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INFLUENCE OF 5,10,15,20-TETRAKIS(4-PYRIDYL)-21H,23H-PORPHYRIN ON THE CORROSION OF STEEL IN AQUEOUS SULFURIC ACID

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The inhibition ability of dissolved 5,10,15,20-tetrakis(4-pyridyl)-21H,23H-porphine (TPyP) on the corrosion of carbon steelin H_2SO_4 5% was investigated by evaluating the mass loss from the volume of the evolved hydrogen and by direct weight measurements at different temperatures.Results indicated that the presence of TPyP was able to reduce the corrosion rate of steel with over 50% efficiency, depending on TPyP concentration and temperature.The surface state of steel was characterized by AFM before and after the steel sample was corroded in H_2SO_4 solution (5%), the smoothing and uniforming effect of porphyrin being obvious, especially at higher temperature.

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1. Introduction

High-molecular-weight organic compounds having in their molecular composition oxygen, nitrogen, and sulfur atoms have been proved to be corrosion inhibitors for carbon steel in various aggressive environments. The presence of π bonds in the structure of the organic compounds enhances the efficiency of the corrosion inhibition [1-5], such compounds providing the ability to get adsorbed on the metal surface.

Porphyrins are capable to develop supramolecular structures on metal surfaces as a result of metal-porphyrin and porphyrin-porphyrin interactions [6-7]. The molecules of porphyrins can reconfigure the electron distribution of the aromatic ring and changetheir properties in order create ordered molecular layers.

Such structures are supposed to be mixed corrosion inhibitors, the electrode surface being protected by the film barrier avoiding the diffusion of electroactive species towards the electrode surface and the accumulation of such species in its proximity.The building of the protective barrier by adsorption of porphyrin molecules [8] and the corrosion inhibiting effect are affected by the properties of such molecules, a result of some factors such as:peripheral functional groups, steric influence, electron density at donor centers.The ordered porphyrin layer may be obtained by self-assembly as a result of chemisorption, vapor deposition and more accurate thin film techniques deposition Langmuir-Blodgett.

In the last decade the corrosion of carbon steel in aqueous mineral acid was investigated and the effect of porphyrins as corrosion inhibitors was put into evidence [9-13].

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Porphyrinsarecomplexing agents for the iron ions from the steel surface, creating active centers for further ordered additional layersformation.

In the present paper the effect of dissolved 5,10,15,20-tetrakis(4-pyridyl)-21H,23H-porphine (TPyP) on the corrosion of steel in H_2SO_4 5%, a very corrosive solution, is investigated. The influences of working parameters (porphyrin concentration, temperature) on the corrosion rate and metal surface configuration are investigated.

2. Experimental

Carbon steel in the form of fibers for concrete reinforcing (length: 51.7 mm, diameter: 1.0 mm, total surface: 163.3 mm^2, specific surface: $0.46013x10^{-3}$ m^2/g, average mass: 0.3549 g) were used. The tested steel, C55 specimens, 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,was produced by MECHEL CampiaTurzii.TPyP was obtained according to previously published data [14].

The requiredchemicals were of analytical reagents grade and used as received.

Atomic force microscopy studies (AFM) were performed by using Nanosurf® EasyScan 2 Advanced Research AFM (Switzerland), equipped with a stiff (450μm × 50 μm × 2 μm) piezoelectric ceramic cantilever (spring constant of 0.2 $N\cdot m^{-1}$) with an integral tip oscillated near its resonance frequency of about 13 kHz. AFM images were obtained in contact mode and are quantitative on all three dimensions. The surface imaging investigations were done in ambient conditions.

Method for corrosion tests.

Before being tested for corrosion, the steel fibers were well washed with warm water and detergent and rinsed with warm water, distilled water and acetone, in the mentioned succession. After drying at 120°C (approx. 10 min.) the fibers were stored in a desiccator.

For each experiment 10 fibers were weighed and subjected to corrosion in 300 ml H_2SO_4 5% or H_2SO_4 5% containing different concentrations of TPyP, at various temperatures. The evolved hydrogen was captured an measured. Finally the corroded fibers were washed out with water, distilled water, and dried at 120°C. After weighing, the samples were kept in a desiccator before AFM analysis.

The mass loss of the steel sample during the corrosion process was calculated from the volume of the evolved hydrogen, and confirmed by weight measurements. The corrosion rate was calculated from the mass modification (m_{cor}) and expressed in grams per unit area in unit time (mass loss: M_L) or in mm/year (penetration rate: P).

3. Results and discussion

H_2SO_4 5% was chosen for the investigation of TPyPcorrosion inhibiting capabilities because it is a very aggressive medium for carbon steel sustaining an accelerated corrosion process. In addition, TPyP is very soluble in this solution.Thecorrosion rate was determined firstly in the absence of TPyP and it is strongly depending on the temperature, as can be seen in Table 1.

Table 1. Corrosion rate of carbon steel in H_2SO_4 5% without TPyP

t^o (^oC)	t (min)	m_{cor} (mg)	M_L ($gm^{-2} h^{-1}$)	P ($mmyear^{-1}$)
25	48	6.6	5.04	5.6
37	23	6.8	10.83	12.1
46	15	7.6	18.53	20.6

The surface of the metal sample was investigated by AFM. The image for the not corroded sample is presented in Figure 1. Corrosion changes the metal surface especially at higher temperature, when changes are dramatic, even at significantly shorter exposure time, aspects presented in Figure 2 and Figure 3 for 25 and 46^{o}C respectively.

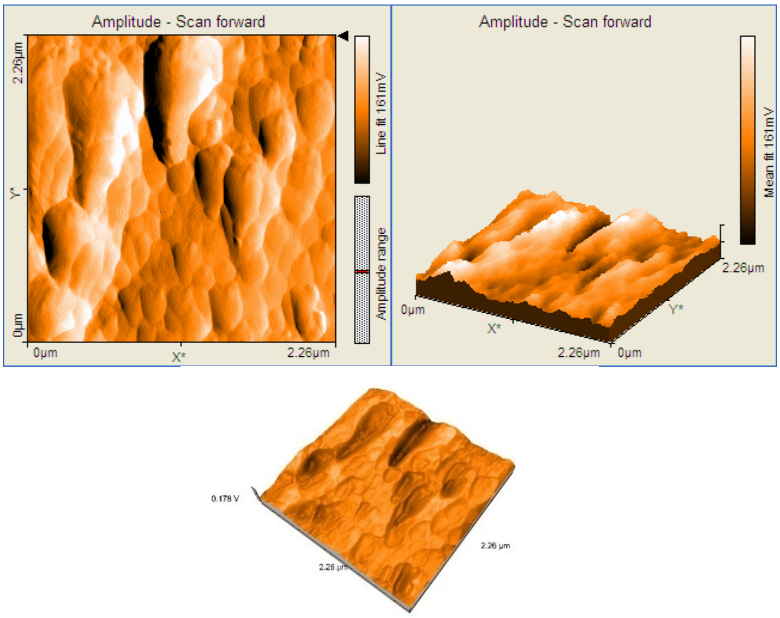

Fig. 1. 2D and 3D AFM images for the not corroded carbon steel surface.

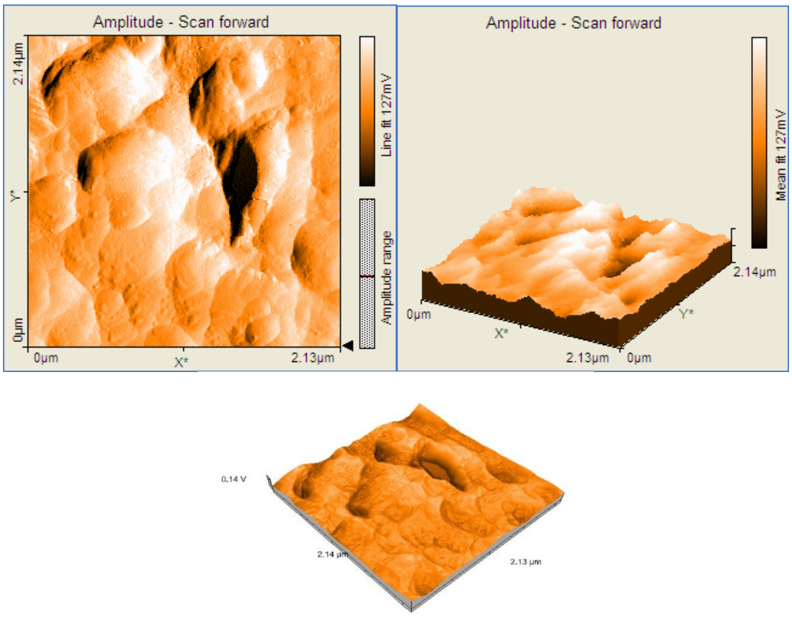

Fig. 2. 2D and 3D AFM images for the corroded carbon steel surface at 25^{o}C in 5%H_2SO_4.

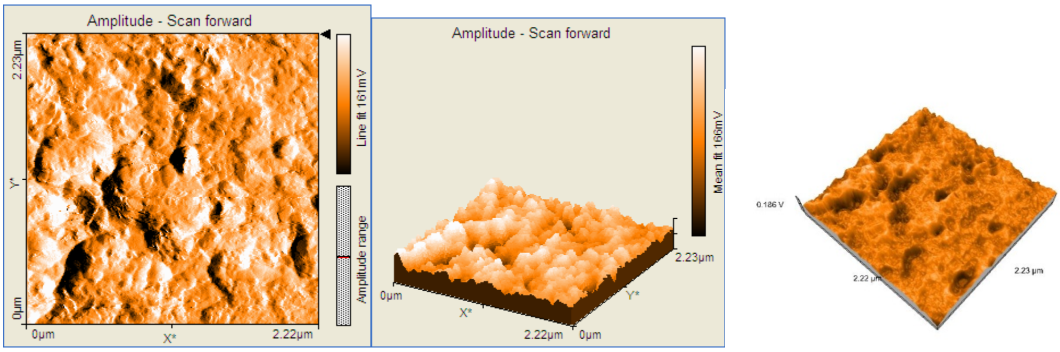

Fig. 3. 2D and 3D AFM images for the corroded carbon steel surface at 46^{o}C in 5%H_2SO_4.

The presence of TPyP decreases the rate of corrosion. The protective action of TPyP is dependent on its concentration in the acid solution.The results obtained for different concentrations of TPyP (c_{porf}) at ambient temperature are presented in Table 2 and for higher temperature in Table 3.The efficiency of inhibition (I_{eff}) is also calculated.

The presence of the porphyrin in the solution modifies the metal surface, as can be seen in Figures4 and 5. The changes are given by the supramolecular assemblies generated by the interactions between TPyP and the metal. The smoothingand uniformingeffect of porphyrin is obvious, especially at higher temperature, Figure 5.

Table 2. Influence of TPyP concentration on the corrosion rate of carbon steel in H_2SO_4 at room temperature.

c_{porf} (mM)	t^o (^{o}C)	t (min)	m_{cor} (mg)	M_L (g $m^{-2} h^{-1}$)	P (mm $year^{-1}$)	I_{eff} (%)
0.00	24-25	56	7.4	4.83	5.4	-
0.03	24-25	55	5.4	3.57	4.0	26.1
0.04	25	55	4.7	3.13	3.5	35.3
0.13	26	59	4.2	2.61	2.9	45.9
0.18	25-26	60	4.0	2.42	2.7	49.8
0.23	25-26	53	3.1	2.15	2.4	55.5
0.30	25-26	57	3.5	2.26	2.5	53.2

Table 3. Influence of TPyP concentration on the corrosion rate of carbon steel in H_2SO_4 at 44^{o}C.

c_{porf} (mM)	t^o (^{o}C)	t (min)	m_{cor} (mg)	M_L (g $m^{-2} h^{-1}$)	P (mm $year^{-1}$)	I_{eff} (%)
0.00	43	20	6,8	12.62	14.1	-
0.02	43	32	7.6	8.67	9.7	31.2
0.03	43-44	19	3.8	7.63	8.5	39.5
0.06	44-45	19	3.3	6.49	7.2	48.5
0.10	42-43	19	2,9	5.76	6.4	54.3

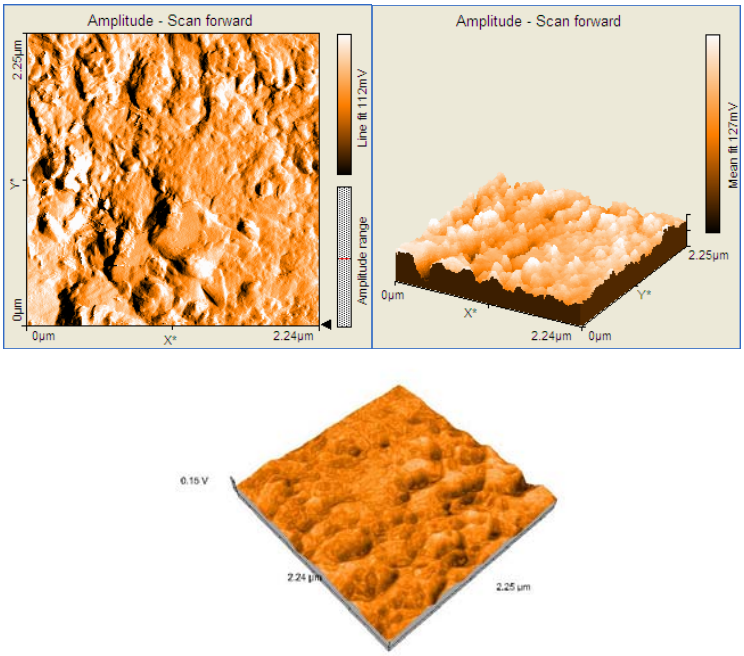

Fig. 4. 2D and 3D AFM images for the corroded carbon steel surface at 25°C in H_2SO_4 5% containing TPyP 0.23 mM

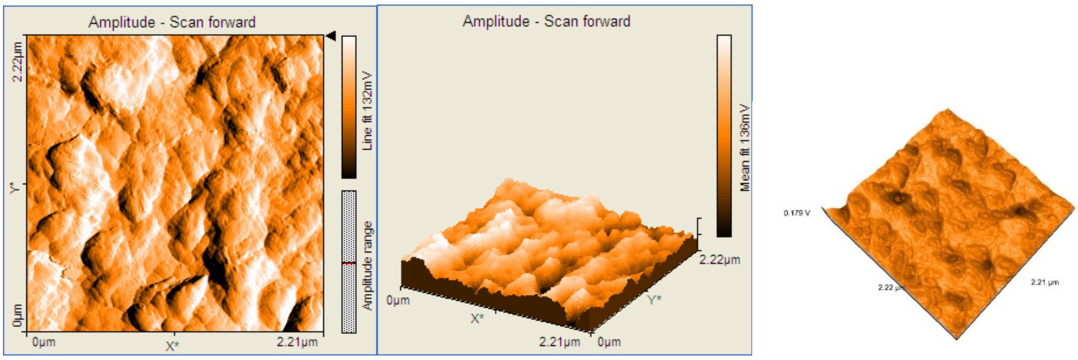

Fig. 5. 2D and 3D AFM images for the corroded carbon steel surface at 44°C in H_2SO_4 5% containing TPyP 0.03mM

The topography of the surfaces were evaluated by AFM measurements, by comparing the following roughness parameters: average surface roughness (Sa, *n*m), maximum peak height (Sp, *n*m), maximum valley depth (Sv, nm) for the best corrosion protection obtained, taking into consideration the best porphyrin concentration.

Table 4. Comparative AFM topography results of the surfaces in each range of temperatures that produced the best inhibition effect, with and without porphyrin

c_{porf} (mM)	**t^o (^{o}C)**	**The surface roughness (Sa, nm)**	**The maximum peak height (Sp, nm)**	**The maximum valley depth (Sv, nm)**	**Best values of I_{eff} (%)**
0.23	25-26	21	68	-110	55.5
WithouthTPyP	25-26	36	130	-130	
0.10	42-43	32	120	-150	54.3
WithouthTPyP	42-43	46	150	-180	

From Table 4 it is obvious that, in each temperature range, the presence of porphyrin produced evident diminution of the surface roughness and protect from advanced corrosion.

The surfaces are more uniform and triangular aggregates of porphyrin, same oriented, and of the same sizes (around 200-250 nm) have been deposited, as can be seen in Figure 5. This is in agreement with the previously discussed phenomenon of generation of porphyrin aggregates in acid media [15-17].

The corrosion rate decreases considerable as the TPyP concentration increases (Figure 6). The influence is stronger at high temperature and at low concentration. Over a certain concentration ofTPyP, the corrosion rate decreasing becomes less pronounced, probably due to the total coverage of the metal surface and to the limited stability of the porphyrinic film in H_2SO_4 5% (due to its high solubility).This is the reason why the inhibiting effect ofTPyP is changing with porphyrin concentration in the manner presented in Figure 7.

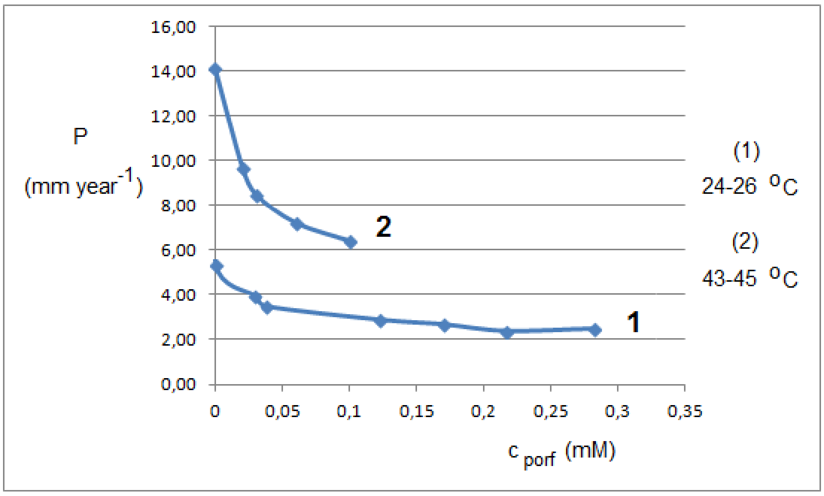

Fig. 6. Dependence of corrosion rate on TPyP concentration

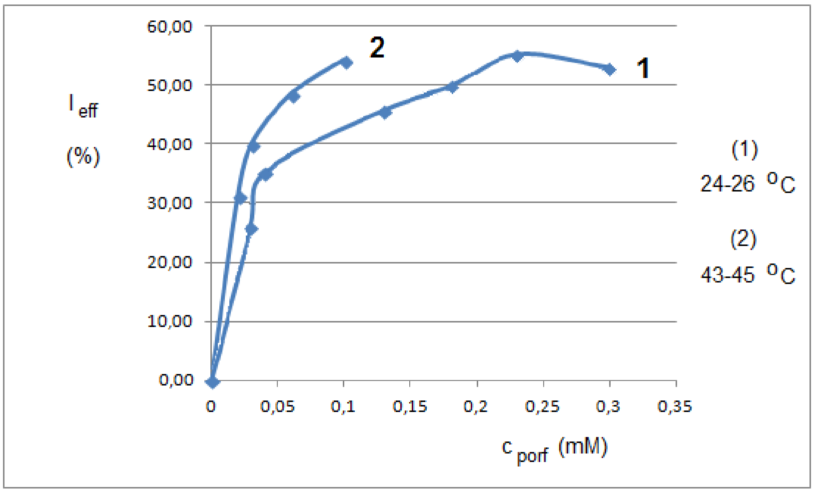

Fig. 7. Dependence of the inhibiting effect on TPyP concentration

4. Conclusions

5,10,15,20-tetrakis(4-pyridyl)-21H,23H-porphine has an inhibiting effect in case of the corrosion of carbon steel in H_2SO_4 5%. The inhibition ability of TPyP was investigated by evaluating the mass loss from the volume of the evolved hydrogen and by direct weight measurements. Experiments were done at different TPyP concentrations and temperatures.

Results indicated that the presence of TPyP reduces the corrosion rate of steel with over 50% efficiency. The inhibiting action of TPyP is depending on its concentration and temperature. The surface state of steel was characterized by AFM before and after the steel sample was corroded in H_2SO_4 solution putting into evidence a smoothing and uniformingeffect produced by porphyrin.

Acknowledgements

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