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## New Directions in Corrosion Inhibitor Design



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### ABSTRACT

There have been two main approaches used to construct Structure-Property Relationships for use in the design of better organic corrosion inhibitors. In one approach, additivity models are used to piecemeal select functional groups to build the corrosion inhibitor. This approach makes the assumption that each functional group in the corrosion inhibitor molecule contributes a unique, independent and additive increment to the corrosion inhibition efficiency. In the second approach, a range of 'descriptors' calculated from the molecular structure (these can be molecular electrostatic potentials, quantum mechanical energies, connectivity indices, etc) are regressed against the corrosion inhibitor efficiencies. Both of these approaches have drawbacks. Models using the functional group approach cannot predict the performance of new materials that do not have functional groups in the database. The second approach suffers from chance correlations when large numbers of descriptors are regressed against the corrosion performance. We will present the results of our recent work that provides a quantum mechanical foundation under the functional group approach allowing excellent prediction of corrosion inhibitor performance using just a few variables.

Keywords: corrosion inhibitor, quantum mechanical, hydrophobicity, dative bonding

### INTRODUCTION

The properties that determine the efficiency of corrosion inhibitors operating through adsorption include their solubility, their rate of diffusion to a metal surface, their hydrophobicity and the strength of their absorption to the metal (or metal oxide) surface. Within a coating, inhibitor solubility becomes a constraint because if the concentration is too high, osmotic blistering causes degradation of the coating. In contrast, organic inhibitors that have very low solubility may require days or weeks to migrate to the metal surface and reach effective equilibrium coverage [1]. Effective corrosion inhibitors also displace water from the metal/metal-oxide surface and can provide a hydrophobic barrier at the metal/metal-oxide surface. Finally, an organic corrosion inhibitor must bond strongly to the metal/metal-oxide to provide high levels of equilibrium coverage at lower concentrations.

We believe that organic compounds offer the best promise for the development of new low-toxicity corrosion inhibitors to replace the more toxic inorganic inhibitors such as hexavalent chromates. The chemical space for organic corrosion inhibitors is still relatively sparsely evaluated when one considers the magnitude of potential new organic compounds that could be synthesized. For example, it has been estimated that the combination of just four elements (e.g. C, N, O, and S) with up to 30 non-hydrogen

atoms would generate  $10^{60}$  unique molecules [2]. In this large chemical space, there are many organic molecules not yet tested that could be effective corrosion inhibitors when coupled with an appropriate delivery system. Considering the extensive time it takes to fully evaluate new corrosion inhibiting compounds, it is clear that high throughput computational methods are needed to select molecular structures for experimental evaluation. We discuss our recent work in the development of new descriptors and structure-activity models for predicting corrosion inhibitor efficiencies from structure.

## QUANTUM MECHANICAL DESCRIPTORS IN CORROSION INHIBITOR SCIENCE

Quantum Mechanical Quantitative Structure Activity Relationships (QM-QSAR) are generally developed by calculating either atom (*e.g.* charge), group (*e.g.* group electronegativity) or molecular (*e.g.* molecular orbital energies) properties and then regressing them against the corrosion inhibition efficiencies [3]. The regression methods that have been applied include ordinary linear least squares, non-linear regression, neural networks, self-organizing maps and genetic function approximation [3,4].

Both local and molecular descriptors are widely used in the development of QM-QSARs. Among the most important local features that are used in QM-QSAR models are charge distributions [5]. Atomic charges have been a key concept in the understanding of many types of chemical reactions, and they are central to the interpretations of a number of other phenomena, such as dipole moments and nuclear magnetic resonance (NMR) chemical shifts. As mentioned above, they also are important parameters in molecular structure–property and structure–activity relations. Consequently, a great many schemes, both quantum chemical and empirical, have been proposed for partitioning the electronic density distribution among the atoms of a molecule.

Computed molecular descriptors are commonly used in developing structure/corrosion-inhibitor activity relationships. Examples of such descriptors include dipole moments, molecular surface area, molecular volume, density, electronic parameters (HOMO, LUMO etc.), polarizabilities, refractive index, distribution/partition coefficients, as well as thermodynamic parameters [3]. HOMO (Highest Occupied Molecular Orbital) and LUMO (Lowest Unoccupied Molecular Orbital) energies have often been found to have high correlation with the corrosion inhibitor activity, but often the correlation only works for a homologous set of molecules [6]. Unfortunately, even with a set of similar molecules, sometimes no correlation between the calculated electronic properties and the corrosion inhibitor activity is found [7]. Recently the use of Density Functional Theory based concepts such as chemical hardness, absolute electronegativity and extent of electron transfer have been used [8].

Unfortunately, molecular descriptors such as those described above are not transferable across diverse sets of molecules (*i.e.* the concept of group additivity). Moreover, in an in-house survey of the corrosion inhibitor literature, we found a number of examples where HOMO and LUMO energies were correlated with corrosion inhibition, but the free energy of adsorption was less than 20-30 kJ/mole. These values imply physisorption of the inhibitors wherein the electrostatic effects dominate bonding between the inhibitor and the metal surface (covalent bond formation generally results in values of >40 kJ/mole for the free energy of adsorption). Thus, the correlations that were previously found by some researchers may be due to other factors that correlate to the HOMO/LUMO energies or their gaps.

A better modeling approach would provide a prediction of whether the interaction between the inhibitor and the metal surface is through physical attraction (*e.g.* electrostatic, van der Waals or hydrogen bonding forces) or bond formation such as covalent or dative bonding. Furthermore, the magnitude of the computed descriptors should correlate with the amount of surface coverage provided by the inhibitor under a given set of conditions. Finally, for high throughput screening, we do not want to have to run through a full quantum mechanical calculation each time we want to screen a new molecule. Therefore, a better modeling approach would allow us to predict the properties of new molecules built up from molecular fragments. In this paper we discuss the results of the use of LogP and a proprietary bonding parameter designated herein as PBP to model corrosion inhibitor efficiencies.

## RESULTS AND DISCUSION

**Model Structure.** In our studies of corrosion inhibitors and their inhibition efficiencies we have observed many similarities between designing corrosion inhibitors and designing therapeutic drugs. Both corrosion inhibitors and drugs must dissolve in water. They need to have enough solubility in water to provide the desired effect, but if there is too high a concentration either toxicity (drugs) or osmotic blistering (corrosion inhibitors) may occur. Another similarity is that drugs need to partition through a hydrophobic cell membrane and corrosion inhibitors partition from water to a (more) hydrophobic metal surface. Finally, both drugs and corrosion inhibitors must react with the active sites (e.g. enzyme cavities and metal atoms respectively) to provide their therapeutic/corrosion-inhibiting effects.

While surveying the therapeutic drug literature, we discovered that the toxicity endpoints for a wide range of compounds had a quadratic relationship with LogP [9-11]. We had previously observed in our work (and the work of others [12], Figure 1) that for a series of corrosion inhibitors having the same head group and hydrophobic tails of increasing length, that the corrosion inhibiting efficiency of the series could be fully explained by a quadratic equation in LogP.

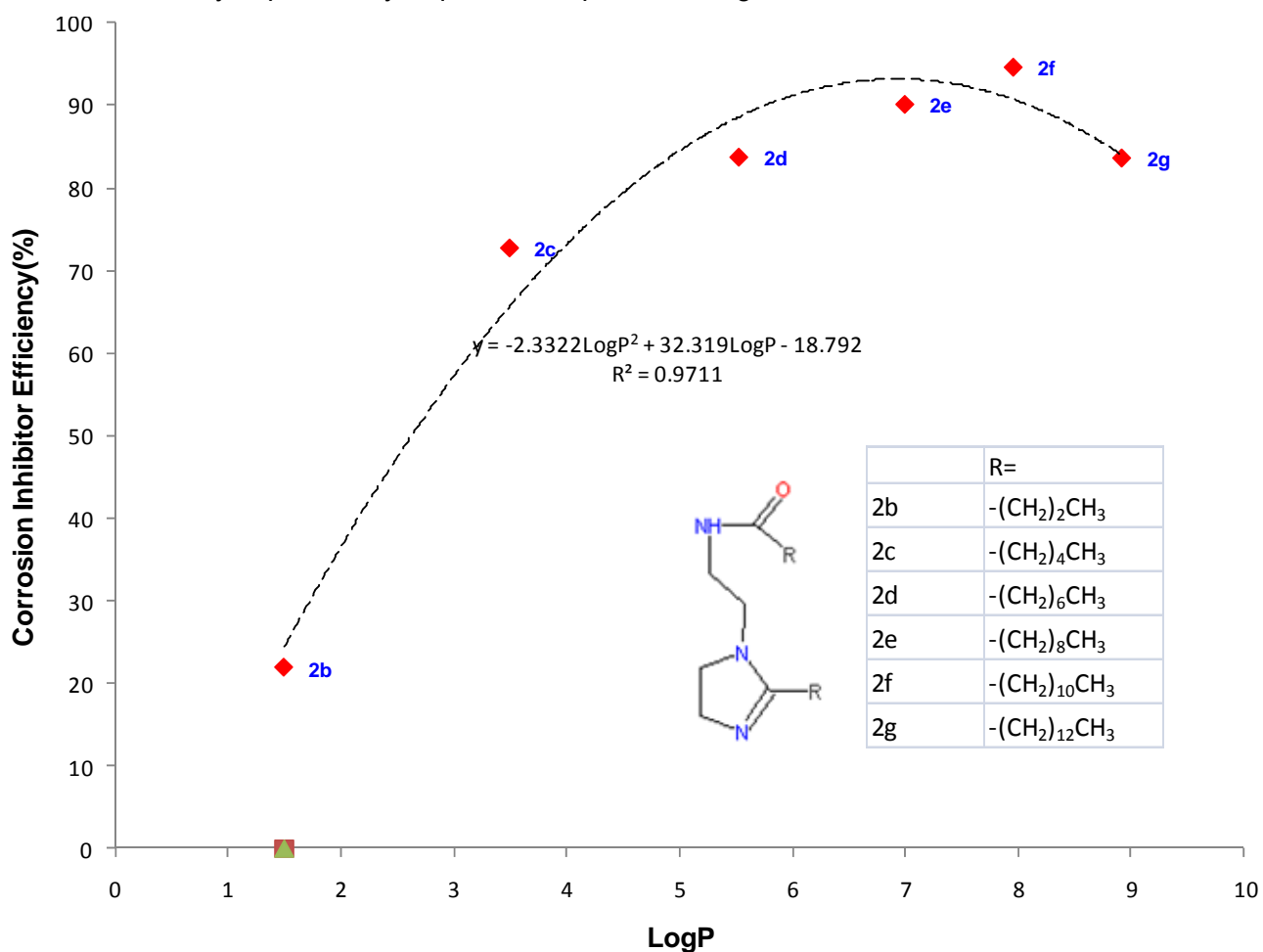


Figure 1 Quadratic relationship between LogP and corrosion inhibitor efficiency

We have identified a rationale for the observed quadratic form of the relationship. The rationale has its basis in the fact that most organic corrosion inhibitors follow either Langmuir or Frumkin adsorption isotherms. If we start with the assumptions that 1) the corrosion rate is proportional to the number of sites that are corroding, 2) that the organic corrosion inhibitors act by adsorbing onto and thereby

blocking the active corrosion sites and 3) the corrosion inhibition efficiency is related to the number of sites blocked we get:

$$CIE(\%) = 100 * \left( \frac{i_{corr(blank)} - i_{corr(blocked)}}{i_{corr(blank)}} \right) \quad (1)$$

where CIE(%) is the corrosion inhibitor efficiency.

The Langmuir isotherm describes (for the majority of organic corrosion inhibitors) the relationship between the concentration of the inhibitor (C), the surface area covered by the inhibitor (e.g. the # of sites blocked) and the equilibrium adsorption constant. The Langmuir isotherm is defined as:

$$K_{ads}C = \left( \frac{\theta}{1-\theta} \right) \quad (2)$$

where  $K_{ads}$  is the equilibrium adsorption constant, C is the concentration and  $\theta$  is the inhibitor coverage. From thermodynamics we know  $\Delta G_{ads} = -RT \ln K_{ads}$  and  $-\Delta G_{ads}/RT = \ln K_{ads}$  and therefore:

$$e^{\frac{-\Delta G_{ads}}{RT}} \cdot C = e^{\ln K_{ads}} \cdot C = K_{ads}C = \left( \frac{\theta}{1-\theta} \right) \quad (3)$$

It is well known that functions such as  $e^x$  can be expressed in expanded form such as a Taylor series. In mathematics, a Taylor series is a representation of a function as an infinite sum of terms calculated from the values of its derivatives at a single point. If the series is centered at zero, the series is also called a Maclaurin series. It is common practice to use a finite number of terms of the series to approximate a function. The Maclaurin expansion of  $e^x$  is given by the expression:

$$e^x = \sum_{n=0}^{\infty} \frac{x^n}{n!} = 1 + x + \frac{1}{2!}x^2 + \frac{1}{3!}x^3 + \frac{1}{4!}x^4 + \dots \quad (4)$$

Using the substitution of  $-\Delta G/RT$  for x we get:

$$e^{\frac{-\Delta G_{ads}}{RT}} = \sum_{n=0}^{\infty} \frac{x^n}{n!} = 1 + \left( -\frac{\Delta G}{RT} \right) + \frac{1}{2!} \left( -\frac{\Delta G}{RT} \right)^2 + \frac{1}{3!} \left( -\frac{\Delta G}{RT} \right)^3 + \frac{1}{4!} \left( -\frac{\Delta G}{RT} \right)^4 + \dots \quad (5)$$

and

$$e^{\frac{-\Delta G_{ads}}{RT}} = \sum_{n=0}^{\infty} \frac{x^n}{n!} = 1 + \left( -\frac{\Delta H}{RT} - \frac{\Delta S}{R} \right) + \frac{1}{2!} \left( -\frac{\Delta H}{RT} - \frac{\Delta S}{R} \right)^2 + \frac{1}{3!} \left( -\frac{\Delta H}{RT} - \frac{\Delta S}{R} \right)^3 + \frac{1}{4!} \left( -\frac{\Delta H}{RT} - \frac{\Delta S}{R} \right)^4 + \dots \quad (6)$$

We can bridge Equation 6 to the equations for conic sections. In two dimensions the general equation for conic sections is:

$$Z = aX^2 + bY^2 + cX + dY + eXY + constant \quad (7)$$

and through axis rotation we can get rid of the cross terms:

$$Z = aX^2 + bY^2 + cX + dY + constant \quad (8)$$

This equation is equivalent to the Maclaurin expansion to the second term or:

$$e^{-\frac{\Delta G_{ads}}{RT}} = CIE(\%) = a \left(\frac{\Delta H}{RT}\right)^2 + c \left(\frac{\Delta H}{RT}\right) + b \left(-\frac{\Delta S}{R}\right)^2 + d \left(-\frac{\Delta S}{R}\right) + constant \quad (9)$$

LogP is defined as the logarithm of the ratio of concentrations of a compound in the two phases of a mixture of two immiscible solvents at equilibrium. The most widely used partition constant is based on water as one solvent and a second hydrophobic solvent such as 1-octanol. The partition constant is thus a measure of how hydrophilic ("water loving") or hydrophobic ("water fearing") a compound is. We believe that LogP is a good proxy for the latter two terms of Equation 9. To partition from the water to the metal/metal-oxide surface, the organic compound must lose its shell of water molecules (a change in entropy for the water molecules forming the cavity around the organic) and also displace water molecules from the metal/metal-oxide surface (again a change in entropy for the water molecules).

For organics such as those shown in Figure 1, bonding to the metal surface does not significantly change for a series of similar molecules, and with the assumption that LogP is a good proxy for the entropic term, Equation 9 simplifies to:

$$e^{-\frac{\Delta G}{RT}} = CIE(\%) = bLogP^2 + dLogP + constant \quad (10)$$

Hence, we see a good quadratic fit to CIE(%) with LogP in Figure 1. LogP values were calculated using the online application at [www.vcclab.org](http://www.vcclab.org). For a series of compounds exhibiting a wider range of bonding energies, both the enthalpy and entropy terms in Equation 9 would be required. In the next section we discuss the use of LogP and a proprietary bonding parameter (PBP) to model a wide range of corrosion inhibiting compounds.

**Application of the Model to Corrosion Inhibition.** In addition to the entropic term in Equation 9 there is also an enthalpic term. A good proxy for this enthalpic term is the bonding energy of the corrosion inhibitor to the metal surface. Unfortunately, calculations using a large representative slab of the surface are too computationally expensive to be useful for screening large numbers of molecules. Therefore, we evaluated potential proxy structures and found that Fe(OH)<sub>3</sub> was a surprisingly good proxy for the oxide covered iron surface. Using Gaussian 09 and the functional/basis-set M06/6-311+G(d,p) we calculated the Self Consistent Field (SCF) energies for the inhibitor, for Fe(OH)<sub>3</sub> and for the inhibitor:Fe(OH)<sub>3</sub> complex. The "stabilization energy" corresponds to the SCF energy of the inhibitor:Fe(OH)<sub>3</sub> complex minus the calculated SCF energies of the inhibitor and Fe(OH)<sub>3</sub>. Several hundred of these energies were calculated and then used to screen descriptors that correlated with the SCF stabilization energies. We identified a proprietary bonding parameter that linearly scales with the SCF stabilization energies (Figure 2). In Figure 2, the upper line represents inhibitors with no hydrogen bonding to Fe(OH)<sub>3</sub> and the lower line represents inhibitors with hydrogen bonding (in addition to the main bonding between the inhibitor and the metal atom) to Fe(OH)<sub>3</sub>. Having identified a suitable bonding parameter we then evaluated its use as a proxy for the enthalpic term in Equation 9.

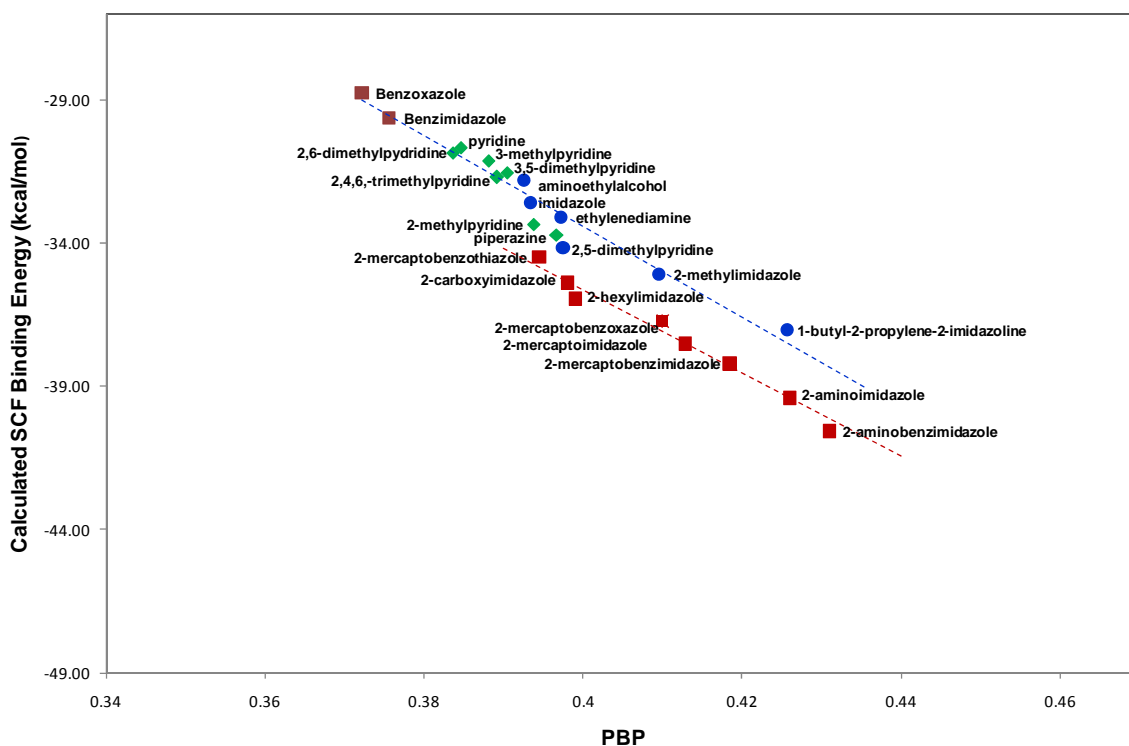


Figure 2. Correlation of proprietary bonding parameter with SCF stabilization energy.

Zhang and coworkers [13] evaluated the corrosion inhibition efficiencies (CIE(%)) for a set of 33 compounds, including amines, imidazolines, imidazoles and benzimidazoles. We found that a comparison of the LogP and PBP values for the compounds in the dataset allow separation of the compounds into three classes. In Class 1 (comprising the compounds piperazine, aminoethylalcohol,

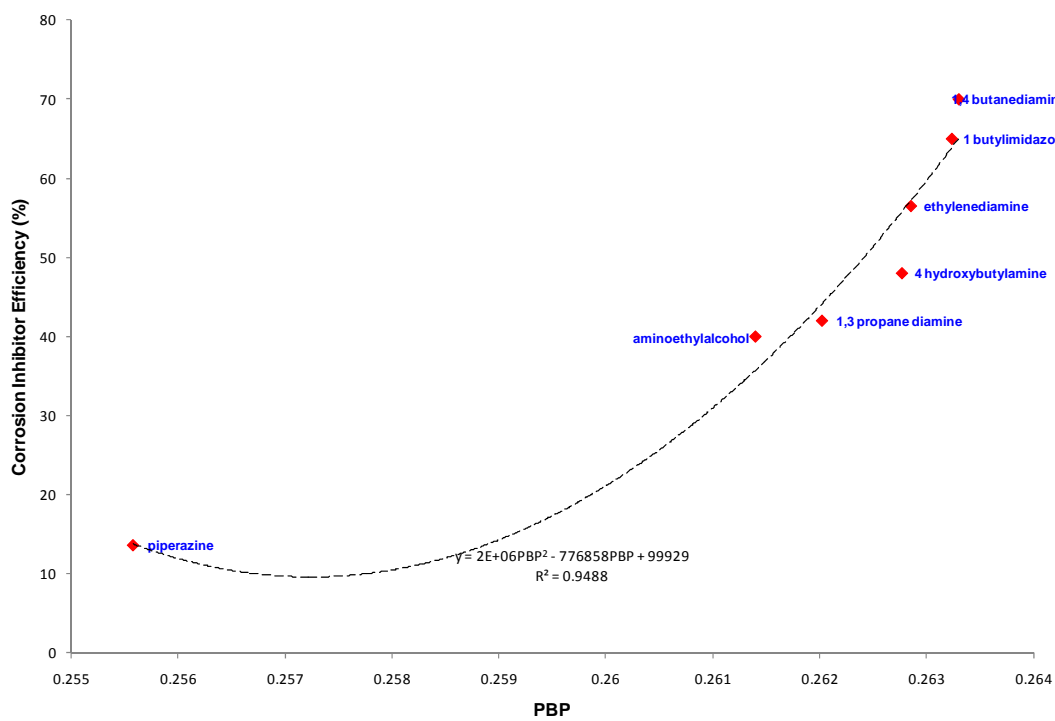


Figure 3. Correlation between PBP and CIE(%) for a water-soluble subset of the Zhang et al. dataset [13]

1,3-propane diamine, 4-hydroxybutylamine, ethylenediamine, 1-butylimidazolyl and 4-butanediamine), the compounds are all water soluble (i.e. they all have small or negative LogP values). For these compounds we found that the corrosion inhibitor efficiencies could be modeled using PBP in the quadratic form (Figure 3). For these water soluble compounds the contribution from the entropic term is small and the corrosion inhibition efficiencies are dominated by the enthalpic term. A second class comprises compounds with high LogP values (e.g. 2-(3-pyridyl)benzimidazole, 2-phenylbenzimidazole, 2-phenylimidazole, 2-(11-amino)phenylbenzoimidazole, 2-benzylbenzimidazole, benzimidazole and 2-hexylimidazole). These compounds (all imidazoles and benzimidazoles) exhibit similar PBP values and as mentioned above have high LogP values. Therefore, these compounds can be fit using just LogP in the quadratic form (Figure 4).

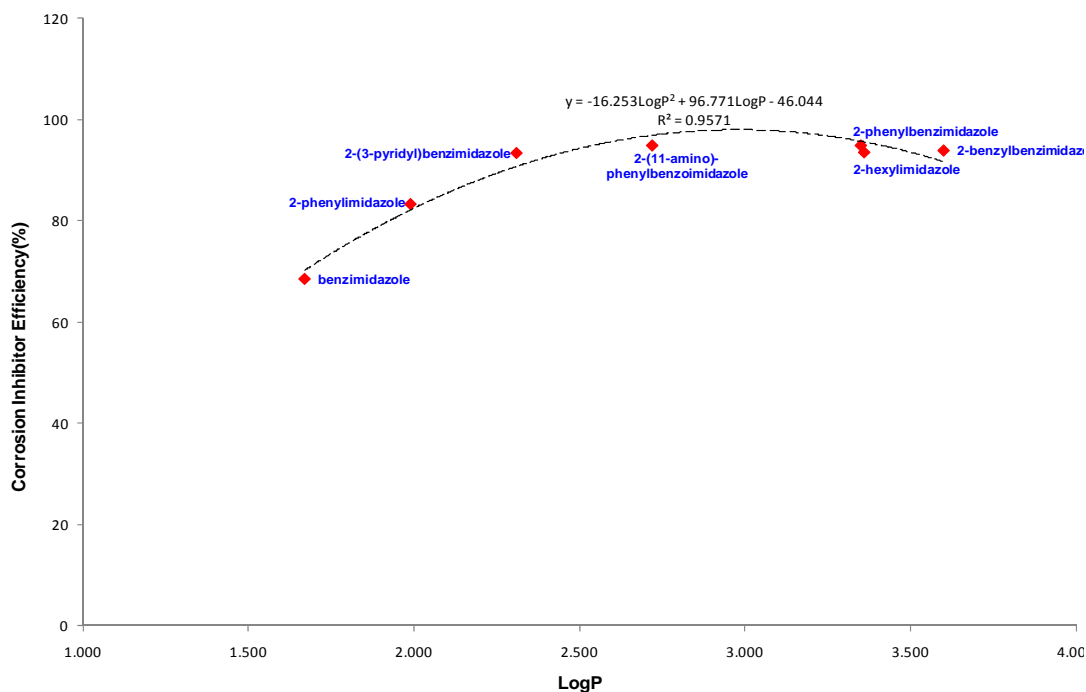


Figure 4. Correlation between LogP and CIE(%) for the hydrophobic subset of the Zhang et al. dataset [13]

In the third class of compounds, the values for LogP and PBP are intermediate in nature and neither descriptor dominates the corrosion inhibitor efficiencies. For this class of inhibitors in the Zhang et al. dataset [13] we found it was possible to fit the corrosion inhibitor efficiencies using both LogP and PBP (Figure 5). It may be possible to fit the entire set (Class 1-3) of compounds using truncated power splines. With truncated power splines the function  $f(n) = \langle f(x) - \alpha \rangle$  is equal to  $f(x) - \alpha$  if  $f(x) - \alpha > 0$  and equal to 0 if  $f(x) - \alpha$  is less than 0. The symbol  $\alpha$  is called knot. The objective of fitting with truncated power splines is to identify knots that segregate the data set into segments that can be fit with the appropriate basis functions. Thus we may be able to partition the Zhang et al [13] dataset using LogP and PBP and their associated knots.

We have successfully applied the model framework using the quadratic forms of LogP and PBP to over thirty corrosion inhibitor studies. A few additional illustrative examples are provided below. Hackerman and coworkers [14] have studied the inhibitive properties of a series of heterocyclicdiazoles including 3-amino-1H-isindole (AIN), indazole (IND), imidazole (IMZ), 4-bromoimidazole (BIM), 4-methylimidazole (MIM), pyrazole (PYR), 4-sulfopyrazole (SOP), and 4-nitropyrazole (NOP). The corrosion inhibitor studies for the cold rolled steel panels were carried out in aqueous solutions of 1M HCl. This group of compounds is roughly characterized by low to moderate PBP values and low to moderate LogP values. The most effective compound (AIN) has the highest PBP value and the second highest LogP of the group. The least protective compound (SOP) has the next to lowest PBP value and the smallest (e.g.

the most water soluble) LogP. Since the compounds were characterized by intermediate values of LogP and PBP the corrosion inhibitor efficiencies were fitted using the double quadratic form of LogP and PBP. The result is shown in Figure 6

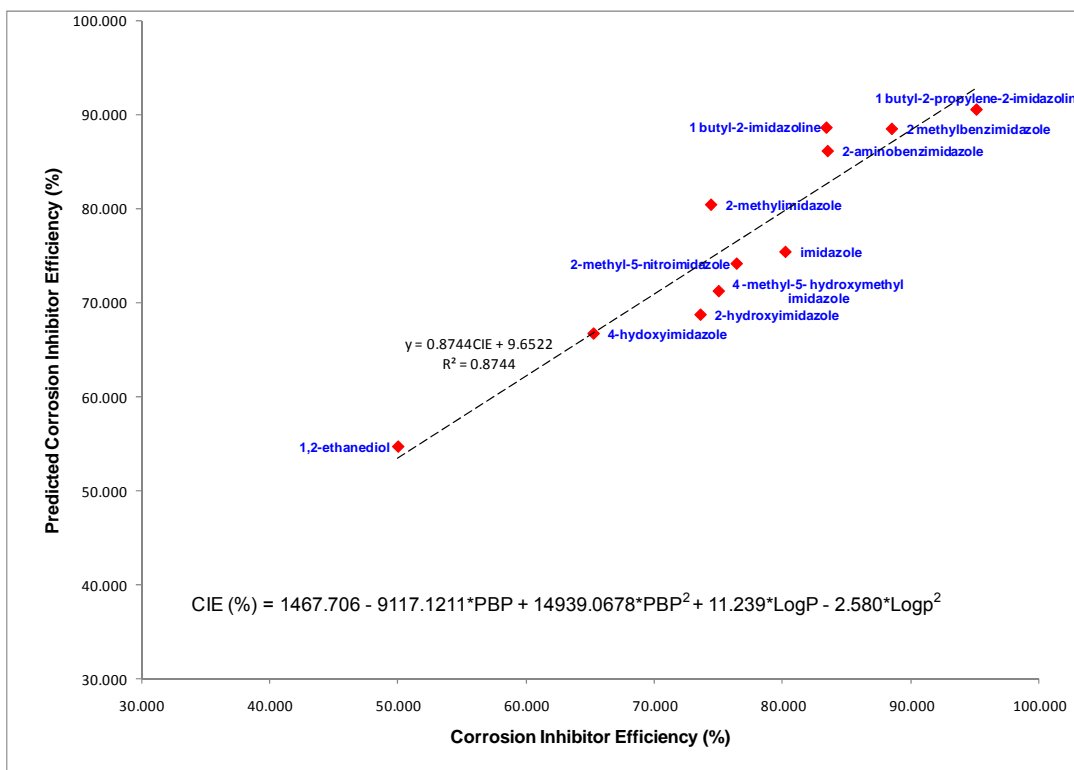


Figure 5. Plot of CIE(%) and predicted CIE(%) using a two parameter fit for compounds having an intermediate set of LogP and PBP values (Zhang et al [13])

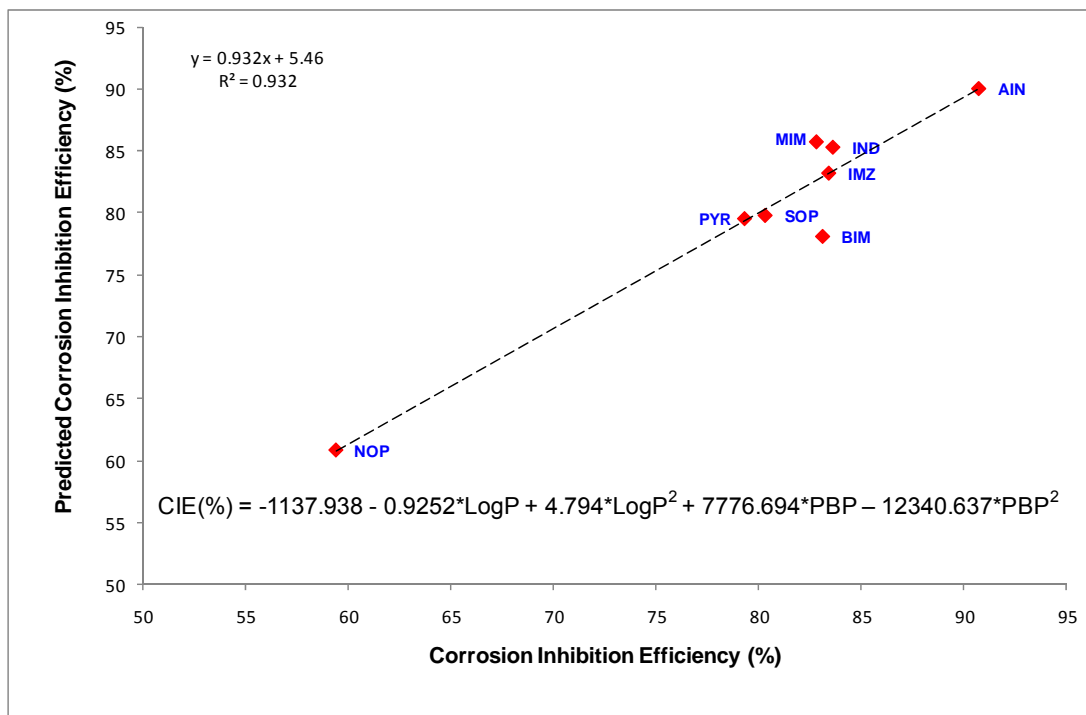


Figure 6. Plot of CIE(%) and predicted CIE(%) using a two parameter fit for compounds having an intermediate set of LogP and PBP values Babić-Samardžija et al [14])



Since the quadratic form was developed using the relationship between the Langmuir isotherm and the free energy of adsorption at equilibrium, we also expected that the quadratic form arrived at in Equation 10 could be applied to the free energies of absorption of organic corrosion inhibitors on steel. Popova and coworkers [15,16] studied the adsorption of a series of benzimidazoles, indole, benzothiazole, benzotriazole and benzothiadiazole on cold rolled steel in aqueous HCl. In these studies the authors did not find a simple correlation between electronic parameters (e.g. HOMO, LUMO, etc) and the inhibitor efficiencies even though the series of benzimidazoles represents a homologous set of compounds. The values of LogP and PBP for compounds in Popova et al. [15,16] were regressed against free energies of adsorption using the quadratics (i.e. quadratic in LogP, PBP and the dipole moment (DM)). An excellent fit was obtained and the results are shown in Figure 7.

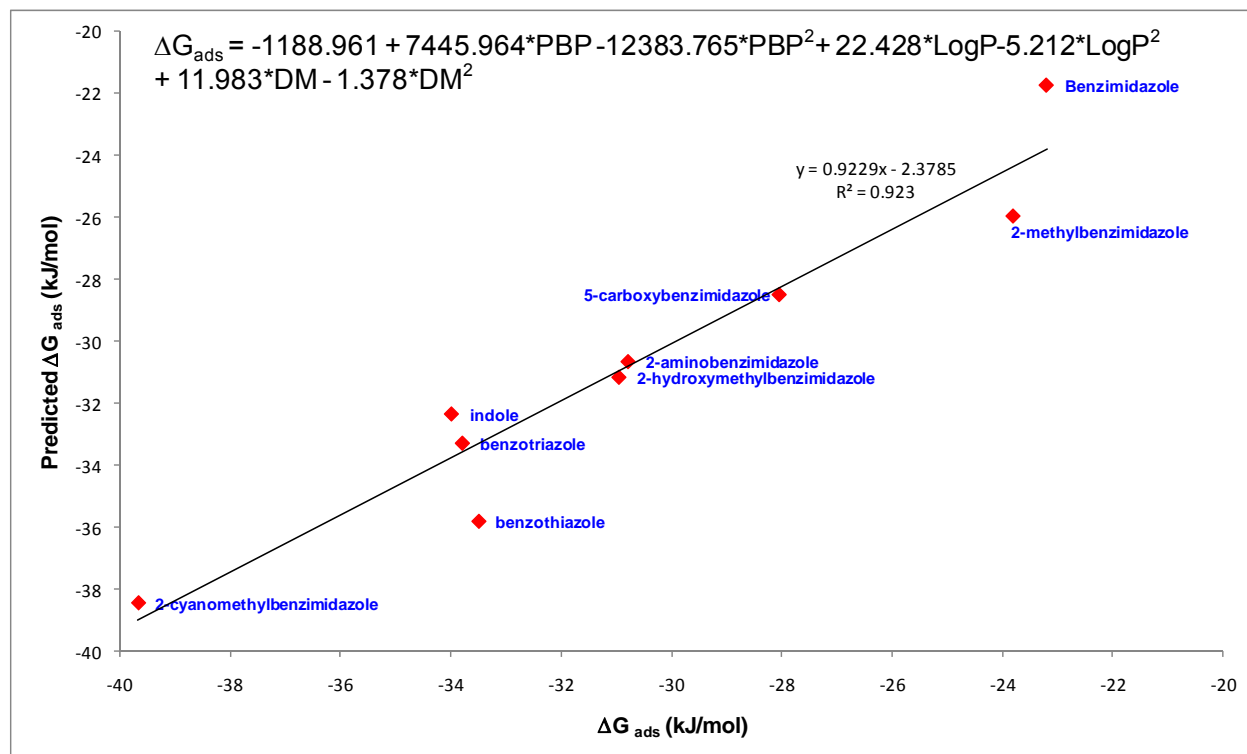


Figure 7. Plot of  $\Delta G_{ads}$  and predicted  $\Delta G_{ads}$  using a three parameter fit for compounds having an intermediate set of LogP and PBP values (Popova et al [15,16])

The adsorption isotherms of the compounds studied by Popova et al [15,16] were found to be best described by a Frumkin isotherm. The Frumkin isotherm differs from the Langmuir isotherm by providing for interactions between adsorbed molecules. Typically, interactions between molecules adsorbed on a metal surface are dipole-dipole interactions [17]. Dipole-dipole interactions can be stabilizing if the molecules are adsorbed parallel to the surface or destabilizing if the molecules are adsorbed perpendicular to the surface [17]. Thus in Figure 7, the best fit to the free energies of adsorption includes the quadratic form of the dipole moment (DM) of the organic compounds as an additional factor in addition to PBP and LogP.

In addition to the results presented above, we have also applied the quadratic forms of LogP and PBP to several other studies. In Ramachandran et al. [18] a series of imidazolines with pendent tails ranging from  $C_7$  to  $C_{21}$  in length were studied for their corrosion inhibiting properties. As we observed for the compounds studied by Duda et al. [12], a simple fit using the quadratic form of LogP could be obtained:

$$CIE(\%) = -5.365 * \text{LogP}^2 + 62.915 * \text{LogP} - 92.865 \quad (r^2 = 0.943) \quad (11)$$

All of the corrosion inhibition studies that we initially evaluated have been for cold rolled mild steel in aqueous HCl. We have begun to apply the new modeling approach to other metals (e.g. copper) and alloys (aluminum and brass and stainless steel). Cardoso et al. [19, 20] have studied the effect of amines, thioureas and unsaturated alcohols on the corrosion of 22%-Cr stainless steel (austenitic-ferritic) [19] and 13%-Cr stainless steel (martensitic) [20]. We made the assumption that the protective nature of stainless steels is due to the predominance of chromium oxide on the metal surface. Therefore, the surface proxy for high chromium stainless steels should be  $\text{Cr}(\text{OH})_3$ . We calculated PBP for the interactions of the inhibitors with  $\text{Cr}(\text{OH})_3$  and regressed PBP along with LogP for compounds in Cardoso et al. [19]. We are about halfway through our calculations on the Cardoso et al. datasets but we have included in Figure 8 at least one member from each of the families of inhibitors used in the Cardoso et al. [19] studies (e.g. primary amine, secondary amine, tertiary amine, aromatic amine, thioureas and unsaturated alcohols).

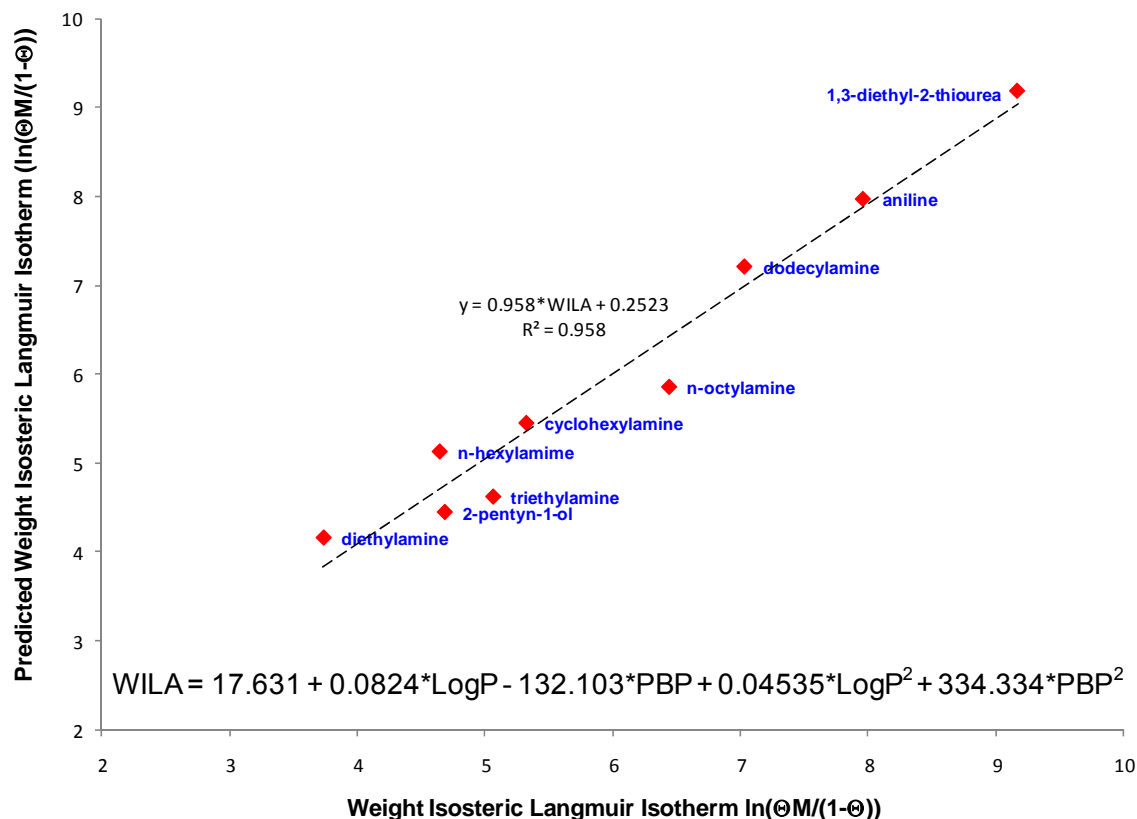


Figure 8. Plot of WILA and predicted WILA using a two parameter fit for compounds having an intermediate set of LogP and PBP values (Cardoso et al [19])

The metric used by Cardoso et al. for corrosion inhibition efficiency is the Weight Isosteric Langmuir Isotherm (WILA,  $\ln(\Theta M/(1-\Theta))$ ) where  $\Theta$  is the coverage and  $M$  is the molecular weight of the inhibitor. As Figure 8 illustrates, a good fit has been achieved for the compounds for which PBP and LogP have been calculated to date. Since we have included one member from each of the families studied by Cardoso et al. [19], we expect to get a good fit to all 23 compounds. Similarly, we also get a good fit for the 13%-Cr stainless steel (martensitic) (Cardoso et al. [20]):

$$WILA = 17.63 + 0.082 * \text{LogP} - 132.10 * \text{PBP} + 0.045 * \text{LogP}^2 + 334.33 * \text{PBP}^2 \quad (r^2 = 0.902) \quad (12)$$

## CONCLUSIONS

A new model framework for correlating the molecular-structure/electronic-properties of corrosion inhibitors and their inhibition efficiencies for cold rolled steel has been developed. The framework is based on the relationship between the Langmuir isotherm and the free energy of adsorption of organic corrosion inhibitors. The free energy of adsorption can be rewritten in a quadratic form using the Maclaurin expansion of  $e^{\Delta G_{ads}}$ . The expansion results in a double quadratic of an entropic term and an enthalpic term. As a proxy for the entropic term we have selected LogP. For the enthalpic term we have identified a proprietary bonding parameter (PBP) that shows a strong linear correlation with the calculated stabilization energy of inhibitor:Fe(OH)<sub>3</sub> complexes. The double quadratic of the two terms provides good fits ( $r^2 > 0.90$ ) for the corrosion inhibition of steel with organic corrosion inhibitors for our 30 systems studied to date. For corrosion inhibitors whose adsorption isotherms are best modeled with a Frumkin isotherm the dipole moment may also be added to account for the interaction between inhibitors. Work is ongoing to develop a master equation to fit all the corrosion inhibitor data to a single QSAR relationship.

In addition to cold rolled steel, the model framework has been extended to stainless steels whose surfaces are predominantly covered with a chromium oxide layer. To model these systems, inhibitor:Cr(OH)<sub>3</sub> complexes were evaluated to provide the appropriate PBP parameters. Preliminary work has shown that the model framework can be applied to aluminum/aluminum-oxide, zinc, magnesium and copper. The new framework allows for new organic corrosion inhibitors to be designed by calculating their respective LogP and PBP values and estimating their inhibition efficiencies.

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