

**UNIVERSITY OF CRAIOVA
FACULTY OF CHEMISTRY**

SUMMARY OF PhD THESIS

**SCIENTIFIC COORDINATOR:
PROF. UNIV. DR. PREDA MIRCEA**

**PhD CANDIDATE:
FLOROIU (AGIU) MIHAELA**

The electrochemically active system metal-environment presents thermodynamic instability due to large amount of free enthalpy. Thus it appears a spontaneous tendency of the system to evaluate to the state characterized by the minimum value of free enthalap, respectively to the state that the metal is found as oxidized (oxides, chlorides, sulfates). Under these conditions metallic materials have a natural tendency to be degraded by electrochemical reactions whose rates are higher or lower depending on the nature, of the corrosive environment with whom it has contact and of the physico-chemical conditions.

Many industrial processes and technological operations involves the participation of acid solutions that induce accelerated evolution toward thermodynamic equilibrium state of metallic materials. The result is that acid solutions present a high electrochemical aggressiveness on iron and its alloys leading to direct loss (consumes important quantities of metallic material) as much as to indirect loss: reduce production by stationary, over-dimensioning of the design to extend the operation, costs of repair or replacement of the significant corrosion, product contamination or damage by explosion of unexpected chemical equipment. Therefore, to ensure sustainability of metallic materials exposed the reduction or even the elimination of the aggressive acid environments is required.

Corrosion products are formed by peripheral electronic transfer of metal to oxidizing species present in acidic environments. One method of minimizing the rate of dissolution process is oxidative acid treatment environment with substances that may act through the following mechanisms:

- ☑ increasing anodic or cathodic polarization;
- ☑ fostering the appearance of a precipitate on the surface of the metal;
- ☑ catalyzing the formation of a stabile passive film;
- ☑ reducing diffusion of ions from solution to metal surface;
- ☑ increasing electrical rezistance of the metal surface.

For the anticorrosive protection were proposed several treatments with organic and inorganic compounds that due to peculiarities of the electronic density distribution and geometry, mediates the creation on the metal surface of an adherent protective film.

The efficiency of inhibition corrosive processes is closely linked to properties of the protective surface film formed on metal surface. The composition of the film is decisive for the efficiency of the protection that the film provides. The quality of the protective film is determined by evaluating the adhesion and its compactness, that has to have high values. The protective action of the film located at the interface metal / aggressive environment depends on how well is electrically isolated.

The present study, which is structured in four chapters, is circumscribing concerns for improving generalized passive film corrosion in solution 1 M HCl of carbon steel, with the following composition: C=0.1 %, Mn = 0.4 %, Si = 0.035 %, Cr = 0.3 %, and the rest till 100% is iron.

Having as support the aspects of phenomenology generalized corrosion of carbon steel in acid environments revealed by the specialized literature, we covered:

⇒ exploiting the anticorrosive potential presented by some inorganic and organic compounds due to the modality in which some electrons in the atomic and steric configuration mediates and modulates interactions uncovalent (physical type interactions) and the covalent (chemical interactions).

⇒ clarifying the contribution of surface film, resulting from the interaction of carbon steel with acid, to delay partial electrochemical reactions using Mössbauer spectrometry.

We set three main areas for study the electrochemical behavior of carbon steel in 1 M HCl solution:

- ◆ Calculation of electrochemical quantities, kinetic and thermodynamic proper corrosion process of carbon steel in 1 M HCl solution in the presence and absence of the following inhibitors:
 - Ammonium polymolybdate (APM);
 - N - ciclohexil benzothiazole sulphenamide (NCBSA);
 - Di – mercaptobenzythiazole (DMBT)
 - Poli (O-2-hidroxietyl) amidon (PETA).
- ◆ Characterization of surface film that confers protection against corrosion by Mössbauer spectrometry and electronic microscopy;
- ◆ Establishing the correlation between the effective anticorrosive action of the compounds mentioned and factors such as: inhibitor concentration, temperature of the corrosive solution, the time exposure of the carbon steel sample at the corrosive solution.

In the first chapter – INHIBITORS AND CORROSION MECHANISMS – are presented the properties of a substance that confers the ability to significantly reduce the current-generating electrochemical reaction rate of corrosion, thus ensuring an effective anticorrosive protection.

There are also mentioned and described in detail the classes of inhibitors, as well as criteria for classification of the inhibiting substances. The mechanisms which hinder or block the move to the state of thermodynamic equilibrium of the system carbon steel - 1 M HCl solution, are also presented and the inhibitory action is explained. A close attention is given to the presentation of the phenomena that are taking place at the interface metal / aggressive environment.

Chapter II – RESULTS OBTAINED ON NATIONAL AND INTERNATIONAL LEVEL REGARDING CARBON STEEL CORROSION IN ACID MEDIA IN THE ABSENCE AND PRESENCE OF THE INHIBITORS – containing the phenomenology of carbon steel corrosion in both acidic solutions uninhibate and treated with various inhibitory substances.

Here are described the results and methods which had been used in numerous studies conducted both nationally and internationally in order to evaluate the corrosion process: the gravimetric method, electrochemical methods. Among the methods used to determine electrochemical parameters, which enable the corrosion process, is treated comprehensive the one that involves the impedance measurements. In this chapter is highlighted and analyzed the influence of temperature and exposure time of the carbon steel sample to the corrosive attack.

In the third chapter – TEST METHODS FOR CORROSION AND EFFICIENCY CORROSION INHIBITOR – is included the description of the principles underlying the methods (gravimetric method, electrochemical methods: galvanostatic, potentiostatic) used to obtain experimental data necessary for the electrochemical parameters calculation. The chapter also contain working methodology for each method separately and the equipment that was used.

An important part of the structure of Chapter III is a presentation of the equation that expresses that the rate of corrosion process represents the contribution of two terms corresponding to the partial electrochemical reactions (anodic reaction and cathodic reaction), meaning the anodic and cathodic terms. This dependence allows one to obtain graphically the primary endpoint of corrosion (i_{cor}) by semi-logarithmic plotting of polarization curves for both the anodic and the cathodic process. Extrapolation of Tafel segments of the corrosion potential ($\eta = 0$) is an effective experimental method for determining the corrosion current.

In Chapter III is extensively described also the Mössbauer spectroscopy equipment, which allowed the analysis of corrosion of carbon steel sample surface in order to obtain information on the mechanism of inhibitory action. Thermogravimetric method is presented also as a method of film surface testing.

The final chapter is the original contribution of the thesis. It contains results from testing the four mentioned inhibitors and their corresponding interpretation. The evaluation of carbon steel corrosion in 1 M HCl solution and inhibitor testing was performed by gravimetric method coupled with tandem electrochemical methods. The morphology of the film with protective action of carbon steel surface was studied using Mössbauer spectrometry and electronic microscopy and for its thermal stability evaluation thermogravimetric method was used. Corrosive acid solutions were analyzed by UV-VIS spectrometry both before and after corrosion test of carbon steel.

For each inhibitor a mechanism of action has been proposed in correlation with the kinetics parameters, electrochemical and thermodynamic data obtained by graphically processing of the gravimetric and electrochemical measurements results. Relevant data for assessing the effectiveness of corrosion protection are presented both in graphical form (which allows viewing of trends and typology) and in tabular form (which offers the advantage of easier correlation of various sizes).

Experimental studies performed have led to the following conclusions:

❶ Carbon steel corrosion in 1 M HCl solution DMBT treated with low-speed occurs with low rates. The interaction between inhibitor molecules and the surface of carbon steel is chemical and leads to the spontaneously formation ($\Delta G_{\text{ads}} = - 32.96 \text{ kJ}\cdot\text{mol}^{-1}$) by self connecting, of an oriented and well ordered monomolecular layer.

Chemical absorption, following a Langmuir type kinetics in a large proportion of DMBT's (adsorption constant $K=13.800 \text{ mol}^{-1}\cdot\text{L}$) produces significant changes in the electrical double layer structure.

The chemical bonds that are established between metal and inhibitor surface are strong due to the presence of the benzothiazole nucleus and sulfur atoms in the molecule's DMBT.

Resulting monomolecular layer on carbon steel surface by self connecting is waterproof and compact, and therefore impeding chloride anion Cl^- near the electrode surface. Consequently, the formation processes are restricted by the Faradic monomolecular layer.

Chemical adsorption of inhibitor molecules does not affect the dissolution mechanism of iron or the reaction of hydrogen depolarisation.

It can also be assumed that the inhibitor acts as a ligand, resulting in complexation of different metal ions present in the carbon steel. Resulting complexes on the surface of the steel forms a stable passive layer that blocks access to the corrosive agent active centers.

For samples immersed in 1 M HCl solution containing DMBT corrosion process is considerably slowed down, forming a compound of Fe^{3+} without a magnetic orientation. The layer that the compound forms has a thickness less than the one in the absence of corrosion inhibitor. Mössbauer parameters of the compound in this case do not differ greatly from those determined for the samples corroded without DMBT. Thus, we believe that the DMBT inhibitor acts as inchoate „rust transformer” and promotes the formation of a compact surface layer.

Elevated inhibitor causes an inhibition of both electrode processes, however the anodic current density decreases more compared to the cathodic current density (the anodic process is mostly inhibited). This finding shows that the presence of inhibitor hinders the process of anodic dissolution and also delays the advancement of the hydrogen depolarisation reaction.

DMBT's efficiency increases with increasing its concentration in 1 M HCl solution, resulting in a maximum (82.2 %) at a concentration of 0.4 mM, very close to that resulting from gravimetric measurements (84.7 %).

② The presence of NCBSA inhibitor in 1 M HCl solution determines delaying generalized corrosion of carbon steel, a possible mechanism of adsorption involves chemical adsorption of NCBSA on the carbon steel surface by forming a compact and stable layer.

Adsorption capacity of the inhibitor on the metal surface is a consequence of mesomer effect that lead to an amfiion capable to react with metal surface. Mesomer effect occurs because of non-participating electron pairs that sulfur and nitrogen atoms has of the side chain The remaining inhibitor molecule contributes to increased adsorption layer thickness.

Transition mechanism in the form of iron ions in solution is not modified by chemical adsorption process NCBSA.

Another plausible mechanism of inhibitory action would be complexation of different metal ions contained in carbon steel by NCBSA, the result being the formation of stable passive film on metal surface.

The rate of degradation of the corrosion layers formed in 1 M HCl solution inhibited with NCBSA (0.019 mg / min) is approximately four times lower than the rate of degradation of the layers of corrosion resulting with the uninhibate solutions(0.072 mg / min).

The loss of mass due to increased degradation of the corrosion layer temperature by 1 °C is higher for carbon steel corrosion uninhibate solution of HCl 1 M (1.39 mg / °C for uninhibate solution and 0.42 mg / °C solutions inhibited).

Carbon steel corrosion potential moves to positive values as the concentration NCBSA in 1 M HCl solution increases, which means that the corrosion current density decreases with increasing concentration of inhibitor.

NCBSA delays reaction depolarisation advancement of hydrogen, but hinders in a greater extend anodic electrochemical reaction.

NCBSA is a less effective inhibitor compared with DMBT.

③ Addition of PETA corrosive environment results in a significant decrease of corrosion rate, implied a considerable reduction of corrosion current density. The result is the formation of stable passive film on metal surface by complexation by PETA of different metal ions existing in the composition of carbon steel.

PETA causes high anticorrosive protection of carbon steel (efficiency is greater than 91 %) due to compact and stable layer that is formed by chemical adsorption on metal surface.

With the PETA anodic polarization potential moving in positive direction the anodic overvoltages increase. On the other hand, cathodic polarization potential moves in negative direction.

Corrosion potential increases with increasing concentration of PETA.

Corrosion potential shift in positive direction is associated with decreased density of corrosion currents. Accordingly, PETA acts as an inhibitor in 1 M HCl solution.

Elevated low density of PETA lead to corrosion currents, namely the increasing inhibition efficiency. From such a concentration of PETA $5 \cdot 10^{-5}$ M we obtain an efficiency of carbon steel corrosion inhibition in HCl 1 M by 99 %.

④ Solution of 1 M HCl treated with PMA has a less corrosive effect on carbon steel, which shows that the presence of PMA causes a significant delay in the process of corrosion.

The process of corrosion inhibitor in the presence of PMA is produced by the same mechanism that follows in the absence of inhibitor, the corresponding activation energies of corrosion processes in the absence and presence of inhibitor are approximately equal (55 kJ/mol – 60 kJ/mol).

Anodic polarization of carbon steel electrode in 1 M HCl solution containing PMA inhibitor showed a decrease of corrosion current density, variation of which is directly proportional to the concentration of inhibitor. Decreasing the corrosion current density is associated with a significant shift of corrosion potential towards less negative (positive values). The fact suggests that the inhibitor acts primarily on the anodic process, which slows in a higher extent.

The initial phase of corrosion involves the formation of a surface film consisting mainly of a mixture of ferrihydrit Fe (III) and FeOOH (α and/or γ) that do not show any crystalline structure and magnetic ordering. The stage preceding the occurrence of crystalline phases forms a gel layer structure, consisting of relatively stable iron oxihydroxizi subsequently depending on the conditions of corrosion oxihydroxizi pass in α and / or γ FeOOH and then the iron oxide (Fe₂O₃).

The PMA inhibitor acts as a „rust transformer” that favors the formation of a compact surface layer, which is revealed by Mössbauer spectrometry analysis of carbon steel surfaces exposed to corrosive attack of 1 M HCl solution inhibited with PMA.