

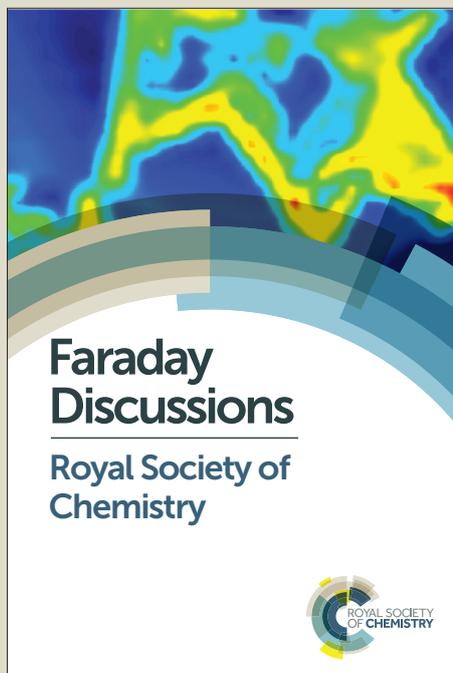
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## ARTICLE

# Multiphysics modelling, quantum chemistry and risk analysis for corrosion inhibitor design and lifetime prediction

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Organic corrosion inhibitors can provide an effective means to extend the life of equipment in aggressive environments, decrease the environmental, economic, health and safety risks associated with corrosion failures and enable the use of low cost steels in place of corrosion resistant alloys. To guide the construction of advanced models for the design and optimization of the chemical composition of organic inhibitors, and to develop predictive tools for inhibitor performance as a function of alloy and environment, a multiphysics model has been constructed following Staehle's principles of "domains and microprocesses". The multiphysics framework provides a way for the science-based modelling of the various phenomena that impact inhibitor efficiency, including chemical thermodynamics and speciation, oil/water partitioning, effect of the inhibitor on multiphase flow, surface adsorption and self-assembled monolayer formation, and the effect of the inhibitor on cathodic and anodic reaction pathways. The fundamental tools required to solve the resulting modelling from a first-principles perspective are also described. Quantification of uncertainty is significant to the development of lifetime prediction models, due to their application for risk management. We therefore also discuss how uncertainty analysis can be coupled with the first-principles approach laid out in this paper.

## Materials Sustainability through Molecular Control of Corrosion

Corrosion control plays a significant role in materials sustainability as it provides one means for the optimization of the stability and longevity of structural materials exposed to either the common elements of nature or the more extreme chemical and/or high-pressure/high-temperature environments encountered in industrial chemical, metallurgical and energy production.<sup>1</sup> Effective corrosion management, including the appropriate selection and application of organic corrosion inhibitors, allows the use of abundant and inexpensive mild steel for the majority of our energy infrastructure (*i.e.* pipelines, refineries), reduces the incidence of costly environmental and safety impacts that would result from corrosion failures, and prevents the need for sourcing more costly and scarce metals that would be required to produce intrinsically corrosion resistant alloys.<sup>2</sup>

Molecular systems deployed for corrosion inhibition are usually selected through intensive experimental testing and then combined with chemical surfactants and biocides to produce a commercial package that is then injected into the pipeline.<sup>2</sup> Successfully designed inhibitor molecules interfere with mechanisms of corrosion in such a way as to reduce the rate of corrosion by at least two orders of magnitude. The inhibitor efficiency (*I.E.*)

quantifies the extent to which corrosion rate without inhibition ( $C_r^0$ ) is reduced to the corrosion rate with inhibition ( $C_r^i$ ), expressed as the percentage decrease:

$$I.E. = 100\% \times (C_r^0 - C_r^i)/C_r^0, \quad [1]$$

Over time the efficiency of the inhibitor is reduced due to equilibrium desorption, mechanical shearing or chemical reactions. Inhibitors are therefore injected either in continuous or batch mode to maintain a protective environment. Inhibitors can also be applied using slow-release agents – polymers that release low-levels of the inhibitor molecules over time – or embedded into coatings and primers.<sup>3,4</sup>

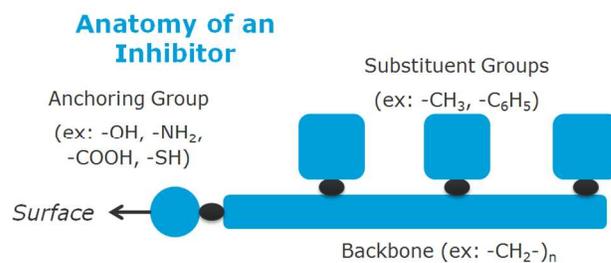


Figure 1. Inhibitor molecule structure provided along with some example chemical fragments for each component.

An inhibitor molecule is typically constituted of three parts: A functional group anchor, a hydrocarbon backbone, and functionalized substituents (Figure 1).<sup>2</sup> From the perspective of a chemist, the design and selection of effective inhibitors should be viewed as the activity of constructing the optimal (anchor, backbone, substituent) triplet for a given materials/environment combination.<sup>5</sup> Whereas some effort has been devoted to this problem, primarily using the quantitative-structure-activity-relations approach (QSAR),<sup>6, 7</sup> our intent here is to present an alternative framework based on combining the principles of corrosion science and engineering, quantum chemistry, computational materials science, as well as electrode kinetics, statistical mechanics and thermodynamics. First, however, we provide an overview of the current state-of-the-art in corrosion inhibitor theory and modeling at the molecular scale.

### Theory and Modeling of Corrosion Inhibitors

The molecular structure of an inhibitor will influence its mechanism of action, suggesting that there may exist an optimal molecular design for a particular application. Characterization by atomic force microscopy, quartz crystal microbalance and electrochemical impedance measurements has shown that corrosion inhibitor molecules adsorb onto metal surfaces, and it is generally believed that the formation of this adsorption layer provides the corrosion protection.<sup>8-11</sup> The extent to which the metal surface is covered by the inhibitor is called the surface coverage,  $\theta$ , which usually ranges from 0 to 1 although it is entirely possible for multilayers to form too.  $\theta$  is related to the inhibitor concentration in solution and the Gibbs free energy of adsorption,  $\Delta G_{ads}$ , by the appropriate adsorption isotherm (*i.e.* constant temperature relation). The most common isotherm for describing adsorption is the Langmuir isotherm, but alternatives exist, such as the Temkin isotherm and the Freundlich isotherm.<sup>12</sup> The distinction between the various models is related to the nature of the interactions between the adsorbing molecules. Assuming non-interaction, the Langmuir isotherm is frequently applied to fit observed inhibitor behavior,<sup>13</sup> with general form:

$$K = \frac{\theta}{(1-\theta)C_A} = \exp\left[-\frac{\Delta G_{ads}}{RT}\right], \quad [2]$$

This isotherm model relates the coverage  $\theta$  to the concentration of inhibitor molecule A,  $C_A$ , and the adsorption equilibrium constant,  $K$ .  $RT$  is the product of the ideal gas constant,  $R$ , with temperature,  $T$ .

Given a particular materials/environment combination, the inhibitor efficiency can be considered an intrinsic property of the inhibitor molecule itself (for a given concentration) and so it should be derivable from quantum theory. According to quantum mechanics, all the information one needs to know about a system can be obtained from the wavefunction, which, in turn, is obtained as the solution to the Schrodinger equation:  $\mathcal{H}\Psi = E\Psi$ , in which the quantum mechanical operator  $\mathcal{H}$  contains the physical terms that contribute to the system energy and  $E$  is an eigenvalue.<sup>14</sup>  $\Psi$  is the quantum mechanical wavefunction that is related to the probability density of the electrons in the system (this density,  $\rho$ , is given by  $|\Psi|^2$ ). Any observable quantity  $\langle A \rangle$  can be determined by taking the expectation value of the appropriate quantum mechanical operator  $\mathcal{A}$  applied to the wavefunction via the equation:

$$\langle A \rangle = \int_{-\infty}^{+\infty} \Psi^* \mathcal{A} \Psi dx = \langle \Psi | \mathcal{A} | \Psi \rangle. \quad [3]$$

The angular brackets on the right introduce Dirac notation and the \* indicates the complex conjugate.<sup>14</sup>

Over the latter half of the 20<sup>th</sup> century, powerful techniques were derived alongside the development of microcomputers that allowed the wavefunctions of molecular systems to be obtained with great accuracy.<sup>15-18</sup> Unfortunately, deducing inhibitor efficiency directly from the wavefunction is non-trivial: the operator representing inhibitor efficiency must somehow capture all the relevant information regarding the target material and environment! Instead, Vosta and Eliasek (and then, later, many others)<sup>6, 19-24</sup> introduced the approach utilized in drug design, of attempting to correlate readily computable molecular descriptors (such as the dipole moment or energies of the frontier molecular orbitals) with the inhibitor efficiencies obtained from experiment using the method of linear (and, later, non-linear) regression (Figure 2). Following this approach inevitably leads to a “black-box” approach. The systems of equations derived that relate inhibitor efficiency to molecular properties are generally opaque to the underlying physics involved in inhibition. Consequently they are of little utility for inhibitor prediction, have very poor transferability between different classes of inhibitors, cannot be applied to different materials/environment combinations, and the uncertainties are not quantified.

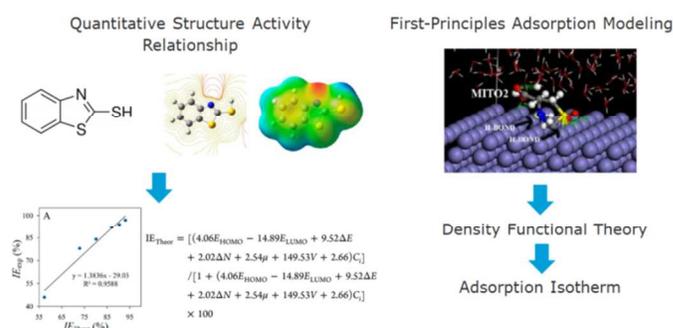


Figure 2. The QSAR approach compared to the first-principles adsorption modeling approach via DFT/atomistic simulation and the construction of an isotherm.<sup>19, 25</sup>

Around the year 2000, the quantum mechanical approaches that were so successful in the molecular realm were becoming capable of simulating surfaces with significant complexity, including metal surfaces with adsorbed molecular species.<sup>26-30</sup> The standard technique for solving the quantum mechanical equations for solid-state systems is known as density functional theory (DFT),<sup>31, 32</sup> and requires the electron density of a material (or material/molecular system),  $\rho$ , to be self-consistently solved according to the Hohenberg-Kohn theorem which computes the energy  $E$  from  $\rho$ .<sup>33-35</sup>

$$E = \int \rho(r)v(r)dr + T[\rho] + \frac{1}{2} \iint \frac{\rho(r_1)\rho(r_2)}{r_{12}} dr_1 dr_2 + E_{xc}[\rho] \quad [4]$$

$v(r)$  is the electrostatic field of atomic nuclei,  $T[\rho]$  is the kinetic energy functional, the double-integral provides the electron-electron interaction (although a self-interaction term is incurred when calculated this way), and  $E_{xc}[\rho]$  is a correction for the errors in the kinetic energy functional and the electron-electron double-integral.

The approaches for quantum chemistry (i.e. molecules) and DFT (i.e. solids and surfaces) have reached a high degree of convergence, such that it is common to find molecular systems treated with DFT and solids treated with quantum chemistry (such as the linear combinations of atomic orbitals).<sup>36</sup> Yet DFT has some important shortcomings that cannot be systematically improved using our current understanding of many-body physics. These shortcomings follow from uncertainty regarding the correct form for the corrections captured by the term  $E_{xc}[\rho]$ .<sup>37</sup> Because of this, all DFT predictions contain an as yet unquantifiable error, and, although much effort has been expended to identify approximate electron correlation functionals that perform well under certain sets of conditions,<sup>28, 38</sup> there is no standard means for estimating the accuracy of a given quantity computed from the self-consistent densities obtained via DFT, even when experimental data is used for “calibration”.<sup>39</sup>

Despite this significant issue, which is an active area of research, DFT is commonly used and considered to have close to “chemical accuracy”. With regards to the particular context of corrosion and interfacial science, density functional theory can be used for predicting the adsorption behavior of materials/molecular systems.<sup>26</sup> For example, DFT has also begun to be applied to explore the mechanisms of inhibition: Kokalj et al. considered the adsorption of a series of molecules on the surface of copper, and computed the binding energies directly from DFT, using them to estimate an adsorption isotherm for the inhibitor and making parallels to the mechanism of inhibition (Figure 2).<sup>40</sup>

One mechanistic simplification that has been applied to relate both experimental and theoretical quantities to the inhibitor efficiency is to assume that the inhibitor efficiency is equivalent to the surface coverage,  $\theta$ . This identity implies that a surface completely covered with inhibitor (i.e. one monolayer, in adsorption parlance) must have a 100% inhibitor efficiency, that is, a corrosion rate of zero.<sup>13</sup>

$$I.E. = 100\% \times \theta \quad [5]$$

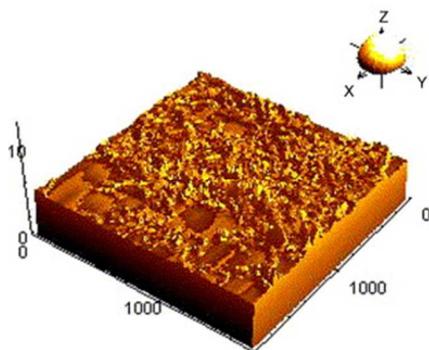


Figure 3. 3D Atomic Force Microscope (AFM) image of mild steel with inhibitor showing loose packing of inhibitor molecules.<sup>10</sup> Scale is in nm.

As observed in Figure 3 a metal surface that is entirely covered with an inhibitor may not have an identically zero corrosion rate.<sup>7, 8, 41, 42</sup> The extent to which corrosion is inhibited will depend upon the efficiency with which the surface is packed: molecules having a bulky topology may leave “gaps” through which metal

atoms can dissolve.<sup>7</sup> This “packing factor” will also be a function of the microstructure of the exposed material surface. Furthermore, the adsorbed inhibitor molecules are in *dynamic* equilibrium with solution, leaving transient opportunities for the underlying metal atoms to dissolve, possibly even dissolving while tethered to an anchoring group. It has also been proposed that some inhibitors act not by blocking the surface dissolution reaction, but instead by blocking the corresponding cathodic reduction reaction, which supplies the counterbalancing electronic and ionic currents that allow dissolution.<sup>2</sup> In the case of pipeline corrosion control, inhibitors have been shown to modify multiphase flow, decreasing the tendency for water to contact the surface.<sup>43</sup> Consequently, there remain many chemical and physical factors that need to be included in a predictive, mechanistic model for corrosion inhibition. In this paper, we argue that such a predictive model can be achieved through an integrated multiphysics modeling approach that includes quantum chemical evaluation of fundamental molecular properties, but also goes beyond that to include aspects of surface adsorption, materials microstructure, and environmental factors such as pH, co-dissolved species and the global properties of the system, such as % water cut and flow rate. Such an approach will be inherently multiphysics in nature, and so we now proceed to briefly introduce the advent of multiphysics modeling and simulation in the materials and chemical sciences.

### Trends in Multiphysics Modeling of Corrosion

Material failures, including corrosion, frequently occur due to the compounding effects of multiple phenomena rather than from one single physical or chemical process acting alone. For this reason models based on an entirely reductionist philosophy will always be insufficient for the purpose of modelling risk, and, in this case, predicting the extent to which risk may be reduced by the application of corrosion inhibitors. Examination of the recent modelling literature in corrosion and related failure modes (such as stress corrosion cracking) reveals the following main modelling approaches in use today:

- Thermodynamic Models
- Fluid Dynamics
- Electrochemistry and Mass Transport
- Atomistic and Quantum Chemistry
- Microstructural Evolution
- Damage Mechanics
- Empirical Modelling

While these methods are most frequently used in isolation (since scientists tend to have narrowly defined fields of expertise), it is widely recognized that interdisciplinary multiscale and multiphysics approaches are required to provide effective engineering tools (Integrated Computational Materials Engineering, ICME).<sup>44, 45</sup> The multiscale modelling paradigm is built upon the recognition that the types of physics occurring at small time and length scales are distinct from those occurring at longer time and length scales. Multiphysics models combine phenomena such as heat and mass transport, or electrode kinetics with fluid mechanics (i.e. not necessarily at different scales and so distinct from multiscale).

As an example of a multiphysics problem-solving approach, molecular dynamics simulations of interactions between the molecules that constitute an oil reservoir were used to predict its megascale thermodynamic properties.<sup>46</sup> The problem of stress-corrosion cracking has seen a lot of attention using multiscale methods that connect long-range stress fields treated via finite element continuum mechanics with atomistic simulations.<sup>47</sup>

Multiphysics and empirical approaches form the subspace of the much larger set of integration tasks that are required to build effective models for materials performance.<sup>48, 49</sup> The circo diagram in Figure 4 embeds these technical scientific and empirical approaches into the larger space of modelling tasks that includes uncertainty quantification and informatics, and draws some connections between them to demonstrate possible integration pathways. Uncertainty quantification includes activities such as the application of Bayesian inference relations,<sup>50</sup> experimental testing and validation, field data collection, damage accumulation models,<sup>51</sup> Monte Carlo simulation,<sup>52</sup> first-order and second-order reliability methods (FORM/SORM),<sup>53</sup> and the identification of knowledge gaps.<sup>54</sup> The informatics tasks include multiphysics simulation,<sup>55</sup> open source code sharing and distribution, machine learning,<sup>52</sup> expert team construction, and data-handling protocols.<sup>56</sup>

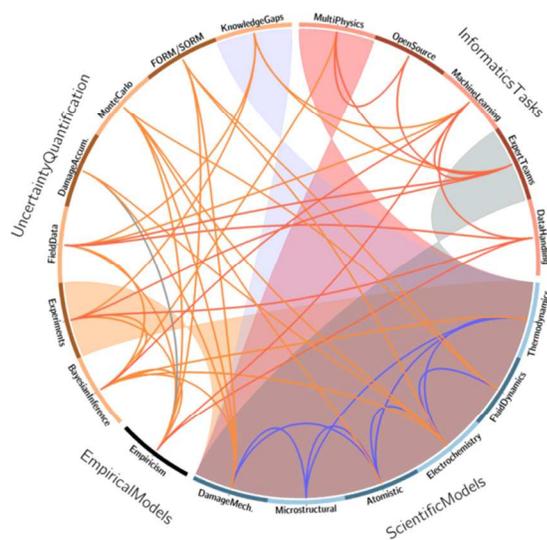


Figure 4. The construction of useful models for materials performance, including models for the design of effective corrosion inhibitor systems, requires the integration of scientific, empirical, uncertainty quantification and informatics tasks.

Given this trend towards integrated computational materials engineering, how does one go about constructing a comprehensive integrated model? Due to the interdependence between chemical environments, flowing oil/water mixtures, materials microstructure, mechanical effects and stochastic behavior, the prediction of the materials/environment response is a non-facile problem that requires a multiphysics approach. Furthermore, the environmental and microstructural conditions in the field will not directly coincide with those in the laboratory, and hence modeling is required to extrapolate laboratory knowledge into applications for

the field with the provision of appropriate bounds on the uncertainty. One approach for beginning to deal with multiphysics phenomena was proposed by Staehle in the microprocess-centric approach, which divides the physical system into a set of *domains* and *microprocesses*.<sup>57</sup> By categorizing the phenomena that lead to the accumulation of corrosive behavior and changes in the material integrity across the domains of the global system – the bulk environment, near-surface environment, the passive film, the near-surface metal and the bulk metal (Figure 5) – a systematic framework was established for predicting the rates of corrosion and the incidence of failures, including those which may not have yet been experienced in the field (unknown unknowns).

By necessity such a framework requires the integration of high-level characterization tools, systems monitoring, experts across the fields of chemistry and materials science, experimental testing and high-fidelity modeling from the atomic scale through to the systems level. Examples were provided in Staehle's original paper for how this approach could be used to predict hitherto unforeseen failure modes from sulfur and lead-assisted stress corrosion cracking in a light water reactor environment.<sup>57</sup>

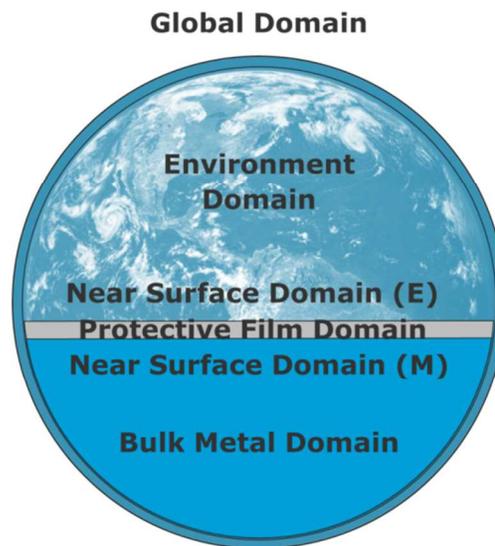


Figure 5. Schematic illustration of the decomposition of a global corrosion via the domains-microprocesses sequence approach.<sup>57</sup>

Despite the apparent appeal of attempting to rigorously model a complex system like a corrosion pipeline entirely from first-principles (like quantum chemistry or atomistic simulation, for example), even given the most optimistic estimates of future available computing power, the task itself would be entirely intractable.<sup>58,59</sup> Considering that 1 km of pipeline could include approximately  $10^{15}$  micron-sized grains and precipitates, with a similar order of magnitude of grain boundaries, and each grain comprising  $\sim 10^{15}$  atoms, even a simulation that operates at the mesoscopic level of grains would be too complex to be computationally tractable. Instead, it makes more sense to decompose the corrosion phenomena into distinct length scales according to their heterogeneity. For instance, megascale conditions,

such as local climates might vary on the length scale of 10's of kilometers ( $10^4$  m). Soil quality, on the other hand, might vary on the order of meters ( $10^0$  m). Galvanic cells and other electrochemical conditions would vary on the level of centimeters to millimeters ( $10^{-3}$ - $10^{-2}$  m). Microstructural variations within the material occur on the length of the grain size, sub-microns to tens of microns ( $10^{-7}$ - $10^{-5}$  m). Atomic scale heterogeneities, including point-, line- and planar-defects take place over nanometer and sub-nanometer scales ( $10^{-10}$ - $10^{-8}$  m). Thus it would suffice to explore, using advanced characterization and *ab initio* models, the contributors of microstructural effects under the possible set of variations that may be introduced at the higher length scales. Since the materials microstructure is likely to remain similar at points along the multi-kilometer stretches of material, appropriate parameters from the lower length scale could be used in the higher length scale models. Thus, the hierarchical approach to multiscale modeling provides an efficient pathway to obtaining an integrated approach. A similar breakdown and integrated multiscale approach has been proposed by Cole and Marney, using the four sub-categories of electrochemical activity, oxide scales, local macro-environmental parameters (eg: soil pH), and general external environmental factors (eg: seasonal variations), drawing from the extensive models developed by soil scientists and hydrologists.<sup>60</sup>

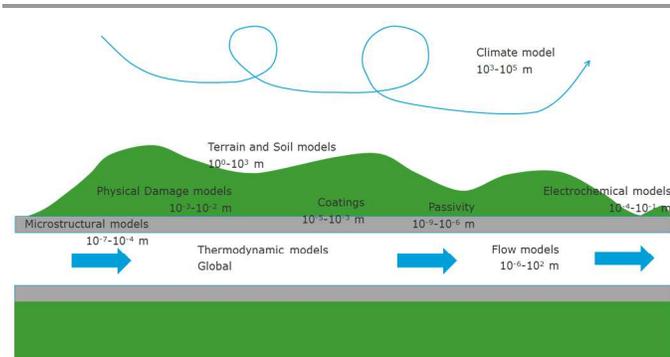


Figure 6. Illustration of the integrated modeling approach to pipeline corrosion, showing a number of contributing factors that are amenable to modeling at various length scales.

### An Integrated Multiphysics Corrosion Inhibition Model

In this section we now apply the domains and microprocesses approach to develop a multiphysics framework for the prediction of inhibitor efficiencies and eventual inhibitor design. In this way we will construct the phenomenological links between the inhibitor performance as a corrosion suppressor and the molecular properties of the inhibitor in a way that also incorporates the role of the materials and environment conditions.

We first identify the relevant domains, with reference to the schematic provided in Figure 5. The environment domain is the content of the pipeline, in this context a hydrocarbon oil of complex composition with some fractional water cut, which may in turn contain carbonates, sulphides, chlorides and other inorganic and organic aqueous neutral and ionic species, including the applied inhibitor. Processes that are relevant to inhibitor performance in this domain will include partitioning of the inhibitor molecule to either

the aqueous or hydrocarbon phases, acid-base equilibria in the aqueous phase, the association of ions to form salts or dissolved ion-pairs, and the aggregation of species to form micelles. The fluid is also in a state of mass transport by convection and so flow processes are also relevant including the entrainment of water by the hydrocarbon under certain conditions of temperature, flow velocity and water cut.<sup>61-66</sup>

The near surface domain will have two possible natures depending on the relative metal/water and metal/oil interfacial energies and the water cut. In the case of an oil-wetted surface, corrosion will already be significantly reduced, and hence the role of the inhibitor will be less relevant. In the case of a water-wetted surface, corrosion can become significant, and hence the role of the inhibitor becomes critical. The near surface domain in this case will be dominated by three key processes: mass transport of inhibitor and corrosive species towards the surface, and the mass transport of corrosion products away from the surface, and the possible reaction of corrosion products with either the inhibitor or other molecules and ions in solution, which may reprecipitate as scale-formers.<sup>67, 68</sup>

The surface domain is the domain in which the inhibitors may adsorb or desorb and form a corrosion inhibiting film. The film will retard chemical reaction by occupying metal sites through the formation of chemisorbed or physisorbed layers. The film properties, such as the nature of dynamic equilibrium and the permeability of the film to cation and anion transport, will determine the extent to which corrosion is reduced. Inhibitors may adsorb as neutral molecules, or as dipolar films consisting of a charged inhibitor (anionic or cationic) with a counteranion pair.<sup>63, 69-71</sup>

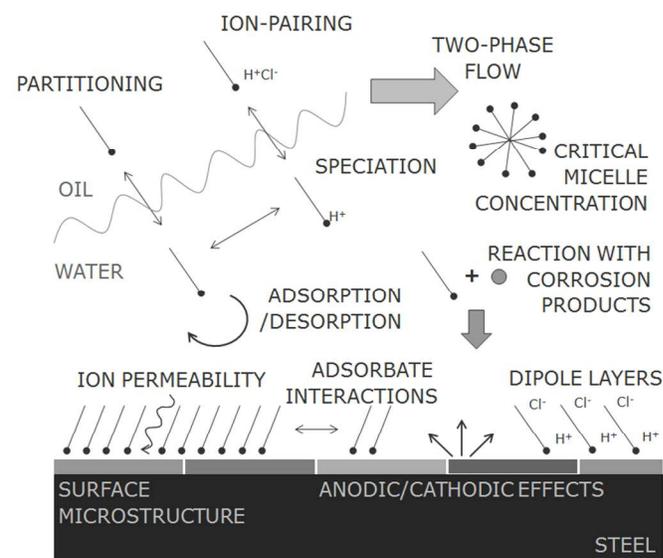


Figure 7. Processes that affect the overall efficiency of a corrosion inhibitor across the environment, near-surface environment, surface and near-surface metal domains.

Globally, the system will be subject to certain temperatures and pressures, morphological features, such as joints, welds, stress-states and Galvanic effects.

On the metallic side, processes in the near-surface domain will dictate what types of surfaces are exposed to the environment.

The materials microstructure will determine the relative distribution of cathodic and anionic corrosion sites, for example. Heterogeneities in the surface can drive certain localized corrosion modes, such as pitting.<sup>68, 72, 73</sup>

These domains and processes relevant to the overall mechanism of inhibitor action are presented schematically in Figure 7, and tabulated in Table 1.

We now proceed to outline some of these processes in more detail and provide ways in which the suite of modelling tools presented in Figure 4 can be applied to develop a comprehensive molecules-to-materials approach for corrosion inhibitor modelling and design.

Table 1. Domains, processes and primary components.

Domain	Micro-process	Constituents
<b>Environment</b>	Partitioning Acid-base equilibria Ion-pairing Micellization Convection Solubility of gases Entrainment	Hydrocarbon oil of complex composition Water Carbonates, sulphides, chlorides and other inorganics Organic aqueous neutral and ionic species
<b>Near surface environment</b>	Oil versus water wetting Mass transport Reaction with corrosion products Precipitation	Oil Water Diffusion layers Corrosion products Scales
<b>Surface</b>	Adsorption (chemisorption, physisorption) Desorption Diffusion Corrosion Cathodic, anodic processes	Inhibitor Metal ions Oxygen Hydrogen (H <sup>+</sup> , H <sub>2</sub> ) Water
<b>Near-surface metal</b>	Localized corrosion Defect mobility Galvanic coupling Dealloying Corrosion products	Intermetallics and precipitates Passive films Scales Defects (grain-boundaries, dislocations) Depletion layers Residual stress
<b>Global</b>	Macroscopic variations in temperature, pressure and inhibitor concentration Cathodic protection Galvanic coupling/cladding	Joins Welds Pipe stress Cladding

### Speciation of the inhibitor molecule in the environment

Inhibitors can be ionized by reaction with water according to their acid-base properties, which is quantified by the acid dissociation constant, pKa. Cheminformatics techniques, based on functional group recognition, can predict acid dissociation constants for a given molecular structure with a high level of accuracy. Quantum chemical methods based on calculating the free energy of acid dissociation are also available.<sup>74</sup>

Ionized inhibitors can also form ion pairs that affect the oil-water partition coefficient in the presence of anions like chloride. The extent of ion pair formation is also predictable through quantum chemical calculations of the free energy of ion association.<sup>75</sup>

Inhibitors in neutral or ion-pair states can also form micelles that will limit their ability to form self-assembled monolayers on exposed metal surfaces.<sup>61, 76</sup> This latter effect is measured by the critical micelle concentration and can be predicted to some extent from classical molecular dynamics or quantum chemical calculations, although such tools are not widely available.<sup>77-83</sup>

### Partitioning of the inhibitor species between the oil and water phases

Inhibitor molecules partition unequally between water and oil, depending upon their molecular hydrophobicity/hydrophilicity. In order to inhibit aqueous corrosion, there must be sufficient inhibitor molecular concentration to maintain an equilibrium surface coverage over the metal. This tendency is quantified by the oil-water partition coefficient, Log P. A higher value of Log P will mean fewer inhibitor molecules are available to act against corrosion in the water phase. Numerous methods are available to compute Log P, but this is primarily in the context of n-octanol as a solvent; more polar than most hydrocarbon media. Quantum chemical techniques have been developed for a much larger group of solvents, including numerous hydrocarbons of relevance to the oil and gas industry.<sup>84, 85</sup> Further work needs to be performed to determine whether or not correlations from single component hydrocarbons can be made to the crude oil environment as a whole, or what descriptors can be taken from a crude assay, for example, that would enable effective partition coefficients to be estimated from first-principles, or some key experimental values in one, two or a few simpler solvent mixtures.

Ultimately the extent of partitioning will be a composite quantity of the water cut, the Log P quantity, the pKa, the extent to which micelles form and ion-pairs migrate across the oil/water interface. Chemical thermodynamics models can be used to integrate these variables and obtain the ultimate concentration of inhibitor present in the aqueous versus crude oil phases.<sup>86</sup>

### Impact of the inhibitor upon multiphase flow

The separation of oil and water into two-phase flow depends upon the surface tensions between oil-water, water-metal, and oil-metal interfaces.<sup>65</sup> Each of these surface tensions can be affected by small concentrations of inhibitor species, since their bifunctional nature tends to lead to concentration at interfaces. These surface tensions can be predicted from molecular dynamics simulations or the classical density functional theory applied to liquids.<sup>87-89</sup> Once the surface and interfacial tensions are determined from first-principles or experiments then the values can be inserted into fluid mechanics expressions to predict whether or not water entrainment or multiphase flow occurs, and whether or not the surface becomes oil wet or wetted with water.

### Migration of the inhibitor molecule to the metal surface across the hydrodynamic boundary layer

Under flowing conditions, transport of the inhibitor from the bulk solution phase to the metal/water interface will depend upon the diffusion of the molecule across the hydrodynamic boundary layer. Thus flow rate and the molecular structure of the inhibitor, as well as the surface quality, will influence the effective concentration of inhibitor near the surface.<sup>90</sup> Molecular dynamics simulations can be used to generate diffusivity data that can then be used in the effective near-surface models. Similar factors apply to the diffusivity of corrosion reactants, products, and potential products of the reaction of inhibitor molecules with the corrosion products. Diffusion constants can then be applied in mesoscale models that combine reaction kinetics with mass transport, such as reaction-kinetic models or Lattice-Boltzmann simulations.<sup>91-93</sup>

### Identification of the solid surface phases available for inhibitor adsorption

Mild steel in an oil and gas environment will have surface phases that could consist of oxides, oxy-hydroxides, hydroxides, sulphides, carbides, carbonates and, under severe acidic corrosion, bare iron surfaces.<sup>29, 74, 68, 72</sup> Other solid surfaces that may be present include sand and formation fines, and organic deposits such as asphaltenes and paraffins.<sup>61, 94</sup> The inhibitor-surface interaction will be different for each phase, and so will the overall inhibitor efficiency. Thermodynamic methods can be used to predict stable surface phases, but these may need to be coupled with kinetic stability diagrams that take metastability into account, since it is known that the most thermodynamically stable phase is not always the phase that is observed to form in the field.<sup>95</sup> Characterization, thermodynamic prediction of microstructures, and microstructural models like phase field theory could be used as predictive tools to generate the surface microstructures most likely to prevail under distinct materials/environment conditions.<sup>96-98</sup>

### Formation of self-assembled monolayers on the solid surface phases

The physics of formation of chemisorbed layers on solid surfaces is described by the theory of adsorption isotherms, most commonly the Langmuir isotherm, although other variants also exist.<sup>12</sup> The key parameter controlling the formation of these layers is called the Gibbs' free energy of adsorption. This value can be inferred from experimental analysis (given certain assumptions) or predicted directly from first principles calculations using density functional theory. The latter method has been reviewed earlier in this paper and is a field of current research activities, due to the recent appearance of robust codes that can compute the structure and energy associated with chemisorbed phases at solid/fluid interfaces with considerable accuracy. Another approach that has been applied is to approximate chemisorption energies by replacing the quantum chemical calculation of a surface with the quantum chemical calculation of a representative metal-oxy or oxy-hydroxide coordination complex interacting with the inhibitor molecule.<sup>99</sup> In some cases these may lead to faster computations, although with a reduction in the information that may be needed to fully capture the surface/inhibitor interaction. The same authors also used the Log P (n-octanol/water partition coefficient) to estimate the change in entropy associated with inhibitor adsorption.

### Prediction of the corrosion rates of metallic surface phases with inhibitor self-assembled layers

In adsorption-centric studies of the mechanism of chemical inhibition of corrosion it is commonly assumed that the extent of surface coverage by the inhibitor molecule corresponds exactly to the extent by which corrosion is reduced. However, we propose herein that this may not exactly be the case, due to porosity of the inhibitor film as a result of imperfect packing, and the dynamic nature of adsorption/desorption of the molecules composing the surface film.<sup>7, 41</sup> We propose herein that instead there is some reduction in corrosion rate for the covered metal surface, which is not necessarily 100% effective. The reduced rates of corrosion in the presence of inhibitor films can be investigated by contrasting different techniques for measuring inhibitor adsorption (quartz crystal microbalance for example) with changes in capacitance and/or the corrosion current. First principles and atomistic-based models of inhibitor packing efficiency on the surface can also be used to estimate the extent to which a maximally covered surface provides total coverage of metal atom sites. Newly emerging simulation techniques, like reactive force field, may also be able to simulate the kinetic processes associated with the dynamic dissolution and reformation of the protective inhibitor surface layer, and thus provide direct estimation of the corrosion rates in the presence of inhibitor versus no inhibitor.<sup>100</sup> Inhibitor molecules may also reduce corrosion through other mechanisms, such as reaction with corrosion products to form scales that act as diffusion barriers, thus limiting corrosion.<sup>67</sup>

### Model Evaluation and Uncertainty Quantification

One rarely discussed feature of quantum chemical and atomistic modelling is the uncertainty in the evaluated molecular descriptors, such as the energy, geometry and other derived quantities. This challenge has been recognized recently, and some new density functional theory approaches devised that directly incorporate uncertainty via Bayesian error estimation.<sup>101</sup> Furthermore, statistical uncertainty can be derived in a natural way from molecular dynamics and Monte Carlo simulations, since they are inherently ensemble methods.<sup>102</sup> For the purpose of lifetime prediction and comparing potential new inhibitor candidate molecules, it is necessary to consider the meaningful differences between the predictions that would be made by slight variations in the choice of theoretical methods, and what are the inherent uncertainties based upon the model approach used and the assumptions contained therein.

The foremost means of quantifying the accuracy of a model is to compare the predictions of a model with a reliable validation dataset in order to evaluate the error in the model prediction. This method should be augmented with more sophisticated treatments, such as exploring the nature of error propagation through the model. This should be based on the model's set of assumptions, uncertainties in the data provided as model inputs, uncertainties in the data used for validation, and fundamental uncertainties that arise due to limitations in our understanding of the physics of the problem (known as *epistemic* or knowledge-based uncertainty).<sup>51, 101, 102</sup> These latter categories of error can be more

challenging to quantify, and are rarely investigated due to the academic emphasis on making models deeper and more theoretically rigorous rather than more relevant to engineering use.

Uncertainty quantification has been incorporated in the integrated multiscale modelling pathway shown in Figure 4. Some methods used in recent literature to evaluate model uncertainties include Bayesian inference,<sup>103</sup> comparing model predictions with experiments and available field data, integration into damage accumulation models,<sup>51</sup> and examination through the use of Monte Carlo and/or first- and second-order reliability methods (FORM/SORM).<sup>53</sup>

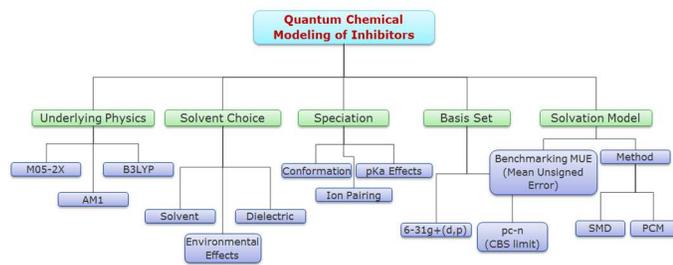


Figure 8. Sources of uncertainty that arise from different model design decisions that must be made when simulating molecular properties in a solvated environment from first-principles.

With respect to quantum chemical-based prediction of the molecular contributions to corrosion inhibition, the methods used to compute the properties of the inhibitors are subject to various critical decisions that need to be made in setting up the problem. For example, the basis function sets used to represent electron density can be made more or less complete, depending upon how much computer time or memory is available to perform the computation.<sup>104</sup> In addition, there are competing semi-empirical approaches that have been developed as a way to emulate the effects of a surrounding organic or aqueous medium.<sup>105</sup> A list of the possible decisions that could be made when constructing such a model is shown in Figure 8. These include the underlying physics model, the choice of solvent, the molecular conformation, the electronic basis set, and the representation of solvent. In the ideal case, transferability between different decisions should lead to similar outcomes but this is not guaranteed. When these sources of variation are taken into account, it is possible to gain an appreciation for the uncertainty in the predictions made by these otherwise highly rigorous theoretical methods.

## Summary and Conclusions

To conclude, this paper presents a new approach to the molecular-based modeling and design of corrosion inhibitors that is based upon a phenomenological breakdown of the critical factors that affect the efficiency of a corrosion inhibitor. The objective was to focus the molecular search by providing constraints upon the molecular suitability based upon the mechanisms of corrosion inhibition, spanning the various domains and processes via which the inhibitor interacts with the corrosion system. As most of the factors outlined above are able to be modeled with state of the art modeling and simulation techniques, we propose that a team-wise effort across

these categories of mechanistic response be applied to construct an integrated multiphysics inhibitor model.

Despite the effort to be comprehensive, we acknowledge that there may be several domain/process combinations that were omitted from the model. As an example, consider that, within the global domain, some factors affecting a molecule's suitability for application as a chemical inhibitor may include the toxicity and environmental impact, the cost of synthesis, and its interaction with other chemicals that may be part of the chemical package (scale inhibitors, demulsifiers, hydrate inhibitors and biocides). Along those lines, the intrinsic molecular stability regarding thermal decomposition or reaction with water should also be given consideration and be used to constrain the design search. Such examples demonstrate the importance of creativity and team-building in reviewing the list of possible processes to incorporate within the integrated multiscale model.

Given that modern computational solution of molecular level problems has become a tractable and relatively inexpensive affair, the integrated multiscale modeling approach should be highly promising in future models of inhibitor efficiency and an attractive, science-based alternative to the proliferation of regression based theory/experiment correlations abundant in the literature today.

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