

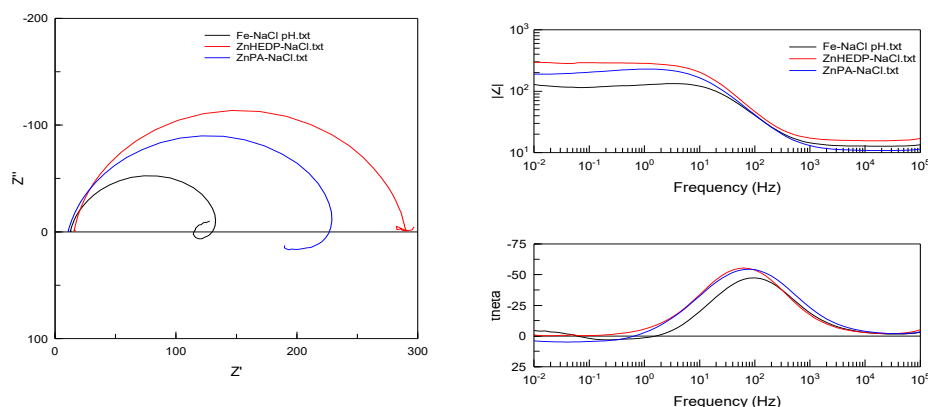
## ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY STUDY OF ZINC METAL PHOSPHONATES IN SALINE SOLUTION

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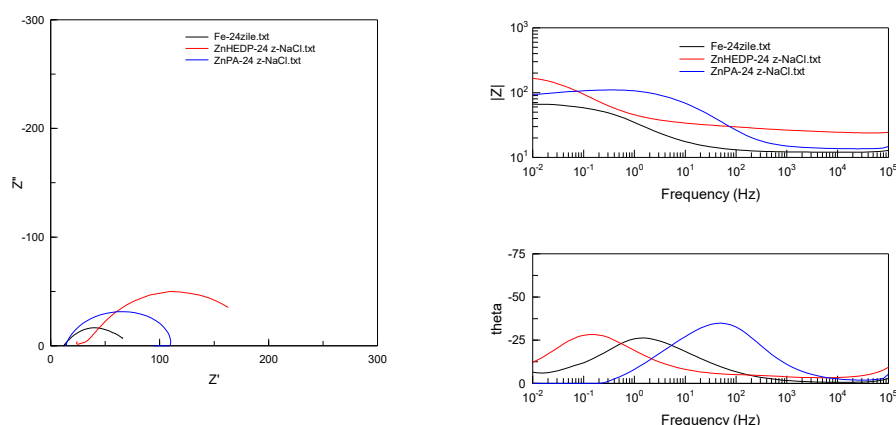
Organic phosphonates such as diphosphonic acids, aminophosphonic acid, and hydroxyphosphonic acid have been the subject of more extensive studies. The structure of phosphonates affects corrosion inhibition efficiency (IE). The concentration of 1-hydroxyethane-1,1-diphosphonic acid (HEDP) influences IE. Therefore, a reduced concentration of HEDP is beneficial. In contrast, if the concentration of HEDP exceeds the optimal value, the protective efficiency decreases because the protective oxide layer dissolves. The primary mechanism that makes corrosion inhibitors effective lies in their ability to adsorb onto the metal surface or react with metal cations to form insoluble compounds. This process results in the formation of a protective layer that shields the metal from the surrounding corrosive environment, thereby blocking aggressive ions from reacting with the metal surface. In addition, phosphonic acids can react with metal cations to form stable, sparingly soluble compounds, further reducing the corrosion rate. These mechanisms are crucial for extending the lifespan of materials and improving the durability of metals exposed to harsh environments [1].

Electrochemical impedance spectroscopy spectra (EIS) (figure 1 and figure 2) were performed to evaluate the corrosive effect of chloride ion on iron in the absence and presence of organic phosphorus compounds. Before each determination, metal phosphonates were dissolved in 3% NaCl solution acidified to pH~2.5 adjusted with HNO<sub>3</sub>. The examined metal phosphonates, ZnHEDP and ZnPA were hydrothermally synthesized at 80°C from Zn and HEDP and PA [2]. The impedance measurements were made using the FRA module of the Autolab 302N device, in the frequency range between 0.1-106 Hz and an AC amplitude of 10 mV. For each recorded spectrum, 60 points were collected, with a logarithmic distribution of 10 points per decade. Experimental EIS data were modeled with an electric equivalent circuit (ECE), using the modeling procedure of ZView 3.0 software (Scribner Associates, Inc.) to determine electrochemical parameters for this study.



**Figure 1.** a) Nyquist plot, b) Bode representation (logarithm of the impedance modulus  $|Z|$  and phase angle as a function of the logarithm of frequency  $f$ , recorded after 60 minutes immersion in 3% NaCl solution at pH 2.5, with and without inhibitor addition.

The values obtained for electrochemical parameters for iron immersed in ZnHEDP indicate the formation of a thicker and more compact layer in the presence of this metal-phosphonate during the first 60 minutes of immersion.



**Figure 2.** a) Nyquist plot, b) Bode representation (logarithm of the impedance modulus  $|Z|$  and phase angle as a function of the logarithm of frequency  $f$ , recorded after 24 days immersion in 3% NaCl solution at pH 2.5, with and without inhibitor addition.

Analyzing the EIS data after 24 days of immersion, it was observed that the stability of the metal-phosphonates and the amount of phosphonic acid released and reaching the metal surface determine the effectiveness of the inhibitor. The released phosphonic acid has the ability to form Fe–O–P bonds.

The polarization resistance ( $R_p$ ) values decrease in the order ZnHEDP > ZnPA > Fe. The lower  $R_p$  values for ZnPA are the result of the smaller amount of phosphonic acid released through hydrolytic attack, which leads to the formation of an incomplete layer on the iron surface. It is also possible that the ZnPA inhibitor is significantly more stable than the ZnHEDP compound.

[1] K.M. Shwetha, B.M. Praveen, K.D. Bharath, Results Surf. Interfaces 16 (2024).

[2] A. Visa, B. Maranescu, A. Bucur, S. Iliescu, K. D. Demadis, Phosphorus Sulfur Silicon Relat. Elem. 189 (2014) 630.