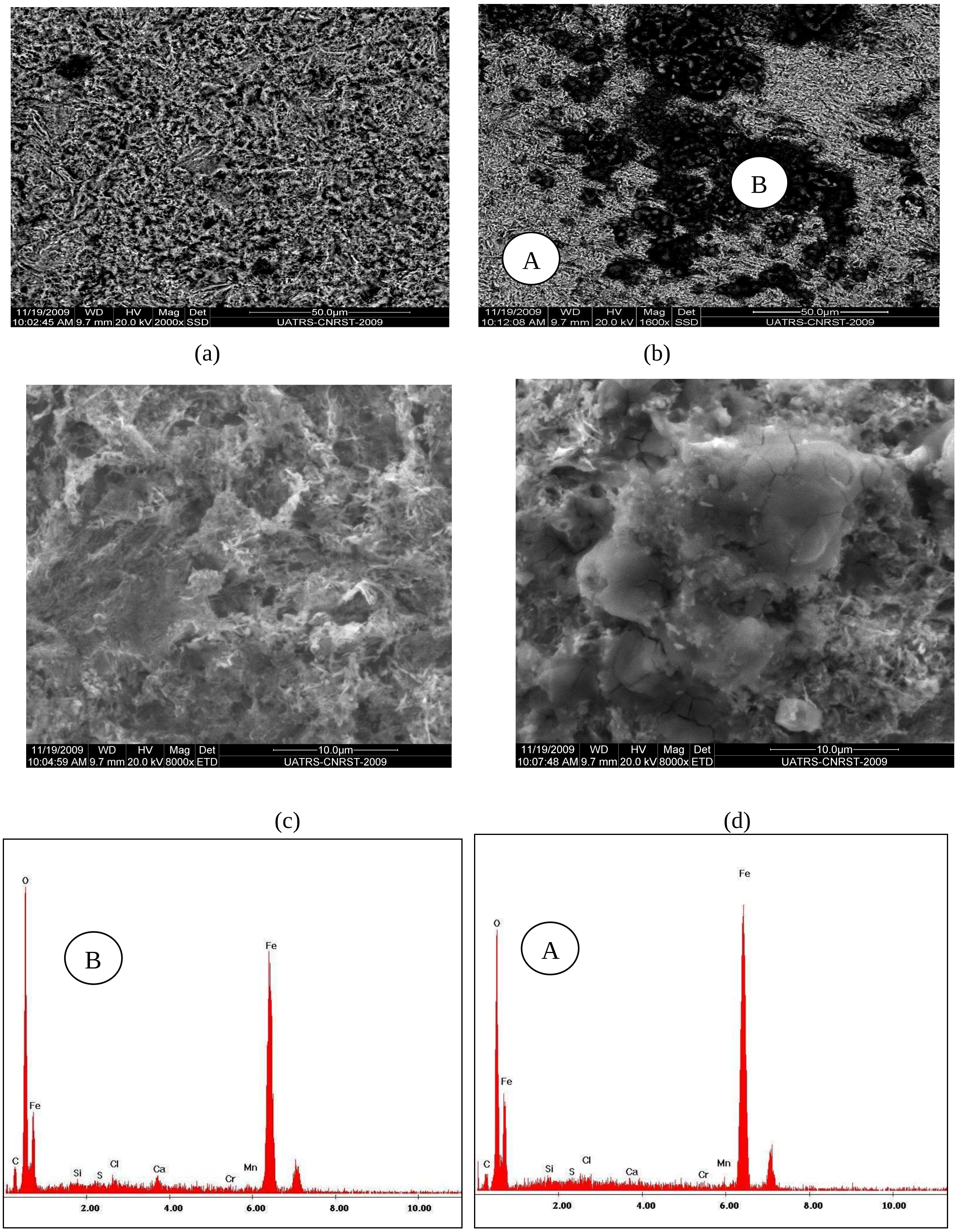
Sample	Iron (Fe)	$E = (M_i - M_f)/M_i$ (%)	Phosphor (P)	
	ICP Analyze (mg/L)		Calculated value (mg/L)	ICP Analyze (mg/L)
Blank	$M_i = 148.3$	—	—	
ATMP	$M_f = 40.01$	73.02	465	389.65

Table 3. Analyze EDX of treated substrates.

Elements	Zone A Mass (%)	Zone B Mass (%)
C	6.8	9.31
O	22.37	28.16
S	0.18	0.18
Cl	0.47	0.51
Cr	0.65	0.75
Mn	1.16	1.56
Fe	68.37	59.52

Table 4. EDX analysis of three zones.

Elements	Zone A Mass %	Zone B Mass %	Zone C Mass %
C	5.93	3.04	7.47
N	1.55	1.91	1.93
O	19.61	2.11	4.72
P	0.61	0.87	1.08
S	0.12	0.42	0.51
Cl	0.17	0.43	0.24
Cr	0.68	0.67	0.89
Mn	0.83	0.92	1.47
Fe	70.51	89.64	81.69

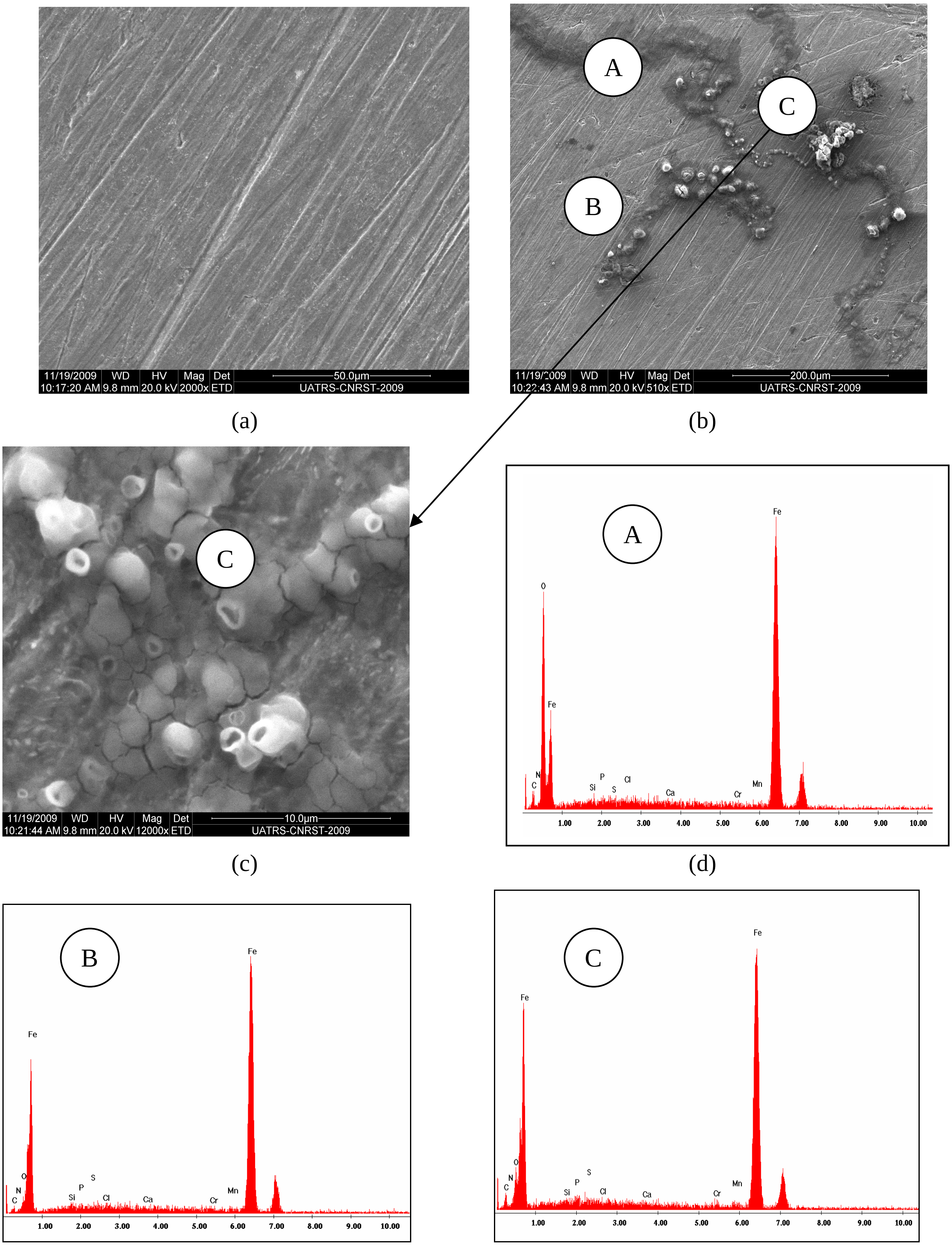


(a) (b)

(c) (d)

(e) (f)

Fig. 2. (a-d) SEM observation of the carbon steel surface after 24 h of immersion in 1 M HCl; (e-f) EDX analysis of the carbon steel surface after 24 h of immersion in 1 M HCl.



(a) (b) (c) (d) (e) (f)

Fig. 3. (a-c) SEM observation of the carbon steel surface after 24 h of immersion in 1 M HCl in the presence of 10^{-1}M of the ATMP; (d-f) EDX analysis of the carbon steel surface after 24 h of immersion in 1 M HCl in the presence of 10^{-1}M of the ATMP.

3.4. X-ray photoelectron spectroscopy

XPS technique was used to investigate the composition of the organic adsorbed layer on the C38 steel surface in normal hydrochloric medium by ATMP. In this way, the high-resolution peaks for C 1s, O 1s, P 2p, N 1s and Fe 2p for carbon steel surface after 24 h of immersion in 1 M HCl solution containing 10^{-1} M of ATMP. All XPS spectra contained complex forms, which were assigned to the corresponding species through a deconvolution fitting procedure (a non-linear least squares algorithm with a Shirley base line and a Gaussian–Lorentzian combination) using the XPS Peak-Fit 4.1 software.

The deconvolution of the high resolution Fe $2p_{3/2}$ XPS spectrum consists in four peaks (Fig. 4). These peaks may be assigned as being due to iron in environments associated with iron oxide and hydroxide. Indeed, the first peak located at 707 was assigned to metallic iron (Fe^0) [28, 29]. The second peak at a BE ~ 711.0 eV assigned to Fe^{3+} was attributed to ferric compounds such as Fe_2O_3 (i.e., Fe^{3+} oxide) and/or Fe_3O_4 (i.e., Fe^{2+}/Fe^{3+} mixed oxide) and FeOOH (i.e., oxyhydroxyde), [30,31], while that located at around 713.8 eV is attributed to the presence of a small concentration of $FeCl_3$ on the metal surface [32]. The last peak, observed at 717 eV is probably ascribed to the satellites of the ferric compounds.

The O 1s spectrum (Fig. 5) envelops was fitted by three peaks. The first peak located at lower binding energy (530.4 eV) can be attributed to O^{2-}, and in principle could be related to the bond with Fe^{3+} in the Fe_2O_3 and/or Fe_3O_4 oxides [33]. The second peak (located at approx. 531.8 eV) is ascribed to OH^-, and is attributable to oxygen in hydrous iron oxides, such as FeOOH and/or $Fe(OH)_3$ [34]. Finally, the small peak may be assigned to the oxygen atoms of adsorbed water with characteristic binding energy of 533 eV [35-37].

The P 2p XPS spectra for ATMP treated carbon steel surface displayed three peaks (Fig. 6). The first peak is located at a binding energy of (133.5 eV) it is attributable to the phosphonates. The second peak has the largest contribution and is mainly attributed to $CH_2P(O)(OH)_2$ [38-41]. The characteristic binding energy values of this coordinate phosphate is (134.2 eV). The last peak at binding energy (132.8 eV), we are not can be attributed.

The C 1s spectra of ATMP treated carbon steel surface show three peaks profile (Fig. 7). The largest peak can be attributed to the C–H with characteristic binding energy of 284.7 eV [42]. The second peak may be assigned to the carbon atoms bonded to nitrogen in C–N bonds in the ATMP ring at 286.7 eV [43-45]. The last peak may be ascribed to the carbon atom of the C–O or C–P bond in the ATMP ring at 288.9 eV.

The N 1s XPS spectrum is fitted into two components (Fig. 8). The peaks for ATMP were located at a binding energy of 400.1 eV and 403 eV; they are attributable to the $N(CH_2)^{3-}$ of ATMP.

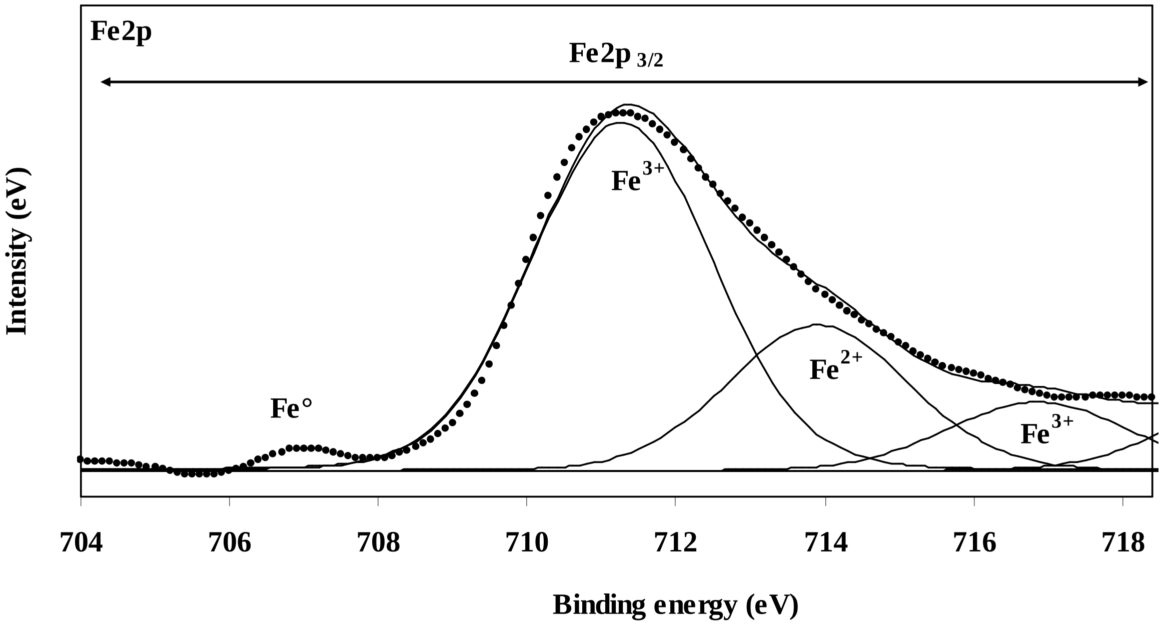


Fig. 4. The XPS deconvoluted profiles for Fe 2p for carbon steel after 24 h immersion period in 1 M HCl in the presence of 1×10^{-1} M of ATMP at 30°C.

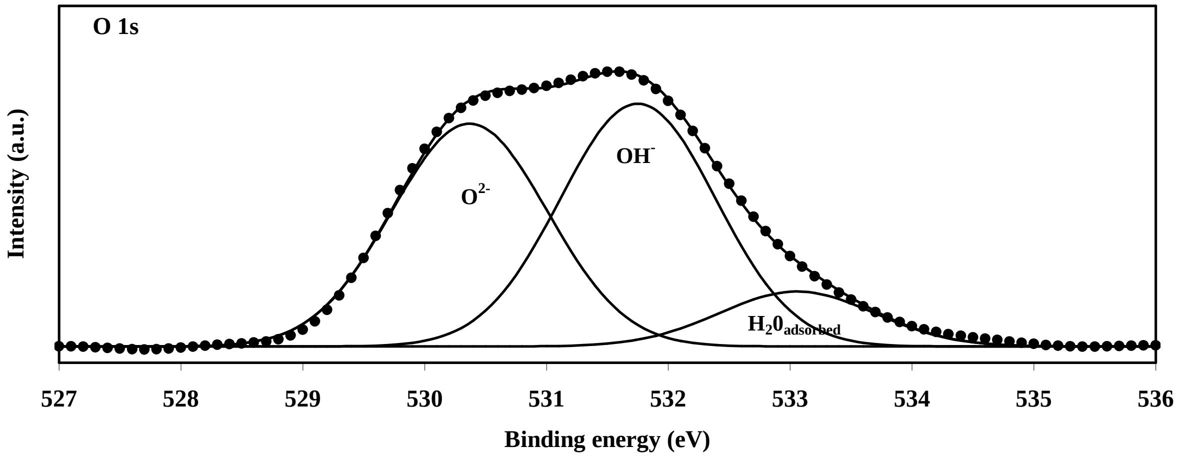


Fig. 5. The XPS deconvoluted profiles for O 1s for carbon steel after 24 h immersion period in 1 M HCl in the presence of 1×10^{-1} M of ATMP at 30°C.

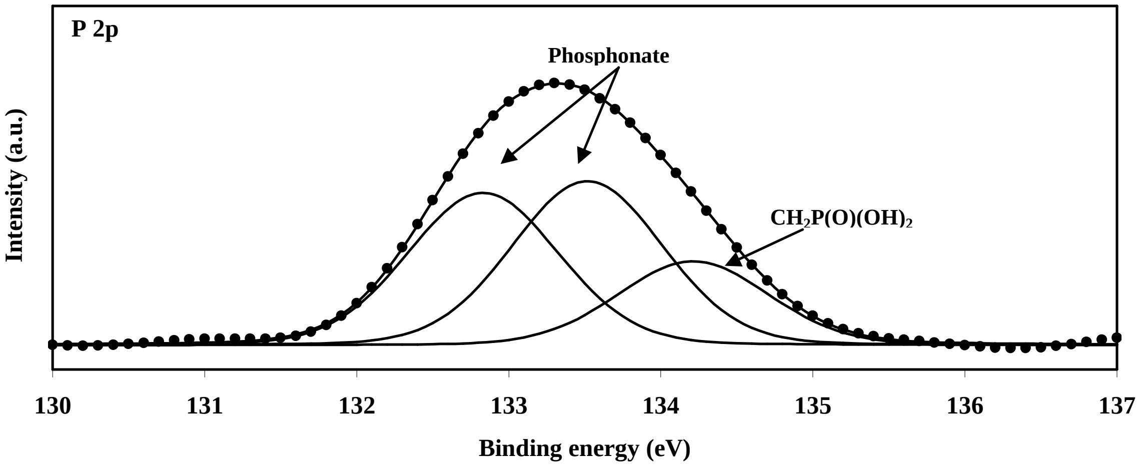


Fig. 6. The XPS deconvoluted profiles for P 2p for carbon steel after 24 h immersion period in 1 M HCl in the presence of 1×10^{-1} M of ATMP at 30°C.

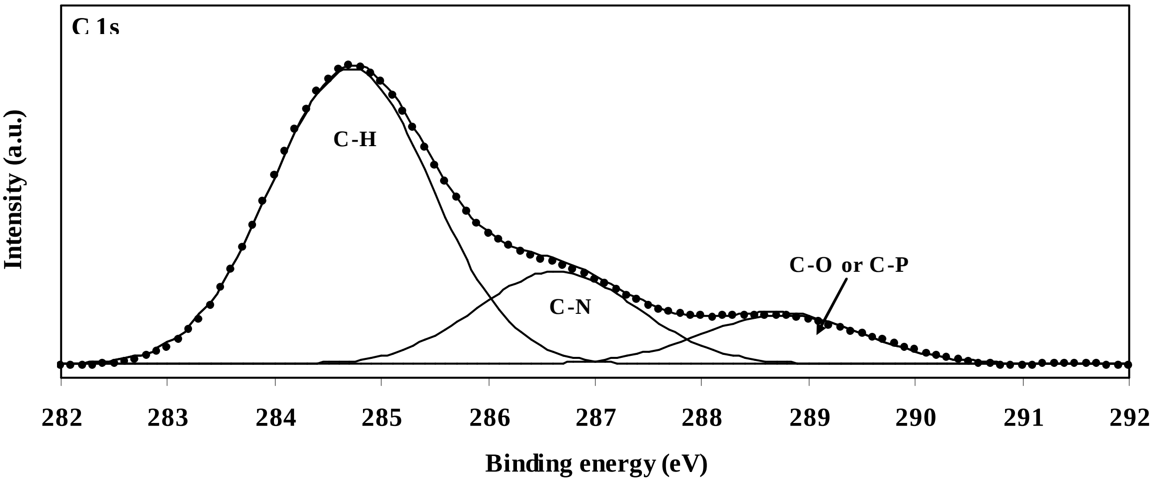


Fig. 7. The XPS deconvoluted profiles for C 1s for carbon steel after 24 h immersion period in 1 M HCl in the presence of 1×10^{-1} M of ATMP at 30°C.

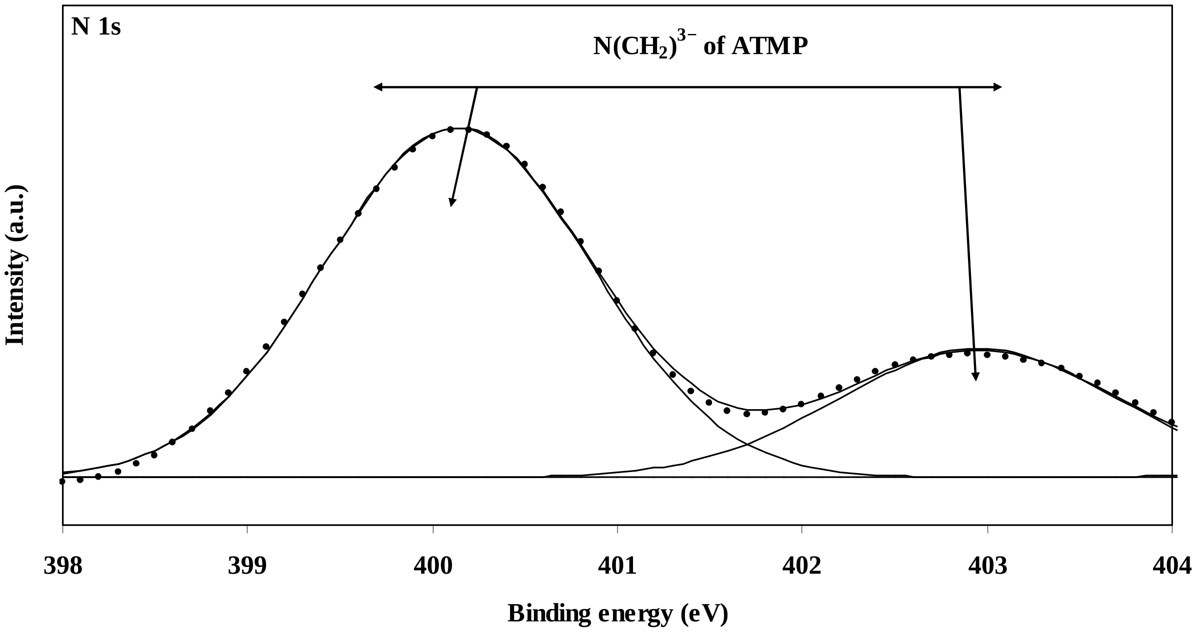


Fig. 8. The XPS deconvoluted profiles for N 1s for carbon steel after 24 h immersion period in 1 M HCl in the presence of 1× 10^{-1} M of ATMP at 30°C.

The results of the XPS confirm the presence of the ATMP on the carbon steel surface. Our previous study demonstrated the inhibitive effect of the ATMP on the corrosion of the carbon steel in 1 M HCl [25]. Indeed, the obtained thermodynamic parameter (ΔG^0_{ads}) indicated that the adsorption mechanism of ATMP on carbon steel surface involves two types of interactions, predominant physisorption (ionic) and weak chemisorption (molecular).

During the present study, we confirmed the inhibition effect of ATMP and demonstrated via the techniques surface (SEM-EDX, XPS) the presence of the ATMP on the steel surface. The obtained results are in good agreement with the previous study, and allowed to approach better the mechanism of inhibition of this molecule (ATMP).

Conclusion

In this work, chemicals (weight loss, ICP) methods were used to study the ability of ATMP to inhibit the corrosion of alloy in aerated stagnant 1 M HCl solutions. The principle conclusions are:

i. The corrosion of carbon steel in 1 M HCl solutions is significantly reduced upon the addition of ATMP.
ii. A surface film of inhibitor is formed on the electrode surface via electrostatic adsorption.
iii. EDX, XPS analysis and SEM examinations of the electrode surface confirmed the existence of such adsorbed film.

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