

Rust phase transformation in the presence of mangrove tannins

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Abstract

The transformation of rust in the presence of 5 g L⁻¹ tannins extracted from mangrove barks was studied. Pre-rusted samples prepared resulted in the formation of predominantly lepidocrocite and magnetite. Partial transformation of rust components, particularly lepidocrocite in the presence of mangrove tannins was found to occur when observed via infrared spectroscopy, X-ray diffraction and SEM analysis. The anti-corrosive properties of the mangrove bark extracts seem to be related to the tannins which are capable of chelating with Fe³⁺ giving a highly stable, and insoluble ferric-tannate complexes. A molecular modeling study of the reaction of catechin, a flavanoid of mangrove tannins with Fe³⁺ to form a ferric-tannate complex was performed to explain the adsorption mechanism of tannins on iron. The correlation between the electronic density of the catechin molecule and the inhibiting properties is reported.

1. Introduction

The known hazardous effects of most synthetic corrosion inhibitors are the reasons for the search of safer and environmentally friendly natural products. Plant extracts are viewed as an incredibly rich source of naturally synthesized chemical compounds that can be extracted at low costs. Naturally occurring substances such as vanillin [1], *Opuntia* extracts [2], lawsonia extract [3], natural honey [4] and extracts of chamomile, halfabar, black cumin and kidney bean [5] are some of the recent studies on corrosion inhibition for different metals in various environments.

Tannins are polyphenols that occur only in vascular plants such as leaves, needles, barks heartwood, seeds and flowers. Tannins exist primarily in condensed and hydrolysable forms. Natural tannin extracts have been employed since the turn of the last century in leather industry. Recent development of their industrial uses as adhesives, flocculants, depressants, viscosity modifier agents and more recently as corrosion inhibitors reflects their importance as industrial raw materials. Electrochemical studies have shown that tannins extracted from the barks of mangrove trees are excellent corrosion inhibitors of steel at very low pH. The mechanism of inhibition at this pH was due to the chemisorption of tannin molecules while at higher pH, inhibition was achieved via formation of ferric-tannates [6].

Contradictory opinions have been referred to in the literature particularly on the nature of the iron-tannate and its interaction with the rusted steel due to the diversity of the material used in different studies. Studies have included the use of tannic acid [7-10], gallic acid [11], oak tannin [12,13], pine tannin [14] and mimosa tannin [15]. In order to establish the correlation between the ferric-tannate formation and the low inhibition efficiency observed at high pH from the electrochemical studies, phase transformations of pre-rusted steels in the presence of tannins were evaluated. In this work the quantum chemical calculations are conducted to analyse the relationship between the molecular structure and properties of ferric-tannate complex and its inhibitory mechanism.

2. Experimental procedure

2.1 Phase transformation studies

Mild steel plates obtained from ARCELOR, France were washed with distilled water and ethanol prior to sample treatments. Pre-rusted samples were prepared by subjecting the mild steel plates to the salt spray chamber according to the ASTM B 117 [16] standard procedure (6 hours exposure in 5 % (w/v) NaCl at 98 % humidity, 1.0 mL hr⁻¹ spray rate, 1.0 kg cm⁻³ of pressure and followed by drying in an oven at 40 °C) The pre-rusted plates were immersed in 5 g L⁻¹ mangrove tannin solution at pH 4.0 for 24 hours. The changes in the rust structures were observed via X-ray diffractions, SEM and FTIR analyses. The SEM analysis was carried out using SEM S-2500 Hitachi Thermo NORAN equipped with an energy-dispersive X-ray spectrometer and prior to the SEM studies the surface was gold or carbon-coated using a vacuum evaporator Edwards Auto 306. A Perkin Elmer System One spectrometer was used to obtain the FTIR spectrums while a Goniometre C diffractometer, incorporating a cobalt radiation ($\lambda=1.78892 \text{ \AA}$) was used to obtain the X-ray diffraction patterns.

2.2 Computational Details

For calibration purposes, computations were performed in two steps. Initial calculation was performed using MOPAC available in CAChe version 5.0 program. The semi empirical AM1 [17] method was first used to generate various stable structures of lowest energy conformations. This is represented as a function of three dihedral angles: $\angle \text{FeOCC}$ (+90.0, 180.0, -90.0) at A, B and C rings. These binding sites are denoted as A_1 , A_2 , B_1 , B_2 , C_1 and B_1B_2 (between two phenolics) and the atomic numbering for catechin molecule are as shown in Figure 1. PRECISE keyword was used to ensure stable geometry.

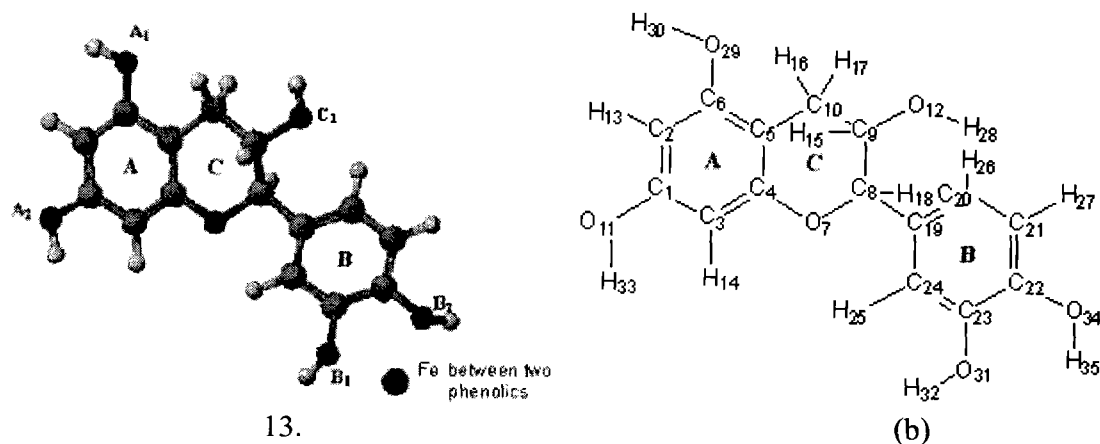


Figure 1: (a) The labeling of phenolic positions (d) Atomic numbering for catechin molecule

In the second step, single point energy calculations were performed on each of the optimized structures derived from the semi empirical calculation using the hybrid Becke3 exchange functional and Perdew and Wang correlation functional (B3PW91 method) [18] using 6-31G** basis set, available in Gaussian03, to compute more accurate energy values and other quantum properties. The verification of the structures as a minimum on the potential energy surface, PES was carried out using FREQ that yielded all positive frequencies.

3. Results and discussions

3.1 Transformation studies

From the X-ray diffraction, XRD pattern in Figure 2, the pre-rusted sample was found to consist of mainly lepidocrocite and magnetite and traces of goethite. The XRD pattern indicated the reduction of several lepidocrocite peaks in favour of ferric-tannate formation after the addition of mangrove tannins.

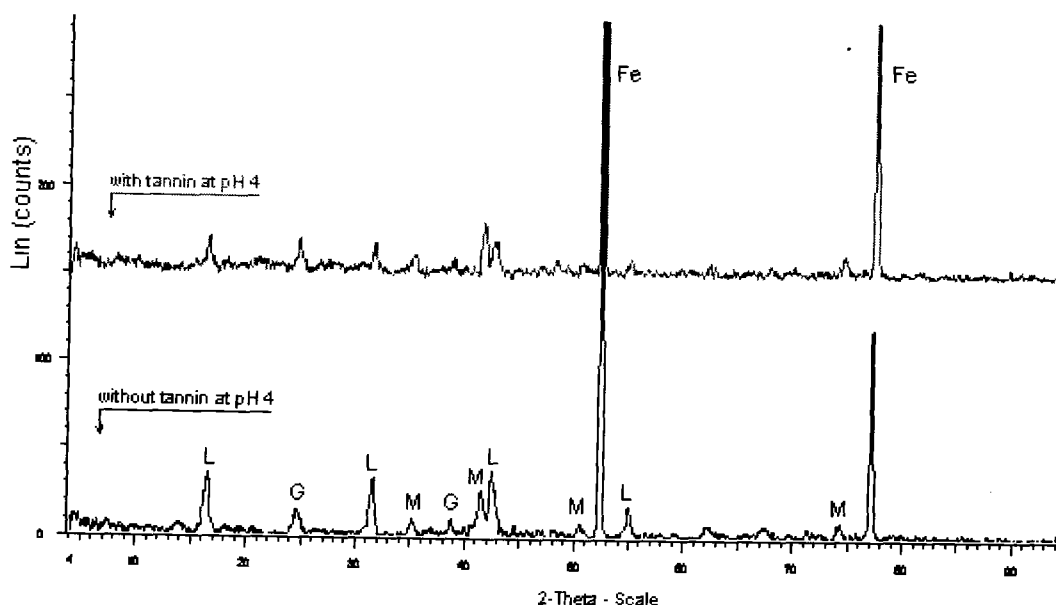


Figure 2 Phase transformation of bare rust surface when treated with 0.5 % mangrove tannins.

Similarly the FTIR spectrum in Figure 3 exhibited the presence of lepidocrocite (1022 , 891 and 474 cm^{-1}), goethite (800 cm^{-1}) and magnetite (571 cm^{-1}) in the untreated pre-rusted sample. Upon treatment of tannins, ferric-tannate peaks at 1163 , 1104 , 1054 and 811 cm^{-1} were evident. A reduction in the intensity of the lepidocrocite peak was also observed. The principal magnetite peak at 571 cm^{-1} may have been superimposed by the broad 626 cm^{-1} peak.

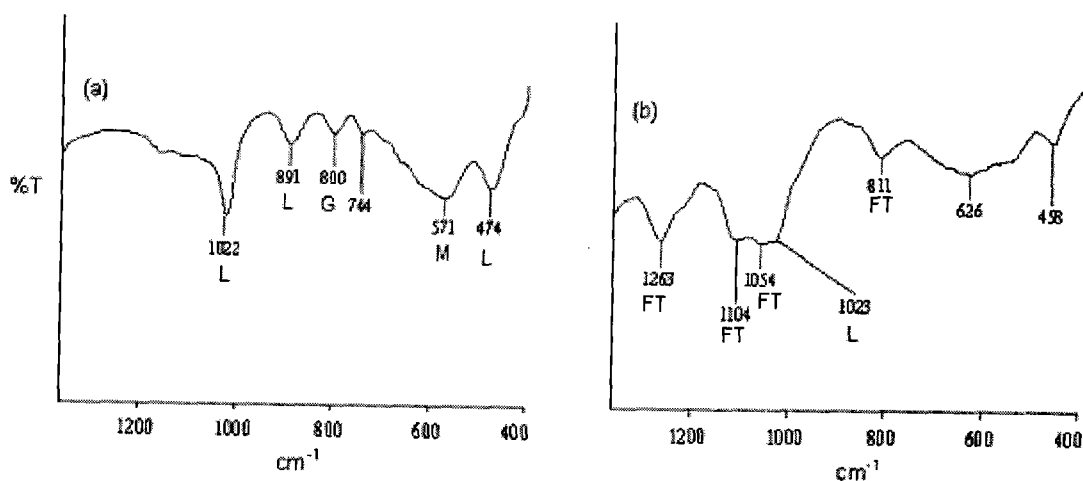


Figure 3 FTIR spectrum of (a) bare rust and (b) converted rust samples: FT-ferric-tannate, G-goethite, L-lepidocrocite, M-magnetite.

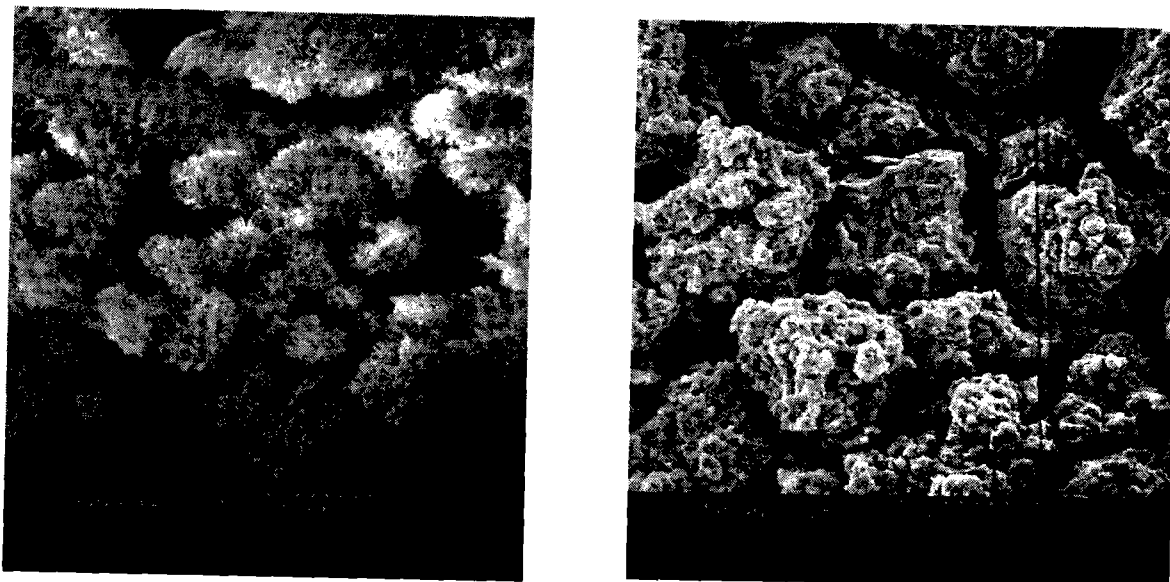


Figure 4 SEM micrographs of pre-rusted steel surface (a) before tannin immersion and (b) after tannin immersion.

Figure 4 shows the SEM micrographs of the rust surfaces before and after immersion in the mangrove tannin solution at pH 4.0. The pre-rusted sample shows basically coral-like structures distributed in a random manner. This structure disappeared with the tannin treated samples and was replaced by a coarse layer with cracks of irregular shapes. A closer inspection of the surface of each crack revealed tiny flowered-like structures stacked on top of one another. Unconverted rust structures were observed underneath the transformed tannins.

The above results indicated that partial transformations of rust into ferric-tannates without other oxide or oxyhydroxides as reaction products. Depolymerisation of mangrove tannins in the presence of phloroglucinol nucleophiles in acidic ethanol followed by the separation of flavan-3-ols and their phloroglucinol adducts using reversed phase high performance liquid chromatography resulted in the identification of four major flavanoids namely catechin, epicatechin, epicatechin gallate and epigallocatechin [19]. The proximity of hydroxyl groups on the aromatic rings of the flavanoid monomers enables the mangrove tannin to chelate the iron (II) and iron (III) ions forming iron-tannates. In the presence of oxygen, Fe (II) tannate is oxidized to the Fe (III) form, a blue-black insoluble complex, which impedes steel corrosion. However the lack of adhesion of tannates as shown from SEM micrographs inferred a physical adsorption of deposits and the cracked morphology of deposits provided easy penetration of moisture into the cracks leading to the formation of new rust. This resulted in a low protective behaviour. Hence the correlation between ferric-tannate formation and the low inhibition efficiency observed at high pH from the electrochemical studies was established.

3.2 Molecular modeling

The energy calculated using both the AM1 semi empirical method and B3PW91/6-31G** calculations of the optimized complexes for each phenolic position indicated that position C₁ with Fe-O-C-C dihedral angle of +90° has the lowest total energy, followed by binding at position B₁B₂ (∠FeOCC -90°). At C₁ (∠FeOCC +90°) position, the breaking of two bonds was observed, namely between C₉ and C₁₀ as well as between O₁₂ and H₂₈ which was confirmed by bond order calculations. Whilst, a new bond between Fe³⁺ and H₂₈ (1.56 Å) was formed (bond order of 0.983).

At B₁B₂ position and dihedral angle of -90°, Fe³⁺ forms bonds with two oxygen atoms i.e. O₃₁ and O₃₄. The bond length of Fe₃₆O₃₁ and Fe₃₆O₃₄ are 1.965 Å and 1.958 Å respectively, both within the normal experimental Fe-O distance (1.875 – 2.042 Å). Apparently, binding at this site is due to the electron-donating properties of the phenolic oxygen and the electron-deficient Fe³⁺. The lengthening and shortening of bonds are also observed, and are consistent with the electron transfer from catechin to the metal ion. Bond order calculations showed that the interaction between Fe³⁺ with O₃₁ and O₃₄ resulted in a value of 0.653 and 0.650 each, indicating a weak single bond being formed.

The HOMO-LUMO energy gap, ΔE_{HOMO-LUMO} of Fe³⁺-tannate shows that the binding at B₁B₂ has the largest energy gap indicating the stability of the complex. The structure of this stable complex is as shown in Figure 5. Conversely, the HOMO-LUMO smaller energy gap value for C₁ ring signifies a less stable complex. The results from the energy calculations and ΔE_{HOMO-LUMO} values show that this B₁B₂ conformation is the most stable form of ferric-tannate compared to the other OH positions while binding at position C₁ is unlikely to form a ferric-tannate complex.

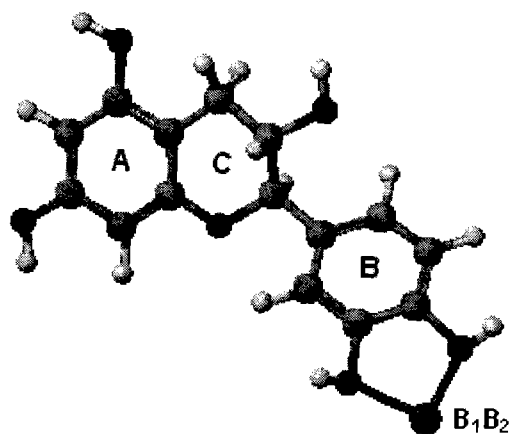


Figure 5 The most stable ferric-tannate complex with B₁B₂ conformation

4. Conclusion

Partial transformation of rust into ferric-tannates was found to occur with the addition of mangrove tannins leading to a low inhibitive behaviour. The mechanism of adsorption of catechin onto the iron surface has been established via theoretical calculation using both semi empirical and density functional theory. The most probable

position of adsorption occurs on the B ring of the two phenolic positions following the electron donating properties of the phenolic OH groups in catechin.

5. References

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