

# Corrosion inhibition and adsorption properties of some manganese metal complexes on mild steel in sulfuric acid solutions

H.T. Rahal,<sup>1</sup> \* A.M. Abdel-Gaber,<sup>2</sup>  R. Al-Oweini<sup>3</sup> and R.N. El-Tabesh<sup>4</sup>

<sup>1</sup>Department of Chemistry, Faculty of Science, Lebanese International University, Al Khyara, West Bekaa, Lebanon

<sup>2</sup>Department of Chemistry, Faculty of Science Alexandria University, Ibrahimia, P.O. Box 426, Alexandria 21321, Egypt

<sup>3</sup>College of Arts and Sciences, University of La Verne, La Verne, CA 91750, USA

<sup>4</sup>Department of Chemistry, Faculty of Science, Beirut Arab University, P.O.Box 11-50-20, Riad El Solh 11072809 Beirut, Lebanon

\*E-mail: [hananrahal88@yahoo.com](mailto:hananrahal88@yahoo.com)

## Abstract

Metal complexes are frequently employed in industry as key compounds in medicinal chemistry. The interaction between metal complexes and metal surfaces is crucial in corrosion chemistry. Open circuit potential-time measurements, electrochemical impedance spectroscopy (EIS), and potentiodynamic polarization techniques are used to investigate the effects of two manganese metal complexes,  $\text{Mn}_2(\text{PAB})_4(\text{Phen})_2$  and  $\text{Mn}_2(\text{PAB})_3(\text{Phen})_2(\text{OH})$  abbreviated as  $\text{MnP}_4$  and  $\text{MnP}_3\text{OH}$ , on the corrosion of mild steel in sulfuric acid solutions. The chemical and structural characteristics of the complexes are confirmed using powder X-ray diffraction, thermal gravimetric analysis and FTIR. Both complexes act as potential corrosion inhibitors, with inhibition efficiencies of 90% at  $10^{-3} \text{ mol}\cdot\text{L}^{-1}$ . Potentiodynamic polarization curves suggest that  $\text{MnP}_4$  and  $\text{MnP}_3\text{OH}$  are anodic type inhibitors. The impedance responses indicate that the corrosion process of mild steel is activation controlled. The obtained results revealed that the inhibition efficiency decreases with increasing temperature, which is suggestive of physical adsorption mechanism. The corrosion inhibition mechanism was further corroborated by the values of kinetic and thermodynamic parameters obtained from the experimental data.

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## 1. Introduction

Despite the fact that mild steel has numerous technological applications, its poor corrosion resistance, particularly in acidic media used in pickling and cleaning, limits its use [1–11]. As a result, mild steel corrosion is a primary concern for corrosion scientists and material technologists. The most widely applied method for suppressing the corrosion rate of metals, particularly in acid solutions, is the use of inhibitors [12–18]. There are two major classes of inhibitors: inorganic and organic. The anodic type of inorganic inhibitors includes

chromates, nitrites, molybdates and phosphates, and the cathodic type includes zinc and polyphosphate inhibitors. The film forming class is the major class of organic inhibitor as it includes amines, amine salts and imidazolines – sodium benzoate mercaptans, esters, amines and ammonia derivatives [19]. Several organic molecules with nitrogen, oxygen, sulfur, phosphorus, and aromatic rings have the ability to adsorb to metal surfaces and act as inhibitors [8, 20–23]. Metal complexes are increasingly receiving a lot of attention from scientists, especially in the fields of chemistry and material science [24]. Owing to their unique properties, they are widely used as catalysts for chemical reactions in pharmaceutical industry, stabilizers or precursors in sol-gel processes as well as corrosion inhibitors [25]. Metal complexes or metal organic frameworks (MOFs) are considered as a group of compounds, either metal ions or clusters, harmonized with organic ligands to form one or higher dimensional structures. Thus, metal complexes are formed by coupling transition metals with organic ligands to form an organometallic complex [26]. The substitution of the ligand molecule and changes in the existing chemical structures lead to the synthesis of a wide range of transition metal complexes, some of which have proven to be efficient corrosion inhibitors. According to Mahdavian and Attar [27], the interaction of transition metal complexes with mild steel or any metallic surface is greatly affected by the activity and nature of the ligand and the standard electrode potential of the metal cation. It is reported that the presence of aromatic rings and heteroatom-rich ligand are likely to enhance the adsorption of the inhibitors on the metal's surface promoting effective corrosion inhibition [28–30]. Adam *et al.* [31] declared higher corrosion inhibition efficiency for the Cu(II) complex compared with the Co(II) complex containing the same ligand. Therefore, reasonably regulating the metal ions coordination center and the ligand is key to developing metal complexes that are good corrosion inhibitors.

Several studies have been conducted on the use of metal complexes in the field of corrosion inhibitors chemistry. In different acidic media at room and elevated temperatures, various ligands of the metal complexes Co(II), Ni(II), Zn(II), Cu(II), Mn(II), Cr(II) and Sn(II) have shown good corrosion inhibition properties for mild steel [27, 32–34]. Transition metal complexes derived from Schiff's base are more effective inhibitors due to their greater size and compactness, while metal-organic blends have also shown synergistic effects [35–39].

There has been an emerging demand for transition metal complexes in rendering the corrosion rate of metals in a variety of aggressive environments. Singh and co-workers [29] synthesized and tested the efficiency of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) complexes with 2-aminobenzoic acid (phenyl-pyridin-2-yl-methylene)-hydrazide. The obtained results showed appreciable corrosion inhibition efficiency for mild steel in 1 M HCl solution and the metal complexes showed a better inhibition effect than the corresponding ligand. Devika *et al.* [16] reported the corrosion behavior of three metal [Co(II), Ni(II), and Fe(III)] complexes of antipyrine based azo dye ligand for soft-cast steel in 1 M HCl acid solution using experimental and theoretical methods. The study revealed that the ligand and their metal complexes show good inhibition efficiency, with Ni complex showing significant

inhibition efficiency at an optimum concentration of 25 mg/L. Heteroleptic complexes of four divalent metals, Co, Ni, Zn, and Cd with dithiophosphonates and N-donor ligands were successfully synthesized, characterized and tested for the corrosion inhibition of mild steel in 1 M HCl solutions [30]. The paper reported excellent corrosion inhibition potentials of the metal complexes with inhibition efficiencies of 75.20% (Co), 89.41% (Zn), 90.60% (Cd) and 91.78% (Ni) when applied at 100 ppm to mild steel in 1 M HCl. Similar results were reported by Nassar *et al.* [40]. In a new study, Haruna *et al.* [41] evaluated the inhibition efficiency of newly synthesized Schiff's base derived from the reaction of 2-amino phenol and 2-hydroxy-1-naphthaldehyde and its Co(II) and Mn(II) complexes on the corrosion of copper in 1 M HCl solution using the weight loss method. The results showed that inhibition efficiency increased with increasing inhibitors concentration. The negative values of Gibb's free energy of adsorption ( $\Delta G_{\text{ads}}$ ) confirmed the physical adsorption of the inhibition process which is inconsistent with Langmuir adsorption isotherm. In the same concept, recently, Liu *et al.* [28] tested the inhibitive properties of 2,2'-bipyridine-3,3'-dicarboxylic acid (bpda) and its transition metal complexes including Ni(bpda)<sub>2</sub>, Zn(bpda)<sub>2</sub> and Mn(bpda)<sub>2</sub>, on the corrosion inhibition of carbon steel in 0.5 M HCl. The results revealed that the metal complexes exhibit higher inhibition efficiencies compared to the bpda ligand, among which Ni(bpda)<sub>2</sub> is the most effective for inhibiting corrosion. Accordingly, the superior corrosion inhibition performance of the three complexes could be attributed to their good adsorption abilities. Ade *et al.* [42], Kashyap *et al.* [43] Verma *et al.* [44] and Abdel-Gaber *et al.* [45] proved that transition metal complexes of the Schiff's base are capable of retarding the corrosion rate of mild steel in acidic conditions.

Gupta *et al.* [46] indicated that the ligand and its metal complexes had a significant inhibitory effect on the corrosion of mild steel in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution, and the Mn(II), Co(II) and Cu(II) complexes showed better inhibition than the ligand. Additionally, El Tabesh *et al.* [47, 48] showed that mixed ligand copper and manganese complexes have a remarkable effect on the corrosion inhibition of carbon steel in 0.5 M H<sub>2</sub>SO<sub>4</sub> solutions. Baboukani *et al.* [49] found that Co complex with a Schiff's base ligand is a moderate mixed type (with predominant anodic character) inhibitor for the corrosion of 316 L stainless steel (SS) in 0.1 H<sub>2</sub>SO<sub>4</sub> solution. Electrochemical tests revealed that increasing the concentration of Co complex increases the corresponding inhibition efficiency upto a concentration of 100 ppm.

Moreover, in an attempt to search for high performance, effective and ecofriendly corrosion inhibitors in neutral media, the macrocyclic compartmental ligand: (2*E*)-3,6,10,13-tetramethyl-2,7,9,14-tetraaza-1,8(1,4)dibenzenacyclotetradecaphane-2,6,9,13-tetraene (PDHDH) and its Ni(II), Cu(II) complexes proved to be excellent inhibitors for on the corrosion of Cu10Ni alloy in 3.5% NaCl. Their protection capacity reached upto 95.7% at 100  $\mu$ M additive concentration [50]. Additionally, in oilfield, the anticorrosion properties of *N'*-phenylbenzohydrazide and its metal complex derivatives (Cu, Mn, Co) on the corrosion of mild steel in oilfield produced water were reported by Mahross *et al.* [51]. The obtained data proved that metal complexes acted as anodic-type inhibitor. Their inhibition activity

was attributed to their physical and chemical adsorption on the mild steel surface resulting in an effective protective barrier. Quantum chemical calculations confirmed experimental data and showed that NPB–Cu has the lowest  $E_{\text{Gap}}$  value (1.053 eV) indicating that it could have better performance as corrosion inhibitor.

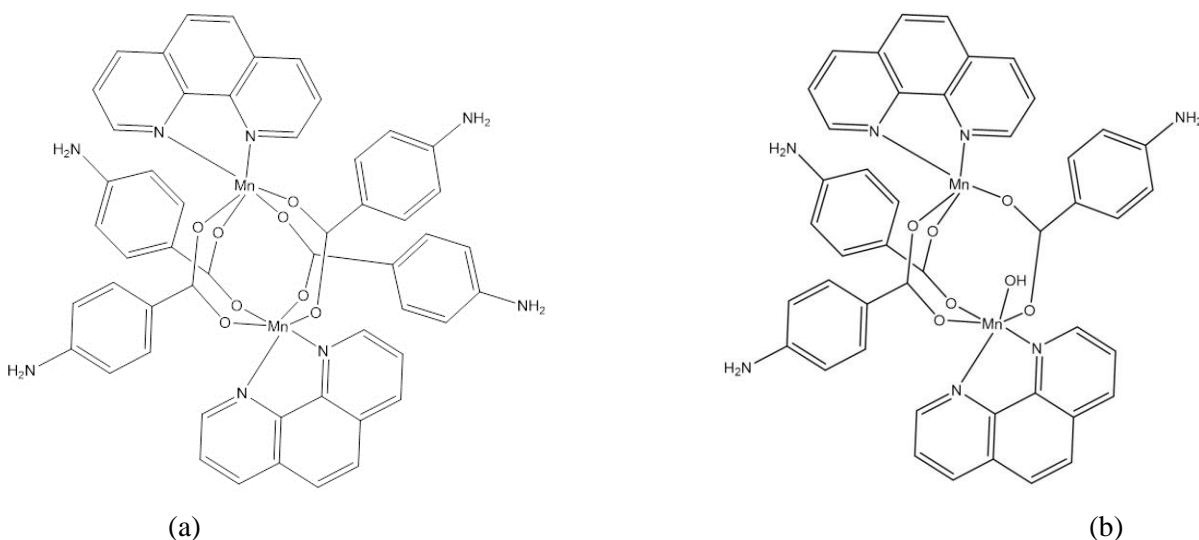
In light of the above few reports on the corrosion inhibition properties of transition metal complexes, the present work looks into the influence of two manganese metal complexes on the corrosion of mild steel in a 0.5 M sulfuric acid solution. The challenge of this study is the preparation and functionalization of novel Mn complexes from simple ligands by a simple method achieving high inhibition efficiencies (90–93%) as well as proposing an inhibition mechanism of metal complexes for the corrosion of mild steel in an acidic environment.

## 2. Experimental Techniques

### 2.1. Solution Preparation

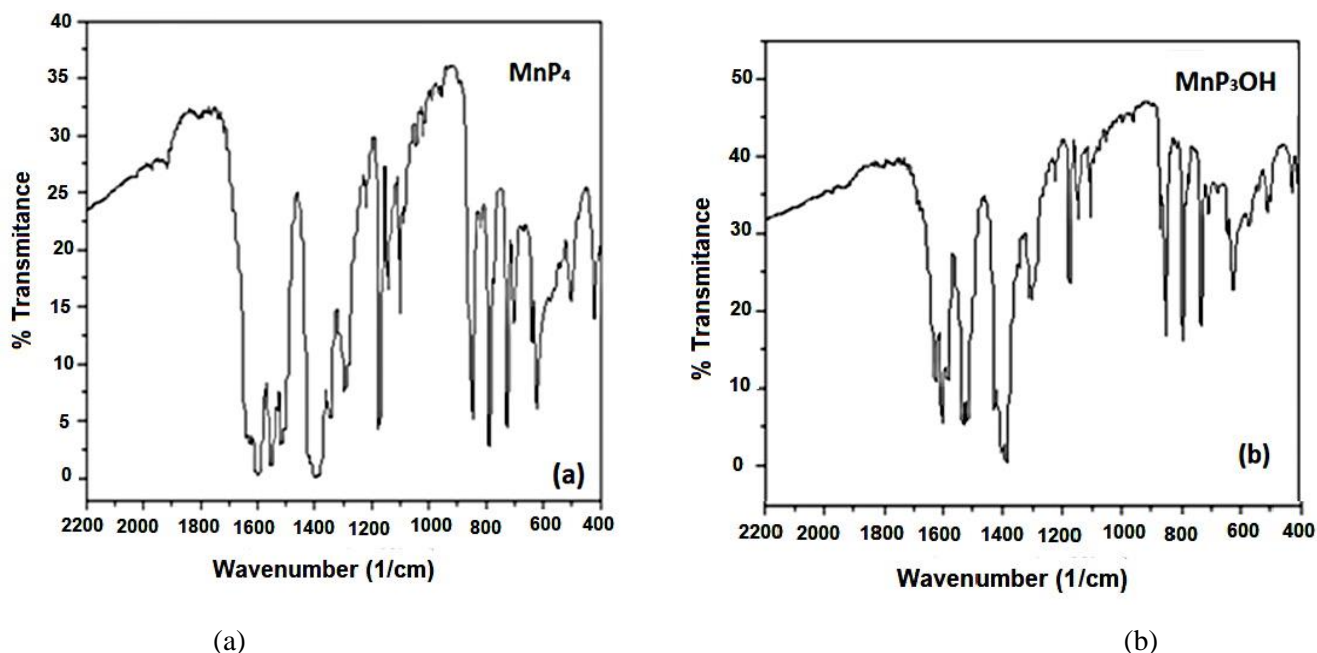
Distilled water was used to dilute 0.5 M sulfuric acid ( $\text{H}_2\text{SO}_4$ ) solutions from 80% analytical grade (Scharlau chemical industries) concentrated acid. As previously stated, the tested solutions were prepared using pure ethanol (99.8%, Riedel-de Haen) and distilled water [47, 48].  $\text{MnP}_4$  was prepared by the reaction of an equimolar amount of each of *p*-aminobenzoic acid, phenanthroline and  $\text{MnSO}_4 \cdot \text{H}_2\text{O}$  in methanol at  $50^\circ\text{C}$ . However,  $\text{MnP}_3\text{OH}$  was synthesized by the reaction of equimolar of each of *p*-aminobenzoic acid, phenanthroline and  $\text{Mn}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$  in methanol at room temperature.

Powder X-Ray Diffraction (XRD BRUKER D8 Advance X-Ray Diffractometer) employing copper  $\text{K}\alpha$  radiation, thermal gravimetric analysis (TGA Labsys SETERAM computerized thermal analyzer) were used to confirm the chemical and structural properties of complexes. Figure 1 (a and b) shows the structural formula of the manganese complexes  $\text{MnP}_4$  and  $\text{MnP}_3\text{OH}$ .



**Figure 1.** Structural formula of the used Mn-metal complexes  $\text{MnP}_4$  (a) and  $\text{MnP}_3\text{OH}$  (b).

Nicolet-Avatar 370 FTIR analysis was used to characterize the Mn complexes. The FTIR spectra for  $\text{MnP}_4$  and  $\text{MnP}_3\text{OH}$  complexes are shown in Figure 2 (a and b). The spectra of the phenanthroline complex in both figures are characterized by strong bands observed in three frequency areas, specifically between  $700$  and  $900\text{ cm}^{-1}$ , between  $1125$  and  $1250\text{ cm}^{-1}$ , and between  $1400$  and  $1650\text{ cm}^{-1}$  [52]. The coordination of deprotonated *p*-aminobenzoic acid to manganese was observed at  $1581\text{ cm}^{-1}$  and  $1396\text{ cm}^{-1}$ , which are assigned to the asymmetrical and symmetrical COO vibrational modes, respectively [53]. Peaks in the range of  $450$ – $630\text{ cm}^{-1}$  may be assigned to Mn–O stretching vibration band present in both  $\text{MnP}_4$  and  $\text{MnP}_3\text{OH}$  complexes [54].



**Figure 2.** FTIR spectra of Mn-metal complexes  $\text{MnP}_4$  (a) and  $\text{MnP}_3\text{OH}$  (b).

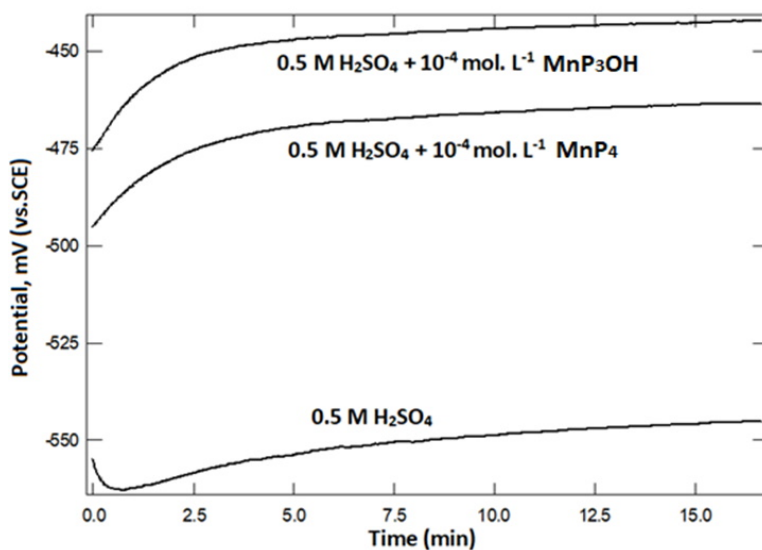
## 2.2. Electrochemical Studies

Electrochemical studies (electrochemical impedance spectroscopy (EIS) and polarization measurement) were performed by connecting the Gill AC transfer function analyzer ACM instrument (UK) to a three-electrode electrochemical cell setup. A detailed description of the electrochemical techniques used in these experiments was previously discussed [7, 48].

## 3. Results and Discussions

### 3.1. Open Circuit Potential (OCP) measurements

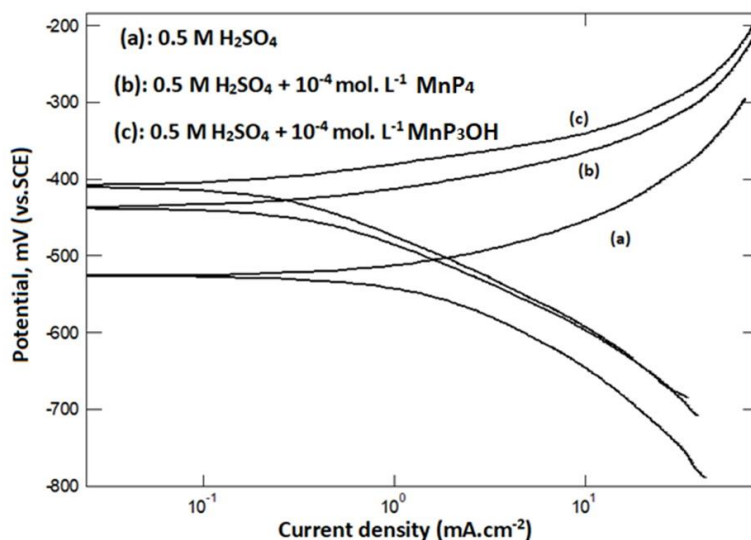
Figure 3 shows that mild steel acquires its equilibrium potential after 15 minutes of immersion in  $0.5\text{ M H}_2\text{SO}_4$  solutions. In the presence of  $10^{-4}\text{ mol}\cdot\text{L}^{-1}$   $\text{MnP}_4$  and  $\text{MnP}_3\text{OH}$ , the equilibrium potential shifted towards less negative values, indicating their effect on the anodic dissolution of mild steel in sulfuric acid solutions [5, 55].



**Figure 3.** Variation of open circuit potential as a function of time for mild steel in 0.5 M  $\text{H}_2\text{SO}_4$  solution in the absence and presence of  $10^{-4} \text{ mol}\cdot\text{L}^{-1}$   $\text{MnP}_4$  and  $\text{MnP}_3\text{OH}$  complexes at  $30^\circ\text{C}$ .

### 3.2 Potentiodynamic polarization curve measurements

Figure 4 shows that the addition of  $\text{MnP}_4$  and  $\text{MnP}_3\text{OH}$  complexes shifts the anodic branch of the polarization curves to a lower current density, indicating suppression of the anodic dissolution of steel and therefore classifying them as anodic type inhibitors. The electrochemical polarization parameters including the corrosion potential ( $E_{\text{corr}}$ ), corrosion current density ( $i_{\text{corr}}$ ), anodic and cathodic Tafel slopes ( $\beta_a$  and  $\beta_c$ ) for mild steel in 0.5 M  $\text{H}_2\text{SO}_4$  in the absence and presence of  $10^{-4} \text{ mol}\cdot\text{L}^{-1}$   $\text{MnP}_4$  and  $\text{MnP}_3\text{OH}$  complexes at  $30^\circ\text{C}$  are listed in Table 1.



**Figure 4.** Potentiodynamic polarization curves for mild steel in 0.5 M  $\text{H}_2\text{SO}_4$  in the absence and presence of  $10^{-4} \text{ mol}\cdot\text{L}^{-1}$   $\text{MnP}_4$  and  $\text{MnP}_3\text{OH}$  complexes at  $30^\circ\text{C}$ .

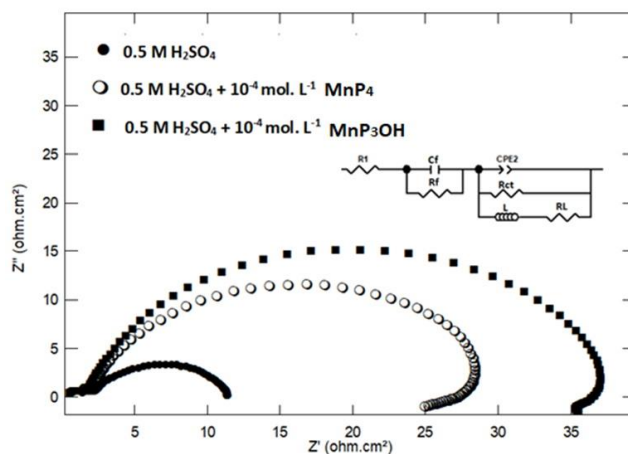
**Table 1.** The electrochemical polarization parameters for the corrosion of mild steel in in 0.5 M H<sub>2</sub>SO<sub>4</sub> in the absence and presence of 10<sup>-4</sup> mol·L<sup>-1</sup> MnP<sub>4</sub> and MnP<sub>3</sub>OH complexes at 30°C.

| Inhibitor<br>(mol·L <sup>-1</sup> ) | E <sub>corr</sub><br>(mV vs. SCE) | β <sub>a</sub> | -β <sub>c</sub> | i <sub>corr</sub><br>(mA·cm <sup>-2</sup> ) |
|-------------------------------------|-----------------------------------|----------------|-----------------|---|
|                                     |                                   | mV/decade      |                 |   |
| 0.00                                | -532                              | 99             | 147             | 1.694                                       |
| MnP <sub>4</sub>                    | -456                              | 72             | 108             | 0.581                                       |
| MnP <sub>3</sub> OH                 | -421                              | 59             | 124             | 0.437                                       |

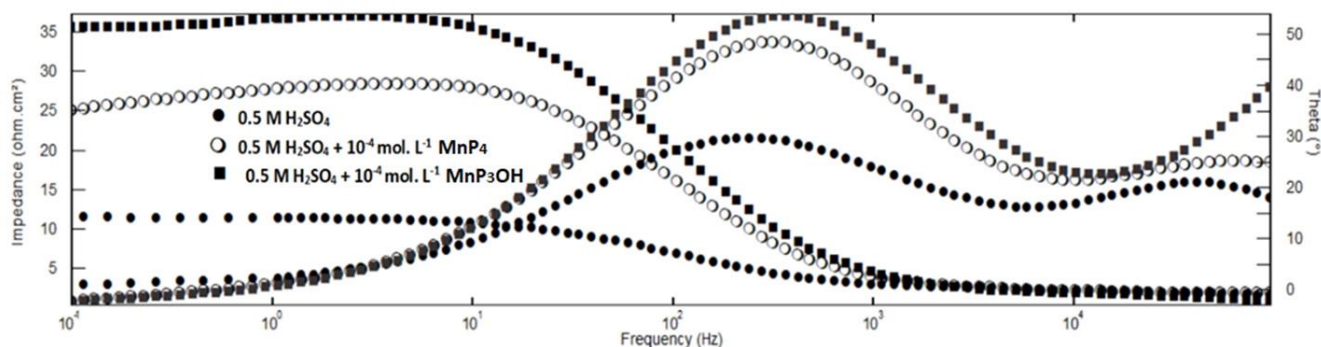
Inspection of the tabulated data revealed that the corrosion current density ( $i_{\text{corr}}$ ) decreases with the addition of both complexes. Moreover, the addition of MnP<sub>4</sub> and MnP<sub>3</sub>OH shifts the corrosion potential  $E_{\text{corr}}$  to more positive values.

### 3.3 Electrochemical impedance spectroscopy results

Based on Nyquist representations, Figure 5 displays two depressed capacitive semicircles. The first depressed capacitive loops were generated by dispersion effects due to surface roughness and inhomogeneities during corrosion [56, 57]. The second semicircle, on the other hand, indicates that mild steel dissolution happens under activation control and may possibly be due to the charge transfer reaction and the time constant of the electric double layer. In the presence of MnP<sub>4</sub> and MnP<sub>3</sub>OH complexes, the depressed semicircle is followed by a low-frequency inductive loop. The inductive loop shows the presence of a Faradic process on free electrode sites, that may be credited to the relaxation of intermediates governing the anodic process on the electrode surface produced by adsorption species such as FeSO<sub>4</sub> [58] or inhibitor species [59, 60]. It might also be explained by the re-dissolution of the passivated surface at low frequency [61]. The diameter of the produced capacitive semicircles increases as the concentration of both complexes rises [5, 11].

**Figure 5.** Nyquist plots for mild steel in 0.5 M H<sub>2</sub>SO<sub>4</sub> in the absence and presence of 10<sup>-4</sup> mol·L<sup>-1</sup> MnP<sub>4</sub> and MnP<sub>3</sub>OH complexes at 30°C.

The Bode plots (the impedance modulus  $|Z|$  and the phase angle theta) shown in Figure 6 indicate that the presence of both complexes increases the impedance modulus, indicating that they retard the corrosion rate of mild steel in sulfuric acid solution. In these plots, the phase angle values are less than 90 indicating the presence of non-ideal capacitances and confirming the presence of inhomogeneities in the system. Additionally, the phase angle value increases with the addition of both complexes. This might be owing to the reduction of the capacitive behavior at the mild steel surface as a result of its lower dissolution rate in the presence of both complexes [62].



**Figure 6.** Bode plots of mild steel in 0.5 M  $\text{H}_2\text{SO}_4$  in the absence and presence of  $10^{-4} \text{ mol}\cdot\text{L}^{-1}$   $\text{MnP}_4$  and  $\text{MnP}_3\text{OH}$  complexes.

The equivalent circuit, inserted in Figure 5, was used to analyze the obtained spectra for both complexes in sulfuric acid. The components of this circuit were extensively described in previous work [48]. The ideal double layer capacitance ( $C_{dl}$ ) could be obtained from the non-ideal double layer capacitance  $Q_{dl}$  using equation 1 [7]:

$$C_{dl} = \frac{(Q \times R_{ct})^{1/n}}{R_{ct}} \quad (1)$$

The percent inhibition efficiency ( $\%P$ ) was calculated using equation (2):

$$\%P = \frac{(R_{ct} - R_{ct0})}{R_{ct}} \times 100 \quad (2)$$

$R_{ct0}$  and  $R_{ct}$  are the charge transfer resistance ( $\text{Ohm}\cdot\text{cm}^2$ ) values in the absence and in the presence of  $\text{MnP}_4$  and  $\text{MnP}_3\text{OH}$  complexes, respectively.

The electrochemical parameters with  $\%P$  obtained from electrochemical chemical measurements are given in Table 2. As can be seen, the  $R_{ct}$  and  $\%P$  values increase while  $C_{dl}$  values decrease with increasing  $\text{MnP}_4$  and  $\text{MnP}_3\text{OH}$  concentrations in sulfuric acid solutions. This drop in  $C_{dl}$  values is due to the adsorption of  $\text{MnP}_4$  and  $\text{MnP}_3\text{OH}$  complexes on mild steel surfaces and the formation of a protective barrier that prevents metal diffusion into the bulk [48].



**Table 2.** The electrochemical impedance parameters for the corrosion of mild steel in 0.5 M H<sub>2</sub>SO<sub>4</sub> containing different concentrations of MnP<sub>4</sub> and MnP<sub>3</sub>OH complexes.

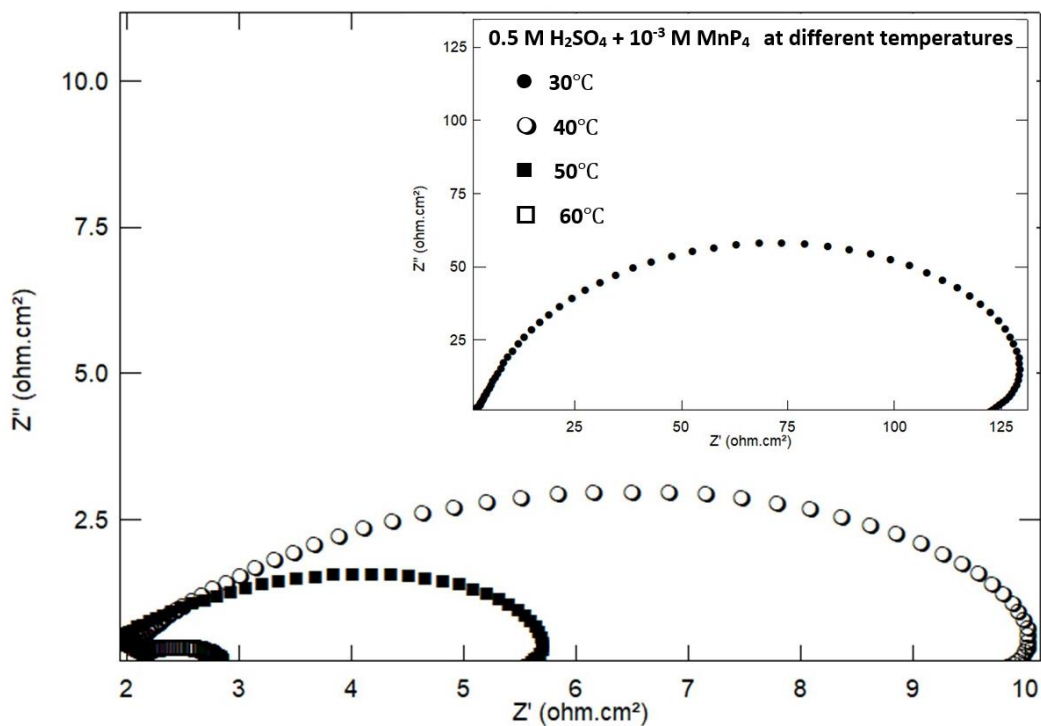
|                     | Conc.,<br>mol·L <sup>-1</sup> | R <sub>s</sub><br>Ω·cm <sup>2</sup> | C <sub>f</sub><br>μF/cm <sup>2</sup> | R <sub>f</sub><br>Ω·cm <sup>2</sup> | R <sub>ct</sub><br>Ω·cm <sup>2</sup> | Q <sub>dl</sub><br>μF/cm <sup>2</sup> | n    | C <sub>dl</sub><br>μF/cm <sup>2</sup> | L<br>H·cm <sup>2</sup> | R <sub>L</sub><br>Ω·cm <sup>2</sup> | %P   |
|---------------------|-------------------------------|-------------------------------------|--------------------------------------|-------------------------------------|--------------------------------------|---------------------------------------|------|---------------------------------------|------------------------|-------------------------------------|------|
| MnP <sub>4</sub>    | Blank                         | 1.54                                | 1.56                                 | 2.30                                | 9                                    | 6500                                  | 0.83 | 61563                                 | –                      | –                                   | –    |
|                     | 1×10 <sup>-5</sup>            | 0.84                                | 1.83                                 | 1.09                                | 14.9                                 | 369                                   | 0.85 | 1687                                  | 0.00072                | 51                                  | 39.1 |
|                     | 2×10 <sup>-5</sup>            | 0.75                                | 2.06                                 | 1.56                                | 15.2                                 | 344                                   | 0.85 | 1559                                  | 0.0154                 | 156                                 | 40.8 |
|                     | 1×10 <sup>-4</sup>            | 0.35                                | 1.53                                 | 1.25                                | 27.6                                 | 250                                   | 0.83 | 1528                                  | 44.42                  | 197                                 | 67.5 |
|                     | 2×10 <sup>-4</sup>            | 0.73                                | 1.98                                 | 1.64                                | 32.8                                 | 241                                   | 0.83 | 1514                                  | 50.48                  | 200                                 | 72.6 |
|                     | 4×10 <sup>-4</sup>            | 0.68                                | 2.25                                 | 1.41                                | 43.4                                 | 227                                   | 0.83 | 1492                                  | 60.49                  | 210                                 | 79.2 |
|                     | 5×10 <sup>-4</sup>            | 0.50                                | 1.05                                 | 1.11                                | 103                                  | 98                                    | 0.85 | 498                                   | 320                    | 583                                 | 91.2 |
|                     | 1×10 <sup>-3</sup>            | 0.50                                | 0.98                                 | 1.19                                | 137                                  | 82                                    | 0.87 | 331                                   | 322                    | 1036                                | 93.4 |
| MnP <sub>3</sub> OH | 1×10 <sup>-5</sup>            | 0.54                                | 2.00                                 | 1.54                                | 18.5                                 | 2808                                  | 0.83 | 25956                                 | 0.00181                | 149                                 | 51.4 |
|                     | 5×10 <sup>-5</sup>            | 0.56                                | 1.65                                 | 1.57                                | 22.4                                 | 2493                                  | 0.84 | 19994                                 | 0.00187                | 254                                 | 59.8 |
|                     | 1×10 <sup>-4</sup>            | 0.12                                | 1.68                                 | 1.58                                | 40.3                                 | 1204                                  | 0.86 | 6974                                  | 0.0170                 | 255                                 | 77.7 |
|                     | 3×10 <sup>-4</sup>            | 0.53                                | 1.85                                 | 1.52                                | 59.5                                 | 1200                                  | 0.87 | 6375                                  | 0.0189                 | 818                                 | 84.8 |
|                     | 5×10 <sup>-4</sup>            | 0.54                                | 1.72                                 | 1.55                                | 100                                  | 1147                                  | 0.87 | 6540                                  | 0.0195                 | 911                                 | 91.7 |
|                     | 1×10 <sup>-3</sup>            | 0.55                                | 1.64                                 | 1.62                                | 151                                  | 1132                                  | 0.88 | 5853                                  | 226                    | 913                                 | 94.0 |
|                     | 2×10 <sup>-3</sup>            | 0.55                                | 0.80                                 | 1.54                                | 159                                  | 90                                    | 0.87 | 376                                   | 8556                   | 1769                                | 94.3 |

Comparing the efficiency of the tested MnP<sub>4</sub> and MnP<sub>3</sub>OH metal complexes to mixed Ligands Cu complexes reported previously [48], it could be observed that Cu complexes acted as mixed type inhibitors whereas Mn complexes were anodic type inhibitors. However, both Cu and Mn complexes were effective at reducing the corrosion of mild steel and have nearly the same efficiency of 90–94% for 1×10<sup>-3</sup> M. As previously mentioned, hetero-atoms rich ligands as well as the metallic ion present in the complex alter the interaction between the metallic complex and the metal's surface affecting the inhibition efficiency.

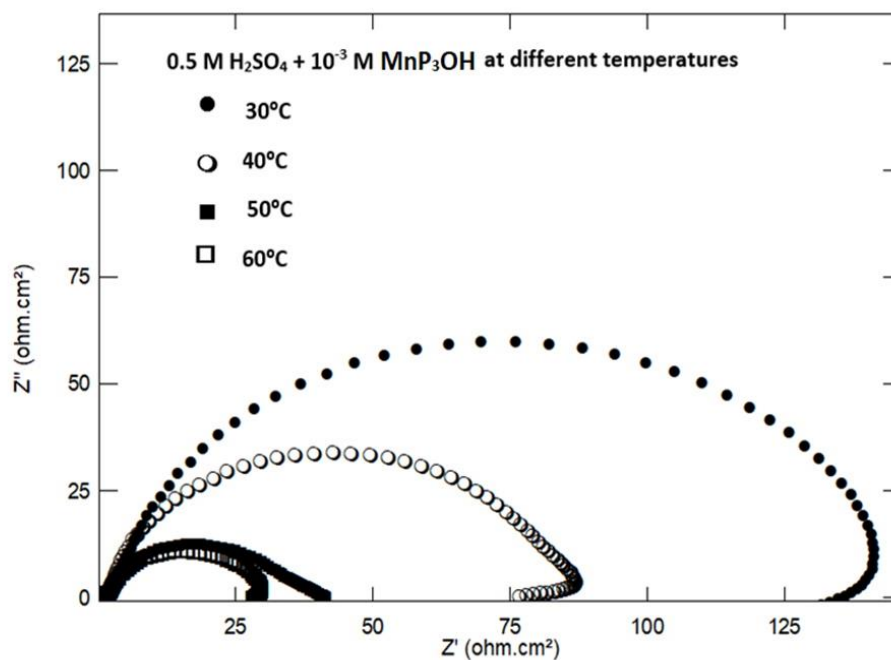
### 3.4. Thermodynamics activation parameters

The calculation of the activation parameters is fundamentally important to illustrate the inhibition mechanism. The thermodynamic parameters ( $\Delta E^*$ ,  $\Delta H^*$ ,  $\Delta S^*$ , and  $\Delta G^*$ ) for the dissolution of mild steel in sulfuric acid solution in the absence and presence of 1×10<sup>-3</sup> M MnP<sub>4</sub> and MnP<sub>3</sub>OH complexes were obtained using Arrhenius and the transition state equations [7, 21] and presented in Table 3. Nyquist plots at different temperatures (Figures 7 and 8) were used to obtain the corrosion rates that were taken as the reciprocal of R<sub>ct</sub> values. It is clear that increasing temperature decreases the size of the depressed semicircles which indicates an increase in the corrosion rate of mild steel. This behavior could be explained on

the basis that the increase in temperature results in desorption of the metal complex from mild steel surface [63].



**Figure 7.** Nyquist plots for steel in sulfuric acid solution in the presence of the  $1 \times 10^{-3}$  M MnP<sub>4</sub> at different temperatures.



**Figure 8.** Nyquist plots for steel in sulfuric acid solution in the presence of the  $1 \times 10^{-3}$  M MnP<sub>3</sub>OH at different temperatures.

**Table 3.** The activation parameters of mild steel in sulfuric acid solution in the absence and presence of  $1 \times 10^{-3}$  M  $\text{MnP}_4$  and  $\text{MnP}_3\text{OH}$  complexes.

| Solution                | $\Delta E^*$<br>$\text{kJ}\cdot\text{mol}^{-1}$ | $\Delta H^*$<br>$\text{kJ}\cdot\text{mol}^{-1}$ | $\Delta S^*$<br>$\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ | $\Delta G^*$<br>$\text{kJ}\cdot\text{mol}^{-1}$ |
|-------------------------|---|---|--|---|
| $\text{H}_2\text{SO}_4$ | 28  | 25  | -181   | 79.8  |
| $\text{MnP}_4$          | 142   | 139   | 176  | 85.7  |
| $\text{MnP}_3\text{OH}$ | 50  | 47  | -130   | 86.4  |

Inspection of the tabulated data show that the activation energy ( $\Delta E^*$ ) and enthalpy of activation ( $\Delta H^*$ ) increases in the presence of  $\text{MnP}_4$  and  $\text{MnP}_3\text{OH}$  complexes indicating the geometric blocking effect of the adsorbed cationic or neutral complex molecules on the mild steel surface [63]. Furthermore, the positive values of  $\Delta H^*$  are an indication of the endothermic nature of the formation process of the activated complex. Negative entropy ( $\Delta S^*$ ) value in the presence of  $\text{MnP}_3\text{OH}$  denotes that the activated complex represents an association rather than a dissociation step [64, 65]. However, the positive value of entropy in  $\text{MnP}_4$  indicates an increase in solvent entropy. Moreover, positive value of  $\Delta S^*$  means that an increase in disordering takes place on going from reactants to the activated complex in the presence of  $\text{MnP}_4$  complex [66–69]. The change of free energy of activation ( $\Delta G^*$ ) values estimated in the absence and presence of both metal complexes are arranged in the order of  $0.5 \text{ M H}_2\text{SO}_4 < \text{MnP}_4 < \text{MnP}_3\text{OH}$ . Positive values of  $\Delta G^*$  indicated the formation of unstable activated complex in the rate determining transition state.

### 3.5. Mechanism of inhibition

Transition metal complexes' interactions with mild steel are heavily influenced by their standard electrode potentials, reactivity, and the type of the ligand that might stabilize the metallic complexes. The standard electrode potential of divalent cations follows the order:  $\text{Fe}^{2+}/\text{Fe}$  ( $-0.44 \text{ V}$ )  $>$   $\text{Mn}^{2+}/\text{Mn}$  ( $-1.18 \text{ V}$ ) [27]. Therefore, the reduction of  $\text{Mn}^{2+}$  species on the mild steel surface is not possible due to their highly negative standard electrode potential compared to  $\text{Fe}^{2+}$ . Based on temperature studies, the decrease in inhibition efficiency with rise in temperature is actually suggestive of physical adsorption mechanism [70].

As reported [71], the steel surface in  $0.5 \text{ M}$  sulphuric acid is positively charged, and this surface charge turns to negative owing to sulphate anion adsorption. Thus, the physical adsorption of  $\text{MnP}_4$  and  $\text{MnP}_3\text{OH}$  is due to the adsorption of protonated amino groups over the negatively charged steel surface [72, 73].

The stronger interaction of  $\text{MnP}_3\text{OH}$  with the mild steel surface in  $0.5 \text{ M H}_2\text{SO}_4$  than  $\text{MnP}_4$  may be attributed to the steric hindrance of substitutes in  $\text{MnP}_4$  compared to  $\text{MnP}_3\text{OH}$ . The closeness of the bulky ligands in  $\text{MnP}_4$  causes steric repulsion that hinders its inhibition potential. Such bulkiness disturbs the molecule's planarity, and thus the phenyl rings may be unable to engage closely enough with the metal surface to have direct contact, resulting in lower protection efficiency [73, 74].

Moreover, the presence of hydroxyl group (OH), an electron releasing group, in  $\text{MnP}_4\text{OH}$  increases the donating ability of  $\text{MnP}_4\text{OH}$  molecules toward the mild steel surface by increasing their conjugations owing to presence of unshared electron pairs on the oxygen atoms and therefore enhances the inhibition performance compared to  $\text{MnP}_4$  [75].

#### 4. Conclusion

This study reports the effect of two manganese metal complexes against the corrosion of mild steel in 0.5 M sulfuric acid solution. The obtained data showed that  $\text{MnP}_4$  and  $\text{MnP}_3\text{OH}$  complexes act as effective corrosion inhibitors for mild steel in 0.5 M  $\text{H}_2\text{SO}_4$  solutions. Potentiodynamic polarization curves proved that both complexes behave as anodic type inhibitors retarding the dissolution of mild steel at anodic sites. The inhibition efficiency increases with increasing the concentration of both metal complexes, while it decreases with an increase in temperature. Their inhibitive action was accredited to their physical adsorption on the mild steel surface resulting in an effective protective barrier, that isolates the metal's surface from the acidic harsh environment. However, the stronger interaction of  $\text{MnP}_3\text{OH}$  with the mild steel surface in 0.5 M  $\text{H}_2\text{SO}_4$  than  $\text{MnP}_4$  may be ascribed to the presence of hydroxyl group in the latter as well as the steric hindrance of substitutes in  $\text{MnP}_4$  compared to  $\text{MnP}_3\text{OH}$ . From the obtained results,  $\text{MnP}_4$  and  $\text{MnP}_3\text{OH}$  can be regarded as new potential inorganic inhibitors that can be applied against mild steel corrosion in aggressive solutions in industrial acid cleaning.

#### Conflicts of interest

Authors declare no conflicts of interest.

#### Ethical Approval

This article does not contain any studies with human participants or animals performed by any of the authors.

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