



Evaluation of the inhibitor synergetic effect of aminotris (methylenephosphonic) acid and metallic salts on the corrosion of iron in acidic medium

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Abstract

In the first part of this study, the effect of addition of various cations (Cu^{2+} , Mn^{2+} , Ca^{2+} , Zn^{2+}) and the aminotris-(methylenephosphonic) acid (ATMP) on the inhibition of iron corrosion in 1M HCl were studied using electrochemical methods (polarisation curves and EIS). Results indicate a significant synergistic effect between ATMP and Zn^{2+} . In the second part, the corrosion behaviour of iron in 1M HCl in the absence and presence of different ratios Zn/ATMP was studied using weight loss test and electrochemical techniques. The immersion solutions were analyzed using the spectroscopy induction coupled plasma. The results confirm the presence of synergistic effect between ATMP and Zn^{2+} , which can be attributed to the formation of Zn and ATMP complex. The maximum protection efficiency was observed at the ratio Zn/ATMP: 50%/50%.

Keywords: Aminotris-(methylenephosphonic) acid; Carbon steel; Hydrochloric acid; Corrosion inhibition; Synergistic effect.

1. Introduction

Acid solutions are widely used in industries for pickling, acid cleaning of boilers, descaling and oil well acidizing [1]. The use of inhibitors is one of the most practical methods for protection metal against corrosion, especially in acidic media. Most well-known acid inhibitors are organic compounds containing nitrogen, sulfur, phosphor and oxygen atoms [1- 24]. The selection of the inhibitors depends on the type of acid, its concentration, the temperature and the type of the metallic material. To improve the performance of inhibitors, the presence of another substance in the corrosive medium can have synergistic effects, decrease the amount of inhibitor and reduce the cost [25]. Several authors studied this phenomenon [26-48]. They notice that the addition of different cations in the solution can have synergetic effect on the efficiency of organic inhibitors.

The objective of the present work is to study the inhibitive efficiency of the amino-tris-methylene-phosphonate (ATMP) in the corrosive medium HCl 1M in the presence of mineral salts using weight loss, spectroscopy induction coupled plasma, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS).

2. Experimental method

2.1. Material

The molecular structure of the ATMP is shown in Figure 1. The tested compound, namely aminotris-(methylenephosphonic) acid ($\text{NCH}_2\text{P}(\text{O})(\text{OH})_{2.3}$), (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 5 minutes and then dried at room temperature before use. The acid solutions (1M HCl) were prepared by dilution of an analytical reagent grade 37% HCl with doubly distilled water.

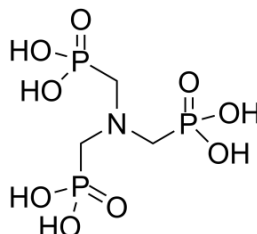


Figure 1: Molecular structure of the aminotris-(methylenephosphonic) acid (ATMP).

2.2. Weight loss test

Gravimetric experiments were carried out in a double glass cell equipped with a thermostated cooling condenser. The solution volume was 100 mL. The carbon steel specimens used have a rectangular form (length=2cm, width=1cm, thickness = 0.2cm). The maximum immersion time was 24 hours at 30°C in non-de-aerated solutions. At the end of the tests, the specimens were carefully washed in acetone under ultrasound and then weighted. Duplicate experiments were performed in each case and the mean value of the weight loss was reported. Weight loss allowed calculation of the mean corrosion rate in $\text{mg cm}^{-2} \text{h}^{-1}$. The percentage inhibition efficiency (IE) was calculated from,

$$IE \% = \frac{W_0 - W_i}{W_0} \times 100 \quad (1)$$

where W_0 and W_i are the weight loss values in absence and in presence of inhibitor.

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 100mL of 1 M HCl without and ATMP and zinc salt, iron, zinc and phosphore in the solution was measured. Analyses were realized on a Jobin Yron ULTIMA 2 with radical aim.

2.4. Electrochemical techniques

The measurements were carried out in a three electrodes electrochemical cell with a platinum counter electrode and a saturated calomel electrode as reference. The potential scan rate was 0.5 mV/s. All potentials are reported vs. SCE.

For polarization measurements, Tacussel-Radiometer model PGZ 301 potentiostat monitored by a PC computer and Voltmaster 4.0 software were used to run the tests and collect and evaluate the experimental data. All test solutions were de-aerated in the cell by using pure nitrogen for 30 minutes prior to the experiment. During each experiment, the test solution was mixed with a magnetic stirrer and the gas bubbling was maintained. Before each Tafel experiment, the carbon steel electrode was allowed to corrode freely and its open circuit potential (OCP) was recorded as a function of time up to 30 minutes. After this time span a steady-state OCP, corresponding to the corrosion potential (E_{corr}) of the working electrode, was obtained. The inhibition efficiency IE was calculated by using the following equation:

$$IE \% = \frac{I_{\text{corr}} - I_{\text{corr}(i)}}{I_{\text{corr}}} \times 100 \quad (2)$$

where I_{corr} and $I_{\text{corr}(i)}$ are referred to corrosion current density without and with addition of inhibitor respectively. Impedance measurements were performed with a Solartron 1255B frequency response analyzer in a frequency range of 10^5 Hz to 10^{-2} Hz with ten points per decade using 10mV peak-to-peak sinusoidal voltage and a Solartron SI 1287 electrochemical interface. ZPlot 2.80 software was used to run the tests and collect and evaluate the experimental data. The working electrode was prepared from a square sheet of carbon steel such that the area exposed to solution was 7.55cm^2 . The impedance spectra were recorded 24 hours after the exposure of the working electrode to the solution (no deaeration, no stirring). The impedance data were analyzed and

fitted with the simulation ZView 2.80, equivalent circuit software. The inhibition efficiency IE was calculated by the following equations:

$$IE \% = \frac{R'_{ct} - R_{ct}}{R'_{ct}} \times 100 \quad (3)$$

where R_{ct} and R'_{ct} are referred to charge transfer resistance without and with addition of inhibitor respectively.

3- Results and discussion

3.1. Results

3.1.1. Effect of the salts addition

To determinate the effect of salts addition on the inhibition power of ATMP, we studied, at first, the behaviour of the steel C38 in solution HCl 1M containing various mixtures ATMP + salt. Table 1 presents the various ratios of concentration ATMP / minerals SALT tested in this study.

Table 1: Composition of the various studied solutions

Compositions	Concentration of ATMP (M)	Chemical formula of the used salt	Concentration of salt (M)
50%Cu 50% ATMP	2.5×10^{-3}	$\text{CuSO}_4, 7\text{H}_2\text{O}$	2.5×10^{-3}
50%Mn 50% ATMP	2.5×10^{-3}	$\text{MnSO}_4, 7\text{H}_2\text{O}$	2.5×10^{-3}
50%Ca 50% ATMP	2.5×10^{-3}	$\text{CaSO}_4, 7\text{H}_2\text{O}$	2.5×10^{-3}
50%Zn 50% ATMP	2.5×10^{-3}	$\text{ZnSO}_4, 7\text{H}_2\text{O}$	2.5×10^{-3}

Fig. 2 shows the obtained Nyquist diagrams of carbon steel in 1M HCl solution in the absence and presence of 50 % of various metallic salts and 50 % of the ATMP.

The corresponding fitted parameters are listed in Table 2.

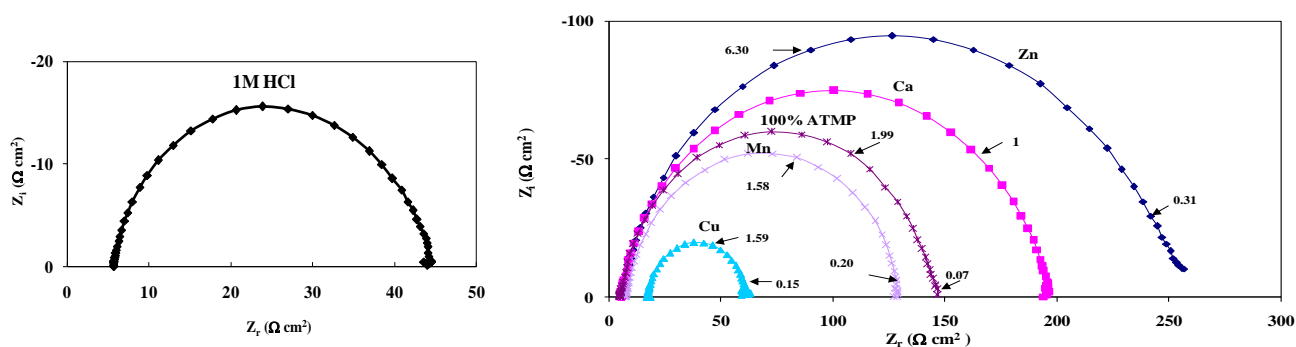


Figure 2: Diagrams of Nyquist of the steel in 1M HCl containing 50 % of various metallic salts and 50 % of the ATMP

Table 2: Impedance parameters and inhibition efficiency values after 24 hours immersion period of carbon steel in 1M HCl without and with inhibitor at 30°C.

Inhibitor	R_s $\Omega \text{ cm}^2$	$10^4 A$ $\text{s}^n \Omega^{-1} \text{ cm}^{-2}$	N	R_{ct} $\Omega \text{ cm}^2$	C_{dl} $\mu\text{F cm}^{-2}$	τ_d s	IE %
Blank	5.7	8.387	0.883	37.42	530.17	0.0198	
50%Zn 50% ATMP	5.9	3.001	0.85	250.8	190.11	0.0477	85.08
50%Ca 50%ATMP	5.12	3.957	0.865	189.6	264.13	0.0501	80.26
50%Mn50%ATMP	7.29	4.962	0.889	121.5	349.43	0.0424	69.2
50%Cu 50%ATMP	17.26	4.975	0.934	43.42	379.4	0.0165	13.81
100% ATMP	4.79	3.995	0.902	140.26	292.1	0.0410	73.32

The capacitive loop corresponds to the charge-transfer reaction which depends either on direct electron transfer at the metal surface or on the electron conduction through the film surface. The depressed form of the HF loop

reflects the surface inhomogeneity of structural or interfacial origin, such as those found in adsorption processes [49]. In this case, the constant phase element, CPE, is introduced in the circuit instead of a pure double layer capacitor to give a more accurate fit [50-52].

The addition of metallic salts in the corrosive medium in the presence of the ATMP is translated by an increase or a decrease in the size of the capacitive loop, depending on the nature of salt. In the presence of ZnSO₄ or CaSO₄, the value of R_{ct} increases and the (C_{dl}) decreases (Table 2). In presence of CuSO₄ or MnSO₄ salts, the value of R_{ct} decreases and the C_{dl} increases.

This result confirms the possible synergic effect of some cations and the ATMP, particularly in the presence of Zn²⁺ ions. The inhibitive efficiency increases in the following order: Zn²⁺> Ca²⁺>ATMP> Mn²⁺> Cu²⁺.

The important synergy effect between the ions Zn²⁺ and the ATMP allowed improving the protective power of the ATMP against the corrosion of the steel in HCl medium.

During the second step of our study, we examined the influence of various ratios Zn / ATMP on the inhibitive efficiency of the steel C38 corrosion in HCl 1M.

3.1.2. The effect of the addition of the ZnSO₄/ATMP on the corrosion inhibition of the steel in HCl media

To optimize the ratio Zn / ATMP, we studied the behaviour of the steel in HCl 1M in the presence of various ratio of Zn / ATMP (Table 3).

Table 3: Various molar ratios of Zn / ATMP used.

Reports Zn/ATMP	Concentration in ATMP (M)	Chemical formula of the used salt	Concentration in Zn (M)
100%Zn (Zn/ATMP=10/0)	0	ZnSO₄, 7H₂O	5 x 10⁻³
80%Zn 20%ATMP (Zn/ATMP=8/2)	10⁻³		4 x 10⁻³
70%Zn 30%ATMP (Zn/ATMP=7/3)	1.5 x 10⁻³		3.5 x 10⁻³
50%Zn 50%ATMP (Zn/ATMP=5/5)	2.5 x 10⁻³		2.5 x 10⁻³
30%Zn 70% ATMP (Zn/ATMP=3/7)	3.5 x 10⁻³		1.5 x 10⁻³
20%Zn 80% ATMP (Zn/ATMP=2/8)	4 x 10⁻³		10⁻³
100%ATMP (Zn/ATMP=0/10)	5 x 10⁻³		0

3.1.2.1. Weight loss Studies

Table 4 gives inhibition efficiency values (IE %), and the corrosion rate obtained by the weight loss method at different ratios of inhibitor (ATMP/Zn) in 1M HCl after 24 hours of immersion at 30°C.

The obtained results show that the presence of Zn²⁺ influences the corrosion rate, and this parameter changes considerably according to the quantity of Zn²⁺. The inhibitive efficiency reaches 86.84 % for a ratio of 50%ATMP and 50%Zn, whereas this rate is 74.78% in presence of 100% of the ATMP. This shows the beneficial effect of ZnSO₄.

We analysed, by ICP, the solutions after 24h immersion of the steel (solution of HCl 1M, a solution of HCl 1M + 5 x 10⁻³M of the ATMP and a solution of HCl 1M + 2.5 x 10⁻³ M of the ATMP + 2.5 x 10⁻³ M of Zn).

The following three elements were analyzed: the iron, the phosphor and the zinc (Table 5).

In the absence of inhibitors, the dissolved iron quantity in solution is very high comparatively to the quantities obtained in the presence of the inhibitors (100%ATMP and 50%Zn50%ATMP), and that the presence of 50 % of Zn in the solution considerably decreased the dissolved iron quantity in the solution. Therefore, we approximately determined the inhibitive efficiency of the steel corrosion in HCl 1M in the presence of the ATMP and of the ATMP + Zn. These percentages are close to the values founded by weight loss measurement.

We also notice that the quantity of Zn present in the solution remains practically unchanged, whereas the concentration of the phosphor considerably decreased. This can be explained by the adsorption of this element on the metallic surface, which is increased in presence of Zn^{2+} .

Table 4: Corrosion parameters obtained from weight loss measurements of carbon steel in 1M HCl containing various concentrations of ATMP/Zn at 30°C.

Inhibitor	Corrosion rate	IE
	($mg\ cm^{-2}\ h^{-1}$)	%
Blank	4.56	
100% Zn	3.74	18
80% Zn 20% ATMP	3.25	28.7
70% Zn 30% ATMP	2.7	40.8
50%Zn 50% ATMP	0.6	86.8
30%Zn 70% ATMP	0.94	79.4
20%Zn 80% ATMP	3.51	23.
100% ATMP	1.15	74.78

Table 5: Results of the ICP analysis

Medium	Fe Analyse ICP (mg/L)	IE % = $(M_i - M_f)/M_i$	P		Zn	
			Theoretical value (mg/L)	Analyse ICP (mg/L)	Theoretical value (mg/L)	Analyse ICP (mg/L)
HCl 1M	$M_i = 148.3$	-----	-----		-----	-----
100% ATMP	$M_{f1} = 40.01$	73.02	465	389.65	-----	-----
50% Zn 50% ATMP	$M_{f2} = 20.76$	86	232.5	102.14	163.55	154.12

3.2.1.2. Electrochemical studies

Figure 3 shows the polarization curves of the steel in HCl 1M without and with addition of various ratios of Zn / ATMP; the temperature is 30°C. The values of the corrosion current densities (I_{corr}), the corrosion potential (E_{corr}), the Tafel slopes (b_c , b_a) and the inhibition efficiency IE(%) for various ratio of Zn/ ATMP are summarised in Table 6.

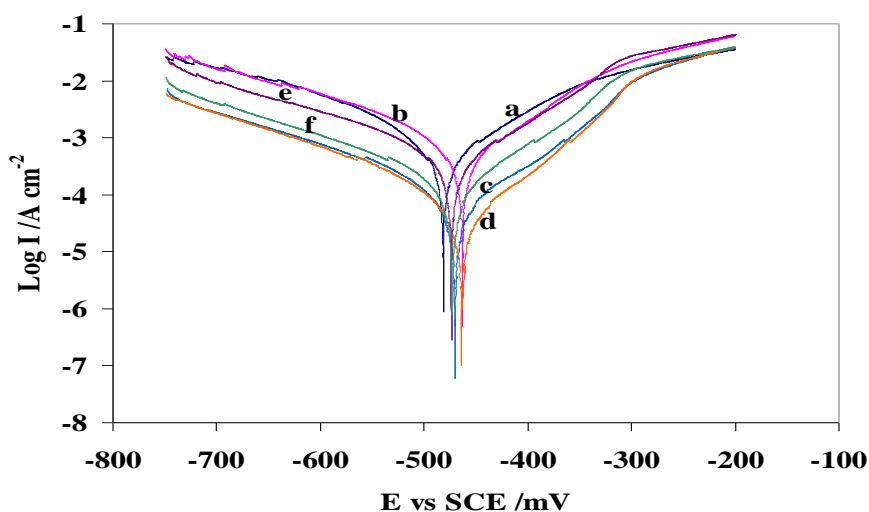


Figure 3: Polarization curves for carbon steel in 1M HCl containing different reports of ATMP/Zn concentrations (a : Blank HCl 1M) ; (b : Zn. /ATMP. = 10/0) ; (c : Zn. /ATMP. = 3/7); (d: Zn. /ATMP. = 5/5); (e: Zn. /ATMP. = 7/3); (f:Zn. /ATMP. = 0/10).

According to the obtained results, we can notice that the current densities I_{corr} decreases with the concentration in $ZnSO_4$ until the ratio $Zn / ATMP = 5/5$. But I_{corr} increases up to this concentration. This result shows the existence of a synergic phenomenon between the ATMP and $ZnSO_4$, depending on the concentration of each others.

The effect of synergy between the ATMP and Zn^{2+} can be explained by the stabilisation of the adsorption of the ATMP on the surface of the steel in presence of Zn^{2+} .

Table 6. Polarization parameters and the corresponding inhibition efficiency for the carbon steel corrosion in 1M HCl containing different ratios of concentrations of ATMP/Zn at 30°C.

Inhibitor Conc. (M)	E_{corr} vs SCE (mV)	I_{corr} ($\mu A\ cm^{-2}$)	b_a (mV dec^{-1})	b_c (mV dec^{-1})	IE %
Blank	- 481.5	569.8	92	188	—
Zn. /ATMP. = 0/10	- 473.2	175.4	84	146	69.22
Zn. /ATMP. = 3/7	- 470.7	155.2	79.7	183.6	72.83
Zn. /ATMP. = 5/5	- 463.9	117.5	76	173.9	79.37
Zn. /ATMP. = 7/3	- 473.9	268.5	87.8	100.5	52.88
Zn. /ATMP. = 10/0	- 463.1	320	79.4	78	43.84

The Nyquist diagrams of iron in presence of 5×10^{-3} M of the amino-tris-methylene phosphonate and $ZnSO_4$ to various ratios, in HCl 1M in 30°C, after 24 hours of immersion are illustrated in Figure 4 and Table 7.

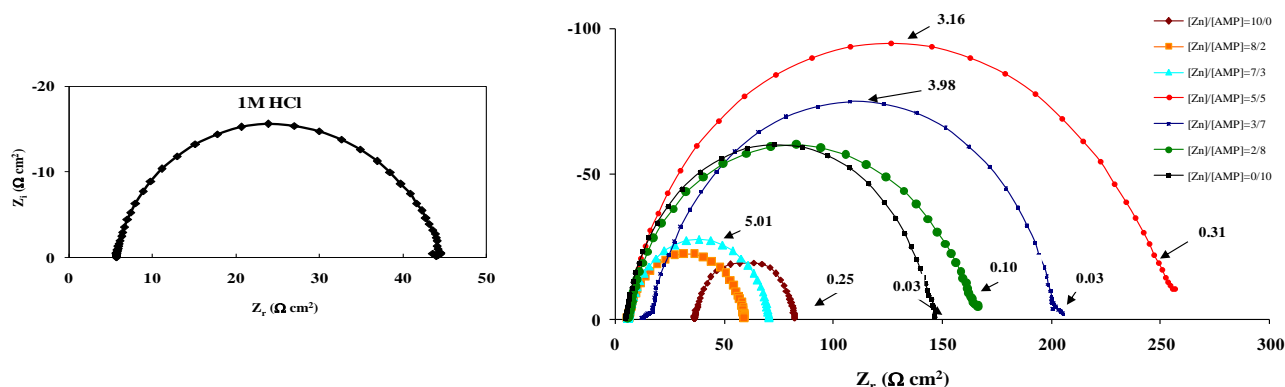


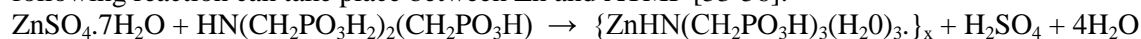
Figure 4: Nyquist Diagrams of the steel in HCl 1M with different ratio of Zn/ATMP.

Table 7: Electrochemical parameters and inhibitive efficiency for the corrosion of the steel in HCl 1M obtained by EIS in the presence of various ratios Zn/ATMP.

Inhibitor	R_s $\Omega\ cm^2$	$10^4 A\ s^n \Omega^{-1}\ cm^{-2}$	n	R_{ct} $\Omega\ cm^2$	C_{dl} $\mu F\ cm^{-2}$	τ_d s	IE %
HCl 1M	5.7	8.387	0.883	37.42	530.17	0.0198	
100% Zn	36.33	7.839	0.878	45.62	493.46	0.0225	17.97
80% Zn 20%ATMP	6.19	7.662	0.885	52.9	505.16	0.0267	29.26
70% Zn 30%ATMP	6.1	7.205	0.892	64.32	496.72	0.0319	41.82
50%Zn 50% ATMP	5.9	3.001	0.85	250.8	190.11	0.0477	85.08
30%Zn 70% ATMP	14.26	3.526	0.849	189.4	217.89	0.0412	80.24
20%Zn 80% ATMP	6.21	7.76	0.883	48.54	502.54	0.0244	22.91
100% ATMP	4.75	3.995	0.902	140.26	292.1	0.0410	73.32

According to these results, we can notice that the presence of Zn in the solution influences clearly the inhibitive behaviour of the ATMP. The value of R_{ct} in the presence of 50%Zn50%ATMP is the most important and the value of C_{dl} decreases and reaches a value of $190\ \mu F\ cm^{-2}$.

The addition of the ZnSO₄, in an optimal concentration, to the solution in the presence of the ATMP, significantly improved the inhibitive efficiency comparatively to the ATMP. The weight loss test, the SIE, and curves E=f (I) show that the presence of Zn in a report Zn/ATMP=5/5 allows to have the best inhibitive efficiency of the steel corrosion in HCl 1M. The ICP analysis of the immersion solutions showed that the presence of Zn allowed a better adsorption of the ATMP on the surface of the steel. In acidic medium, the following reaction can take place between Zn and ATMP [53-56].



The formed complex helps to considerably increase the size of the molecule of ATMP. So, the formed complex adsorbs on the metal covering a larger surface, and thus allows to increase the inhibitive corrosion efficiency of the molecule.

Conclusion

The corrosion of iron was studied using Ac impedance measurements in the presence of ATMP and bivalent cations, such as Zn, Ca, Cu and Mn. The Zn improved the inhibitive corrosion efficiency of the iron in HCl 1M in presence of ATMP.

At optimal ratio Zn/ATMP: 50%/50%, the inhibition may be caused by formation of Zn/ATMP complex. Synergism was determined and analysed quantitatively using various techniques, the presence of Zn allows the adsorption of the ATMP on the surface of the steel.

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