

Investigation of Carbon Steel Corrosion Inhibition by Hydroxamic Acids

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Introduction

Corrosion inhibition by chemical additives is of great importance and become more common in protecting carbon steel particularly for internal corrosion. However, because of more and more restrictive environmental regulations, development of new non toxic, environmental friendly inhibitors are of high priority in corrosion research. In this thesis, non toxic organic compounds, namely hydroxamic acids, were investigated as promising corrosion inhibitors for carbon steel. In the literature only a few studies were published on testing and evaluation of hydroxamic acids as corrosion inhibitor of copper.

Aims of the work

- In order to find a new effective, environmental friendly corrosion inhibitor for carbon steel corrosion in neutral aqueous solutions. Two dihydroxamic acids, namely oxalyl-dihydroxamic acid (C2), and pimeloyl-1,5-di-hydroxamic acid (C7) have been evaluated as corrosion inhibitors for carbon steel in neutral aqueous solution.

- To increase the efficiency of the inhibitor, the influence of metal ions (Cu^{2+} , Mg^{2+} , Ni^{2+} and Zn^{2+}) on the adsorption process and corrosion inhibition of pimeloyl-1,5-di-hydroxamic acid (C7) on carbon steel surface have been investigated.

➤ Formation of self-assembled monolayers (SAMs) using monohydroxamic acids $\text{CH}_3(\text{CH}_2)_n\text{CONHOH}$ with different alkyl length on the carbon steel electrode surface has been investigated.

Methods

Electrochemical techniques (potentiodynamic polarization and ac impedance measurements) have been used to study the corrosion inhibition effect and to understand the inhibition mechanism of carbon steel corrosion in the presence of different additives by measuring the kinetic data of corrosion parameters and by the interpretation of the polarization curves and impedance plots. Surface analysis techniques (X-ray Photoelectron Spectroscopy and Scanning Electron Microscopy) were used to identify the chemical composition, electronic state and the morphology of steel surface.

New Scientific Results

1. The protective effect of oxalyl-dihydroxamic acid (C2) and pimeloyl-dihydroxamic acid (C7) on carbon steel corrosion

- The electrochemical results obtained reveal that after 1h of immersion C7 provided moderate corrosion protection to carbon steel with inhibition efficiencies 65% compared to 91% for C2.
- C7 with a hydrocarbon chain provides less inhibition efficiency than C2 molecule. This has been tentatively attributed to the fact that the C7 with a long hydrocarbon chain probably tend to be adsorbed with only one hydrophilic group (-CONHOH) on the metal surface, see Fig. 1(a).

Around the single C-C bonds, the C7 molecule freely rotates, thus affecting negatively the adsorption process. In contrary, the C2 molecules have a rigid, planar structure which is conducive to surface adsorption and most likely tend to be adsorbed with the two hydrophilic groups onto the metal surface as seen in Fig. 1(b), this leading to stronger adsorption and better inhibition.

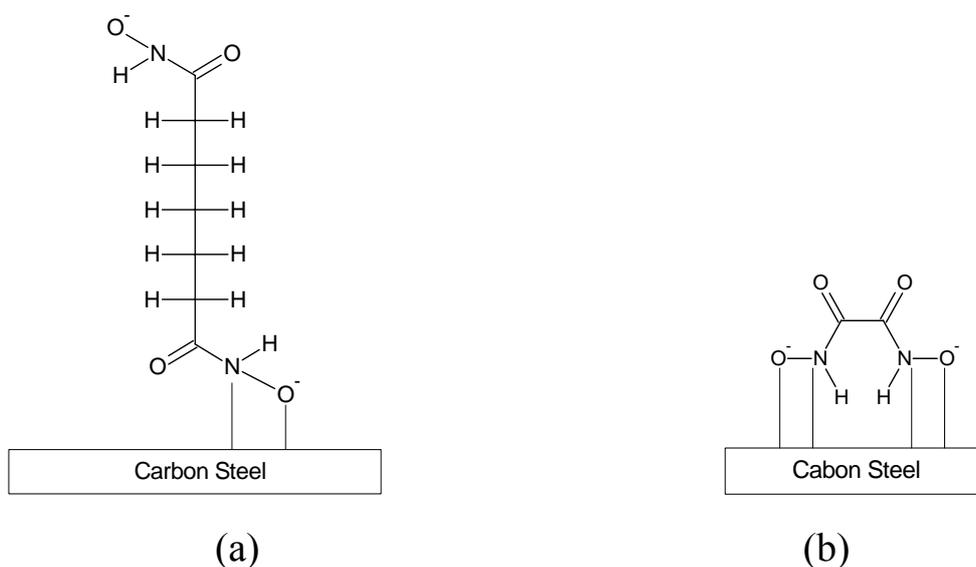


Figure 1. Models of C7 (a) and C2 (b) adsorption on carbon steel surface

- Concentration dependence: a maximum in the inhibitive efficiencies of the both tested molecules is observed at a concentration around 7.5×10^{-4} mol.dm⁻³. At lower concentrations ($c \leq 10^{-4}$ mol.dm⁻³) insufficient adsorption and as a consequence low inhibition efficiency was observed. Higher concentrations ($c > 10^{-3}$ mol.dm⁻³) also result in decrease in the inhibition efficiency.
- Time dependence: the inhibition efficiency of C7 decreases in time gradually. C2 acts as a better corrosion inhibitor, after one hour of

immersion time, its efficiency reaching 91% and remaining almost unchanged after that.

2. Protective Effect of Pimeloyl-Dihydroxamic Acid in the Presence of Metal Ions

- The influence of namely Zn^{2+} , Ni^{2+} , Cu^{2+} , and Mg^{2+} metal ions, on the adsorption process and corrosion inhibition of C7 on carbon steel surface has been investigated. The presence of Zn^{2+} and Ni^{2+} remarkably increases the inhibition efficiency of C7. This is due to the co-adsorption and the formation of stable complexes on the carbon steel surface, that protect the carbon steel from further corrosion. The optimum molar ratio is 1/0.5 for C7/Ni ions and 1/2 for C7/Zn ions. The corrosion potential (E_{corr}) has shifted to more positive values (-539 mV in the presence of Ni^{2+} and -504 mV in the presence of Zn^{2+} as compared to that measured in blank solution, -644 mV), and the anodic currents of the iron dissolution decrease. On the other hand, the presence of Mg^{2+} has no effect on the inhibition performance of C7, because of its low stability constants with hydroxamic acid derivatives.
- Influence of the pH value: additionally to the metal ions, the pH value has a significant influence on the C7 corrosion inhibition, as the complex formation of C7/ metal ions depends on the pH. In addition to pH 7, the effect of C7/ Ni^{2+} and C7/ Cu^{2+} has been also tested at pH 5. It was found that C7/ Ni^{2+} provide better protection at pH 7 than at pH 5. In the case of C7/ Cu^{2+} different behaviour was observed, at pH 7 heavy green precipitation of insoluble material was

formed, but at pH 5 the addition of Cu^{2+} significantly improves the inhibition performance up to 96% efficiency. This is due to the formation of different types of C7/metal ions complexes at each pH value with different compositions, structure and properties.

- XPS analysis was used to identify the chemical composition of the surface layer. N 1s and C 1s regions have been scanned in order to detect the presence and intensity of inhibitor (C7 molecule) in the surface film. The N 1s is present in XPS spectra measured on the surface of carbon steel for all the tested samples. The binding energy at 398 eV is assigned to the N-H group in the organic molecule, which indicates the presence of C7 molecule on the carbon steel surface. The corresponding C 1s spectrum also indicates the presence of the C7 molecules, where the largest peak at around 284.5-284.9 eV, is assigned to the C-C aliphatic bonds, which is related to the carbon chain in the C7. The XPS results are in a good agreement with the electrochemical measurements, where the recorded inhibition efficiencies are proportional to the amount of N and C. The higher the amount of N and C in the surface film the higher the inhibition efficiency, and the lower the amount of O the lower the formation of iron oxides.
- Difference of the functional groups: a comparative study between hydroxamic acid and carboxylic acid has also been performed in order to reveal the role of N in the hydroxamic acid functional group. Selected hydroxamic acids (oxalyl-dihydroxamic acid (C2) and adipoyl-dihydroxamic acid (C6)) and carboxylic acids (oxalic acid (Ox) and adipic acid (Ad)) have been investigated for this purpose. The results show that the C2 has higher protective efficiency (91%)

than Ox (36%) the same result was obtained for the longer inhibitors, C6 has higher protection efficiency (56%) than Ad (13%). Dihydroxamic acids provided a better corrosion protection to the carbon steel under the tested conditions, this shows the importance of the presence of nitrogen atoms which play role in enhanced the inhibition efficiency of dihydroxamic acids. This may be due to the electron releasing $-NH$ group participating in the adsorption process.

3. Corrosion protection properties of monohydroxamic acids (decanoyl hydroxamic acid (C10) and stearoyl hydroxamic acid (C18)) as self-assembled monolayers (SAMs) on carbon steel

- The polarization curves of the modified carbon steel electrodes measured in 0.1 M Na_2SO_4 solution show that the SAM-covered electrodes show more noble behaviour than unprotected steel. The corrosion potential (E_{corr}) has shifted significantly to more positive values (-314 mV in the presence of C10 monolayer and -290 mV in the presence C18 monolayer, compared to that measured for unmodified electrode, -665mV). The anodic current shows the carbon steel dissolution significantly decreases, indicating that hydroxamic acid SAMs work as an anodic inhibitor, throughout the adsorption and blocking the corrosion process. The EIS results show that the charge transfer resistance (R_{ct}) in the presence of C18 SAMs was 4.6 times higher than that of C10 SAMs; in the presence of C10 or C18 layers the corresponding phase angle-frequency plots shows that the phase angle values were kept high in a wide frequency range, even at low frequency region. This demonstrates the formation of a uniform and protective

layer of C10 or C18 on the steel surface with insulating characteristics.

- The change in the SAMs properties of C10 and C18 were monitored in various self-assembling time on freshly prepared carbon steel electrodes. Increasing in the assembling time results in increased inhibition efficiency of both molecules.
- The presence of the SAM layers was proved by wettability measurements. The measured advancing contact angle on the non-modified carbon steel was about 60° , while on the samples modified with C10 and C18 were about 100° and 105° , respectively. After the adsorption of hydroxamic acids through the hydrophilic polar functional groups, their hydrophobic alkyl chains faces the solution, that creating hydrophobic interface, which results in increased contact angle values.
- XPS analysis confirms the presence of hydroxamic acid SAMs on the carbon steel. The N 1s spectra showed two components, one at 400.9-401.2 eV assigned to the N-H group in the organic hydroxamic acid molecule and a second peak at slightly lower binding energy, 399.4-399.8 eV, due to the de-protonated head groups. The corresponding C 1s spectrum also indicates the presence of hydroxamic acid on the carbon steel surface, where the largest peak at 284.8-284.9 eV is assigned to the C-C aliphatic bonds of the hydroxamic acid. The thickness of the hydroxamic acid layers formed on the carbon steel surface was determined by a model that assuming ordered hydroxamic acid monolayer with the head group facing toward the steel surface. The calculated thickness of the organic tail layer $((\text{CH}_2)_n)$ was 1.18 nm for C10 and 2.23 nm for C18 and the head group layer (CONHOH) was estimated to be 0.4 nm for both molecules. The determined total layer

thickness of C18 was 2.63 nm this corresponds approximately to the length of C18 molecule (2.5 nm) which indicates the formation of a single hydroxamic acid layer.

Thesis

1. Oxalyl-dihydroxamic acid (C2) was proven to be a very effective corrosion inhibitor for carbon steel. The high efficiency of C2 is attributed to the adsorption process, where the molecules tend to be adsorbed with the two hydrophilic groups onto the metal surface creating a strong bond and good adhesion between C2 and the substrate.
2. Pimeloyl-dihydroxamic acid (C7) provided moderate corrosion protection on carbon steel with inhibition efficiency of 65% compared to 91% of C2. This has been attributed to the fact that the C7 with long hydrocarbon chain probably tends to be adsorbed with only one hydrophilic group (-CONHOH) on the metal surface. Single C-C bonds allow C7 molecules move and rotate freely, which has negatively affect the adsorption process and, as a consequence, on the inhibition properties. The adsorption process proved to be a key factor in the inhibitor performance.
3. It was confirmed that the addition of Ni^{2+} , Zn^{2+} and Cu^{2+} at the optimum molar ratio significantly enhances the inhibition performance of C7 with inhibition efficiency reaching 95%. This is due to the co-adsorption and the formation of stable complexes on the carbon steel surface, which protects the carbon steel from further corrosion.
4. It was established that the molar ratio of C7/metal ions mixture plays an important role in the inhibition performance on carbon steel corrosion

at pH 7. The best inhibition effect was obtained at molar ratios of $C7/Zn^{2+} = 1/2$, and $C7/Ni^{2+} = 1/0.5$. Correlation was found between the stability constant of C7/metal ion complexes and their inhibition efficiencies. $C7/Ni^{2+}$, $C7/Zn^{2+}$ and $C7/Cu^{2+}$ have considerably high stability constants and high inhibition effects. $C7/Mg^{2+}$ has low stability constant and has no effect on the inhibition property of C7.

5. It was confirmed that the immersion time and pH play also an important role in the inhibition efficiency of C7/metal ions. A continuous build up of inhibitor film takes place which result in increase in the thickness and the persistency with time resulting in formation of a protective layer at the carbon steel surface. The pH-dependent inhibition efficiency of C7/metal ions is related to the formation of different C7/metal ion complexes.
6. Comparative study between a selected hydroxamic and carboxylic acids show that the corrosion inhibition efficiencies of hydroxamic acids are much far better than that of carboxylic acids. The presence of nitrogen atom plays an important role in enhancing inhibition efficiency of dihydroxamic acids, which is due to the electron releasing of -NH- group participating in the adsorption process.
7. Decanoyl hydroxamic acid (C10) and stearoyl hydroxamic acid (C18) successfully deposited in a form of protective self-assembled layers on carbon steel surfaces, reduce the corrosion rate with inhibition efficiencies reaching 96% for C10 and 99% for C18. The increasing assembling time results in increased inhibition efficiency for both molecules, indicating that the formation of hydroxamic acid monolayers on carbon steel surface is a time dependent process.

8. Quantitative evaluation of the XPS data confirms the presence of the hydroxamic acid SAMs on the modified electrode surfaces, with total layer thickness of 1.58 nm for C10 and 2.63 nm for C18 that proves the formation of a monolayer.

Possible applications

The tested di-hydroxamic acid molecules can be used for corrosion protection of water cooling systems equipment. Particularly for malty systems where the equipment consists of different materials such as steel, copper, zinc. In these systems usually different metal ions exist in the flow as a result of corrosion process. It is well known that the presence and accumulation of copper ions on the carbon steel surface cause extra cathodic reactions that lead to increase in the carbon steel corrosion. Furthermore the precipitation of copper ions in certain places in the system reduces to copper metal and creates a galvanic corrosion with carbon steel which increases the corrosion rate as well. This is a common problem in many industrial plants. However we assume that the tested hydroxamic acids can act as efficient corrosion inhibitors and, in addition, prevent the negative effect of such ions (if present in the system) throughout the formation of stable complexes between hydroxamic acids and metal ions which improve the inhibition efficiency instead of causing problems. Hydroxamic acid self-assembled monolayer provide an excellent model system to study the interfacial properties of organic layers and from practical point of view, it can be applied as a temporary corrosion protection for material under storage or transportation.

List of publication

- I. **Abdulmajed Alagta**, Ilona Felhősi, Erika Kálmán, (Di-Hydroxamic Acid as Corrosion Inhibitor for Low Carbon Steel, in the Presence of some Metal Ions) *Ann. Univ. Ferrara, N. S., Sez V. Supp N. 12, vol (2005) 51–62.*
- II. **Abdulmajed Alagta**, Ilona Felhősi, Erika Kálmán (Hydroxamic Acid Corrosion Inhibitor for Steel in Aqueous Solution) *Materials Science Forum Vols. 537-538 (2007) pp. 81-87*
- III. **Abdulmajed Alagta**, Ilona Felhősi, Judit Telegdi, Imre Bertóti, Erika Kálmán (Effect of metal ions on corrosion inhibition of pimeloyl-1,5-di-hydroxamic acid for steel in neutral solution), *Corrosion Science 49 (2007) 2754–2766*
- IV. **Abdulmajed Alagta**, Ilona Felhősi, Imre Bertoti, Erika Kálmán, (Corrosion Protection Properties of Hydroxamic acid Self-Assembled Monolayer on Carbon Steel), *Corrosion Science 50 (2008) 1644-1649.*

List of conferences

- I. **Abdulmajed Alagta**, Ilona Felhősi, Erika Kálmán, (Di-Hydroxamic Acid as Corrosion Inhibitor for Low Carbon Steel, in the Presence of some Metal Ions) 10thEuropean Symp. Corros. Inhibitors (10SEIC) 29August -2 September, Ferrara 2005, Oral presentation.

- II. **Abdulmajed Alagta**, Ilona Felhősi, Erika Kálmán, 5th Hungarian Conference and Exhibition on Materials Science Testing and Informatics, Balatonfüred, 9-11 October 2005, Oral presentation.
- III. **Abdulmajed Alagta**, Ilona Felhősi, Erika Kálmán, (Corrosion Inhibition of Pimeloyl-1,5-di-hydroxamic acid for Carbon Steel in different aqueous electrolyte) *EUROCORR (2007) Abstract 18 and paper in electronic volume.*
- IV. **Abdulmajed Alagta**, Ilona Felhősi, Erika Kálmán (Characterization of Carbon Steel Surface Modified by Hydroxamic Acid Self-Assembled Monolayer) International Conference on Functional Nanocoatings, Budapest 30Mar. 2008 (poster).