# Synergistic effects of aminotris(methylene phosphonic acid) and Zn<sup>2+</sup> on the carbon steel corrosion in acid media: An experimental and theoretical approach

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# Abstract

The corrosion of metals and alloys causes considerable material losses, both in direct and indirect ways, for industry and society every year. Each year, corrosion destroys an amount of steel equivalent to one quarter of annual global production. Across a variety of industries, corrosion results in equipment break down which leads to a major financial loss. While there are several methods to prevent and/or retard corrosion of metallic materials, the use of inhibitors is one of the most effective strategies to ensure the protection of these materials, in environments characterized by contact with aggressive acid media. This study utilized gravimetric analysis, polarization, EIS, adsorption, and computational methods to research the synergistic effects of aminotris(methylenephosphonic acid) (ATMP) and  $(Zn^{2+})$  on corrosion inhibition of carbon steel in hydrochloric acid. The study revealed that the efficiency of the inhibition varies depending on the ATMP/Zn<sup>2+</sup> ratio. For 10<sup>-2</sup> M of ATMP and 10<sup>-3</sup> M of Zn<sup>2+</sup>, the maximum inhibition effect value is obtained. The effects of the synergism depend on both the temperature and ratio of  $ATMP/Zn^{2+}$ . From the results observed in this study, the synergistic parameter was found to be greater than 1. To theoretically analyze the corrosion inhibition performances of studied compounds, DFT and Monte Carlo Simulation approaches are considered. It is important to note that the theoretical acquired data support the experimental observations.

Received: June 9, 2021. Published: September 6, 2021

doi: 10.17675/2305-6894-2021-10-3-24

*Keywords:* carbon steel, acid media, corrosion, adsorption, organic compounds, electrochemical techniques, synergism.

### **1. Introduction**

Carbon steel is an important commodity used in the chemical and petrochemical industries due to its efficient production, cost efficiency, and outstanding mechanical workability [1-3]. These industries face multiple challenges including corrosion, a very damaging chemical and electrochemical operation [3, 4]. Acid solutions are commonly used in the acid pickling, factory washing, acid de-scaling, oil acidification and petrochemical industries [5–7]. Because of their aggressive behavior, hydrochloric, sulfuric, and nitric acids are some of the widely used acids in solution [8-10]. Inhibition ranks alongside material selection, use of protective coatings, and process conditions/environment adjustment as one of the most common methods used for corrosion control. Organic combinations that are strongly polar functional compounds are commonly used corrosion inhibitors, many of which are based on nitrogen, P, S and O [11–31], allowing for adsorption on the surface of the metal, which has been observed to rely on the physicochemical properties of the functional groups and the density of electrons in the donor atom. Most of the organic compounds that have been studied as corrosion inhibitors for iron and low alloy steels are toxic in nature [32–38]. Phosphonates, on the other hand, have been found to have a negligible environmental impact at the levels of concentration necessary to inhibit corrosion [39, 40]. Organic compounds containing groups of  $R-PO(OH)_2$  or  $R-PO(OR)_2$  include phosphonates or phosphonic acids. These phosphonic acids have either been used alone [41-45] or in conjunction with other inhibitors like Zn<sup>+2</sup> [46–49]. This study investigates the synergistic phenomenon and also the mechanistic aspects of carbon steel corrosion inhibition in the presence of Zn-ATMP in 1 M HCl solution.

# 2. Materials and methods

### 2.1. Materials

The zinc salt – phosphonic acid mixture was the corrosion inhibitor used in this work. Zinc sulfate  $(ZnSO_4 \cdot 7H_2O)$  was used as the precursor of  $Zn^{2+}$  ion. The tested compound  $(N[CH_2P(O)(OH)_2]_3)$  is amino tris (methylene phosphonic acid). (ATMP), obtained from Sigma-Aldrich (>97.0 wt% in ATMP), was tested without further purification. Figure 1 shows the molecular structure of ATMP.

The metal used in this study is a carbon steel (C38) (Euronorm: C35E carbon steel and US specification: SAE 1035) 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 balance iron (Fe). The surface pre-treatment was performed for all the experiments by grinding with SiC emery paper (grades 120, 600 and 1200), thoroughly washed with bidistilled water, cleaned with acetone and then dried.



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

#### 2.2. Weight loss measurements

For gravimetric measurements, specimens of carbon steel measuring  $10 \times 10 \times 3$  mm were used. Measurements of weight loss were carried out in a controlled solution of 80 mL in a double walled glass cell for 24 hours at 298 K. The samples were removed from the solution after 24 h, washed, dried and weighted.

The steel's corrosion rate ( $V_{CR}$ ) was calculated using the following equation:

$$V_{\rm CR} = \frac{\Delta W}{St} \tag{1}$$

Where  $\Delta W$  is the average weight loss of three coupons, *S* is the total area of the coupon, and *t* is the immersion time. The studied temperatures ranged from 298 to 333 K.

The inhibition efficiency  $(\eta_W)$  and surface coverage  $(\theta)$  of the corrosion inhibitors were given as follows:

$$\eta_{W} = \left(1 - \frac{V_{\text{CR(inh)}}}{V_{\text{CR(uninh)}}}\right) \cdot 100\%$$
(2)

$$\theta = 1 - \frac{V_{\text{CR(inh)}}}{V_{\text{CR(uninh)}}} \tag{3}$$

Where  $V_{CR(inh)}$  is the corrosion rate in the presence of the inhibitor and  $V_{CR(uninh)}$  is the corrosion rate in its absence of inhibitor. We chose to use eq. 3 because we have made the assumption that our inhibitor is of purely blocking type that act just by surface screening.

To meet scientific standards of replicability, three experiments were performed for each condition separately.

#### 2.3. Electrochemical techniques

At room temperature, for the electrochemical measurements a model composed of threeelectrode cells was used. For the working electrode we used a carbon steel with a surface of  $1 \text{ cm}^2$ . For the reference we used a saturated calomel electrode (SCE); a Pt electrode was used as the counter. All potentials are reported *vs*. SCE. Polarization and AC impedance measurements were performed by the electrochemical measuring device SP150 (Bio-Logic). Using impedance graphing and analysis software, version EC-Lab V11.01, the EIS data were analyzed.

For this analysis, we used electrochemical methods such as, open circuit potential (OCP) measurement, linear potentiodynamic measurements and AC impedance measurements. Before beginning the potentiodynamic polarization measurement, the OCP was calculated for 30 minutes at a rate of 30 mV/s.

The inhibition efficiency,  $\eta_p$ , was calculated from the fitted corrosion current density (*i*<sub>corr</sub>) as follows:

$$\eta_{\rm p} = \frac{i_{\rm corr} - i_{\rm corr(inh)}}{i_{\rm corr}} \cdot 100\%$$
(4)

Where  $i_{\text{corr}}$  is the corrosion current density in the presence of the inhibitor and  $i_{\text{corr(inh)}}$  is the corrosion current density in its absence.

The perturbation amplitude at OCP was 5 mV for the EIS test, and the frequency ranged from 100 kHz to 0.1 Hz. The impedance data was equipped with EC-Lab software V11.01. Thus,  $R_{ct}$  evaluated the inhibition efficiency according to the equation below:

$$\eta_{\rm EIS} = \frac{R_{\rm ct} - R_{\rm ct}^0}{R_{\rm ct}} \cdot 100\%$$
 (5)

Where,  $R_{ct}^0$  and  $R_{ct}$  are the charge transfer resistance values in the absence and the presence of inhibitor.

# 2.4. Adsorption isotherm, thermodynamic and synergism parameters

For this study, in order to learn more about the adsorption mode of ATMP and ATMP/ $Zn^{2+}$  on the metal, at different temperatures but in the same medium (HCl 1 M). Several attempts were made to select the right adsorption isotherms, which allowed us to calculate thermodynamic and synergism parameters using standard equations.

# 2.5. Computational approaches

# DFT calculations

The method of DFT/B3LYP is considered for DFT calculations. The basis set for O, H, C, P and N atoms is favored in the 6-31G(d,p) calculations, while LANL2DZ is used for Zn atoms. In the study of corrosion inhibition efficiencies of molecules, conceptual density functional theory is commonly favoured. Parr and Pearson provided the following equations in the aforementioned theory, using a finite difference method, to measure quantum chemical parameters like softness ( $\sigma$ ), chemical potential ( $\mu$ ), hardness ( $\eta$ ) and electronegativity ( $\chi$ ) using ground state ionization energy (I) and ground state electron affinity (A).

It is evident from the given equations that electronegativity is the negative of the chemical potential while softness is defined as the multiplicative inverse of the hardness [50].

$$\mu = -\chi = -\left(\frac{I+A}{2}\right) \tag{6}$$

$$\eta = (I - A) / 2 \tag{7}$$

$$\sigma = 1/\eta \tag{8}$$

While there are several electrophilicity scales available in the literature, the most important way to use Parr's electrophilicity index [51] ( $\omega$ ) is to estimate the electrophilic strength of molecules. According to the index referred to above, a molecule's electrophilic strength is related to its absolute electronegativity and absolute hardness values and is determined using the equation given below. Chattaraj, on the other hand, defined nucleophilicity ( $\epsilon$ ) as the multiplicative inverse of the electrophilicity index in a manner similar to that of the relationship between hardness and softness.

$$\omega = \chi^2 / 2\eta = \mu^2 / 2\eta \tag{9}$$

$$\varepsilon = 1/\omega$$
 (10)

In corrosion inhibition studies, the fraction of electrons transferred to the metal surface from the inhibitor molecule ( $\Delta N$ ), metal–ligand interaction energy ( $\Delta \psi$ ) and back-donation energy ( $\Delta E_{b-d}$ ) are commonly used parameters. With the assistance of the principle of hardness equalization and Sanderson's principle of electronegativity equalization[52], the equations proposed to measure the fraction of electrons transferred and metal-inhibitor interaction energy have been suggested.

$$\Delta N = \frac{\Phi_{\rm Fe} - \chi_{\rm inh}}{2(\eta_{\rm Fe} + \eta_{\rm inh})} \tag{11}$$

$$\Delta \psi = -\frac{(\Phi_{\rm Fe} - \chi_{\rm inh})^2}{4(\eta_{\rm Fe} + \eta_{\rm inh})}$$
(12)

$$\Delta E_{\rm b-d} = -\frac{\eta_{\rm inh}}{4} \tag{13}$$

where  $\Phi_{Fe}$  is the work function taken as 4.82 eV/mol and  $\eta_{Fe}$  is the absolute hardness of the metal taken as 0.0 eV/mol.  $\chi_{inh}$  represents the electronegativity and  $\eta_{inh}$  the hardness value of the inhibitor molecule. It should be noted that Koopmans Theorem [53] is an important way to calculate all the above parameters since it notes that the negative values of HOMO and LUMO orbital energies correspond to the molecules' ionization energy and electron affinity.

### Monte Carlo simulations

The simulated annealing algorithm was used in conjunction with a Monte Carlo simulation to explain the inhibition mechanism at the atomic level [54, 55].

To define well all bond-types within the studied structures, thus calculating energies, the Universal force field was used. During the simulated annealing process, temperature scanning was performed three times (3 cycles) from a temperature range of 105 to 102 K with 15,000 steps per cycle [56]. During the simulated annealing run, the smart algorithm is used for geometry optimization in which the convergence requirements for energy, force and displacement are 0.001 Kcal·mol<sup>-1</sup>, 0.5 Kcal·mol<sup>-1</sup>·Å<sup>-1</sup> and 0.015 Å, respectively [57].

A simulation box of  $27\text{Å} \times 27\text{Å} \times 68\text{Å}$  including five layers of Fe (110) with 60 Å as a vacuum region was adopted to conduct this simulation. The aqueous phase is known to mimic the actual state, using the "150H<sub>2</sub>O + 2Cl<sup>-</sup> + 2H<sub>3</sub>O<sup>+</sup>" solution composition. By constructing an amorphous cell containing 30 ATMP (or ATMP zinc complex), 3Cl<sup>-</sup> and 3H<sub>3</sub>O<sup>+</sup> [58], the self-diffusivity coefficient (*D*) of the aggressive materials (*i.e.* Cl<sup>-</sup> and H<sub>3</sub>O<sup>+</sup> ions) *via* the ATMP membrane, as well as its zinc complex, was measured.

The designed cell was then relaxed to achieve an overall equal distribution within the cell. The next move was to run a molecular dynamics simulation for 100 ps to assess the mean squared displacements (MSD) of these aggressive species in ATMP and its complex [59].

### 3. Results and Discussion

#### 3.1. Gravimetric measurements

Table 1 shows the results of weight loss measurements of carbon steel in 1 M HCl solution in the absence and presence of inhibitors: aminotris(methylenephosphonic acid) (ATMP),  $Zn^{2+}$ , and the combination of ATMP and  $Zn^{2+}$  during a 24 hours immersion period. The results show that in a 1 M HCl solution, ATMP acts as a strong inhibitor of carbon steel corrosion. Inhibition efficiency increases as inhibitor concentration rises, in a similar fashion to that observed by Labjar *et al.* [42, 44]. This suggests that ATMP has a significant inhibitory effect on steel acid corrosion as it weakens the HCl solution's attack on carbon steel by adsorbing on the steel's surface. In 1 M HCl medium, the presence of  $Zn^{2+}$  had no significant impact on the corrosion inhibition of carbon steel.

A substantial change in inhibitory efficacy was observed by fixing the ATMP concentration at  $10^{-3}$  M and adding different Zn<sup>2+</sup> concentrations, which increased from 52% in the presence of ATMP only, to 75% in the presence of ATMP and  $10^{-3}$  M Zn<sup>2+</sup>. The inhibitory effect of ATMP was not further enhanced by any of the increases in the concentration of Zn<sup>2+</sup>.

A clear improvement in the inhibitory efficacy of ATMP is observed by fixing the concentration of  $Zn^{2+}$  at  $10^{-3}$  M and adding different concentrations of ATMP, increasing the inhibitory efficacy from 80 percent to 98 percent at a concentration of  $10^{-2}$  M, which can

be explained by the existence of an effect of synergy between ATMP and  $Zn^{+2}$  favored more by an increase in ATMP concentration.

**Table 1.** Weight loss measurements and inhibition efficiency for mild steel in 1 M HCl in the absence and the presence of (ATMP) and  $Zn^{2+}$  inhibitors obtained after 24 h immersion at 298 K.

Inhibitor	conc. (M)	Vcr	
ATMP	$\mathbf{Zn}^{2+}$	$(\mathbf{mg}\cdot\mathbf{cm}^{-2}\cdot\mathbf{h}^{-1})$	IE(%)
Blank	Blank	4.57	_
10 <sup>-3</sup>	0	2.18	52.30
$2.5 \cdot 10^{-3}$	0	1.63	64.33
$5 \cdot 10^{-3}$	0	1.28	71.99
$7.5 \cdot 10^{-3}$	0	1.09	76.15
$10^{-2}$	0	0.87	80.96
Blank	Blank	4.57	_
0	10 <sup>-3</sup>	4.13	9.63
0	$2.5 \cdot 10^{-3}$	3.8	16.85
0	$5 \cdot 10^{-3}$	3.76	17.72
0	$7.5 \cdot 10^{-3}$	3.75	17.94
0	10 <sup>-2</sup>	3.73	18.38
Blank	Blank	4.57	_
10 <sup>-3</sup>	0	2.18	52.30
$10^{-3}$	10 <sup>-3</sup>	1.11	75.71
10 <sup>-3</sup>	$2.5 \cdot 10^{-3}$	1.82	60.17
10 <sup>-3</sup>	$5 \cdot 10^{-3}$	1.59	65.21
10 <sup>-3</sup>	$7.5 \cdot 10^{-3}$	1.52	66.74
10 <sup>-3</sup>	10 <sup>-2</sup>	1.48	67.61
Blank	Blank	4.57	_
0	10 <sup>-3</sup>	4.13	9.63
10 <sup>-3</sup>	10 <sup>-3</sup>	1.11	75.71
$2.5 \cdot 10^{-3}$	10 <sup>-3</sup>	0.95	79.21
$5 \cdot 10^{-3}$	10 <sup>-3</sup>	0.70	84.86
$7.5 \cdot 10^{-3}$	10 <sup>-3</sup>	0.42	90.81
$10^{-2}$	10 <sup>-3</sup>	0.09	98.03

### 3.2. Electrochemical impedance spectroscopy (EIS) measurements

Figures (2a) and (2b) display the Nyquist plots collected at open circuit potential in the absence and presence of  $10^{-3}$  M Zn<sup>2+</sup> and different concentrations of ATMP alone, as well as  $10^{-3}$  M Zn<sup>2+</sup> plus different concentrations of ATMP after 24h immersion.



**Figure 2.** Nyquist plot for carbon steel in 1 M HCl in the absence and the presence of  $10^{-3}$  M  $Zn^{2+}$  and different concentrations of ATMP (a) and in the absence and presence of  $10^{-3}$  M  $Zn^{2+}/ATMP$  (b).

The charge transfer mechanism is correlated with the double electric layer [60], as shown by the Nyquist plot's semicircular appearance. A capacitive loop is formed by the time constant of the electric double layer and charge-transfer resistance, which is dependent on either direct electron transfer at the metal surface or electron conduction through the film surface.

The HF loop's depressed form shows the surface's structural or interfacial structural inhomogeneity, as seen in adsorption processes [61]. Instead of using a pure double layer capacitor, a constant phase component, CPE, is used in this case to provide a more accurate fit [62]. The impedance function of a CPE has the following equation [63]:

$$Z_{\rm CPE} = A^{-1} (i\omega)^{-n} \tag{14}$$

*n* is a CPE exponent that can be used as a gauge of surface heterogeneity or roughness [64], where *A* is the CPE constant,  $\omega$  is the angular frequency (in rad·s<sup>-1</sup>),  $i^2 = -1$  is the imaginary number, and *A* is the CPE constant. CPE may represent resistance (n = 0, A = R), capacitance (n = 1, A = C), inductance (n = 1, A = L), or Warburg impedance (n = 0.5, A = W) depending on the value of *n*.

Within the studied frequency range, the system could be described by the corresponding structural model of the interface, both without and with inhibitors, as shown in Figure 3. The solution resistance is  $R_{s}$ , and the charge-transfer resistance is  $R_{ct}$  in this circuit.



**Figure 3.** Equivalent circuits used to fit the EIS data of carbon steel in 1 M HCl + xM ATMP without and with  $10^{-3}$  M Zn<sup>+2</sup>.

The impedance data derived from EIS experiments is summarized in Table 2. Inspection of this data reveals that in the presence and absence of  $10^{-3}$  M Zn<sup>2+</sup>,  $R_{ct}$  and  $C_{dl}$  values have an inverse correlation in the entire concentration spectrum ( $R_{ct}$  increases and  $C_{dl}$  decreases with ATMP concentration). The proportional factor A value of CPE varies with the inhibitor concentration on a regular basis, whether in the presence of ATMP alone or in the presence of  $10^{-3}$  M ATMP/Zn<sup>2+</sup> mixtures. It's fair to assume that a protective film covers the metal's surface. In fact, relative to the blank, the increase in *n vs*. ATMP with and without Zn<sup>2+</sup> can be interpreted by a reduction in surface heterogeneity caused by the inhibitor's adsorption at the most active adsorption sites. [65]. The calculated value of the time constant ( $\tau_d$ ) obtained in the absence of ATMP, on the other hand, was found to be 0.0098 s. The addition of ATMP or a  $10^{-3}$  M ATMP/Zn<sup>2+</sup> mixture to the acid solution increases the value of ( $\tau_d$ ). In the presence of ATMP or a  $10^{-3}$  M ATMP/Zn<sup>2+</sup> mixture to the acid solution, the adsorption process time increases exponentially, indicating a slow adsorption process [66]. The  $R_{ct}$ 

stated earlier [67] is used to calculate the  $\eta_{EIS}(\%)$  efficiency of the inhibition. The efficiency of inhibition improves as the concentration of ATMP increases. ATMP's inhibitory potential has been significantly enhanced by the presence of  $Zn^{2+}$ . This is valid for all of the ATMP concentrations that have been studied. The inhibition efficiency values derived from the impedance analysis follow the same trend as weight loss measurements.

**Table 2.** Impedance parameters and inhibition efficiency values for carbon steel after 24 h immersion period in 1 M HCl without and with different concentrations of ATMP only or  $10^{-3}$  M ATMP/Zn<sup>2+</sup> at ambient temperature.

Inhibitor (M	r conc. )	$R_{\rm S}$	$10^4 A$	N	$R_{\rm ct}$	$C_{\rm dl}$	τ <sub>d</sub> (S)	ηειs (%)
ATMP	$\mathbf{Zn}^{2+}$	( <u>sz.cm</u> -)	(S <sup>-1</sup> 2 <sup>-1</sup> Clll <sup>-</sup> )		( <b>32</b> ·CIII <sup>-</sup> )	(µr·cm-)		(70)
Blank	Blank	2.275±0.01	4.953	0.8451±0.002	40.45±0.14	241.90	0.0098	_
$10^{-3}$	0	2.116±0.01	3.980	$0.8459{\pm}0.001$	84.14±0.27	214.40	0.0180	51.93
$2.5 \cdot 10^{-3}$	0	$1.842 \pm 0.02$	3.734	$0.8464 \pm 0.002$	93.59±0.36	203.20	0.0190	56.78
$5 \cdot 10^{-3}$	0	2.316±0.03	3.608	$0.8467 {\pm} 0.003$	122.9±0.41	199.50	0.0245	67.09
$7.5 \cdot 10^{-3}$	0	2.117±0.03	2.970	$0.8760 {\pm} 0.002$	$160.3 \pm 0.48$	193.00	0.0309	74.77
$10^{-2}$	0	2.339±0.02	3.209	$0.8475 {\pm} 0.004$	$182.5 \pm 1.88$	187.00	0.0341	77.84
0	$10^{-3}$	1.119±0.01	5.003	$0.8316{\pm}0.002$	43.5±0.21	230.40	0.0180	7.01
$10^{-3}$	$10^{-3}$	2.122±0.02	3.025	$0.8816 {\pm} 0.004$	$156.4 \pm 0.57$	200.80	0.0314	74.14
$2.5 \cdot 10^{-3}$	$10^{-3}$	$1.715 \pm 0.02$	2.659	$0.8759{\pm}0.003$	229.1±2.13	178.90	0.0410	82.34
$5 \cdot 10^{-3}$	$10^{-3}$	$2.207 \pm 0.01$	1.870	$0.8861 {\pm} 0.002$	263.1±4.18	127.00	00334	84.63
$7.5 \cdot 10^{-3}$	$10^{-3}$	3.222±0.01	1.286	$0.8744{\pm}0.001$	327.9±4.87	81.66	0.0268	87.66
$10^{-2}$	$10^{-3}$	$2.442 \pm 0.02$	0.571	$0.9206 {\pm} 0.003$	838.3±5.61	44.00	0.0369	95.17

# 3.3 Potentiodynamic tests

Figures (4a) and (4b) illustrate potentiodynamic polarization data for our metal in 1 M HCl for various concentrations of ATMP alone and ATMP/Zn<sup>2+</sup> mixture. Table 3 describes the kinetic corrosion parameters measured from these experiments using the extrapolation method [14], such as corrosion potential ( $E_{corr}$ ) and corrosion current density ( $I_{corr}$ ). The addition of ATMP or the ATMP/Zn<sup>2+</sup> (10<sup>-3</sup> M) combination lowers both the cathodic and anodic currents, preventing the carbon steel electrode from being acidically attacked in 1 M HCl. With the addition of ATMP or a mixture of ATMP/Zn<sup>2+</sup> (10<sup>-3</sup> M). For the studied inhibitors: ATMP or ATMP/Zn<sup>2+</sup>, indicating that the "hydrogen evolution reaction" for the cathodic process is controlled by activation and that the mechanism of this process is not modified by the addition of ATMP or ATMP/Zn<sup>2+</sup> [68–71]. The results suggesting that these inhibitors were first adsorbed onto the metal's surface and impeded by attempting to block

the metal surface's reaction sites without changing the mechanism of the anodic reaction [72].

The electrochemistry of corrosive metals is well understood to include two or more half-cell reactions. The surface of low carbon steel is positively charged in HCl solutions [73].

The chemisorption process involves charge sharing or charge transfer from the inhibitor molecules to the metal surface. It's possible when the surface has both a positive and negative charge [74].

As previously mentioned, physical adsorption is the result of electrostatic attractive forces between organic ions or dipoles and the metal's electrically charged surface.

The electric field present at the metal/solution interface is responsible for the metal's surface charge [75]. The surface charge will describe the location of the corrosion potential  $(E_{\text{corr}})$  with respect to the respective zero charge potential (PZC)  $E_q = 0$  [76]. When the difference  $\Psi = [(E_{\text{corr}} - E_q = 0)$  is negative, the electrode surface acquires a negative net charge, and the adsorption of cations is favored. On the other hand, the adsorption of anions is favored when  $\Psi$  becomes positive. The  $P_{zc}$  of iron in a hydrochloric acid solution was reported to be -530 versus SCE. As a result, the value of  $\Psi$  is nearly +80 mV versus SCE, and the metal surface acquires a positive charge [77]. Cationic ATMP species do not adsorb, but chloride ions do, and the surface becomes negatively charged. Due to electrostatic attraction, the protonated ATMP molecules are physically adsorbed on the metal surface, providing some inhibition. The presence of  $10^{-3}$  M Zn<sup>+2</sup> thus improves inhibition efficiency.

It is clear from Table 3 that  $I_{corr}$  values decrease substantially as the ATMP concentration increases, and even more so as the  $10^{-3}$  M Zn<sup>2+</sup>/different ATMP concentrations rise.

The inspection of the results obtained indicates that ATMP and the  $10^{-3}$  M ATMP/ Zn<sup>2+</sup> mixture demonstrate inhibitory properties across the entire concentration spectrum examined, and that the effectiveness of protection  $\eta_p$  (%) improves in both cases as the concentration of ATMP increases. It is also obvious that the  $10^{-3}$  M Zn<sup>2+</sup>/different ATMP mixture shows higher performance than ATMP, which can be correlated to the synergistic effect existing between ATMP and Zn<sup>2+</sup>. The inhibiting nature of ATMP and the  $10^{-3}$  M ATMP/ Zn<sup>2+</sup> mixture is also confirmed by potentiodynamic tests, the inhibiting efficiency values determined from the results of the potentiodynamic polarization method display the exact pattern as those collected from EIS data and gravimetric measurements.



**Figure 4.** Polarization curves of carbon steel in 1 M HCl with varying concentrations of ATMP in the absence of  $10^{-3}$  M Zn<sup>2+</sup> (a) and with varying concentrations of ATMP in the presence of  $10^{-3}$  M Zn<sup>2+</sup> (b).

Inhibitor conc. (M)			<b>T</b> ( <b>A</b> -?)	
ATMP	Zn <sup>2+</sup>	$- E_{\rm corr}  vs.  SCE  (mV)$	Icorr (µA·cm <sup>2</sup> )	$\eta_{ m P}$
Blank	Blank	-454.8	560.7	
$10^{-3}$	0	-444.5	390.5	30.35
$2.5 \cdot 10^{-3}$	0	-443.9	347.0	38.11
$5 \cdot 10^{-3}$	0	-451.2	246.2	56.09
$7.5 \cdot 10^{-3}$	0	-448.5	208.3	62.85
$10^{-2}$	0	-444.7	132.65	76.34
0	10 <sup>-3</sup>	-459.6	512.0	8.68
$10^{-3}$	$10^{-3}$	-444.5	187.9	66.48
$2.5 \cdot 10^{-3}$	$10^{-3}$	-455.9	173.6	69.03
$5 \cdot 10^{-3}$	$10^{-3}$	-434.5	119.4	78.70
$7.5 \cdot 10^{-3}$	$10^{-3}$	-429.2	87.0	84.48
$10^{-2}$	10 <sup>-3</sup>	-441.6	59.2	89.44

**Table 3.** Polarization parameters and the corresponding inhibition efficiencies for the corrosion of carbon steel in 1 M HCl containing different concentrations of ATMP or  $10^{-3}$  M ATMP/ Zn<sup>2+</sup>.

# 3.4. Effect of inhibitor concentration and solution temperature

# 3.4.1. Effect temperature

The weight loss of mild steel at 1M HCl was measured in the absence and presence of various concentrations of ATMP or  $10^{-3}$  M ATMP/Zn<sup>2+</sup> at different temperatures of 298 K to 333 K. The results are shown in Table 4.

**Table 4.** Corrosion parameters obtained from weight loss for carbon steel in 1 M HCl containing various concentrations of ATMP or  $10^{-3}$  M ATMP/ Zn<sup>2+</sup> at different temperatures.

Inhib conc.	itor (M)	VCR (mg cm <sup>-2</sup> h <sup>-1</sup> )			or $V_{CR}$ M) $(\operatorname{mg} \operatorname{cm}^{-2} \operatorname{h}^{-1})$ IE (%)			θ					
ATMP	$\mathbf{Zn}^{2+}$	298K	313K	323K	333K	298K	313K	323K	333K	298K	313K	323K	333K
Blank	Blank	4.57	6.93	11.6	18.33	_	_	_	_				
10 <sup>-3</sup>	0	2.18	5.73	9.93	16.37	52.3	17.32	14.33	10.67	0.523	0.1732	0.1433	0.1067
$2.5  10^{-3}$	0	1.63	4.62	8.7	14.39	64.33	33.41	24.92	21.47	0.6433	0.3341	0.2492	0.2147
5 10-3	0	1.28	3.92	7.1	12.09	71.99	43.44	38.81	34.02	0.7199	0.4344	0.3881	0.3402
7.5 10 <sup>-3</sup>	0	1.09	3.32	6.35	10.77	76.15	52.12	45.27	41.21	0.7615	0.5212	0.4527	0.4121
$10^{-2}$	0	0.87	2.78	5.15	9.12	80.96	59.94	55.57	50.24	0.8096	0.5994	0.5557	0.5024

Inhib conc.	itor (M)	V <sub>CR</sub> (mg cm <sup>-2</sup> h <sup>-1</sup> )			$\begin{array}{c c} \mathbf{Or} & \mathbf{V}_{\mathrm{CR}} \\ \mathbf{M} & (\mathbf{mg} \ \mathbf{cm}^{-2} \ \mathbf{h}^{-1}) \end{array} \qquad IE (\%)$					θ			
ATMP	$\mathbf{Zn}^{2+}$	298K	313K	323K	333K	298K	313K	323K	333K	298K	313K	323K	333K
0	10 <sup>-3</sup>	4.13	6.44	10.83	17.47	9.63	7.16	6.62	4.73	0.0963	0.0716	0.0662	0.0473
$10^{-3}$	$10^{-3}$	1.11	2.45	5.77	9.98	75.71	64.6	50.22	45.57	0.7571	0.646	0.5022	0.4557
$2.5 \ 10^{-3}$	$10^{-3}$	0.95	2.08	4	7.88	79.21	69.98	65.51	57.01	0.7921	0.6998	0.6551	0.5701
5 10-3	10 <sup>-3</sup>	0.7	1.67	3.25	6.13	84.86	75.87	71.97	66.52	0.8486	0.7587	0.7197	0.6652
7.5 10 <sup>-3</sup>	$10^{-3}$	0.42	1.37	2.8	5.51	90.81	80.21	75.87	69.94	0.9081	0.8021	0.7587	0.6994
10 <sup>-2</sup>	10 <sup>-3</sup>	0.09	1.04	2.45	4.97	98.03	85	78.91	72.85	0.9803	0.85	0.7891	0.7285



**Figure 5.** Inhibitor efficiency *vs* different temperatures (a) in the presence of different concentrations of ATMP (b) in the presence of  $10^{-3}$  M ATMP/Zn<sup>2+</sup>.

In both the absence and presence of  $Zn^{2+}$ , the performance of inhibition increased as the concentration of ATMP increased. However, the performance of the inhibitor reduces as visible in Figures (5a) and (5b), as the temperature increases. The evolution of hydrogen at the metal's surface hastens at excessive temperatures, resulting in thin-film desorption and a reduction in inhibitor efficacy. Table 4 suggests that corrosion rate increases along with increases in temperatures. It means that temperature has a robust effect on the desorption of the adsorbed inhibitor at the metal's surface. The presence of  $Zn^{2+}$  has significantly improved the resistance of carbon steel to corrosion even if the temperature will increase.

As per the following equation, the corrosion reaction activation parameters can be defined as an Arrhenius-type process:

$$V_{\rm CR} = k \exp(-E_{\rm a}/RT) \tag{15}$$

In which  $E_a$  is the apparent corrosion energy of activation, R is the universal constant of gas and k is the pre-exponential factor of Arrhenius.

Straight line (Figure 6) was given by a plot of  $\ln V_{CR}$  versus 1/T whose slope and intercept were used for the  $E_a$  calculation. Table 5 summarizes the following results, in the absence or presence of  $Zn^{2+}$ ,  $E_a$  increased with increasing ATMP concentration, and all  $E_a$ values within the concentration spectrum analyzed were greater than the uninhibited solution. The increase in  $E_a$  in the presence of ATMP alone and  $10^{-3}$  M ATMP/Zn<sup>+2</sup>, can be described as physical adsorption. Indeed, a higher energy barrier for the corrosion phase in the inhibited solution is related to physical adsorption or poor chemical bonding between the inhibitor species and the steel surface [34, 67]. According to Szauer and Brand [68], the increase in activation energy might well be attributed to a significant decrease in the inhibitor's adsorption on the carbon steel surface as the temperature rises. As a result of the increased area of metal exposed to the acid environment, the corrosion rate increases.

Results display that including ATMP its own or  $10^{-3}$  M ATMP/Zn<sup>+2</sup> to the acid medium increases the value of  $E_a$  with the increasing inhibitor concentrations. The growth in activation energies with increasing inhibitor concentration reasons the physical adsorption of inhibitor molecules on the metal's surface [78]. Previous studies have proven that adsorption of the inhibitor at the metal's surface forms a physical barrier that decreases the metal's reactivity in electrochemical corrosion reactions [19, 79].

Based on transition state theory, both the enthalpy and entropy of activation were determined using the alternate form of the Arrhenius equation:

$$V_{\rm CR} = \frac{RT}{Nh} \exp\left(\frac{\Delta S_{\rm a}^0}{R}\right) \exp\left(-\frac{\Delta H_{\rm a}^0}{RT}\right)$$
(16)

Where  $\Delta S_a$  signifies activation entropy,  $\Delta H_a$  is the activation enthalpy, *h* represents Planck's constant, *N* denotes Avogadro's number, and *T* and *R* are the absolute temperature, and the universal gas constant respectively.

A linear plot of  $\ln V_{CR}/T$  versus 1/T was drawn (Figure 7) using Eq. (8), with a slope of  $(-\Delta H_a/R)$  and an intercept of  $[\ln(R/Nh) + \Delta S_a/R]$ , by which the values of  $H_a$  and  $S_a$  were determined (Table 5).



**Figure 6.** Arrhenius plots for C38 steel corrosion rates  $\ln V_{CR}$  versus 1/T in 1 M HCl in absence and in presence of different concentrations of ATMP and in absence and in presence of  $10^{-3}$  M ATMP/Zn<sup>+2</sup>.

Inhibitor conc. (M)		${m E}_{f a}$	$\Delta H_{a}$	$\Delta S_{\mathbf{a}}$	$E_{\mathrm{a}}$ – $\Delta H_{\mathrm{a}}$
ATMP	Zn <sup>2+</sup>	(kJ·mol <sup>−1</sup> )	(kJ·mol <sup>-1</sup> ·K <sup>-1</sup> )	$(\mathbf{J} \cdot \mathbf{mol}^{-1} \cdot \mathbf{K}^{-1})$	(kJ·mol <sup>−1</sup> )
Blank	Blank	32.86	30.24	-130.68	2.62
$10^{-3}$	0	47.59	44.97	-86.58	2.62
$2.5 \cdot 10^{-3}$	0	51.72	49.10	-75.13	2.62
$5 \cdot 10^{-3}$	0	53.03	50.42	-72.59	2.61
$7.5 \cdot 10^{-3}$	0	54.33	51.72	-69.65	2.61
$10^{-2}$	0	55.42	52.80	-67.83	2.61
10 <sup>-3</sup>	10 <sup>-3</sup>	44.54	41.92	-91.91	2.62
$2.5 \cdot 10^{-3}$	$10^{-3}$	49.61	47	-87.44	2.61
$5 \cdot 10^{-3}$	$10^{-3}$	51.12	48.5	-84.73	2.62
$7.5 \cdot 10^{-3}$	$10^{-3}$	60.65	58.04	-56.57	2.61
$10^{-2}$	$10^{-3}$	94.94	92.32	47.59	2.62

**Table 5.** Calculated values of kinetic thermodynamic parameters for carbon steel in 1 M HCl in the absence and presence of different concentrations of ATMP only and in presence of  $10^{-3}$  M ATMP/Zn<sup>2+</sup>.

Table 5 shows that all the  $\Delta H_a$  values are positive, suggesting the endothermic nature of the dissolution of carbon steel in the studied corrosive setting. The table additionally indicates that  $\Delta H_a$  differs in the same way as  $E_a$ , but with  $E_a$  values higher than those of  $\Delta H_a$ . This implies that a gaseous process, namely a hydrogen evolution reaction accompanied by a decrease in overall volume, must be involved in the corrosion process [80]. Since the  $E_a$ and  $\Delta H_a$  values are identical, the well-known thermodynamic relationship defined by Eq. (17) can be verified.

$$E_{\rm a} - \Delta H_{\rm a} = RT \tag{17}$$

Table 5 displays the numerical parameters of the difference between  $E_a$  and  $\Delta H_a$  for the different systems. The corrosion phase is known as a unimolecular reaction [81] since the standard value of 2.62 kJ/mol falls in the range of the *RT* values of 2.47 and 2.77 kJ/mol at 298 and 333 K, respectively. The adsorption of ATMP and  $10^{-3}$  M ATMP/Zn<sup>2+</sup>slows carbon steel's dissolution in a solution of HCl (1 M); ( $\Delta S_a$ ) values are high and negative, implying that the adsorption slows the mentioned dissolution process. It also means that the activated complex represents an association rather than dissociation in the rate-determining process [43, 47]. When comparing the ( $\Delta S_a$ ) values for ATMP inhibited and uninhibited solutions, it is obvious that the ( $\Delta S_a$ ) values for ATMP inhibited solutions are less negative. When the  $10^{-3}$  M ATMP/Zn<sup>2+</sup> mixture is present, the values of ( $\Delta S_a$ ) tend to become positive as the ATMP concentration increases. A rise in ( $\Delta S_a$ ) is usually interpreted as the appearance of a condition on the way from reactants to the activated complex [37, 82].



**Figure 7.** Transition-state plots for C38 steel corrosion rates  $\ln I_{corr}/T$  versus 1/T in 1 M HCl in absence and in presence of different concentrations of ATMP and in absence and in presence of  $10^{-3}$  M ATMP/Zn<sup>2+</sup>.

### 3.4.2. Adsorption isotherm

ATMP prevents carbon steel corrosion by being adsorption on the surface of the metal [43, 70]. Adsorption demonstrates the action of adsorbed molecules on the surface of the metal (electrode surface). The adsorption isotherm provides fundamental knowledge about the inhibitor's interaction with the steel's surface. Several isotherms, like Frumkin, Langmuir, and Temkin, were attempted to match. A straight line with the estimated unit slope was drawn using  $C_{inh}/\Theta vs$ .  $C_{inh}$  ( $\Theta$ -surface coverage) values.

As shown in Figure 8, adsorption in the presence of ATMP alone or ATMP/Zn<sup>2+</sup> fits the Langmuir adsorption isotherm. The adsorbate concentration in the bulk of the electrolyte  $(C_{inh})$  is related to the degree of surface coverage ( $\Theta$ ), and  $K_{ads}$  is the adsorption equilibrium constant, according to Langmuir's assumptions (18).

$$\frac{C_{\rm inh}}{\theta} = \frac{1}{K_{\rm ads}} + C_{\rm inh}$$
(18)

The parameters acquired from the adsorption isotherm Eq (11) are the linear regression coefficient ( $R^2$ ), the standard free energy of adsorption ( $\Delta G_{ads}^0$ ), and the equilibrium constant ( $K_{ads}$ ):

$$\Delta G_{\rm ads}^0 = -RT\ln(55.5K_{\rm ads}) \tag{19}$$

Where *R* is the universal gas constant and 55.5 is the concentration of water in solution in mol·L<sup>-1</sup>. Table 6 lists the  $\Delta G_{ads}^0$  and  $K_{ads}$  values that were calculated.



**Figure 8.** Langmuir adsorption isotherm (a) in the presence of different concentrations of ATMP (b) in the presence of  $10^{-3}$  M ATMP/Zn<sup>2+</sup>.

As temperature values increase, the adsorption technique equilibrium constant ( $K_{ads}$ ) in the presence of  $10^{-3}$  M ATMP/Zn<sup>2+</sup> decreases (Table 6). The adsorption strength of the inhibitor at the carbon metallic surface is measured in  $K_{ads}$ . At lower temperatures, the addition of  $10^{-3}$  M ATMP/Zn<sup>2+</sup> results in better  $K_{ads}$  values, suggesting that it was firmly adsorbed onto the carbon metallic surface. The inhibition efficiency barely decreased with increasing temperature as a result of improved desorption of  $10^{-3}$  M ATMP/Zn<sup>2+</sup> from the metal surface.

Negative  $\Delta G_{ads}^0$  values suggest spontaneous adsorption and a stable adsorbed layer at the carbon metal surface. Values of  $\Delta G_{ads}^0$  up to  $-20 \text{ kJ} \cdot \text{mol}^{-1}$  are related to physisorption, while those around  $-40^{\circ}\text{kJ} \cdot \text{mol}^{-1}$  or better are related to chemisorption [83]. As a result of sharing or transferring electrons from organic molecules to the steel surface to shape a coordinate form of a bond. Previously, Labjar *et al.* [84] formerly tested ATMP adsorption on carbon metal surfaces involves two types of interactions: important physisorption (ionic) and vulnerable chemisorption (molecular). This behavior is clarified by the fact that adsorption becomes less favorable as the experimental temperature increases, implying that physisorption is more important than chemisorption in corrosion inhibition [85]. The presence of  $10^{-3}$  M ATMP/Zn<sup>2+</sup> increased the absolute values of  $\Delta G_{ads}^0$ , implying that the adsorption process of  $10^{-3}$  M ATMP/Zn<sup>2+</sup> on carbon steel in 1.0 M HCl solution at the studied temperatures displays a physical adsorption and an increasing chemical adsorption than ATMP alone.

Inhibitor	Temp. (K)	<b>R</b> <sup>2</sup>	Kads (M <sup>-1</sup> )	$-\Delta G^{0}_{ads}$ (kJ·mol <sup>-1</sup> )	$\Delta H_{ads}$ (kJ·mol <sup>-1</sup> ·K <sup>-1</sup> )	$\Delta S_{ads}$ $(\mathbf{J} \cdot \mathbf{mol}^{-1} \cdot \mathbf{K}^{-1})$
	298	0.9978	1111.11	27.32		
ATMP only	313	0.9902	212.76	24.40	50.02	-85.7
	323	0.9736	153.84	24.30	-52.23	
	333	0.9869	119.27	24.28		
$10^{-3}$ M $7n^{2+}$	298	0.9935	1666.66	28.33		
different concentrations of ATMP	313	0.9968	1428.57	29.35	14 64	16.2
	323	0.9995	1111.11	29.61	-14.04	40.3
	333	0.9993	909.09	29.98		

**Table 6.** Thermodynamic parameters for the adsorption of ATMP only and  $10^{-3}$  M ATMP/Zn<sup>2+</sup> on the C38 steel in 1 M HCl at different temperatures.

The following equation (20) can be used to measure the other thermodynamic functions  $(\Delta H_{ads}^0 \text{ and } \Delta S_{ads}^0)$ :

$$\Delta G_{\rm ads}^0 = \Delta H_{\rm ads}^0 - T \Delta S_{\rm ads}^0 \tag{20}$$

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Figures (9a) and (9b) indicates the plot of  $\Delta G_{ads}^0$  as opposed to *T* which offers straight traces with slopes of  $-\Delta S_{ads}^0$  and intercepts of  $\Delta H_{ads}^0$ . The acquired values of  $\Delta H_{ads}^0$  and  $\Delta S_{ads}^0$  are given in Table 6. The acquired value of  $\Delta H_{ads}^0$  is negative, implying that the adsorption technique at the C38 metallic surface is exothermic. The value of  $\Delta H_{ads}^0$  may divulge crucial information about the sort of inhibitor adsorption. An endothermic adsorption technique ( $\Delta H_{ads}^0 > 0$ ) is surely attributed to chemisorption [76], whilst an exothermic adsorption technique ( $\Delta H_{ads}^0 < 0$ ) may involve either physisorption or chemisorption, or a combination of both processes. In an exothermic section, the absolute value of  $\Delta H_{ads}^0$  distinguishes chemisorption from physisorption. The approximate enthalpy of physisorption (ionic) and vulnerable chemisorption ( $-52.23 \text{ kJ} \cdot \text{mol}^{-1}$ ) for ATMP is higher than the standard physical adsorption phase of ATMP on carbon steel surface most likely involves two types of interactions: physisorption (ionic) and vulnerable chemisorption (ionic) and vulnerable chemisorption (ionic) and vulnerable chemisorption (ionic) and vulnerable chemisorption (ionic).

The presence of  $10^{-3}$  M ATMP/Zn<sup>2+</sup> increased the values of  $\Delta H_{ads}^0$ , implying that the adsorption phase of  $10^{-3}$  M ATMP/Zn<sup>2+</sup> on carbon steel in 1.0 M HCl solution at the studied temperatures includes a physical adsorption and greater essential chemisorption than withinside the presence of ATMP alone.

The value of  $\Delta S_{ads}^0$  for ATMP is negative (Table 4), suggesting that before adsorption, the ATMP molecules circulate freely within the bulk solution, whilst the inhibitor molecules adsorbed onto the moderate steel surface act in a more orderly way as adsorption progresses, resulting in a lower entropy. Positive values of  $\Delta S_{ads}^0$  for 10<sup>-3</sup> M ATMP/Zn<sup>2+</sup> indicate that adsorption is correlated with an increase in system dysfunction [87-88].

The incorporated model of the Van't Hoff equation, represented by Eq. (21), can also be used to derive  $\Delta H_{ads}^0$  and  $\Delta S_{ads}^0$  [89].

$$\ln K_{\rm ads} = -\Delta H_{\rm ads}^0 / RT + \text{Constant}$$
(21)

Figure 10 indicates the plot of  $\ln K_{ads}$  as opposed to 1/T, which produces straight lines with slopes of  $(-\Delta H_{ads}^0/R)$  and intercepts of  $(\Delta S_{ads}^0/R + \ln(1/55.5))$ . The measured  $\Delta H_{ads}^0$ utilizing the Van't Hoff equation are  $-52.22 \text{ kJ} \cdot \text{mol}^{-1}$  for ATMP and  $-14.64 \text{ kJ} \cdot \text{mol}^{-1}$  for  $10^{-3}$  M ATMP/Zn<sup>2+</sup>, indicating physisorption and exothermic behavior of the ATMP molecule at the metal surface. The values of  $\Delta H_{ads}^0$  obtained acquired by both techniques are in proper consensus.

Furthermore, the concluded  $\Delta S_{ads}^0$  values of  $-85.7 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$  for ATMP and 46.3  $\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$  are very close to those acquired in Table 6.



**Figure 9.** Variation of  $\Delta G_{ads}^0$  versus *T* on C38 steel in 1 M HCl containing (a) ATMP only; (b)  $10^{-3}$  M ATMP/Zn<sup>2+</sup>.



Figure 10. Vant't Hoff plots for the C38 steel/ATMP/1 M HCl and C38 steel/ $10^{-3}$  M ATMP/Zn<sup>2+</sup>/1 M HCl.

### 3.4.3. Synergism considerations

The efficiency of the additives was assessed by the inhibition coefficient  $\gamma$  [90]:

$$\gamma = V_{\rm CR0} / V_{\rm CR} \tag{22}$$

Where  $V_{CR0}$  and  $V_{CR}$  are the corrosion rate in the absence and in the presence of an inhibitor or mixture, respectively.

The mutual effect of inhibitors in mixtures was assessed by the coefficient of mutual effect  $\sigma$ :

$$\sigma = \gamma_{\rm mix} / (\gamma_1 \cdot \gamma_2) \tag{23}$$

where  $\gamma_{mix}$ ,  $\gamma_1$  and  $\gamma_2$  are the experimental inhibition coefficient of the mixture and the inhibition coefficients of components ATMP and  $Zn^{2+}$ .

The results found of the values of the inhibition coefficient and the coefficient of mutual effect are grouped in the Table 7.

When  $\sigma$  nears 1, there is no activity between the molecules of the inhibitor, whereas  $\sigma > 1$  indicates a synergistic activity. While if  $\sigma < 1$ , the antagonistic behavior predominates, possibly due to competitive adsorption.

The values of  $\sigma$  in Table 7 are almost all greater than unity, suggesting, the ATMP and  $Zn^{2+}$  have a synergistic effect. In general,  $Zn^{2+}$  improved ATMP's inhibition efficiency synergistically.

### 3.5. Quantum chemical calculation methods

Frontier orbital energies, hardness, softness, electronegativity, chemical potential, electrophilicity, nucleophilicity, the amount of electron transition from the inhibitor's molecule to the metal's surface, metal-inhibitor interaction energy, and back-donation energy are some of the parameters that provide useful information about molecule corrosion inhibition activities. The strength of atoms is characterized as chemical resilience, ions, and molecules to electron cloud polarization or deformation according to multiple papers published by Kaya [91].

After introducing the Hard and Soft Acid–Base Principle (HSAB) to science, Pearson introduced the Maximum Hardness Principle [92], which states that hard molecules are more stable than soft molecules. Hard molecules have a high energy gap and are thus ineffective in preventing metal corrosion. Based on the information provided, the corrosion inhibition performance ranking for the studied compounds is as follows: ATMP–Zn complex > ATMP (Figure 11).

Inhibitor (M	r conc. )		V (mg∙ci	C <b>R</b> n <sup>−2</sup> •h <sup>−1</sup> )				γ			σ		
ATMP	Zn <sup>2+</sup>	298K	313K	323K	333K	298K	313K	323K	333K	298K	313K	323K	333K
Blank	Blank	4.57	6.93	11.6	18.33	_	_	_	_	_	_	_	_
$10^{-3}$	0	2.18	5.73	9.93	16.37	2.09	1.21	1.17	1.12	_	_	_	_
$2.5 \cdot 10^{-3}$	0	1.63	4.62	8.7	14.39	2.80	1.5	1.33	1.27	_	_	_	—
$5 \cdot 10^{-3}$	0	1.28	3.92	7.1	12.09	3.57	1.76	1.63	1.51	_	_	_	—
$7.5 \cdot 10^{-3}$	0	1.09	3.32	6.35	10.77	4.19	2.09	1.82	1.70	_	_	_	—
$10^{-2}$	0	0.87	2.78	5.15	9.12	5.25	2.49	2.25	2.01	_	_	_	_
0	10–3	4.13	6.44	10.83	17.47	1.10	1.07	1.07	1.05	_	_	_	_
$10^{-3}$	10–3	1.11	2.45	5.77	9.98	4.12	2.83	2.01	1.83	1.77	2.17	1.60	1.56
$2.5 \cdot 10^{-3}$	10–3	0.95	2.08	4	7.88	4.81	3.33	2.90	2.32	1.55	2.06	2.03	1.74
$5 \cdot 10^{-3}$	10–3	0.7	1.67	3.25	6.13	6.53	4.15	3.57	2.99	1.65	2.18	2.04	1.88
$7.5 \cdot 10^{-3}$	10–3	0.42	1.37	2.8	5.51	10.88	5.06	4.14	3.32	2.34	2.25	2.12	1.86
$10^{-2}$	10–3	0.09	1.04	2.45	4.97	50.78	6.66	4.73	3.69	8.73	2.48	1.96	1.75

**Table 7.** Values of the inhibition coefficient and the coefficient of mutual effect for carbon steel corrosion in 1 M HCl as obtained from weight loss measurements.



Figure 11. Molecular structure of ATMP and its zinc complex.

This ranking corresponds with the findings of the experiments. Electronegativity is the capacity of chemical species to withdraw electrons. It is important to remember that molecules with high electronegativity values are ineffective against metal surface corrosion. In light of the calculated electronegativity values, the obtained rating is incompatible with experiments. Another metric used in the study of chemical reactivity is the electrophilicity index, electron donation and electron accepting power of molecules. According to the Minimum Electrophilicity Principle [93], the sum of the electrophilicity index values of products should be less than that of reactants in a chemical reaction. This knowledge indicates that chemical species with low electrophilicity values are more stable than those with higher electrophilicity values. Calculated electrophilicity index values ATMP and its Zn complex are 2.019 and 17.81 eV, respectively. If this is the case, complex molecules should have a greater corrosion inhibitory effect on iron surfaces. This indicates that the findings of this study back up the Minimum Electrophilicity Principle's validity.

According to the determined metal-ligand interaction energy values, The ATMP–Zn complex has a greater interaction with the iron surface. This result backs up the results of the experiment. Back-donation energy is a valuable method for analyzing electron donating abilities of molecules, according to Gomez and coworkers [94], and the energy shift is proportional to the inhibitor molecule's hardness, as shown in the equation above. It's worth noting that the measured  $\Delta_{b-d}$  values exhibit the tendency: ATMP–Zn complex > ATMP (Table 8, Figure 12). This tendency is confirmed by experimental data.

Inhibitor	<i>Е</i> номо (eV)	Elumo (eV)	Δ <i>E</i> (eV)	η (eV)	χ (eV)	Δ <i>N</i> (e)	Δψ (eV)	$\Delta E_{ ext{b-d}}$
ATMP	-6.892	-0.369	6.524	3.262	3.630	0.182	-0.108	-0.815
ATMP–Zn complex	-12.809	-7.195	5.614	2.807	10.002	-0.923	-2.896	-0.702

**Table 8.** Electronic structure parameters of ATMP molecule and its zinc complex.



**Figure 12.** HOMO, LUMO and ESP (red (blue) color refers to negative (positive) potential) map of ATMP and its zinc complex.

The Monte Carlo Simulation method gives computational chemists a lot of control when it comes to anticipating interactions between metal surfaces and inhibitor molecules. The Fe (110) surface was chosen for calculations in this analysis. Monte Carlo simulation was used to find the most robust low-energy configurations of adsorption of ATMP–Zn complex and ATMP on the Fe (110) surface. Figure 13 depicts the outcomes.



**Figure 13.** Side and top-views of the adsorption configuration of ATMP and its Zinc complex onto Fe (110)'s surface.

Adsorption energy is the amount of energy released when an inhibitor molecule binds to a metal's surface. The adsorption energy of good corrosion inhibitors is very low. ATMP and its Zn complex have calculated adsorption energy values of -83.913 and -44.114 kcal/mol, respectively (Table 9).

**Table 9.** Calculated adsorption energy ( $E_{ads}$ ) of ATMP and its zinc complex on the Fe (110) surface under solvation condition.

	ATMP	ATMP-Zn complex
$E_{\rm ads}  ({\rm Kcal \cdot mol^{-1}})$	-44.114	-83.913

This data indicates that its Zn complex is more effective than ATMP at preventing Fe (110) surface corrosion. It is reported that diffusion coefficients calculated reflect the inhibitive performances of molecules. For the Cl corrosive particles, the diffusion coefficients followed the order ATMP > ATMP–Zn complex, while for the H<sub>3</sub>O<sup>+</sup> corrosive particles, the diffusion coefficients followed the order D (L3) ATMP > ATMP–Zn complex (Figue 14, Table 10). These rankings are reflected in the experimentally obtained results.



**Figure 14**. Mean square displacement of  $Cl^-$  (right graph) and  $H_3O^+$  (left graph) ions in the ATMP and its complex membranes at 298 K, as well as the diffusion model of these ions in ATMP membrane (inset of right graph).

**Table 10.** Diffusion coefficient (D) of  $Cl^-$  and  $H_3O^+$  species in ATMP and its zinc complex membranes at 298 K.

Compound	Specie	D (Å <sup>2</sup> ·ps <sup>-1</sup> )
	Cl	0.48014
AIMP	$H_3O^+$	0.00550
ATMD 74 complex	Cl	0.31135
A I MP-Zn complex	$H_3O^+$	0.00480

### 3.6. Mechanism of corrosion inhibition

The chemical composition of the inhibitor, temperature, and electrochemical potential at the steel/solution interface all contribute to the inhibitor's adsorption on the surface of carbon steel. The water molecules in the solvent could adsorb at the steel/solution interface. Adsorption occurs when ions and molecules gather near the steel/solution interface alter the solvent molecules on metal surfaces [95, 96].

The anions are adsorbed, and the steel surface has an extra positive charge in excess of what is needed to balance the charge in accordance with the applied potential. The compounds (unshared pairs of electrons) adsorb extremely well on a variety of electrode surfaces. The relative coordinating power toward the given metal of the various groups present determines the precise nature of the interactions between a metal surface and a molecule.

According to previous studies, the surface charge of steel in HCl solution should be positive. As a result, the anions first bind to the steel surface, generating an excess negative charge that aids physical adsorption of the inhibitor cations. As a result of the Cl<sup>-</sup> and phosphonate ions adsorption, the surface becomes negatively charged. Electrostatic attraction attracts the protonated ATMP molecules to the carbon steel surface. The interaction of nitrogen atoms' unshared pairs of electrons with the vacant d-orbitals of iron atoms can result in free molecule adsorption (chemisorption). This model of adsorption, on the other hand, has no effect. The ATMP molecules are quickly protonated to form ionic forms in an acid solution. The strong defensive properties of this compound are thought to be mainly due to electrostatic cation adsorption [42]. When ATMP and Zn<sup>2+</sup> are combined in aqueous solution, ATMP reacts with Zn<sup>2+</sup> to form the [Zn<sup>2+</sup>–ATMP] complex [97]. This complex diffuses to the metal surface, where it binds to Fe(III) ions that are present. On the surface, a dense polymeric network structure is formed by a high degree of cross-linkage and reorganization.

### 4. Conclusion

Based on the above results, the following conclusions have been drawn:

- 1. ATMP, a non-toxic organic compound, was shown to be a successful synergist for corrosion control of carbon steel in acid media when combined with  $Zn^{2+}$ .
- 2. The synergistic effect of adding  $10^{-3}$  M Zn<sup>2+</sup> to ATMP significantly improved corrosion inhibition performance. When ATMP and Zn<sup>2+</sup> are combined in an aqueous solution, ATMP forms a complex with Zn<sup>2+</sup>.
- 3. The inhibitor molecules bind to the mild steel surface, blocking reaction sites and obeying the Langmuir adsorption isotherm.
- 4. The action of synergistic inhibition was confirmed by the coefficient of mutual effect, which was greater than unity.
- 5. With the addition of ATMP and  $10^{-3}$  M Zn<sup>2+</sup> combination, the surface area accessible for corrosive species attack decreases.
- 6. This study's findings are supported by quantum chemical studies.

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