Characterizing the Adsorption Behavior of a Bovine Serum Albumin and a Novel Amino Acid onto Iron and Aluminum

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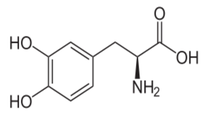
Background

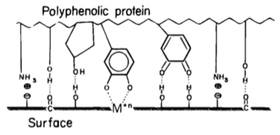
- "Flash rusting" is a kind of corrosion that happens when a cleaned metal surface is exposed to a humid environment for a significant amount of time.
- The corroded surface will subsequently shorten the lifetime of the new coating/surface treatment due to the presence of corrosion products.
- A need exists for an environmentally friendly, aqueously soluble, biopolymer-based corrosion inhibitor that can protect exposed steel surfaces during the paint removal process from undergoing flash rusting.
- Our approach is to look at naturally occurring biopolymers that are known to bind to metal surfaces very strongly, namely those containing L-3,4-dihydroxyphenyl-L-alanine (L-dopa).
- Polyphenolic proteins extracted from ***Mytilus edulis*** foot tissue contain various percentages of L-dopa.

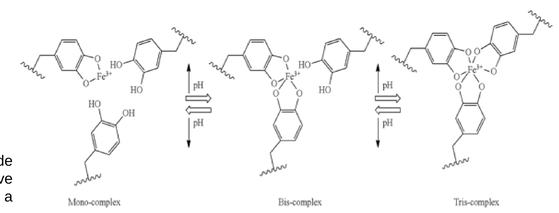
L-3,4-dihydroxyphenyl-L-alanine

- L-3,4-dihydroxyphenyl-L-alanine (L-dopa), a unique catecholic amino acid;
- L-dopa residues are oxidized and cross-linked in quinone-tanning;
- Iron(III) binding to L-dopa forms catechol complexes in a mono, tris- or bis (catecholato) coordination mode.[1]



L-Dopa





Schematic diagram of the various amino acid side chains contained within the mussel adhesive protein and their possible binding interactions at a surface/solution/protein interface. [2]

Objectives

Determine the adsorption characteristics of Bovine Serum Albumin (BSA) and a novel amino acid (L-dopa) onto high strength steel (HY80) and 5083 aluminum alloy.

Methodology

The Bradford protein assay [3] and the Arnow assay [4] are used for BSA and L-dopa determination, respectively, to detect the bulk solution concentration of non-adsorbed protein as a function of time. Based on these methods, the amount of protein adsorbed on metal surfaces can be calculated.

The adsorption isotherm is based on the Langmuir theory.[5-6]

$$Q=KNC(1+KC)$$

$$C/Q=1/NK+C/N$$

C – the equilibrium concentration of the adsorbate in the bulk solution;
Q – the number of macromolecules adsorbed per unit surface area of adsorbent;
N – the maximum number of adsorption sites per unit of surface area of adsorbent;
K – the affinity that the adsorbate molecules have for the adsorption sites.

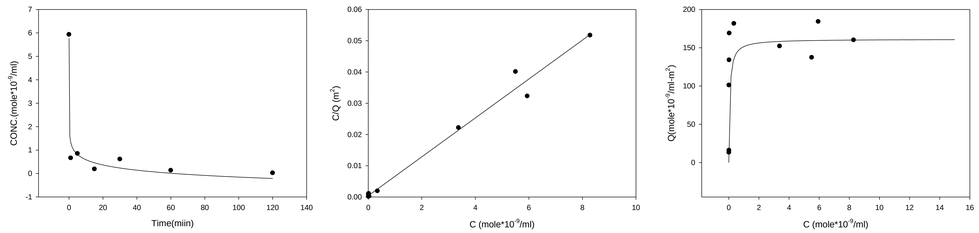
A plot of C/Q versus C should yield a straight line. N and K can be determined from the slope and the y-intercept, respectively. The plotted graph can be compared to the theoretical curve. The optimal equilibrium concentration to achieve maximum adsorption can then be determined.

The adsorption measurements of BSA are made at neutral pH 7.6-7.8. The adsorption measurements of L-dopa are made at pH 3.4-3.5. Measurements of L-dopa at neutral pH are in progress.

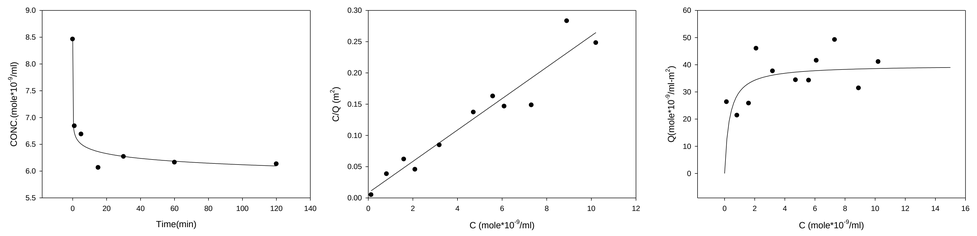
Results

Adsorbate	Adsorbent	Coefficient of Determination R^2	Maximum number of adsorption sites N (mol/m^2)	Affinity constant K (mol^{-1})
BSA	HY80	0.9838	1.6129×10^{-7}	1.55×10^{10}
BSA	Al5083	0.9232	1.2346×10^{-7}	3.0988×10^{9}
L-dopa	Al5083	0.7717	1.311×10^{-6}	3.674×10^{5}

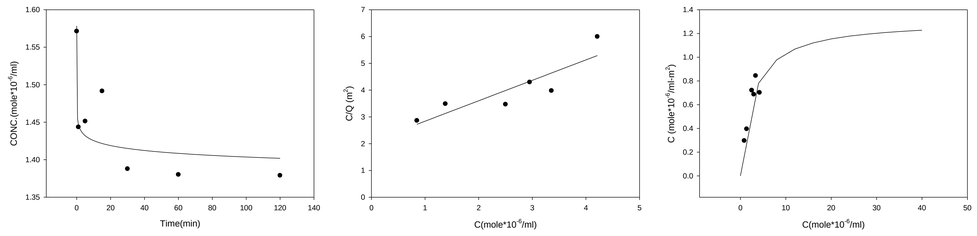
HY80/BSA

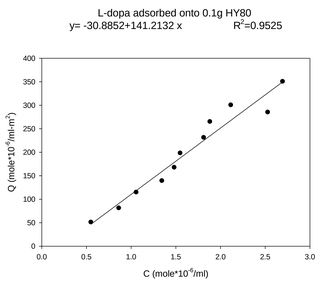


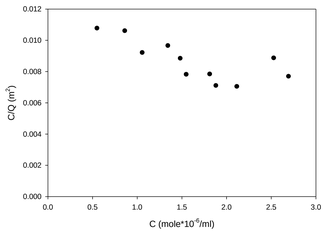
Al5083/BSA



Al5083/L-dopa







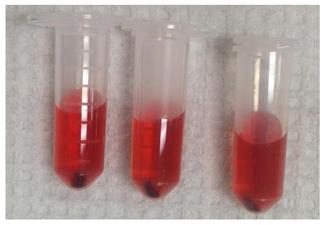


Figure 1. Precipitates form and are at the bottom of tubes after centrifugation at 14,000 rpm.

Discussion and Conclusion

- The results of adsorption sites and affinity constant showed the adsorption behavior of BSA and L-dopa onto HY80 and Al5083 are different.
- The high values of the linear correlation coefficient shows that BSA exhibits Langmuir adsorption behavior. BSA has more adsorption sites and a larger affinity constant on HY80 than Al5083.
- L-dopa has ten times higher of the number of adsorption sites than does BSA on Al5083. The adsorption of L-dopa onto Al5083 cannot be described well by the Langmuir theory.
- At low pH, iron(III) binding to L-dopa forms an insoluble protein-metal complex. Precipitates form during the Arnow assay (Figure 1). L-dopa does not follow Langmuir Isotherm adsorption behavior. With higher concentrations of L-dopa and a longer incubation time, there will be lager concentration differences in the bulk solution, which indicates that L-dopa cannot be an effective corrosion inhibitor by itself.

Future Work

- Tests of L-dopa adsorbed onto HY80 and Al5083 will be performed at neutral pH.
- More data points are needed to determine the adsorption behavior of adsorbates.
- The adsorption behavior of polyphenolic proteins will be tested on HY80 and Al5083.

References

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