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ELECTROCHEMICAL STUDIES ON 5,10,15,20-TETRAKIS (4-PYRIDYL)-21H,23H-PORPHINE AND ITS ZN(II) COMPLEX

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ABSTRACT. The electrochemical characterization of 5,10,15,20-tetrakis(4-pyridyl)-21H,23H-porphine (TPyP) and of Zn(II)5,10,15,20-tetrapyridylporphyrin (ZnPyP) is presented. Voltammetric and corrosion studies were carried out in order to investigate the electroactivity of TPYP and ZnPyP. Cyclic voltammograms obtained on Pt electrode, in H_2SO_4 0.1N or a mixture (1:1 vol.) of H_2SO_4 0.1N and AcCN, present two peaks for oxidation and one for reduction in case of TPyP and two oxidation and two reduction peaks for ZnPyP. The corrosion inhibiting abilities of TPyP and ZnPyP were illustrated by potentiodynamic curves obtained on carbon steel in 1N H_2SO_4, indicating a decrease of the current in the active region of the anodic polarization curves. Corrosion tests monitoring the mass loss of steel were also carried out.

Keywords: 5,10,15,20-tetrakis(4-pyridyl)-21H,23H-porphine, cyclic voltammetry, corrosion inhibition

INTRODUCTION

Porphyrins are capable to develop supramolecular structures. The molecules of porphyrins can change their properties by reconfiguring the electron distribution of the aromatic ring, thus allowing the accomplishment of some major objectives. Some applications of these compounds are in the fields of fundamental sciences (physics and chemistry), nanotechnologies [1-3], highly strategically technology domains (photovoltaic cells [4]), safety and durability for building engineering (corrosion inhibition [5]), monitoring the quality of the environment (electrochemical sensors [6-8]) and competitive health treatments (PDT therapy of cancer) [9].

The electrochemical behavior of porphyrins was well studied in nonaqueous systems [10]. Porphyrins are electrochemically active substrates and are supposed to be mixed corrosion inhibitors [11].

Porphyrins form highly stable metallic complexes having a great potential as corrosion inhibitors [12, 13]. Their planar molecules containing four pyrrole subunits present bonding sites for complexes formation at the

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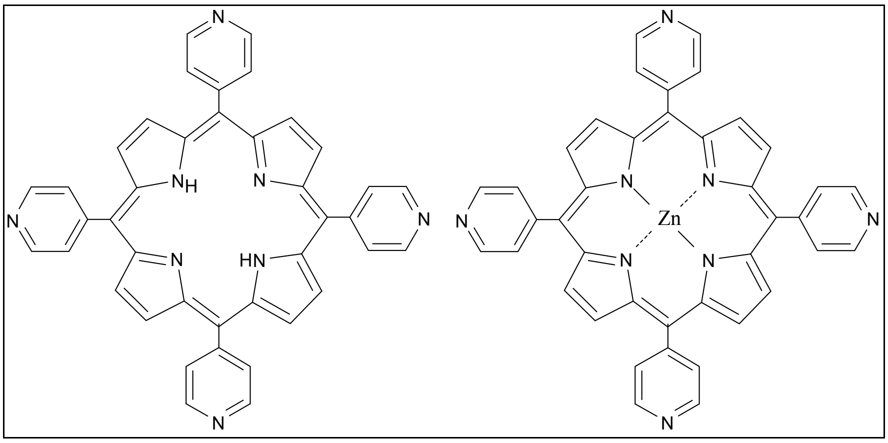
nitrogen atoms. The whole molecule structure shows conjugated double bonds due to the –CH= bridging groups and thus, a very mobile electronic system. These properties are very important in the adsorption process of these compounds on diverse metals surfaces.

The present paper presents the voltammetric studies regarding the electrode reactions of 5,10,15,20-tetrakis(4-pyridyl)-21H,23H-porphine (TPyP) and Zn(II)5,10,15,20-tetrapyridylporphyrin (ZnPyP), with the corresponding structures presented in Scheme 1, and their corrosion inhibition effect.



Scheme 1

The adsorption of TPyP and ZnPyP on the metal surface occurs as a result of electrostatic forces between the electric charge on the metal and the high polarizability of the organic substrate molecules. The interaction of TPyP and ZnPyP with the metal interface, covered with oxides and water molecules, is even more favored by the presence of the four pyridyl *meso*-substituents.

When iron is immersed in an aqueous phase, water molecules adsorb on its surface. Porphyrin molecules are adsorbed in their turn, by replacing the water molecules, this being considered the first step of metal-porphyrin interaction (Scheme 2):

$$[\mathrm{PORPHYRIN}]_{\mathrm{soln}} + [\mathrm{nH_2O}]_{\mathrm{adsorbed}} \rightleftharpoons [\mathrm{PORPHYRIN}]_{\mathrm{adsorbed}} + [\mathrm{nH_2O}]_{\mathrm{soln}}$$

Scheme 2

In a second step, the porphyrinic compound, in its adsorbed state, can form a Fe(II) coordination complex with the Fe^{2+} ions located on the metal surface, these compounds having a corrosion inhibitor activity given by both their high stability and low solubility in the solution.

RESULTS AND DISCUSSION

The voltammetric investigations on TPyP, Figure 1, and on ZnTPyP, Figure 2, revealed the existence of the following oxidation and reduction potentials (V/SCE): TPyP: ε_{pa1} = 0.0 and ε_{pc1} = - 0.1 ($\varepsilon_{1/2}$ = - 0.05) and ε_{pa2} = 1.37 (irrev.); ZnTPyP: ε_{pa1} = 1.1, ε_{pc1} = 0.45 ($\varepsilon_{1/2}$ = 0.77) and ε_{pa2} = 1.49, ε_{pc2} = 1.05 ($\varepsilon_{1/2}$ = 1.27).

By using a mixture of aqueous H_2SO_4 and AcCN, the electrode reaction peaks are the same, as can be seen in Figure 3, the organic co-solvent having no influence on the reaction mechanism.

The corrosion inhibition of porphyrin-base TPyP and metalloporphyrin ZnPyP was investigated on carbon steel in H_2SO_4. The results are presented in Figure 4 and demonstrate that both compounds present an important inhibition effect on the corrosion process of carbon steel. The decrease of the critical current density for passivation (in the active region) is significant, but there is also some influence as inhibitor in the transpassive region (the oxygen evolution) and on the cathodic hydrogen evolution reaction. It is also notable that the onset potential for the active region is the same in every solution. However the potential corresponding to the peak as well as the onset of passivation (i.e. Flade potential) is decreased by the inhibitor.

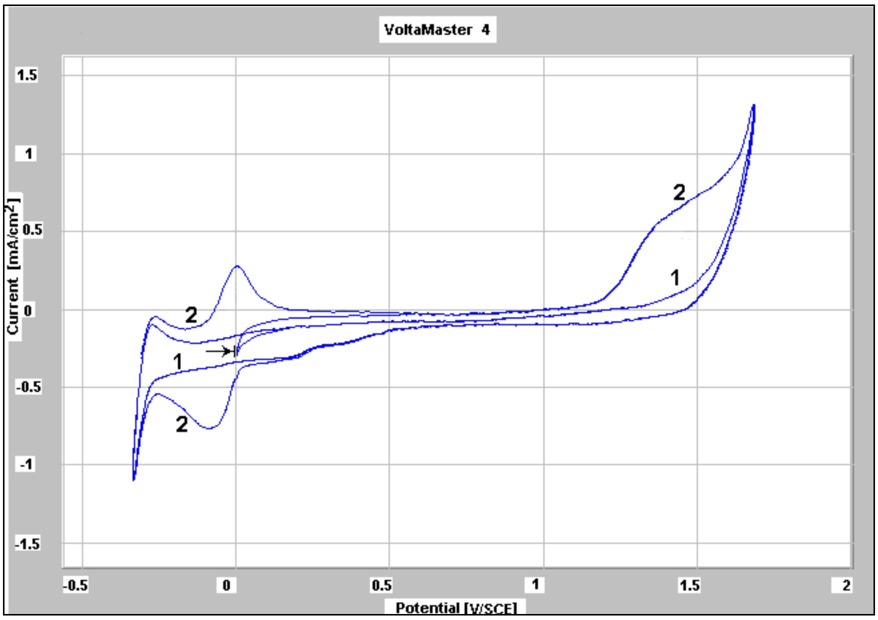


Figure 1. Cyclic voltammograms of TPyP (Pt electrodes, scan rate 50 mV/s, ref. SCE, 25°C); curve 1: H_2SO_4 0.1N, curve 2: H_2SO_4 0.1N + TPyP 1.5 mM

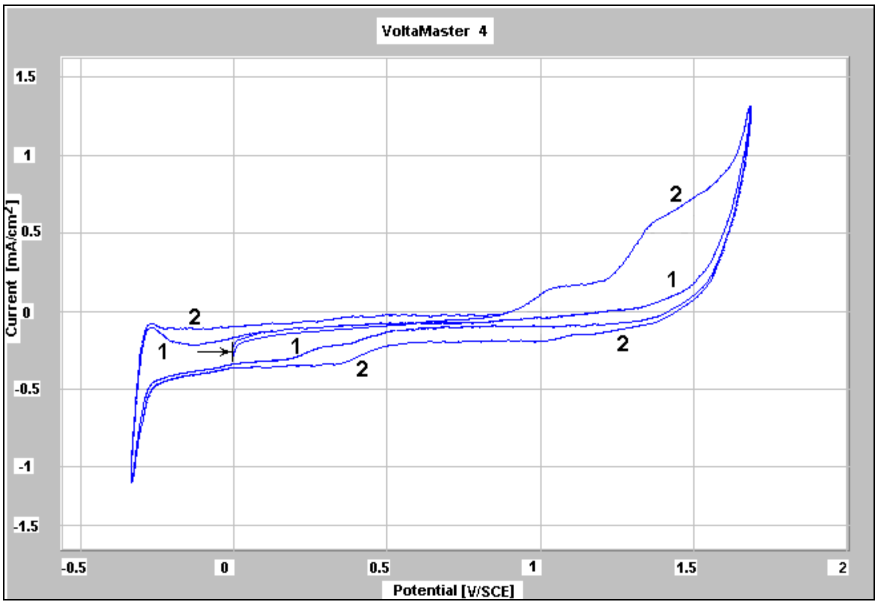


Figure 2. Cyclic voltammograms of ZnPyP (Pt electrodes, scan rate 50 mV/s, ref. SCE, 25°C); curve 1: H_2SO_4 0.1N, curve 2: H_2SO_4 0.1N + ZnPyP 1.0mM

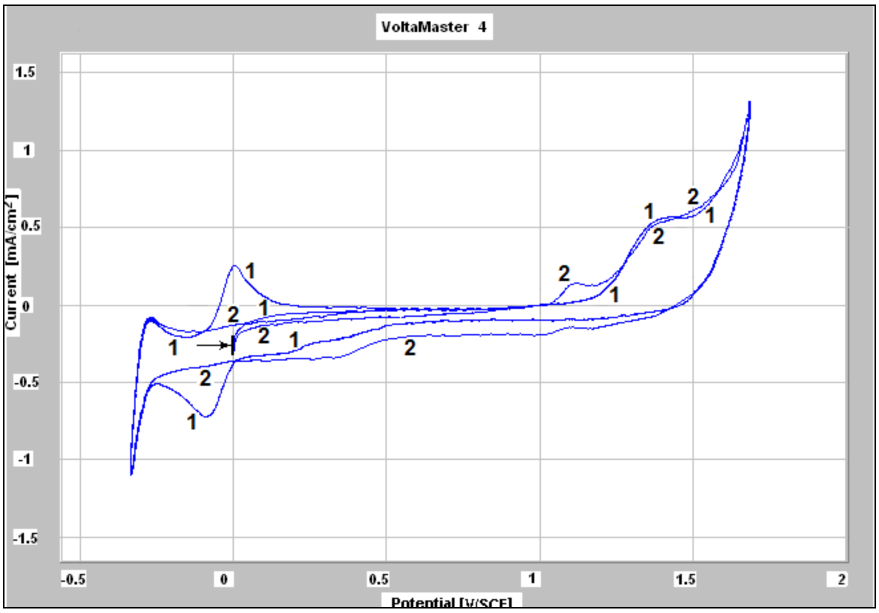


Figure 3. Cyclic voltammograms of TPyP and ZnPyP (Pt electrodes, scan rate 50 mV/s, ref. SCE, 25°C); curve 1: H_2SO_4 0.1N + AcCN (1:1 vol.) + TPyP 1.5 mM, curve 2: H_2SO_4 0.1N + AcCN (1:1 vol.) + ZnPyP 1.0mM

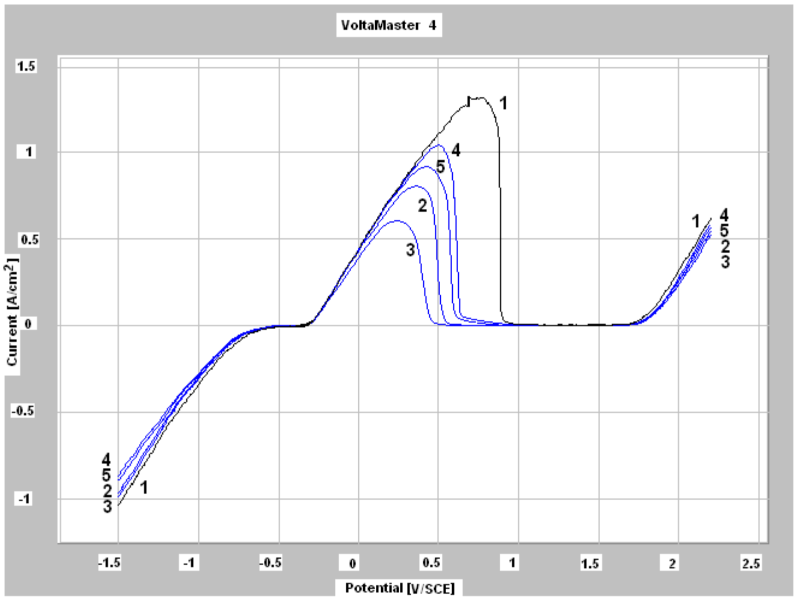


Figure 4. Potentiodynamic curves obtained on carbon steel in H_2SO_4 1N, scan rate 100 mV/s, 25°C. Porphyrin conc., mM: without porphyrin (curve 1), 0.08 TPyP (2), 1.3 TPyP (3), 0.37 ZnPyP (4) and 0.75 ZnPyP (5).

Corrosion tests monitoring the mass loss of steel were also carried out. Measuring the mass loss of steel during the corrosion process the results presented in Table 1 were obtained. The testing method consisted in measurement of the volume of hydrogen evolved during the corrosion process. The inhibiting efficiency is in the range of 30-50% for this very aggressive medium, depending on the inhibitor concentration and the temperature.

Table 1. The effect of TPyP concentration on the corrosion rate of carbon steel in H_2SO_4 5%, at 25°C, after 1.5 hours.

TPyP concentration, mM	Mass loss, g/(m^{2}day)	**P**, mm/year	Inhibition efficiency, %
0	109.68	5.1	-
0.05	84.00	3.9	23
0.1	75.36	3.5	31
0.2	64.56	3.0	41
0.5	60.24	2.8	45
1.0	58.08	2.7	47

CONCLUSIONS

TPyP and ZnPyP present electrochemical activity. They are oxidized/ reduced on platinum electrode, in aqueous H_2SO_4 medium. From the influence of these compounds on the passivation curve of carbon steel in H_2SO_4, and from mass loss measurements, an important corrosion inhibition activity is to be noticed.

EXPERIMENTAL SECTION

Voltammetric studies were made using a three-electrode cell and a potentiostat VOLTALAB PGZ 301 Dynamic – ETS Voltammetry – Radiometer Copenhagen with a VoltaMaster 4 program, at room temperature. The working electrodes were carbon steel (for corrosion inhibition studies) and platinum (for cyclic voltammetry). Counter electrode and reference electrode were always platinum and SCE. Other experimental specifications are given at the proper locations.

Carbon steel C55 specimens, produced by MECHEL Campia Turzii, in the form of fibres for concrete reinforcing, containing: 0.53-0.61% C, 0.44-0.45% Mn, 0.23-0.25% Si, max 0.01% S, max 0.01% P, max 0.03% Al, max 0.06% Cu, max 0.03% Cr, max 0.06% Ni, max 0.09% Mo, the remainder Fe were used.

Porphyrins were obtained according to previous published literature data [14].

The mass loss of the steel during the corrosion process was calculated from the volume of the evolved hydrogen, and confirmed by weight measurements.

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