DOCTORAL DISSERTATION

STUDY OF CARBON STEEL CORROSION INHIBITION
IN ACID MEDIUM

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SUMMARY

Acids are intensively used in different industrial technological processes : crude oil and gases extraction and processing, decaping of metallic pieces by oxides, industrial cleaning and other chemical and petrochemical operations. Also, on fractionary distillation of oil, due to salt hydrolise, result acids with distructive effect on installations. In rafinaries, acid corrosion is an important and expensive aspect of activity, which causes production losses, inneficient processes, suplemental costs and for corrosion control compounds.

Using inhibitors is one of the most practical methods for anticorrosion protection, especially in acid media, from all methods and technics, tried and used.

Inhibitors are compounds which controls, reduce or delay reactions between metal and environment, when are used in small amounts. The last aspect present economic interest. Between the studied categories of inhibitors, organic inhibitors presents a great interest for their effects on reducing corrosion processes in miscellaneous domains.

The corrosion inhibition efficiency by organic compounds, depends with layer structure and properties formed on the metallic surface, many of these organic compounds acting by adsorbtion on the metal surface.

The inhibition power by organic inhibitors, was analised throw many characteristics such as : molecular volume, molar mass, molecular structure, heteroatoms nature form molecule etc.

Organic compounds containing nitrogen and sulphur atoms, have a great interest in using as corrosion inhibitors for carbon steel, because they showed superior inhibition efficiencies to organic compounds only with nitrogen atoms, or only with sulphur atoms. Identification and evaluation of corrosion organic inhibitors of carbon steel in acid media, are important aspects to be solved practically, industrially and teoretically.

The aim of this study is to analyse the inhibition effect of two inhibitors in hydrochloric acid solution 2M :
- N-(2-hidroxy) tiosemicarbazide, HBTC and
- N-acetyl p-aminobenzene sulfonamide, APAS.

The hydrochloric acid solution was chosed, for intense use in miscellaneous domains and for his high agresivity showed on carbon steel.

Behind the practical objectives, this study also wants a better understanding of processes that take place on the carbon steel surface in time of immersion in hydrochloric acid solution 2M, with different concentrations of HBTC or APAS.

For achievement of the study were used weight loss and potentiostatic measurements, rounded up with scanning electron microscopy (SEM) and Mössbauer spectrometry of carbon steel surface.

The working electrode, was made from carbon steel, with following composition (weight %) :

C	Si	Mn	Ni	Cr	Fe
0,1	0,035	0,4	0,3	0,3	rest

The study has 3 chapters and is based on a large volume of reference materials.

In first chapter are systematized bibliographical dates of definition and corrosion categories, with development of electrochemical corrosion phenomenon for carbon steel. Are approached also essential elements for characterization of corrosion inhibitors, and in the end are shown dates about investigation in speciality literature of a carbon steel mixed type corrosion inhibitors, in different acid solutions, presentation finalized with conclusions about the mechanisms that produce carbon steel corrosion inhibition. This exposure about some of the best known mixed type corrosion inhibitors, was necessary for situation in the context of study theme.

In second chapter are described work methods, experimental and calculation sequences, characteristical functions, mathematical judgements. Also are mentioned working standards, about some of activities in the study.

Chapter I and II together makes first part of study. The second part of the study is formed from chapter III, which contains research results about carbon steel corrosion inhibition in hydrochloric acid solution 2M, with different concentrations of organic compounds HBTC and APAS, obtained from weight loss and potentiostatic measurements, associated with scanning electron microscopy and surface Mössbauer spectrometry. (CEMS).

Chapter III begins with carbon steel surface characterization in hydrochloric acid solution 2M which will be used for comparison in next stages of experiment.

Weight loss and electrochemical conduct of carbon steel diluted in HCl 2M solution

The gravimetrical measurements based on hidrogen volumetrical determinations, had permited calculation and representation of corrosion rate and corrosion penetration, according with the experiment temperatures.

In both situations the drawings do not present liniar evolutions in the way that they start with induction corrosion periods, due the corosion rates rise in value with the temperature, the most increased being at 45^0C and especially at 55^0C.

Using average values for corrosion rate from weight loss data, the representation of these values according with the temperature are exponential, fact which shows a fast and substantial development of the corrosion pending with temperature increase. The exponential ecuation is $y = 1,6974e^{0,0731x}$.

The same element is relieved from the penetration index I_p, which present a value (105,2 mm/year) at 55^0C of aproximative 9 times higher compared with I_p value at 25^0C (11,226 mm/year).

A liniar variation is seen in the drawing representation of the formed hidrogen volumes during the temperature experiment. Here, as well, the experiment temperature increesing efect is obviously reflected at 45^0C and especially at 55^0C.

From the weight loss point of view is seen that carbon steel corrosion developing process in HCl 2M solution is maximal in the last third of the experiment period.

It comes up also that the steel carbon corosion speed values, depend by the experiment period in which the weight loss measurements are done.

The activation energy values, graphical and analitical determined are about 59 KJ/mol.

For the electrochemical measurements it was used the potentiostatical method in a standard electrochemical cell with 3 electrodes. The main used electrode was the calomel-electrode, being used through a Luggin capilar. The measurements fullfilling source was a KEITHLEY 2420 3A SOURCE METER with data prelucration con computer.

For anode and cathode polarisation was done a set of five determinatios at the room temperature, taking in consideration the most reproductible replicas.

It is seen high values for i_{cor} ($i_{cor} = 0,35$ mA/cm^2), b_a ($b_a = 102$ mV) which shows the carbon steel corosion process in HCl solution 2M is intens also at surface as profound the metal mass.

The slope b_a with high value, shows that the steel carbon is very active and the anode desolving reaction is intense. The coroded carbon steel surface in solution of HCl 2M, examined on a electronic microscope VEGA TESCAN, is noticed by the intensity of the corrosion parts, alteration of the metalic texture, noticed and confirmed elements by the Mössbauer spectroscopic measurements. The doublet figures for the coroded item in HCl 2M, shows the presency of Fe^{3+}, α, β, γ-FeOOH and $Fe(OH)_3$ compounds.

Carbon steel corrosion inhibition in HCl 2M solution, using as inhibitor HBTC, in different concentrations

In this sequence the will was to investigate the determined efects of different concentrations of HBTC in HCl 2M solution, regarding carbon steel corosion inhibition. All measurements had been done at room temperature.

From the weight loss point of view, had been determinated corrosion rates as gravimetrical values k_g and penetration index I_p, as well in HCl 2M solution without inhibitor as in HCl 2M solution with HBTC having the concentrations : 0,1 mM; 0,2 mM; 0,3 mM; 0,4 mM.

The presency of HBTC in HCl 2M solution, determinate the following decreasings of the corrosion rate ($g·m^{-2}·h^{-1}$) :
- at c = 0,1 mM, reduction is 45%;
- at c = 0,2 mM, reduction is 53%;
- at c = 0,3 mM, reduction is 65%;
- at c = 0,4 mM, reduction is 75%.

Same differencies can be observed also in the case of corrosion rate considered as corrosion penetration. Is clear the produced effect by the increasing of HBTC concentration in HCl 2M solution, over the decreasing of carbon steel corosion speed and over the size values of the percentage inhibition eficiency from weight loss (at c = 0,4 mM HBTC, P = 74,25%, and P = 44,2% at c = 0,1 mM HBTC).

From the graphical representation it is seen as well, the increasing of P values in the same time with the increasing of HBTC concentrations.

The inhibition effect of the carbon steel corrosion determined by the presency of HBTC in HCl 2M solution, is the result of HBTC molecules adsorbtion on the metal surface through the existing interaction between the couple of unparticipant electrons from the nitrogen and sulphur atoms, parts present in the lateral wing of the HBTC molecules and the metal.

It is possible to be formed on the carbon steel surface of some complexes by HBTC molecules (as ligand) and different steel metal cations, which are conducting at a stabil pasiv layer on the metal surface.

Adsorbtion is also confirmed by the increased value of the eqiulibrium constant (adsorbtion-desorbtion) $K = 5676 M^{-1}L$ and adsorbtion entalphy which is indicating a spontaneously adsorbtion process.

As in the previous sequence, the experimental figures drive to a Langmuir adsorbtion isoterm.

The carbon steel polarity curves for investigated HBTC concentrations, shows in comparision with the no inhibitor polarity curves, the action of HBTC as mixt inhibitor with stronger effect over the metal disolving reaction. The same elements are noticed by the electrodinamic parameters values determinated by Tafel straight lines.

Electrochemical percentage determined inhibition efficiency has close values to the weight loss one (at c = 0,4 mM, $P_g = 74,25\%$ and $P_e = 73,3\%$).

Through electronic microscopy of the carbon steel surface samples, after corrosion in HCl 2M solution having 0,1mM HBTC; 0,2 mM HBTC; 0,3 mM HBTC; 0,4 mM HBTC, it is noticed the existency of a thin film at the carbon steel surface and the reduction of the corrosion centers intensity.

The CEMS spectrum of the coroded sample in HCl 2M solution with HBTC, shows that the depth of the coroded surface is smaller due to the inhibitor presency. In the same respect, the corrosion process is considered slow down, being formed a superficial compound of Fe^{3+}, without any magnetic arangement. Counting its relative area, this compound has a smaller thickness than the layer formed in the no inhibitor corrosion process.

Mössbauer parameters of the compound in this case, are not significant different in comparision with the compounds found in the no inhibitor solution for the coroded sample. New parameters can be associated to other superficial compounds as feryhydrates. Is well known that feryhydrite is a forerunner for other demanded oxyhydroxides.

We consider that HBTC inhibitor act as a incipient "rust transformer" favourising formation of a "superficial closed layer". The inhibitor transform some constituents of rust into corrosion inhibiting oxide phases.

It was determined $3,33 \times 10^{-4}$ M HBTC concentration as optimal concentration and in next study has been done detailed analysis for that inhibitor concentration.

Electrochemical and gravimetrical behaviour of carbon steel in solution of HCL 2M consisting of $3,33 \times 10^{-4}$ M HBTC

The target is the investigation of the presency effect of $3,33 \times 10^{-4}$ M HBTC in HCl 2M solution towards carbon steel corrosion inhibition.

The operation part specifique running was to use a single concentration of HBTC in the HCl 2M solution. The experiment was runned at four temperatures, also in HCl 2M solution without inhibitor, as well as in HCl 2M solution with HBTC mentioned concentration.

The carbon steel corosion rates revealed as weight loss values k_g, at the experiment temperatures, are serious decreased in HCl 2M solution with HBTC, in comparision with solution without HBTC. The decreasion is more pronounced at temperatures of 25^0C and 35^0C (7 times, and 4 times). At the temperatures of 45^0C and 55^0C the decreasing of the corrosion rates are cantitative smaller (3,5 times, and 2,65 times). Is obvious the inhibition effect of the carbon steel corrosion due to the presency of the HBTC, effect with a maxim value at 25^0C.

According with the increasing of the temperature, the corrosion rates rise, the most important difference being between the corrosion rate at 55^0C and 45^0C obvious seen in the grafic and in the HCl 2M solution with $3,33 \times 10^{-4}$ M HBTC. This item is wellseen in the graphical representations of the formed hidrogen volumes, penetration index I_p, corrosion inhibition coeficient C.

Corrosion average rates representations ($k_{g\ mediu}$) of the carbon steel for the HCl 2M solution with or without inhibitor, have exponential form, having in the following order the ecuations :

1) $y = 1,6449 e^{0,0736x}$ for the solution without inhibitor and

2) $y = 0,1153 e^{0,1046x}$ for the solution with $3,33 \times 10^{-4}$ M HBTC.

The maximal values of the procentual inhibition efficiency are recorded at 25^0C temperature, the average value being 85,78%. To the other temperatures the inhibition efficiency values are decreasing, the smallest being at temperature of 55^0C (the average value is 62,30%).

The average value at all inhibition efficiency experiment temperatures is 74,21%.

The graphical representation of the inhibition percentage efficiency average values is notifying its decreasing with the temperature.

Time variation graphic of the inhibition eficiency at the experiment temperatures, have, relatively, a logarithmic form. The activation energy determined for the solution with HBTC, is with aprox. 43% higher, than the activation energy from the solution without inhibitor, as for 86,07 KJ/mol compared with 60KJ/mol, revealing that the energy border for the corrosion reaction, rise in the presency of the inhibitor, and the corosion reaction shall be rejected by the carbon steel surface spots, with high activation energy characteristics.

Analitical determined values for the activation energy are near graphical determined values, accordingly 59,41 KJ·mol^{-1} and 85,43 KJ·mol^{-1}.

To study the HBTC molecules adsorbtion mechanism were calculated standard adsorbtion free energy values which are negative (spontaneous adsobtion) very close with a chemosorbtion process. K values, determined in the same way, even high signifying an

intense adsorbtion, decrease with the rising of temperature from $1,799 \times 10^4$ at 25^0C, to $0,496 \times 10^4$ at 55^0C mean 3,62 times.

This might means the (HBTC) inhibitor molecules absorbtion intensity reduction at the surface of the carbon steel and developing of a desorbtion inhibitor process, at the surface of the carbon steel.

As well as the activation energy, the activation entalpy, is increased in the inhibitor presency, meaning 82,45 KJ·mol^{-1} compared with 57,2 KJ·mol^{-1} proving a increasing of the energetical border for the corosion reaction in presency of HBTC.

Potentiostatical method applied at the room temperature, finalised with the drawing of the polarity curves and Tafel segment extrapolation, had confirmed the corosion inhibition effect of the carbon steel in HCl2M solution in the presence of HBTC ($3,33 \times 10^{-4}$ M), proving that this one is a mixt inhibitor as well through displaying the potential values in both directions as through modifications of the Tafel slope segments. The corrosion current is reduced from 0,53 mA/cm^2 to 0,106 mA/cm^2, the percentage inhibition efficiency electrochemical determined being 80%.

This experimental sequence in which it was used HBTC compound at a single concentration, had proved the carbon steel inhibition corrosion effect in HCl 2M solution and emphasize the temperature influence over the developing of the processes, in the same solution of hydrochloric acid.

The carbon steel corrosion inhibition in HCl 2M, using as inhibitor APAS, in different concentrations

It was intended to investigate determined effects of different concentrations of APAS in HCl 2M solution over the carbon steel corrosion. It had been in mind the fact that the elements from APAS molecules which can favourise the adsorbtion of APAS molecules at the carbon steel surface, are relative identical with the one from HBTC molecules, and the molecular bigger mass (214 – APAS compared with 195 – HBTC) might be able, as well , to favourise the adsorbtion.

From the weight loss point of view, had been determinated the corrosion rates (k$_g$) and penetration index I$_p$, also in HCl 2M solution without inhibitor as well in HCl 2M solution with APAS having the following concentrations : 0,1 mM; 0,2 mM; 0,3 mM; 0,4 mM.

APAS presency in HCl 2M solution, is determinating the following decreasings of the corrosion rate, (g·m^{-2}·h^{-1}) :

- at c = 0,1 mM, reduction is 46%;
- at c = 0,2 mM, reduction is 55%;
- at c = 0,3 mM, reduction is 64%;
- at c = 0,4 mM, reduction is 75%.

The same differences can be observed in the case of corrosion rate noticed as penetration of the corrosion. It is obvious the carbon steel corrosion rate decreasing effect obtained through increasing of APAS concentration and over the values of the percentage inhibition eficiency from weight loss (at c = 0,4 mM, P = 74,2%, and P = 45,7% at c = 0,1 mM).

Carbon steel corrosion inhibation due to the presency of APAS in HCl 2M solution, is the result of the adsorbtion of APAS molecules at the metal surface, by the couple of sulphur

unparticipant electrones forming a link metal-sulphur and/or the adsorbtion of APAS on the carbon steel surface, by the nitrogen atom. It is possible to use the interpretation that it is formed a complex between the APAS molecules as ligand and different metalic atoms from the carbon steel net.

Adsorbtion is confirmed by the increased value of equilibrium constant (adsorbtion-desorbtion) K = 6675,5 M^{-1}·L and by the free standard adsorbtion entalphy $\Delta G_{ads}^{0} = -31,75 KJ \cdot mol^{-1}$ which indicate a spontaneously adsorbtion process.

Adsorbtion isotherm which corespond to the experiment figures, is Langmuir isoterm. Carbon steel polarity curves for APAS investigated concentrations shows, compared with the obtained potentiostaticaly polarity curves in no APAS HCl 2M solution, that the APAS inhibitor is manifestig itself as a mixt inhibitor, but with main anodical action (strongly influencing the metal disolving reaction). In the same respect, the electrochemical parameters values determined from Tafel straight lines confirm the fact that APAS is a mixt inhibitor with majoritaire anode action.

The inhibation percentage efficiency electrochemical determined, is close in value to the weight loss one (la c = 0,4 mM APAS, P_g = 74,2% şi P_e = 76,5%).

The examination of the coroded samples in HCl 2M solution and in HCl 2M solution with APAS experimented concentrations through electronic microscopy relieves the formation of a thin film on the carbon steel surface.

Mössbauer spectroscopy indicate in the coroded samples case in HCl 2M solution with APAS, that the corrosion processes are considerably slown down. As well the Mössbauer spectroscopy shows that a Fe superficial compound was formed without a magnetic arrangement on the sample surface. At this stage the principal corrosion product is a oxyhydroxide non-stoechiometrical amorphus of Fe^{3+}, consisting of a mixture of α, β si γ - FeOOH.

The Mössbauer parameters of the compound found on the coroded sample in the solution consisting inhibitor, is not significantly different compared to the coroded sample parameters in HCl 2M solution without inhibitor.

We consider that APAS inhibitor behaviour is like a "rust transformer" and is favourising formation of a "superficial closed layer". The inhibitor transform some constituents of rust into corrosion inhibiting oxide phases.