

ELECTROCHEMICAL AND COMPUTATIONAL SCREENING OF NON-TOXIC ORGANIC REPLACEMENTS FOR HEXAVALENT CHROMATE CORROSION INHIBITORS.

Ronald Cook, Jeannine Elliott and Shaun Sapp
TDA Research, Inc. 4663 Table Mountain Drive, Golden CO 80403

ABSTRACT

Hexavalent chromates have long been recognized as the "gold standard" in corrosion protection. However, increasingly stringent health and environmental regulations are restricting the use and disposal of chromates. The primary mechanism by which chromates arrest corrosion on aerospace aluminum alloys is through inhibition of the oxygen reduction reaction (ORR) at copper-based cathodic half-cells. Other inorganic anions and inorganic cations are much less effective than chromates. Recent studies for example have shown that Ce^{3+} (an often touted replacement for chromates) is 1000 times less effective than CrO_4^{2-} at inhibiting the ORR, whereas certain organic thiols (e.g. 2,5-dithiol-1,3,4-thiadiazole) are ten times more effective than Ce^{3+} as inhibitors for the oxygen reduction reaction (ORR) at copper containing cathodic half-cells. We have used a rotating disc copper electrode and computational modeling to develop Quantitative Structure Property Relationships for organic inhibitors of the ORR. In our studies we have identified organics that are highly active for ORR inhibition. We will present the results of these studies and discuss the relationships between the organic structures and inhibition of the ORR for developing improved organic corrosion inhibitors for aerospace aluminum alloys.

Keywords corrosion, QSPR, chromates non-toxic, oxygen reduction reaction

INTRODUCTION

The corrosion of military equipment and facilities is a significant and ongoing problem. In total, corrosion costs the Department of Defense \$20 billion annually and is the number one cost driver in military life-cycle costs¹. The primary defense against the corrosion on aerospace aluminum alloys is the diligent use of protective organic coatings. In typical practice, the metal surface(s) are first treated with a chemical agent to passivate or seal the surface and are then coated with an organic coating (typically an epoxy primer) that contains a corrosion inhibitor. While the overall durability of protective coatings has improved remarkably in recent years, thereby reducing materials and manpower costs, the development of new corrosion inhibitors has not kept pace. Today's most effective and most widely used corrosion inhibitors are the soluble chromates (developed over 50 years ago). The toxic properties and environmental costs of chromates are well documented and their use and disposal are therefore strictly regulated. Much research has been conducted on chromate replacements in the hope that an understanding of their mechanism of action would lead to identification of lower toxicity materials with the same effectiveness. However, to date alternative corrosion inhibitors have not provided the same level of corrosion protection as chromates. This performance gap has hindered the adoption of low-toxicity alternative for corrosion protection of aircraft. Further, non-chromates have generally been very sensitive to the application and system they are used. For example, they may have satisfactory performance in one coating while performing poorly in another coating system.

Several factors are important when considering new materials to provide corrosion inhibition for aluminum aerospace alloys. First, the materials must provide strong corrosion inhibition for either the anodic or cathodic corrosion mechanism. Secondly, the corrosion inhibitor must be able to be delivered and transported efficiently to where it is needed to provide active corrosion protection. And finally, it must have low toxicity.

Studies of the mechanisms of corrosion protection by chromates are being used to guide the development of new inhibitors. Frankel and McCreery² and others (e.g. Kendig and Buchheit³) have identified how soluble hexavalent chromates are thought to inhibit the corrosion. Chromates are stored in a chromate conversion coating and/or in a primer coating. Upon exposure to water or salt-water solutions the hexavalent chromium in the conversion coating is released to a concentration of approximately 10^{-4} M. The chromates in the primer (e.g. SrCrO_4) have limited solubility in water and release hexavalent chromium to 10^{-3} M at equilibrium. In both cases the slightly soluble hexavalent chromium is readily transported through the coating to the corrosion site where it stops corrosion either by inhibiting anodic dissolution or by interfering with the cathodic half-cell reaction (e.g. oxygen reduction) that occurs at copper sites in the Al-Cu alloys. Inhibition of the cathodic half-cell occurs when Cr(VI) binds to the copper surface and is irreversibly reduced to form an insoluble Cr(III) hydroxide.

Components of a good chromate replacement should therefore include mechanisms for delivery (storage and release), transport (through the coating/pretreatment to the metal substrate) and inhibition of corrosion on the metal of interest. For aircraft aluminum alloys like AA2024 and AA7075, the copper in the aluminum (and the cathodic oxygen reduction reaction that takes place on it) is what drives the corrosion process. Therefore, potential corrosion inhibitors must be able to stop the oxygen reduction reaction at the copper sites by poisoning the reduction reaction or blocking oxygen access cathodic sites.

There are a large number of possible alternative corrosion inhibiting pigments. The first to consider is other inorganic materials. Examples include cerates, lanthanides, molybdates, vanadates, borates, silicates and various salts of these materials. None of these inorganics are effective one-to-one replacements for chromates, although some metavanadate salts nearly match chromate performance for cathodic inhibition. The other possible classes of corrosion inhibitor replacements are organic molecules. One would expect from the large number of organic compounds that are available for vapor phase corrosion inhibition and corrosion inhibition in liquid medium, that many of these compounds would be candidates for protective coating applications. That is not the case, however. This is because organic corrosion inhibitors must meet multiple necessary criteria to be effective in the coatings or pretreatment applications. These include limited solubility in organic solvents and some but not excessive solubility in water, an effective specific gravity of ~ 2 to 5, absence of deleterious effects on coating's mechanical properties (e.g. plasticization) and most importantly they must not interfere with the curing process or react with the resin so as to be locked into the resin and not available for inhibition. Organic corrosion inhibitors generally have functional groups (like amines, thiols, carboxylic acids) that can react with the coating resins during cure, locking them in to the matrix where they are unavailable for transport to the corrosion site.

The development of new delivery vehicles for corrosion inhibitors (e.g. microcapsules, ion exchanged clays, functionalized nanoparticles, etc) has renewed interest in organic corrosion inhibitors as these delivery systems allow the organic corrosion inhibitors to be protected during cure and released in a controlled manner. The organic corrosion inhibitor is embedded into a carrier that acts as a reservoir for the corrosion inhibitor releasing it when it is needed. So-called smart carriers provide a triggering mechanism for release of the corrosion inhibitor only when needed. Some examples of smart corrosion inhibitors are galvanic release of corrosion inhibiting organic anions from conducting polymers⁴ and pH triggered release of corrosion inhibitors from surface modified boehmite nanoparticles⁵. In this paper we discuss the use of rotating disk electrodes coupled with quantitative structure property modeling to select organic molecules having low toxicity for chromate replacement in epoxy primers.

EXPERIMENTAL PROCEDURE

The ability of the organic inhibitors to inhibit oxygen reduction was carried out according to the methods described by Kendig and coworkers⁶. In depth studies of the corrosion of high strength aerospace alloys (AA2024 and AA7075) have shown that the corrosion is driven by the reduction of oxygen at copper containing intermetallics (or copper redistributed/redeposited from dealloying of the intermetallics). Kendig and coworkers⁶ have shown that rate of the oxygen reduction reaction (ORR) at rotating copper electrodes in oxygenated aqueous electrolytes is an effective tool for screening inhibitors for the ORR. The measurement of the effectiveness of inhibitors for the oxygen reduction reaction is carried out at rotating copper disk electrodes (RCDE). A copper cylinder is inserted into a Teflon fitting (Pine Instruments, Inc) and polished to a bright finish, rinsed with deionized water and then air-dried. The RCDE is then immersed in a 5% NaCl solution and preconditioned at 2000 rpm and -1.2V (vs. a saturated calomel reference electrode, SCE) for sixty (60) seconds followed by 750 seconds at -0.7V (vs. SCE). The rotation rate is then varied between 10 and 2500 rpm in a random order while measuring the oxygen reduction currents at each rotation rate. The resulting currents are plotted against the square root of the rotation rate. The ratio of the slope of the line of the solution without the inhibitor to the slope of the line of the solution with the inhibitor is designated r . In actual use the metric $1/r$ is used. $1/r$ gets larger (e.g. a more effective inhibitor) as the slope of the line for the inhibited solutions gets smaller.

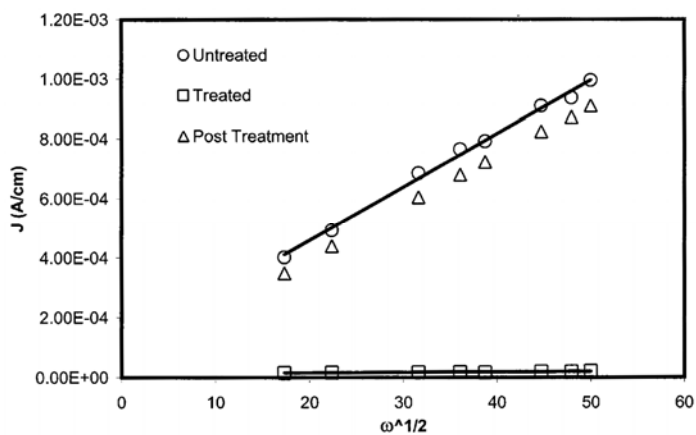


Figure 1. Inhibition of the ORR on a copper RDE by an organic salt

Computation of solubility (LogS) and lipophilicity (LogP) were carried out using the software provided by the Virtual Computational Chemistry Laboratory at www.vcclab.org. Electronic parameters for the organic molecules were carried out at the B3LYP 6-31G+d level using Gaussian 03. Regression analyses were carried out using the multi-linear regression analysis algorithm in XLSTAT[®] and non-linear models were fit using an in-house developed genetic function approximation approach using Genehunter[®] and Excel[®].

RESULTS

A review of the literature on the action of non-oxidizing organic corrosion inhibitors shows that the mechanism of their corrosion inhibition is primarily that of a strongly adherent protective film. The best materials readily displace water and aggressive ions from the metal surface and also provide a barrier to migration of water, oxygen and electrons through the film to the metal surface. Numerous Quantitative Structure Property Relationship (QSPR) studies have shown that various electronic parameters calculated from the energy minimized structures of organic molecules have high correlations with corrosion protection. These quantum mechanical parameters include the energies of the HOMO and LUMO orbitals, the HOMO-LUMO energy gap, the polarizability and the dipole moment⁷⁻⁹.

After examining the corrosion inhibitor literature, we decided that the most promising molecular descriptors for corrosion inhibitors should be: 1) computable from their 2D molecular structures, 2) be already used in current methods for computing aqueous solubility (LogS) and oil/water partition coefficients (LogP) and 3) be proxies for binding strengths of the corrosion inhibitors to the metal surfaces. As mentioned above, many QSPRs relating quantum mechanical properties computable from the molecular structure to corrosion inhibiting efficiencies have been developed. Such studies⁷⁻⁹ have found that the energies of the Highest Occupied Molecular Orbitals (HOMO) and Lowest Unoccupied Molecular Orbitals (LUMO), the energy gap between the HOMO and LUMO and related parameters correlate well with corrosion efficiency. We have combined these parameters into a single parameter representing the ability of organic molecules to take up or release electrons to the metal surface. In addition, it is also possible that due to steric effects or if the metal surface is charged, that electrostatic forces (instead of the formation of covalent bonds) may play a major role

in determining the adsorption strength of organic corrosion inhibitors to the metal surface. Therefore we also included the dipole moment in the molecular descriptor pool.

Simple linear regression of the four descriptors do not generate good models ($r^2 = 0.65$) Non-linear regression methods (e.g. genetic function approximation) provided excellent results between the experimentally measured $1/r$ values and those predicted from the molecular structures using the four molecular descriptors. Figure 2 shows the results of the regression of the descriptors to the $1/r$ values for a small set of 13 organic corrosion inhibitors that were evaluated. As the plot shows, even for the small set used for training the GP algorithm, good fits were achieved for both the training set and the out of sample verification set.

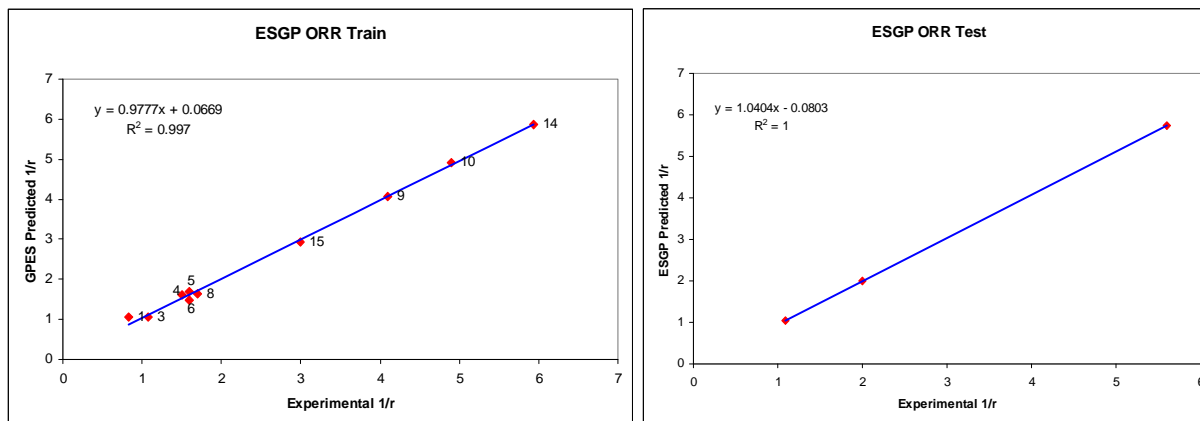


Figure 2. Fit of experimental and predicted $1/r$ values for training and test sets

Another goal of the modeling work is to identify organic structures that have low toxicity in addition to having high corrosion protection efficiencies. In reviewing the literature for toxicity modeling of organic molecules we found that LogS , LogP , dipole and quantum chemical descriptors are often used to model toxicities of therapeutic drugs. We also found that there are many similarities between the properties of drugs and the properties of corrosion inhibitors. For both applications the organics need to have some solubility in water (LogS) and also a certain level of lipophilicity (e.g. partitioning into the fatty tissues compared to partitioning from water to the metal surface). Also for both applications the organics need to bind to the active site and have low or no toxicity. Therefore we evaluated the same set of four molecular descriptors that we used for inhibition of the oxygen inhibition reaction for toxicity. For the initial evaluation we used toxicity of the organic structures to fish. This was in part because leaching of the organics from the coatings could eventually result in their reaching streams, rivers and lakes and becoming a problem to fish species.

The need to assess the toxicity of new chemicals and drugs quickly has led to the development of quantitative structure property relationships for prediction of toxicity from their two-dimensional structures. For example the U.S. EPA provides a web-based (and downloadable) program to calculate toxicities of a wide variety of organic structures towards fish. Because toxicity often derails the development of new drugs in the later stages of drug development the Pharmaceutical Industry has also developed many structure-toxicity algorithms. Thus we used the EPA-vetted toxicity prediction algorithm (ECOSAR) to predict the toxicities towards fish for the organic structures that were studied using rotating copper disk electrodes and then regressed the same four parameters that we used in the corrosion inhibitor prediction against the toxicities. The toxicities are given as the log of the concentration of the organics having a LC_{50} after 14 days exposure.

As seen in Figure 3 the molecular descriptors developed for prediction of corrosion inhibition of the oxygen reduction reaction on copper are also very good descriptors for fish toxicity as predicted using the EPA program ECOSAR. Therefore the same four molecular descriptors can be used to rank molecular structures for both corrosion inhibitor efficiency and fish toxicity and perhaps other toxicities as well.

Using the models we have developed to date we have generated a list of low toxicity corrosion inhibitors for the oxygen reduction reaction. These materials have either been purchased or synthesized and then incorporated into nanostructured carriers based on surface modified boehmite nanoplatelet technology. The organic corrosion inhibitors were incorporated into the nanostructured carriers using a method known as incipient wetness (i.e. the nanostructured materials were heated under vacuum to 120°C and then a water solution containing the organics were added to the dried evacuated powders). The resulting powders were then incorporated into an epoxy primer and are currently being evaluated using the ASTM B-117 salt fog standard.

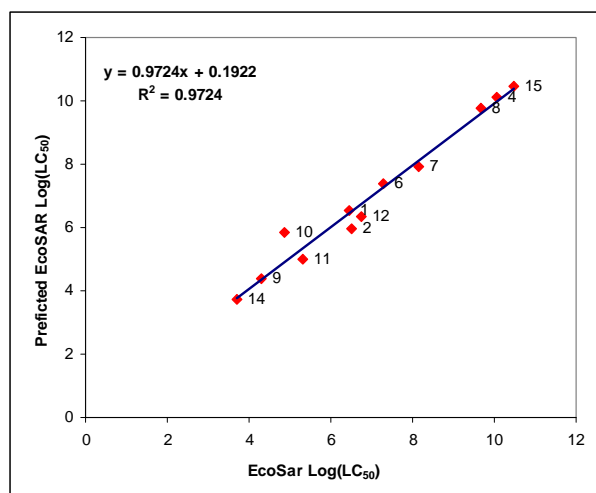


Figure 3 Fit of ECOSAR against predicted Log(LC₅₀) values.

CONCLUSIONS

In summary, we have identified four molecular descriptors that are highly effective in predicting the inhibition of both the oxygen reduction reaction (a proxy for their inhibition effectiveness on aerospace Al-Cu alloys) and for toxicity of the organics towards fish. There are good reasons to expect that these molecular descriptors (or ones similar to them) will also be effective in predicting toxicities to other species and perhaps their mutagenicities and carcinogenicities. The models have been used to predict additional organic structures that are currently undergoing evaluation in epoxy primers.

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