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Effect of Zn ions on corrosion inhibition of aminotris (methylenephosphonic) acid for carbon steel in acidic solution

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Abstract : The synergistic effect of zinc ions on the corrosion inhibition of carbon steel in 1M HCl solutions by aminotris-tris (methylene phosphonic) acid (ATMP) has been studied using electrochemical impedance spectroscopy (EIS), Tafel polarisation method, gravimetric measurement and inductively coupled plasma (ICP). The results revealed significant synergistic effect between ATMP and Zn^{+2} which depend on the molar ratio, temperature and immersion time. The presence of Zn^{2+}/ATMP induces a decrease in anodic and cathodic currents. They act as a mixed–type inhibitor. The addition of zinc ions in acidic solution containing ATMP induces the formation of stable complexes and stabilizes the adsorption of ATMP on the steel surface. The synergistic effect was observed between Zn^{2+} and ATMP with an optimum molar ratio of Zn^{+2}/ATMP = 5/5.

Keywords : Aminotris-(methylenephosphonic) acid; Zinc ions; Carbon steel; Acid inhibition; ICP; EIS.

INTRODUCTION

The use of corrosion inhibitors is one of the most practical methods for metal corrosion protection in different medium. Most well-known acid inhibitors are organic compounds, that act by adsorption on the steel surface, through heteroatoms, such as nitrogen, sulfur, phosphorus and oxygen atoms as well as through triple or conjugated double bonds or aromatic rings[1-24]. The inhibitors efficiency depends on the medium, the temperature and the type of the metallic material used.

Synergistic inhibition is an effective method to improve the inhibition action of inhibitor in the presence of another substance in the corrosive medium, to decrease the amount of usage and to reduce the cost of the inhibitor in acidic media[25]. Synergetic inhibition effect on the corrosion inhibition mechanism has been reported by several authors[26-47]. In previous studies, some researchers found that the addition of metal ion improves the inhibitor performance of organic compounds as inhibitor for steel in acidic solutions[48,49].

In our previous studies[50-52], the inhibitor effect of ATMP on the corrosion of iron steel in 1 M HCl was investigated. The results showed that the inhibition efficiency increased with ATMP concentration reaching a maximum at 10^{-1}M of ATMP. The corrosion inhibition is mainly controlled by a physisorption process. The objective of the present work is to investigate the synergistic influence of zinc ions on the performance of the amino-tris-methylene-phosphonate (ATMP) as a corrosion inhibitor compound for carbon steel in 1M HCl using gravimetric measurement, ICP and electrochemical techniques (potentiodynamic polarization and EIS methods).

EXPERIMENTAL

Chemicals and solutions

The inhibitor, 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 molecular structure of ATMP is shown in Figure 1. Zinc ions are used in the form of sulphate salt ($ZnSO_4 \cdot 7H_2O$).

In this study, we examined the influence of various ratios of Zn^{2+}/ATMP on the corrosion rate of carbon steel in 1M HCl solution (TABLE 1). In all cases, the total concentration of Zn^{2+} and ATMP used was $5x10^{-3}$ M.

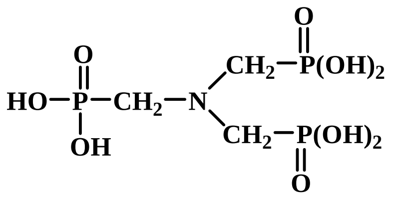

Figure 1 : Aminotris-(methylenephosphonic) acid (ATMP).

Tests were performed on carbon steel coupons with a 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 using emery paper SiC (grades 120, 600 and 1200); they were rinsed with distilled water, degreased with acetone under ultrasound 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 bi-distilled water.

TABLE 1 : Various ratios Zn^{2+} / ATMP used

Ratios Zn^{2+}/ATMP	Concentration in ATMP (M)	Concentration in Zn^{2+} (M)
100% Zn^{2+} (Zn^{2+}/ATMP = 10/0)	0	5 x 10^{-3}
70% Zn^{2+} 30%ATMP (Zn^{2+}/ATMP = 7/3)	1.5 x 10^{-3}	3.5 x 10^{-3}
50% Zn^{2+} 50% ATMP (Zn^{2+}/ATMP=5/5)	2.5 x 10^{-3}	2.5 x 10^{-3}
30% Zn^{2+} 70% ATMP (Zn^{2+}/ATMP=3/7)	3.5 x 10^{-3}	1.5 x 10^{-3}
100% ATMP (Zn^{2+}/ATMP = 0/10)	5 x 10^{-3}	0

Gravimetric test

Gravimetric experiments were carried out at 30°C in a double glass cell equipped with a thermostated cooling system. The solution volume was 100 mL. The carbon steel specimens used have a rectangular form (length=2cm, width=1cm, thickness = 0.2cm). All weight loss tests were done in an atmospheric environment for 24h. After 24 hours, the specimens were removed, carefully washed in acetone under ultrasound, dried and then reweighted. The experiments were done in duplicate in each case and the average value of weight loss was reported. The corrosion rate (in mg $cm^{-2}.h^{-1}$) was calculated using the following equation[53].

$$V = \frac{\Delta P}{S.t} \qquad (1)$$

Where ΔP is the average weight loss, S the total surface area and t is immersion time.

The inhibition efficiency (η) was calculated as follows[53]

$$\eta(\%) = \frac{V - V_{inh}}{V} x100 \qquad (2)$$

where V and V_{inh} are the corrosion rate values in the absence and in the presence of inhibitor.

Spectroscopy induction coupled plasma

The sample was ionised by injecting it in plasma of argon. Analyses were performed on a Jobin Yron ULTIMA 2 with radical aim. The calibration is made in the same solution of HCl to eliminate the effect of matrix.

EIS measurements

Electrochemical measurements were performed in a conventional three electrode cell with a platinum electrode as a counter electrode and a saturated calomel electrode (SCE) as the reference electrode. All potentials are reported versus SCE.

EIS measurements were performed using a Solartron 1255 FRA system and a Solartron ECI 1287. Impedance spectra were obtained in the frequency range of 100 KHz to 0.01 Hz with ten points per decade. An AC sinusoid ±10mV was applied at the corrosion potential (E_{corr}). The EIS tests were performed in a polymethyl methacrylate (PMMA) cell with a capacity of 1000 mL at 30±1 °C, using a thermostat. The working electrode was prepared from a square sheet of carbon steel such that the area exposed to solution was 7.55cm^2. The inhibition efficiency (η) was defined as,

$$\eta(\%) = \frac{R_{ctcorr}{}^{-1} - R_{ctcorr(inh)}{}^{-1}}{R_{ctcorr}{}^{-1}} \times 100 \qquad (3)$$

where R_{ct} and $R_{ct(inh)}$ were charge transfer resistance without and with addition of inhibitor, respectively.

Potentiodynamic polarization

Polarization measurements were carried out using Tacussel-Radiometer model PGZ 301 measurement system. A carbon steel cylinder pressed into a Teflon holder acted as a working electrode (WE). Its working area of 1 cm^2 remained precisely fixed. A fine Luggin capillary was placed close to the working electrode to minimize ohmic resistance. All test solutions were deaerated in the cell by using pure nitrogen for 30 min 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 up to 30 min. After this time a steady-state OCP, corresponding to the corrosion potential (E_{corr}) of the working electrode, was obtained. The anodic and cathodic polarization curves were recorded at a constant sweep rate of 0.5mVs^{-1}.

RESULTS AND DISCUSSION

Weight loss measurements

The addition effect of [Zn^{+2}]/[ATMP] at different ratio on carbon steel corrosion in 1M HCl was studied by weight loss at 30°C after 24h of immersion. The inhibition efficiency η % and the corrosion rate are given in TABLE 2. Clearly, efficiency depends on the ratios [Zn^{+2}] / [ATMP]. When only Zn^{2+} was added to the solution, the value of η % was relatively low. When ATMP was added, the efficiency increased. The efficiency was increased from 17.98% to 86.84% when 2.510^{-3}M ATMP and 2.510^{-3}M Zn^{2+} were used together, indicating that a synergistic effect exist. There are two domains and the beneficial effect of Zn^{2+} depends on its concentration on solution. For concentration of Zn^{2+} less than 2.5x10^{-3}M, the efficiency increases with the concentration of Zn^{2+} witch stabilize the adsorption of ATMP on the steel surface and form a stable ATMP-Zn2+ complexes[49]. When the concentration of Zn^{2+} is superior to the ATMP concentration, η% decreases because excessive amount of Zn^{2+} may result on the occupancy of the limited actives sites available for the adsorption of ATMP molecules which are necessary to cover the electrode surface to ensure steel protection against the acid corrosion.

Spectroscopy induction coupled plasma

To determinate the synergy effect between the ATMP and the ions Zn^{2+}, the solutions of immersion were analysed by ICP (TABLE 3). These results showed that in the absence of the inhibitors, the dis-

TABLE 2 : Corrosion parameters obtained from weight loss measurements of carbon steel in 1M HCl containing various ratios of concentrations of ATMP/Zn at 30°C.

Inhibitor	Corrosion rate (mg cm^{-2} h^{-1})	η %
Blank	4.56	
100% Zn^{2+}	3.74	17.98
70% Zn^{2+} 30% ATMP	2.7	40.79
50% Zn^{2+} 50% ATMP	0.6	86.84
30% Zn^{2+} 70% ATMP	0.94	79.38
100% ATMP	1.15	74.78

solved iron quantity in solution is very high comparatively to the quantities measured in the presence of the inhibitors (100% ATMP and 5/5 ratio $[Zn^{+2}]/[ATMP]$). The presence of Zn^{2+} and ATMP, in the solution, considerably decreased the dissolved iron quantity in the solution. Consequently, the inhibitive efficiency deducted is in good agreement and confirm the results obtained by the gravimetric test.

The quantity of Zn^{2+} present in the solution remained practically unchanged, whereas the concentration of the phosphor considerably decreased. This can be explained by the adsorption of ATMP on the metallic surface and confirm that Zn^{2+} stabilize the adsorption of ATMP on the steel surface.

Electrochemical impedance spectroscopy studies

The corrosion behaviour of carbon steel in 1M HCl solution in presence of Zn^{2+}/ATMP was also investigated by electrochemical impedance spectroscopy (EIS) at 30°C after 24h of immersion. Nyquist plots of carbon steel in uninhibited and inhibited acidic solutions containing different ratios of $[Zn^{+2}]/[ATMP]$ are given in Figure 2. These diagrams have similar shape for all tested concentrations, indicating that addition of inhibitor induce no change in the corrosion mechanism.

The impedance spectra show a large capacitive loop related to a single charge transfer of the corrosion process. These capacitive loops are not perfect semicircles and are depressed into the real axis as a result of the micro roughness and energetic heterogeneity of the metal surface during the corrosion process[49,50]. The impedance parameters deduced from the analysis of Nyquist diagram and values of efficiency are given in TABLE 4. Double layer capacitance values (C_{dl}) and charge transfer resistance vales (R_{ct}) were obtained from impedance measurements as previously described[54]. To obtain the double-layer capacitance (C_{dl}), the frequency at which the imaginary component of the impedance is maximum (_Z_{imax}) is found and C_{dl} values are calculated from the following equation:

$$f(-Z_{i\,max}) = \frac{1}{2\pi C_{dl} R_{ct}} \qquad (4)$$

The efficiency is calculated by charge transfer resistance as previously described[53]. As shown in Figure 2 and TABLE 4, R_{ct} increased to 250.8 Ωcm^2 and C_{dl} decreased to 190.11 $\mu F\ cm^{-2}$ in presence of Zn^{2+}/ATMP at molar ratio 5/5. A large charge transfer resistance is associated with a slower corroding system. The decrease in C_{dl}, which result from a decrease in local dielectric constant and/or an increase in the thickness of the electrical double layer, suggests that the Zn^{2+}/ATMP function by adsorption at the metal solution/interface. The increase of inhibition efficiency recorded in the presence of Zn ions can be related to the relatively high stability of Zn complexes compared with ferrous complexes[55,56]. The inhibition efficiencies calculated from EIS are in good agreement with those obtained by weight loss measurements and ICP.

Effect of immersion time and temperature

The molar ratio, which acts as best inhibition effect in the studied concentration range, was selected for further investigations. Figure 3 shows the Nyquist diagrams for carbon steel in 1M HCl containing the optimal molar ratio $2.5x10^{-3}$M of Zn^{2+} and $2.5x10^{-3}$M of ATMP ($[Zn^{+2}]/[ATMP]=5/5$) after differents immersion time. After 44 h (Figure 3), the diameter of the semicircle recorded in the presence of the inhibitors increased significantly as compared to shorter exposure times, which indicated the continuous growth of the surface film and the approach in the perfect coverage of the surface film on the metal. The growth of this layer enhanced the corrosion resistance of the metal.

EIS parameters obtained for different immersion timeare given in TABLE 5. R_{ct} value in inhibited solu-

TABLE 3 : ICP analysis results for the different solutions.

		P		Zn^{2+}		
	Fe (mg/L)	Theoretical value (mg/L)	Analyse ICP (mg/L)	Theoretical value (mg/L)	Analyse ICP (mg/L)	η % = $(M_i - M_f)/M_i$
HCl 1M	M_i = 148.3	---------		----------	--------	
HCl + $5x10^{-3}$M ATMP	M_{f1}= 40.01	465	389.65	----------	---------	73.02
$2.5x10^{-3}MZn^{2+}$ + $2.5x10^{-3}$M ATMP	M_{f2}= 20.76	232.5	102.14	163.55	154.12	86

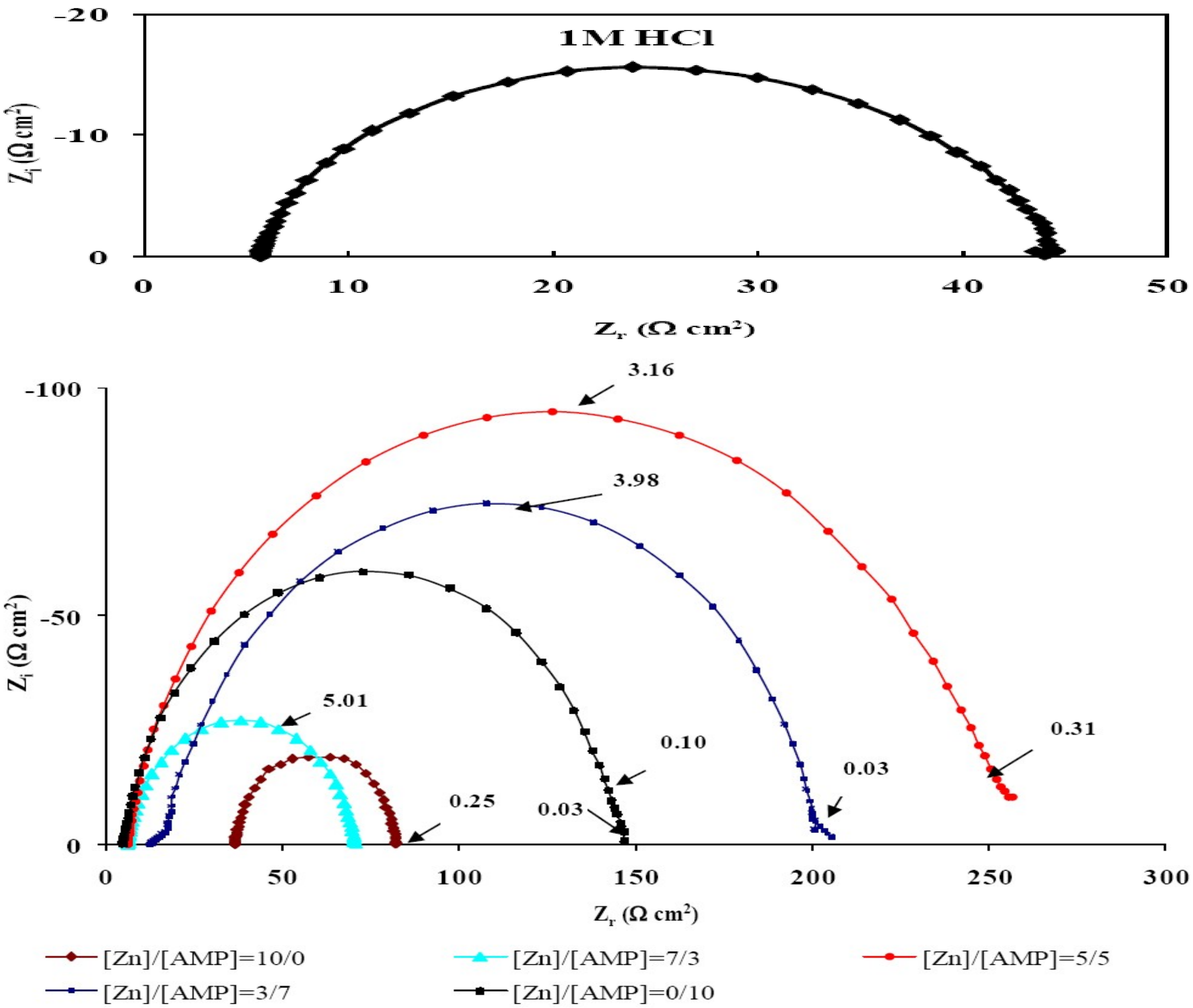

Figure 2 : Nyquist diagrams of the steel in HCl 1M containing different ratios of Zn^{2+}/ATMP.

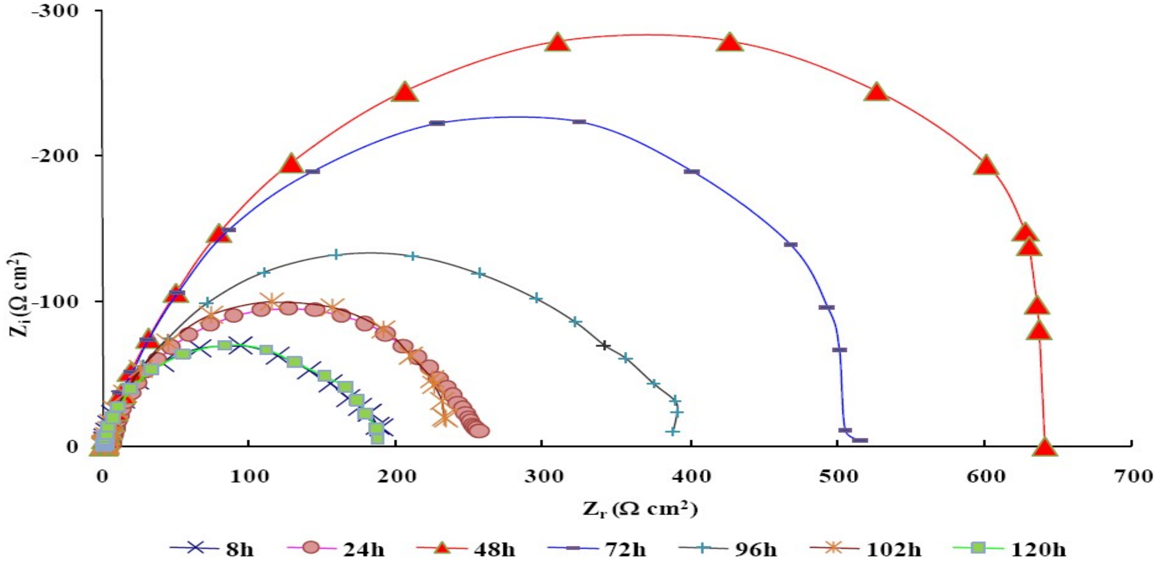

Figure 3 : Nyquist diagrams of the carbon steel in HCl 1M + 5 x 10^{-3}M of (50%Zn^{2+} + 50 % ATMP) at 30°C according to different immersion time.

TABLE 4 : EIS parameters and inhibitive efficiency for the carbon steel in HCl 1M in the presence of various ratios of [Zn^{2+}] / [ATMP]

Inhibitor	10^4 A $s^n\Omega^{-1}cm^{-2}$	N	R_{ct} Ω cm^2	C_{dl} μF cm^{-2}	τ_d s	η %
1 M HCl	8.387	0.883	37.42	530.17	0.0198	
100% Zn^{2+}	7.839	0.878	45.62	493.46	0.0225	17.97
70% Zn^{2+} 30%ATMP	7.205	0.892	64.32	496.72	0.0319	41.82
50% Zn^{2+} 50% ATMP	3.001	0.85	250.8	190.11	0.0477	85.08
30% Zn^{2+} 70% ATMP	3.526	0.849	189.4	217.89	0.0412	80.24
100% ATMP	3.995	0.902	140.26	292.1	0.0410	73.32

TABLE 5 : Electrochemical parameters obtained by S.I.E from the steel in HCl 1M + 5 x 10^{-3}M of (50%Zn^{2+} + 50 % ATMP) in 30°C according to the immersion time.

Immersion time in hrs	10^4 A $s^n\Omega^{-1}cm^{-2}$	N	R_{ct} Ω cm^2	C_{dl} μF cm^{-2}	τ_d S
8	8.99	0.666	188	368.60	0.0693
24	3.001	0.85	250.8	190.11	0.0477
48	5.98	0.445	641	180.85	0.1159
72	8.83	0.557	514	471.09	0.2421
96	8.93	0.667	394	530.11	0.2089
102	8.73	0.783	237	564.14	0.1337
120	8.83	0.85	187	642.58	0.1202

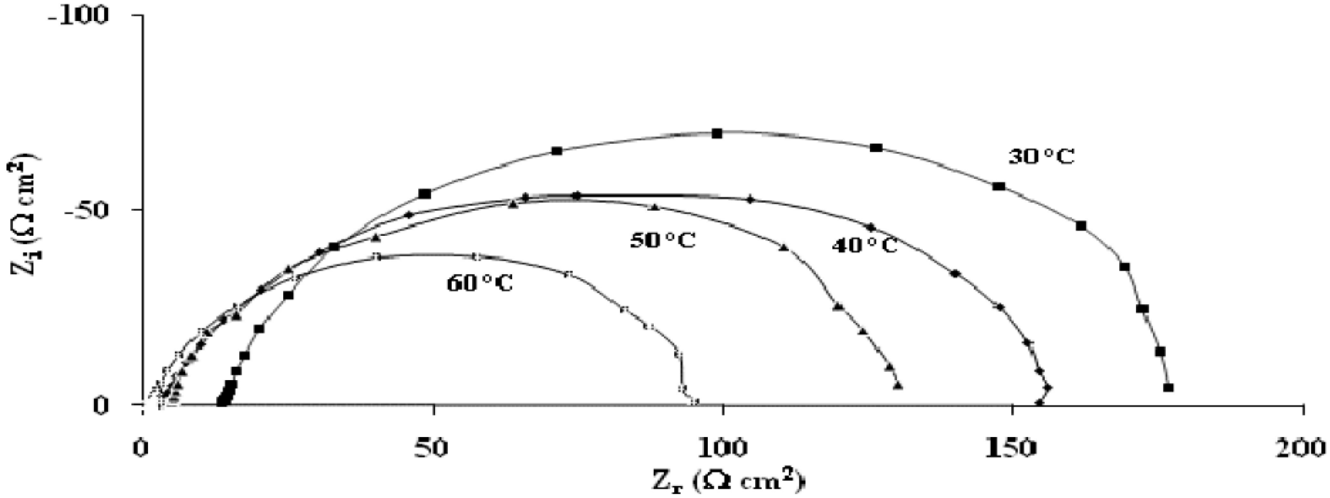

Figure 4 : Nyquist diagrams of the carbon steel C 38 in a solution 1M HCl + 5×10^{-3}M (50% Zn^{2+} + 50 % ATMP) at various temperatures after 2 hrs immersion time.

TABLE 6 : EIS parameters ofthe steel in 1 M HCl + 5 x 10^{-3}M of (50% Zn^{2+} + 50 % ATMP) at various temperatures after 2 hrs of immersion time.

T (°C) of immersion	5 10^{-3}M (50% Zn^{2+} + 50% ATMP)	
	R_{ct} Ω cm^2	C_{dl} μF cm^{-2}
30	177	178.78
40	161	210.90
50	134	211.71
60	95	214.81

tion increased up to 48 h, and then tends to a decrease. After 48 h, a decrease in the R_{ct} value was observed, which may be due to the formation of some defects on the film leading to the access of aggressive ions to the metal/inhibitor interface.

Figure 4 shows the Nyquist diagrams for carbon steel in 1M HCl containing 2.5x10^{-3}M of Zn^{2+} and 2.5x10^{-3}M of ATMP at different temperature after 2 hrs of immersion. For all temperature, spectra exhibit one single semicircle and its diameter decreases with the increase of temperature. The same result is observed with ATMP[50]. The values of R_{ct} decrease with the increase oftemperature range of 30°C to 60°C (TABLE 6).

In order to calculate the activation energy of the corrosion process and investigate the mechanism of inhibition, AC impedance study was performed in the temperature range of 30–60°C in the presence of mixed inhibitor Zn^{2+}/ATMP. The dependence of the corrosion rate on temperature can be expressed by the Arrhenius equation:

$$i_{corr} = A\exp(\text{“}E_a/RT) \qquad (5)$$

where icorr is corrosion current, A is a constant, Ea the activation energy of the metal dissolution reaction, R is the gas constant andT is the temperature. The E_a and DH°a values were calculated from the Arrhenius plots and found to be 19.69 kJ mol^{-1} and 17.05 $KJ.mol^{-1}$ respectively. The decrease in activation energy after the addition of the inhibitor to the 1 M HCl (TABLE 7) solution indicates that chemical adsorption occurs in the first stage[51,57,58]. The value of the energy of activation (Ea) is bigger than the similar value of $\Delta H_a°$ indicating that the process of corrosion involves a gaseous reaction, that of the formation of H_2. Indeed, the average

TABLE 7 : Calculated values of E_a for cabon steel in 1MHCl in presence and in absence of inhibitors

Medium	1M HCl[51]	1M HCl + 510^{-3} M ATMP[51]	1M HCl + 510^{-3} M (Zn^{2+}/ ATMP = 5/5)
E_a ($KJ.mol^{-1}$)	22.92	48.9	19.69

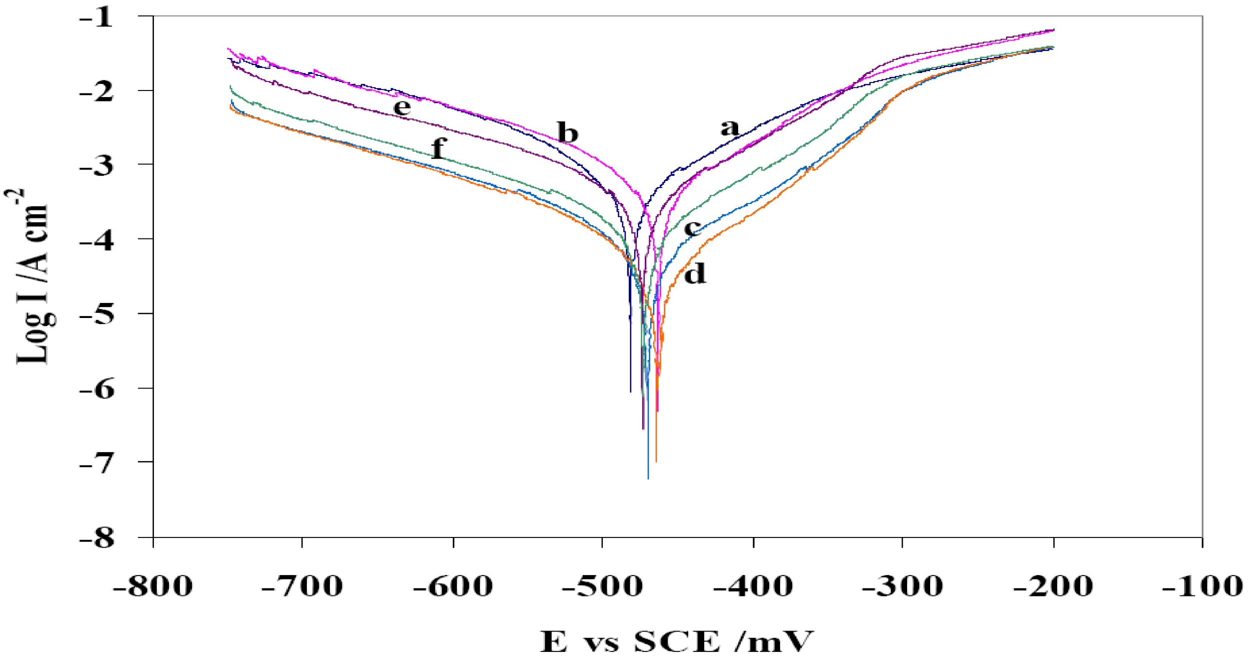

Figure 5 : Polarization curves for carbon steel in 1M HCl containing different ratios of concentrations of ATMP/Zn (a : Blank HCl 1M) ; (b : [Zn] /[ATMP] = 10/0); (c : [Zn] /[ATMP] = 3/7); (d: [Zn] /[ATMP] = 5/5); (e: [Zn] /[ATMP] = 7/3); (f:[Zn] /[ATMP] = 0/10).

TABLE 8 : Polarization parameters and the corresponding inhibition efficiency for the corrosion of carbon steel in 1M HCl containing different molar ratio of ATMP/Zn at 30°C.

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

value of the difference ($E_a - \Delta H°_a$) is apporimatly 2.64 KJmol^{-1} very close to the average value of the product RT (2.68 KJmol^{-1}), where T in the range 30°C – 60°C, this is explained by the fact that the process of corrosion is a unimolecular reaction, characterised by the following equation[59]:

$$E_a - \Delta H°_a = RT$$

Polarization studies

The potentiodynamic polarization curves of the carbon steel inM HCl solution with various molar ratio of Zn^{2+}/ATMP are presented in Figure 5. The related electrochemical parameters, i.e., corrosion potential (Ecorr), corrosion current density (icorr) and inhibition efficiency (IE%) values were calculated from these curves and listed in TABLE 8.

It is clear from Figure 5 that, both anodic metal dissolution of iron and cathodic hydrogen evolution reaction were inhibited after the addition of inhibitors to the aggressive solution. The inhibition of these reactions is more pronounced with the increasing inhibitor concentration while the corrosion potential values are nearly remained the same. These results suggest that Zn^{2+}/ATMP can be classified as mixed type corrosion inhibitor. The cathodic current–potential curves (Figure 5) give rise to parallel lines indicating that the addition of mixed inhibitor Zn^{2+}/ATMP to the 1 M HCl solution does not modify the hydrogen evolution mechanism and the reduction of H^+ ions at the metal surface takes placemainly through a charge transfer mechanism. The inhibitor molecules are first adsorbed onto the surface and, therefore, impedes by merely blocking the reaction sites of the metal surface. In this way, the surface area available for H^+ ions is decreased while the actual reaction mechanism remains unaffected[60]. A higher coverage of the inhibitor on the surface was obtained in solutions with the equal molar concentrations of Zn^{2+} and ATMP.

The zinc ions may compete with the ATMP molecules for adsorption on the metal surface, but the adsorbed Zinc ions stabilize the adsorption of ATMP via interaction between Zn^{2+} and ATMP which form a stable complexe[54].

$$ZnSO_4.7H_2O + HN(CH_2PO_3H_2)_2(CH_2PO_3H) \rightarrow \{Zn[HN(CH_2PO_3H)_3(H_20)_3]\}_x + H_2SO_4 + 4H_2O$$

So that the inhibition ability of ATMP are improved by the combined use of ATMP and Zn^{2+}.

CONCLUSION

In this work, the effect of the Zn^{2+} cations addition on the corrosion inhibition of carbon steel in 1 M HCl, in the presence of the ATMP, was investigated. The addition of Zn^{2+} directly influenced the inhibitive behavior of the ATMP and was dependant on the its concentration, temperature and immersion time.

Addition of Zn^{2+} improves the efficiency of ATMP significatly and the high synergistic effect is clearly shown with an optimumm molar ratio of $[Zn^{+2}]/[ATMP]= 5/5$. The ICP analysis of the immersion solutions showed that the presence of Zn^{2+} enhanced the adsorption of the ATMP on the surface of the steel. The effect of immersion time and solution temperature on the evolution of R_{ct} was also estimated. It was found that the increase of temperature induce a decrease in the value of the transfer resistance and the optimal immersion time is about 48 hrs.

The adsorption of ATMP is stabilised in the presence of zinc ions in the 1M HCl solutions and form a stable complexe.

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