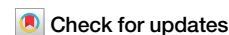


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Molecular modeling applied to corrosion inhibition: a critical review

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In the last few years, organic corrosion inhibitors have been used as a green alternative to toxic inorganic compounds to prevent corrosion in materials. Nonetheless, the fundamental mechanisms determining their inhibition performance are still far from understood. Molecular modeling can provide important insights into those mechanisms, allowing for a detailed analysis of the corrosion inhibition (CI) process. However, CI modeling is frequently underexplored and commonly used in a standardized way following a pre-determined recipe to support experimental data. We highlight six fundamental aspects (A) that one should consider when modeling CI: (A1) the electronic properties of isolated inhibitors, (A2) the interaction of the inhibitor with the surface, (A3) the surface model, (A4) the effect of the anodic and cathodic zones on the surface, (A5) the solvent effects, and (A6) the electrodes' potential effects. While A1-A3 are more frequently investigated, A4-A6 and some more complex surface models from A3 are usually not considered and represent gaps in the CI modeling literature. In this review, we discuss the main features of molecular modeling applied to CI, considering the aforementioned key aspects and focusing on the gaps that the emerging approaches aim to fill. Filling these gaps will allow performing more detailed simulations of the CI process, which, coupled with artificial intelligence (AI) methods and multiscale approaches, might construct the bridge between the nanoscale CI modeling and the continuum scale of the CI processes.

Corrosion inhibitors are extensively used to protect metal surfaces^{1,2}; however, traditional inhibitors, particularly chromates, must be replaced by compounds of lower toxicity³, and thus there is great interest in organic inhibitors⁴⁻⁶. These are usually constituted by elements with lone pair electrons, such as O, N, P, or S, and/or aromatic rings with delocalized π electrons, or certain functional groups such as amines ($-\text{NH}_2$), carboxylic acids ($-\text{COOH}$), alcohols ($-\text{OH}$), phenols, amino acids, etc.^{4,5}. These functional groups are electron-rich centers, which often bond to the metal surfaces via coordinate covalent bonds between the unoccupied d -orbitals of the surfaces and the lone pair/ π electrons in the inhibitor, and back bindings bonds from the free electrons of the metal and the antibonding orbitals of the inhibitor⁶.

However, the exact role of the inhibitors in influencing the corrosion inhibition (CI) process of active metals in saline solutions is not fully understood. The common hypothesis is that the organic inhibitors adsorb on the surface forming a protective film⁷⁻¹¹. In this process, the organic inhibitor (with its attached ligands, and charge and potential variations) moves from the bulk solution toward a surface at a mixed potential (established by the various anodic and cathodic zones), and then interacts with the electric double-layer (EDL), replaces the existing shielding of water

and solute, finally binding to the surface, causing subsequent changes to the charge and potential distributions at the surface and within the molecule. In this regard, the nature of the anodic and cathodic zones and the growth of inhibitors films are determined by both inhibitor-surface and inhibitor-inhibitor interactions, that are present in the first and subsequent inhibitor layers.

All these processes need fine-scale models to not only deepen our understanding of each stage but also to assist in developing strategies such as *inverse design for the discovering inhibitors*. Molecular modeling emerges as an excellent tool to that end, and its use in CI is increasing every year. Nonetheless, realistic models must incorporate six key aspects (A): (A1) the electronic properties of isolated inhibitors, (A2) the interaction of the inhibitor with the surface, (A3) the surface model, (A4) the effect of the anodic and cathodic zones on the surface, (A5) the solvent effects, and (A6) the electrodes' potential effects.

Concerning A1, acidic-basic properties, polarizability, molecular volume, presence of lone-pair electrons, dipolar moment, etc., may enhance/diminish the affinity of the inhibitor to the surface. However, a knowledge of these properties alone is insufficient for predicting and understanding inhibition and must be combined with A2-A6. A2 will

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determine how strong is the inhibitor-surface interaction. A3 is also important for describing the inhibitor-surface interactions. A more detailed and complex surface model will provide a better description of the processes occurring at its interfaces, but at an often prohibitive computational cost. A4 can play a central role in modeling CI since the different reactions that occur there affect the inhibitor-surface interaction, as well as the other secondary reactions that could appear and compete with the adsorption of the inhibitor. A5 is determining in understanding how the inhibitor displaces the solvent molecules from the metallic interface to be adsorbed on it, and also to evaluate the changes in the inhibitor's electronic properties due to the presence of a solvent. Finally, A6 allows for polarizing the complete system: metallic interface, inhibitor, and the solvent (electrolyte). In the metallic surface, the induced surface charges will interact with the polarized electronic structure of the inhibitor, enhancing/diminishing their affinity. Similarly, the induced charges on the inhibitor could influence the formation of the monolayer and subsequent inhibitor layers on the surface. The water molecules at the interface will also be affected by the electrode potential, inducing preferential orientations towards the metallic surface.

In CI modeling, the most common approach is to consider only A1-A3, where the corrosion inhibitor properties are correlated to the experimental CI performance using statistical techniques. A4-A6, and more complex surface models from A3, are rarely investigated or unexplored, which leads to important gaps in the CI literature and an incomplete understanding of the CI process. Emerging modeling tools and methods can address these gaps and, thus, in this paper, we review the most recent works on CI modeling using small organic molecules, focusing on the main advantages and disadvantages of the methodologies used. In this review we discuss the articles that address A1-A3, with a particular focus on more complex surface models for A3, and how emerging methodologies have or could be used to fill the gaps of A4 to A6. It is critical for the advance of this field that more complex phenomena and the corresponding molecular, charge, and potential alignments promoted by the establishment of electrochemical cells, potential, and solvent effects be included in the simulation of CI. The major innovation in this review is thus the critical examination of emerging methods to tackle processes A4 to A6 and how to merge these with the more established methods for A1 to A3. The simulation of these more complex processes requires both larger models and the incorporation of more functionalities (such as potential) into the models and thus the review highlights the development in model structure and mathematical formulations required.

This review is organized as follows: "Theoretical background" discusses the theoretical background involved in the simulations commonly applied to CI and "Theoretical background" discusses the main aspects for the CI modeling, reviewing the most recent works for each of the aspects highlighted before. We also give a focus on the main gaps found in the CI literature to describe some critical phenomena, discussing the most recent works that somehow address those gaps.

Theoretical background

Molecular modeling is a very active research area with applications in many different fields, such as sensors¹², materials design¹³, and drug discovery¹⁴, to name just a few. With the advent of faster computers and optimized methodologies, molecular modeling has become a vital tool for investigating CI. Although molecular modeling is a versatile tool with many methods available, its use in CI is standardized and frequently limited to complement the experimental findings, often relying on QSAR (Quantitative Structure-Activity relationship), or on very simplified models of the structures and the physical and chemical processes. By standardized, we mean molecular modeling performed with oversimplified models, where the employed theory level is insufficient to provide significant insights about the CI.

However, the methodologies available for molecular modeling are very rich and diverse, and could contribute to a much deeper understanding if their full potential would be deployed to the study of the processes involved in CI. As it will be further discussed in "Theoretical background", the recent works applied to CI, especially those intended to develop methods, despite

being scarce, provide important information about the molecular process that occurs during the CI.

From a molecular modeling point-of-view, we can, in principle, describe computationally any atomistic process in materials if we have two basic ingredients. The first one is the knowledge of the interactions between atoms in the material (that is, the interatomic potentials). Those determine the equations of motion for the atoms and the physical evolution of the material at the atomic level. The second one is an algorithm to integrate the equations of motion and obtain physical properties (such as most stable structures, thermodynamic properties, reaction rates, and many others) from the atomic interactions. The variety of available choices for these two ingredients is overwhelming, and well beyond the scope of this review. Here we give a very broad and superficial account of the most popular approaches.

Concerning the interatomic interactions, one could obtain the forces on the atomic nuclei in any material from Quantum Mechanics (QM) by solving the Schrödinger equation (Here we only present the time-independent Schrödinger equation as time dependent phenomena are usually described using the time evolution of stationary states, or through the adiabatic approximation where electrons are assumed to be in their (instantaneous) ground state.) (SE) for its nuclei and electrons:

$$\hat{H}|\Phi(\vec{x})\rangle = E|\Phi(\vec{x})\rangle, \quad (1)$$

where $|\Phi(\vec{x})\rangle$ is the eigen-wavefunction, $\vec{x}$ is the generalized position vector for all nuclei and electrons, $\hat{H}$ is the Hamiltonian operator, and E is eigenvalue. However, the solution of eq. (1) becomes unfeasible even for the simplest molecular systems due to its complexity. To overcome that, a number of approximations are usually assumed. The first one is the Born-Oppenheimer (BO) approximation, where the wavefunctions of nuclei and electrons are decoupled (factorized) since the latter moves much faster. Under such assumption, one ends up with the problem of solving the electronic SE:

$$\hat{H}_e \Psi_n(\{\vec{r}; \vec{R}\}) = E_n^e(\{\vec{R}\}) \Psi_n(\{\vec{r}; \vec{R}\}), \quad (2)$$

where $\hat{H}_e$ is the electronic Hamiltonian, E_n^e is its n -th eigenvalue, Ψ_n is the corresponding electronic wave function, and $\{\vec{r}\}$ and $\{\vec{R}\}$ are the sets of electron and nuclear coordinates, respectively. The wave functions and eigenvalues depend parametrically on the instantaneous positions of the nuclei $\vec{R}$, following their motion adiabatically. $\hat{H}_e$ governs the electrons state, and its general form is given by:

$$\hat{H}_e = \hat{T}_e(\vec{r}) + \hat{V}_{e-\text{Nuc}}(\vec{r}; \vec{R}) + \hat{V}_{\text{Nuc}-\text{Nuc}}(\vec{R}) + \hat{V}_{e-e}(\vec{r}), \quad (3)$$

where the terms in the right hand are the electron's kinetic energy operator and the electron-nucleus, nucleus-nucleus, and electron-electron potential energy operators. If one is able to solve the electrons' SE in Eq. (2), the nuclear problem could then be solved using $E_n^e(\{\vec{R}\})$ as the potential energy surface (PES) where the nuclei move. Normally, the electrons are considered to be in their ground state, so that their energy E_e is their ground state energy. The nuclear dynamics can be obtained considering the nuclei as quantum particles, thus incorporating all quantum effects in the model, or as classical particles (due to their large mass). The latter case is the most frequent one in the modeling of materials, and restricts the quantum effects to the description of the electrons. The nuclei, in this case, move following the Newton laws of classical mechanics, with forces defined by the derivatives of the PES:

$$\vec{F}_i = -\frac{dE_e(\{\vec{R}\})}{d\vec{R}_i}. \quad (4)$$

The electronic SE eq. (2) is still too difficult to be solved but for the simplest molecules, and approximations have to be made. Quantum Chemistry

(QC)¹⁵ provides a plethora of methods that propose approximations to the many-body electronic wavefunctions, with increasing levels of accuracy, from the simple Hartree-Fock (HF) method to sophisticated Configuration Interaction approaches. Quantum Monte Carlo methods (QMC)¹⁶, on the other hand, do not propose explicit functional forms for the wavefunction, but directly compute averages of physical quantities (mainly the energy, typically for the ground state) numerically using stochastic methods by sampling the multidimensional space of the wavefunctions. The advantage of QMC over QC methods is that the scaling with system size is much more favorable, allowing to deal with larger systems, although they are usually restricted to simple properties such as the total energy, and to deal with the ground state. However, both kinds of approaches are usually too expensive computationally to deal with the typical sizes involved in CI, which limits their applicability and impact in this field.

A class of methods that is frequently used to solve the electronic problem is Density Functional Theory (DFT). Here one abandons any attempt to approximate the electronic many-body wavefunction $\Psi_n(\vec{r})$, and focuses on the electronic charge density:

$$\rho(\vec{r}) = N \int d\vec{r}_2 \dots \int d\vec{r}_N |\Psi^*(\vec{r}, \vec{r}_2, \dots, \vec{r}_N)|^2, \quad (5)$$

which depends only on the position $\vec{r}$ where it is evaluated, instead of on the positions of all the electrons, as does the many body electronic wavefunction Ψ . The charge density is thus a much simpler mathematical object. However, despite its simplicity, it suffices to describe the ground state of the system, as shown by Hohenberg and Kohn¹⁷. If one is able to compute the ground state charge density $\rho(\vec{r})$ without resorting to Eq. (5), one could have access to the properties of the system without the knowledge of the wave function. The energy of the ground state would be obtained as:

$$E[\rho(\vec{r})] = T[\rho(\vec{r})] + E_{\text{ext}}[\rho(\vec{r})] + E_{\text{H}}[\rho(\vec{r})] + E_{\text{xc}}[\rho(\vec{r})], \quad (6)$$

where T is the kinetic energy of the electrons, E_{ext} is the energy due to the potential generated by the nuclei and any external field, E_{H} is the Hartree energy (the classical electrostatic energy of the electronic charge density ρ), and E_{xc} the exchange and correlation energy, which describes all the contributions from the electron-electron interactions beyond the Hartree term. The brackets $[\]$ denotes the functional dependence of these terms on the charge density function $\rho(\vec{r})$.

DFT provides a practical way of solving the electronic problem without the complication of finding the many body wavefunction, provided that appropriate expressions for the energy terms entering in Eq. (6) are available (of which only T and E_{xc} are unknown in general). Kohn and Sham¹⁸ provided the first practical approach to compute these terms, using a set of fictitious one-electron wavefunctions $\psi_i(\vec{r})$ to express the charge density ρ :

$$\rho(\vec{r}) = \sum_i |\psi_i(\vec{r})|^2, \quad (7)$$

and an approximation T_0 to the kinetic energy T :

$$T_0[\rho(\vec{r})] = -\frac{1}{2} \sum_i (\psi_i(\vec{r})|\nabla^2|\psi_i(\vec{r}))^2, \quad (8)$$

and taking the expression for the exchange-correlation energy (including the difference between the true kinetic energy T and the approximate T_0) from the homogeneous electron gas (for which very accurate solutions from QMC simulations are available). In this, so-called Local Density Approximation (LDA), the XC energy is just an integral over space involving the energy density calculated in the homogeneous electron gas:

$$E_{\text{xc}}^{\text{LDA}}[\rho(\vec{r})] = \int \rho(\vec{r}) \epsilon_{\text{xc}}^{\text{LDA}}(\rho(\vec{r})) d\vec{r}. \quad (9)$$

Further and more accurate approximations have been developed for the XC functional (like the Generalized Gradient Approximation - GGA, in which the density and its gradients on each point are considered), providing greatly improved results over the original LDA approximation.

Within the Kohn-Sham approach (either within the LDA or with more advanced functionals) the fictitious one-electron wave functions are obtained solving an effective one-particle SE equation:

$$\hat{H}_{\text{KS}} \psi_i(\vec{r}) = \epsilon_i \psi_i(\vec{r}), \quad (10)$$

with H_{KS} being the effective Kohn-Sham one-electron hamiltonian:

$$\hat{H}_{\text{KS}} = -\frac{1}{2} \nabla^2 + v_{\text{ext}}(\vec{r}) + v_{\text{H}}(\vec{r}) + v_{\text{xc}}(\vec{r}). \quad (11)$$

The first three terms in the right-hand side of Eq. (11) are the usual ones (kinetic, external, and Hartree potential), while the last one is obtained from the expression of the exchange-correlation energy functional:

$$v_{\text{xc}}(\vec{r}) = \frac{\delta E_{\text{xc}}}{\delta \rho(\vec{r})} = \epsilon_{\text{xc}}(\rho(\vec{r})) + \rho(\vec{r}) \frac{\partial \epsilon_{\text{xc}}(\rho(\vec{r}))}{\partial \rho(\vec{r})}. \quad (12)$$

In that manner, the previous many-body problem is reduced to a one-electron problem which can be readily solved numerically, enabling the studying of much larger systems compared to the ones that can be investigated through wave-function-based electronic structure methods. This numerical efficiency and the capacity of DFT to reach systems of considerable size (even thousands of atoms in high performance computers) have made it the method of choice in most computations in materials science and chemistry, and in most applications to CI modeling.

The methods reviewed above provide a description of the electronic state and the nuclear dynamics (from the forces obtained from the electronic solution) that stem from the fundamental laws of QM and electromagnetism. As they do not require neither any previous knowledge of the system under study nor empirical parameters, they are usually referred to as first-principles methods. They are highly transferable and can be applied to any system, as they rely only on the fundamental laws of physics and do not require any previous knowledge or parameters fit to any particular system. Therefore, they have a high level of predictive power, and thus are of general applicability. Besides, they provide a detailed microscopic picture of processes in materials. DFT in particular is the first-principles method of choice for practical CI studies, when the behavior of the electrons is a concern (like in the study of chemical reactions), and when one does not wish to use experimental or empirical parameters in the simulation.

Although DFT can be used in the study of large atomistic systems, when the number of atoms involved is beyond a few hundreds or the time scales involved are longer than a few picoseconds, DFT is too computationally demanding, and one has to resort to less expensive approaches. A popular one is Molecular Mechanics (MM), where one retains an atomistic description of the system, but the interatomic forces are not obtained from the electronic structure, but parameterized in the form of a classical interatomic potential $V(\{\vec{R}\})$, commonly referred to as force field (FF), that depends on the positions of the atoms in the system. The FF can be more or less complex, and have different analytical or numerical forms and parametrizations, but have the common feature that they are parametrized and fit to known experimental or theoretical results. Commonly used forms of FFs for small molecules are OPLS-All-Atom (OPLS-AA)¹⁹, OPLS3²⁰, General AMBER Force Field^{21,22}, CHARMM General force field^{23–25}, GROMOS^{26–30}, and Merck Molecular Force Field^{31–35}, which are implemented in software packages such as GROMACS³⁶, NAMD³⁷, LAMMPS³⁸, AMBER³⁹, CHARMM⁴⁰, and OpenMM⁴¹, among others. These FFs contain molecular parameters for a wide range of chemical species^{42,43}. Nonetheless, a common issue of utilizing FF in CI modeling (and in other areas) is the indiscriminate use of unvalidated FFs.

Also, recently, other types of FFs are being developed which do not have an analytical expression and are parameterized using machine learning (ML) approaches⁴⁴. The ML FFs learn about the system through the relationship between chemical descriptors and their properties from patterns in the data⁴⁵. The patterns and structure in data are typically extracted by applying kernel methods, and neural networks based on the atomic representation of the system⁴⁶. In this respect, ML FFs allow to explore efficiently the chemical space and predict some properties of the system with good accuracy. Although the transferability of ML FFs poses a problem when going beyond the specific training conditions^{44,45}, they are a promising approach that may provide in the near future first-principles accuracy at the cost of MM methods.

Once the method to compute the energies and forces is chosen (either using first-principles or classical potentials), one still must solve the equations of motion and obtain the physical properties of the system, like reaction energies, thermodynamics, phase stability, transport properties, etc. For this, two main methods have been used. The first one is Molecular Dynamics (MD)^{47,48}, in which one essentially integrates the Newton's equations of motion for the atoms in the system:

$$\vec{F}_i = m_i \frac{\partial^2 \vec{R}_i}{\partial t^2}, i = 1, 2, \dots, N, \quad (13)$$

obtaining their trajectories as a function of time: $\vec{R}_i(t)$. This is done from the knowledge of the forces (derivatives of the system energy with respect to the atomic positions, as in (4)), discretizing time and approximating the derivatives using finite differences. The trajectories are then obtained for discrete values of time. Time averages over the integrated trajectories for the properties of interest are approximations to the thermodynamic averages. Different MD techniques allow to access different physical properties, over different thermodynamic ensembles: microcanonical (constant NVE), canonical (constant NVT), Grand canonical (constant μ VT), etc.

The second class of methods commonly used to obtain the physical properties form the energy and interaction models are based on Monte Carlo approaches. Here, one does not attempt to follow the dynamics of the system, but to compute properties in equilibrium, from averages of the corresponding operator. The averages are computed using stochastic approaches. In these simulations, a system is evolved to a different state from an ensemble of possible future states, which is accepted or rejected with a certain probability and using some criterion. The equilibrium's state in the system is investigated as a function of the temperature (Metropolis Monte Carlo), or to advance the system's state through time (kinetic Monte Carlo). In Metropolis Monte Carlo, the number of states can be seen as the number of geometries, which are accumulated, and then a potential energy function is calculated for each of them. Thus, a certain thermodynamic property can be computed through the integration:

$$A = \int A(\vec{r}) P(\vec{r}) d\vec{r}, \quad (14)$$

where A is the thermodynamic property, $P(\vec{r})$ is the probability distribution function, and $\vec{r}$ the coordinates. $P(\vec{r})$ is given by:

$$P(\vec{r}) = \frac{\exp\left(-\frac{E(\vec{r})}{k_B T}\right)}{\int \exp\left(-\frac{E(\vec{r})}{k_B T}\right)}, \quad (15)$$

where $E(\vec{r})$ is the energy of the system with coordinates $\vec{r}$ and the denominator is the partition function. $P(\vec{r})$ can be calculated using two methods: a quadrature scheme or Metropolis⁴⁹.

In Kinetic Monte Carlo, the simulation proceeds with a list of all possible discrete reaction steps, and then a probabilistic method is used to select a reaction based on what will occur in a time step. In this case, reactions with a high rate will be preferably selected over those with a slower

rate, and the reaction rates can be obtained from ab-initio simulations. The time step for the selected reaction is evolved based on all possible reaction rates for the current configuration. Once the system is updated, a list of reactions is created, and the probabilistic selection process continues. The main difference between MD and Kinetic Monte Carlo is that MD follows the evolution of the system with time in a continuous manner, whereas in Kinetic Monte Carlo, the events are discrete^{49,50}.

Main aspects for the CI modeling

From a molecular point of view, CI modeling provides invaluable insights into all phenomena that occur during the corrosion process, e.g., oxidation/reduction of the metallic surface and other chemical species present in solution, mass loss in the metallic surface, redistribution of the electronic charge in the inhibitor and the EDL, which functional groups are oriented toward the metal, how the molecule builds up layers on the metallic surface, etc. Those insights allow us to comprehend how atoms-molecules-surface-solvent interact, paving the way to investigating several degrees of freedom of a given problem, individually and collectively, a tricky task when doing experiments. In that manner, one can evaluate with atomistic detail the CI process, bringing light to the inhibition mechanisms.

The choice of the interaction model (mainly between QM and MM models) is related to the desired level of predictability in investigating the target property or phenomenon. However, in CI modeling, because of the system's size usually required in the simulations, often highly accurate methods are prohibitive. QM methods allow us to investigate the electronic and structural properties of the inhibitor, surface, and aqueous interface with more detail than the MM ones since the electrons are explicitly considered in those methods, besides being more transferable and general. In that manner, QM methods may provide important information about the adsorption mechanism of the inhibitor, where, for instance, the π -orbitals of the inhibitor will interact with the surface and with the other ones from other inhibitor molecules, and depending on the coverage and the strength of this interaction, the corrosion inhibitor will adopt a particular adsorption configuration, that potentially could lead to the formation of self-assembled monolayers (SAM)⁵¹. Nonetheless, the lack of computing power often limits the application of QM methods, where, for instance, the solvent effects are not always included. Modeling based on MM is very popular in the CI field, as it is reported in many works in the literature⁵²⁻⁷⁴. That is primarily because of its low computational cost compared to QM methods, allowing, for instance, the inclusion of solvent effects, one of the critical aspects in the CI field.

Many works reported in the literature use molecular modeling only to support experimental observations^{64,69,75-81}. Most works use QM methods to compute molecular properties of isolated inhibitors^{64,69,76-82} which are traditionally attempted to correlate with CI efficiency through electronic properties, such as the ones discussed in the next section. In the following sections, we revise the main works available in the literature, presenting a detailed discussion of the six main aspects of CI modeling highlighted in the introduction.

Electronic properties of isolated inhibitors

The electronic properties of isolated inhibitors can give us a first insight into their CI properties. Most of the works reported in the literature attempt to correlate these properties with the experimental CI performances of the inhibitors. This approach is known as MEPTIC (molecular-electronic properties to inhibition-efficiency correlation)⁸³. This is usually done through simple correlation methods (e.g., linear regression analysis) or more elaborated statistical models such as nonlinear methods (e.g., neural networks, polynomial regressions, ML techniques, etc.)⁸⁴. The more elaborated methods correspond to the QSAR (Quantitative Structure-Activity Relationship) approach, which is usually applied in predicting biological activities or physicochemical properties of compounds, but in recent years has been applied to predict the CI properties of compounds.

MEPTIC. In the MEPTIC approach, trends in the electronic structure of the isolated inhibitors and their similarity with other inhibitors are attempted to correlate with the experimental CI performance, sometimes also aiming to provide insights into its interaction with the surface. Most of the time, the aforementioned molecular properties are calculated using DFT, but some works use wave-function-based methods, such as Møller-Plesset (MP), Coupled Cluster (CC), HF method, etc., and semiempirical methods^{85–88}. The MEPTIC models can be expressed as follows:

$$f(x) = \alpha_1 x_1 + \alpha_2 x_2 + \dots + \alpha_n x_n + \epsilon, \quad (16)$$

where $f(x)$ is the molecular property, x_n the n th molecular parameter, α_n the coefficient (weight) of each parameter, and ϵ the associated error. For example, the CI performance, η , can be expressed as a combination of some coefficients and the energies of the frontier orbitals:

$$\eta = a + bE_{\text{HOMO}} + cE_{\text{LUMO}} + \dots, \quad (17)$$

where a , b , and c are constants determined to fit the model, E_{HOMO} and E_{LUMO} the energies of the HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) orbitals. Once these apparent correlations are determined for a given set of inhibitors and materials, the findings are extrapolated to other systems^{10,83,89,90}. However, this approach may result in erroneous associations, as many of these studies observed the correlations within a restricted set of molecules, or even to any correlation as shown in Fig. 1. The inhibition efficiency (η) in Fig. 1 was calculated as $\eta = (R_p^{\text{inh}} - R_p^{\text{blank}})/R_p^{\text{inh}}$, where R_p^{inh} is the mean polarization resistance of the inhibited sample, and R_p^{blank} the mean polarization of the blank (non-inhibited sample). When a more comprehensive dataset of inhibitors is employed, the apparent correlation might disappear or not be so apparent^{10,84,91–95}. From MEPTIC approach, one can not have any information about the physical and chemical processes that occur during/after the adsorption process because of the lack of explicit interaction between inhibitors and the metallic surfaces, which is not considered in these studies^{96–105}.

Another problem that could appear in MEPTIC is the linear dependence between the variables (molecular properties) used. The linear dependence could appear using two related quantities (e.g., the fundamental gap and the HOMO and LUMO energies), but there might also be other ambiguous and unclear linear dependencies when many parameters are used in the models. To deal with that, there are statistical techniques to identify the causal correlations between the parameters or regularization techniques^{84,106,107}.

Among the electronic properties typically utilized in the MEPTIC approach, the frontier molecular orbitals HOMO and LUMO are the most commonly analyzed in the literature. Those orbitals tend to react with surface states, thereby enhancing the interaction between the inhibitor and the surface. The E_{HOMO} is associated with the molecule's tendency to transfer electrons to the surface, while the E_{LUMO} is related to its tendency to accept electrons from the surface, e.g., in a transition metal from d -orbitals. Consequently, the difference between the HOMO and LUMO energies, often referred to as the HOMO-LUMO gap or fundamental gap ΔE , can indicate the strength of the inhibitor-surface interaction in an indirect way. A higher ΔE implies lower reactivity of the molecule with the surface, whereas a lower ΔE suggests higher reactivity.

However, ΔE is not the sole determinant of the inhibitor's reactivity with the surface or its CI performance. Breedon et al.⁹¹ have criticized that correlation by exploring other molecular parameters, such as molecular ionization and deprotonation energies for a set of 28 small organic molecules using DFT and QMC calculations. They found no clear relationship between experimental CI efficiency, the fundamental gap, and other molecular properties. More recently, Kokalj⁸⁹ discussed the importance of the molecular electron-donating ability and the fundamental gap in CI for a data set of 22 heterocyclic organic inhibitors for Fe in acidic solutions. A weak bilinear dependence with a volcano-like shape on the fundamental gap

was found, but the correlation is too weak to be quantitative. Hence, analyzing only the fundamental gap cannot predict the inhibition efficiency.

Liu et al.¹⁰⁴ studied the inhibition performance of nicotinic acid (NA), nicotinic acid amide (NAA), and 4-methoxypyridine (MP) for the CI of mild steel in acidic solution through experiments and simulations. Their experimental results showed that the inhibitors could prevent the material's corrosion following the trend $\text{NAA} > \text{NA} > \text{MP}$ for CI performance. Then, the CI performance was correlated to molecular properties, such as charge density distributions, HOMO and LUMO energies, and the Hard-Soft Acids and Bases (HSAB) parameters, finding some correlations with their experimental results for CI performance. However, the correlations found, even agreeing with experimental results, should not be generalized to other corrosion inhibitors or materials because, as mentioned before, they can lead to false associations. In this case, the correlations could be more coincidences than true relations.

Another important molecular parameter used in MEPTIC is the dipole moment. This quantity measures the separation of the electric charges within a molecule. There are two arguments for its effect on CI performance. The first one says that a high dipole moment will enhance the molecule's interaction with the metallic surface, leading to higher CI. The second argument says that a lower dipole moment will favor the molecule accumulation on the surface (the lower dipole moment of the molecule reduces its electrostatic repulsion from the charges on the surface), protecting the material against corrosion. Both arguments could be true, even if they seem to be contradictory. In this sense, the effect of dipole moment on the CI properties is non-trivial and depends on several factors, from electrostatic to intermolecular interactions, as well as the dipole's orientation^{90,108}, as shown in Fig. 1.

The HSAB theory has also been applied in the MEPTIC approach to predict the bonding between the inhibitor and the surface, where the molecule is the electron-donor species (nucleophile), and the metallic surface (assuming metals with d -orbitals) is the electron-acceptor one (electrophile) due to its vacant d -orbitals. Accordingly, the corrosion inhibitor would be adsorbed on the metallic surface by its reactive part and block the active sites on the metallic surface, thus preventing it from corrosion. In this sense, the HSAB theory can help to predict the CI properties of specific molecules, but without any information about the CI mechanism. It can also lead to incorrect conclusions due to the lack of robustness of the models used or because there is no correlation at all between the molecular parameters used and the CI efficiency, as shown in Fig. 1. The parameters used for HSAB theory, such as Mulliken electronegativity, chemical potentials, nucleophilicity, electrophilicity, softness, hardness, etc., can be calculated using DFT simulations through simple ground state equations based on the electronic density⁹⁰.

The Fukui indices are additional reactivity descriptors that emerge from the HSAB theory. They provide information about which atoms on the molecule tend to lose/gain electrons, thus determining the strength of certain potential bonding sites (reactive sites) on the corrosion inhibitor. Some of these descriptors are the electrophilic (f^+) and nucleophilic (f^-) indices, which indicate the electrophilic and nucleophilic regions of the corrosion inhibitor, hence the affinity to be adsorbed on the metallic surface. The Fukui indices can be compared for different corrosion inhibitors or molecule derivatives to get insights into which one can perform better as corrosion inhibitor^{3,62,66,69,71,82,84,90,109–119}.

QSAR. The QSAR models can also be used to analyze the dependence of some property of interest (e.g., CI performance) with molecular features. One of the differences between the QSAR models and the MEPTIC approach is that the latter focuses more on the electronic properties of corrosion inhibitors and their correlation with CI. In contrast, the QSAR models are a more versatile modeling approach which can include several molecular descriptors and experimental data to predict the CI. In this sense, the QSAR models are usually more mathematically complex than the MEPTIC ones. Several QSAR models have been applied to different families of organic compounds used as corrosion inhibitors, such as

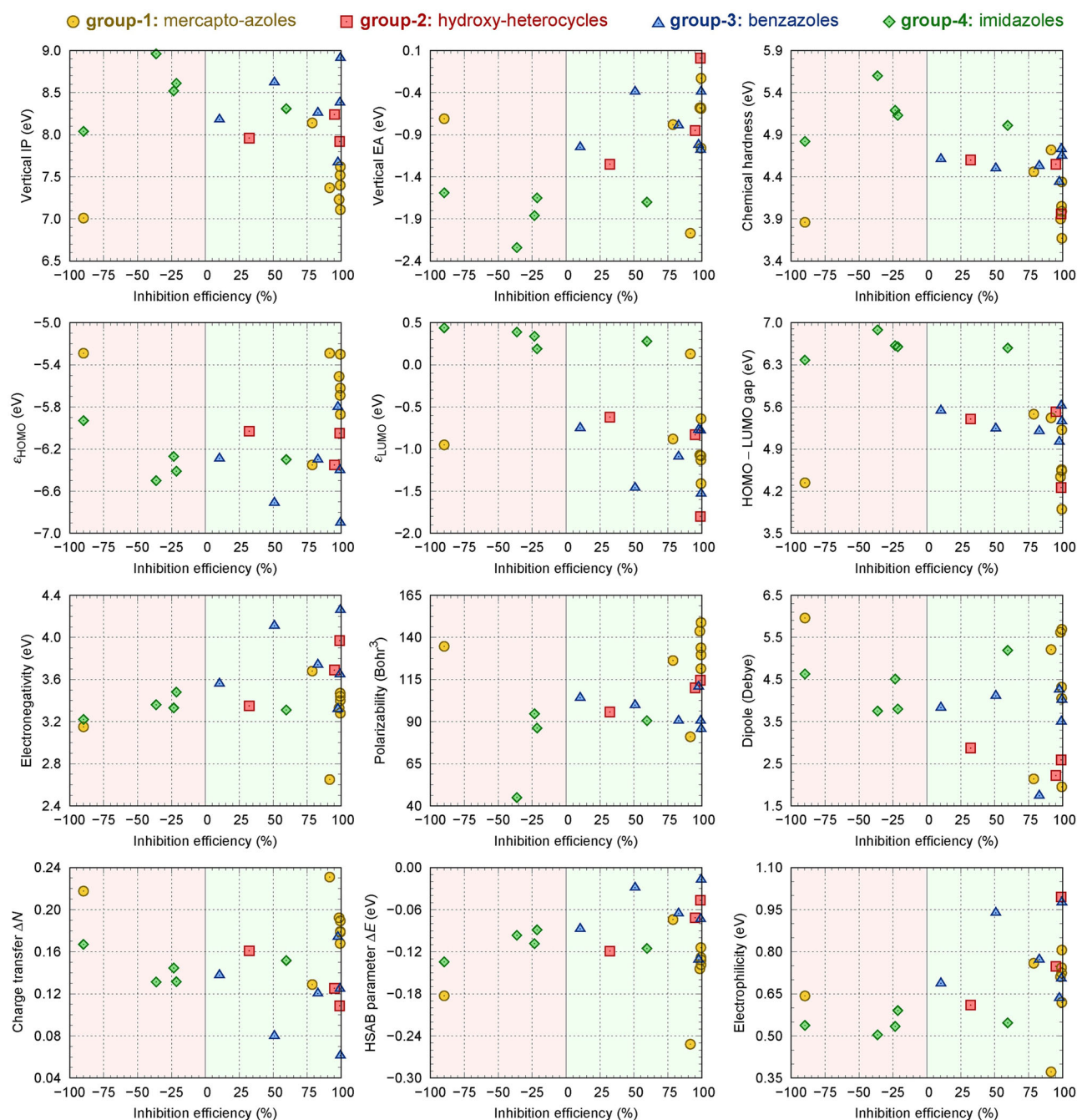


Fig. 1 | Correlations between the experimental corrosion inhibition efficiency and molecular electronic parameters for a set of organic compounds tested as corrosion inhibitors for copper in saline solution. A significant vertical dispersion of points near 100% inhibition efficiency appeared for all the molecular electronic

parameters. This implies that a good inhibitor can present almost any value within a relative broad range. All the details about the molecular electronic parameters, set of organic compounds, and numerical values are reported by ref. 90. Adapted from ref. 90 with authorization.

azoles, imidazoles, amino acids, Schiff bases, etc. To evaluate the fitness and statistical significance of a QSAR model, statistical properties such as Pearson's correlation coefficient (R), coefficient of determination (R^2), mean absolute error (MAE), mean square error (MSE), root mean square error (RMSE), the sum of square errors (SSE), etc., are used^{94,120–122}.

The main issue with the QSAR models typically used in the CI literature is that only a few show statistical robustness, potentially resulting in false correlations between the CI performance and the computed molecular properties⁸³. To identify reliable molecular descriptors for QSAR models, ref. 93 investigated a data set comprising 100 small organic molecules as potential corrosion inhibitors of Al alloys AA2024 and AA7075. Their findings indicated that molecular electronic properties obtained through

DFT (such as electron affinity, ionization potential, E_{HOMO} , E_{LUMO} , among others) lacked sufficient information to generate predictive models for CI performance. However, when these DFT descriptors were combined with other molecular features (e.g., the presence of specific functional groups, molecular topology, van der Waals volume, etc.), along with experimental data, they yielded excellent QSAR models. Winkler's work sets a precedent demonstrating that molecular properties can be linked to CI efficiency, showing that QSAR models can correlate molecular features with CI performance. However, these models do not provide any information about the mechanism of action of the inhibitor.

Another remarkable example of using QSAR models is the work by ref. 123, who studied the CI performance of 28 small organic molecules.

They employed a QSAR approach known as comparative molecular surface analysis (CoMSA), which utilizes distributions of electronegativity, polarizability, and van der Waals volume calculated at the DFT level to identify highly effective corrosion inhibitor compounds. The outcomes of their study revealed the identification of five molecules as prototypes and archetypes for corrosion inhibitors. This demonstrates that these properties projected onto the molecular surface (using the Connolly surface model¹²⁴) can predict the CI potential for small organic molecules.

Currently, Artificial Neural Networks (ANN) have emerged as a nonlinear technique employed to characterize the connection between molecular descriptors and their corresponding molecular properties in a given dataset³. ANN has been used to correlate and predict complex nonlinear relationships without having any knowledge about the underlying mathematical description involved and using an artificial intelligence (AI) approach¹²⁵. An ANN is formed by several simple and highly interconnected processors or neurons (nodes). It is characterized by three main components: node character (processing of the signals by the node), network topology (structure and connections between the nodes), and learning rules (how the weight of the molecular parameters are initialized and adjusted using an algorithm). The nodes in an ANN are usually arranged in three layers: the input, hidden, and output layers³.

Chen et al.⁹⁴ investigated through an ANN the quantitative relationship between structural/molecular features and their experimental electrochemical properties for a data set of 38 corrosion inhibitors. The neural network used was the Bayesian regularization approach, based on a three-layer neural network architecture with an automatic training process to minimize the correlation error. The structural descriptors used in the model considered molecular features such as the number of atoms, number of non-H atoms, number of rings, among others. The experimental properties considered were the corrosion potential, corrosion current, and anodic/cathodic Tafel slopes. Their results showed that the ANN could predict the electrochemical performance of the corrosion inhibitor compounds they used, with combined experimental and molecular properties, when applied to AA-2024-T3 alloys.

In a recent work by ref. 126, a cross-category corrosion inhibitor database was constructed using an ANN (three-level direct message passing neural network, 3L-DMPNN) model with molecular information that incorporates atomic-level, chemical bond-level, and molecular-level details to predict the CI performance of compounds in specific environments. The model's generalization ability was tested by them in 23 organic molecules from the latest literature studies⁹⁴ and 4 molecules tested in the laboratory, finding that the model could accurately predict the CI performance for both highly and slightly efficient corrosion inhibitors at a low computational cost.

In summary, examining the electronic properties of isolated corrosion inhibitors offers insights into their potential interaction with the metallic surface to protect the material from corrosion. However, those analyses are insufficient to conclude that a given molecule might be a good corrosion inhibitor because either using MEPTIC or QSAR approaches often leads to poor or no correlation between the molecule's electronic properties and the experimental CI performance. More advanced QSAR models, when provided with appropriate molecular descriptors, may improve such correlations, but it is always difficult to extend the findings for a given set of molecules to other molecules.

The interaction of the inhibitor with the surface

Addressing the inhibitor's adsorption onto the surface is fundamental in CI modeling. In the CI literature, the adsorption energy (E_{ads}) of the inhibitor on the surface is often used as a parameter to infer the CI efficiency of inhibitors. For the different methods used, E_{ads} is computed in varying ways, but always referring to how strongly a molecule is attached to a surface and displaces solvent molecules, thus blocking electrochemical activity. Several factors, such as the molecular structure and functional groups of a given inhibitor, may influence its adsorption energy on the metals. That affects the alignment (or configuration) of the inhibitor molecules on the surface and,

thus, the adsorption configuration of the molecule on the surface and coverage^{64,69,75–79,81,127–129}.

The accuracy of the energies obtained strongly depends on the computational method employed, and emerging methodologies can provide better descriptions of both energetic and structural properties. For instance, in QM simulations the accuracy will depend on the level of theory used in the calculation (e.g., the specific functional used in DFT), while, in MM simulations, on the FF parametrization (AMBER type, reactive force fields, ML FFs, etc)^{45,130,131}.

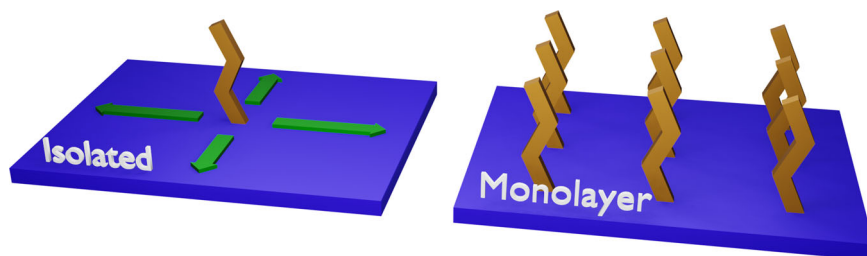
In the context of MD, to assess the system's energy accurately, it is necessary to consider many different configurations, exploring the local energy minima on the system's PES. Most of the papers found in the literature are unclear whether they use a single configuration of the system (e.g., one adsorption structure obtained by structural optimizations) or consider an average over many MD steps.

Several works in the literature report the adsorption energies for inhibitors in different metallic surfaces by means of QM and MM simulations^{5,61,73,114,127,132–139}. Thaçi et al.⁶¹ investigated the CI properties of monocarbonyl analogs of curcumin, specifically (2E,5E)-2,5-di-benzylidenecyclopentanone and (2E,5E)-bis[(4-dimethylamino)benzylidene]cyclopentanone, for Cu, using electrochemical measurements, Monte Carlo and MD simulations with classical potentials. Their simulations showed the ability of both inhibitors to be adsorbed on the surface, protecting it from corrosion, where both molecules adopted a configuration parallel to the surface. They performed the structural analysis using the radial distribution functions, which showed peaks in distances from 1 to 3.5 Å, corresponding to chemisorption on the surface. Kozlica et al.⁵ investigated the combined CI performance of MBI and octylphosphonic acid (OPA) on oxidized Cu (Cu₂O) with different OH/O termination, and a model of oxidized Al(111) surface with the equivalent of 2 monolayers of oxygen atoms and hydroxylated termination (OH/Al₂O₃/Al(111)). Adsorption energies of the inhibitors on the Cu surfaces were computed by them using DFT. Their results showed that MBI adsorbed preferably with the thione and thiolate form to the Cu surface, while the thiol form did not take part in the adsorption process due to the lower stability against the thiolate and thione form. In the case of OPA, they found a similar adsorption tendency. For the Al surfaces, the adsorption of the phosphonic group was addressed in a previous work by them¹⁴⁰, showing an adsorption preference for this group instead of the imidazole and thiol ones. In this case, the interactions governing the inhibitor's adsorption on the oxidized surfaces studied are covalent bonds with either O- or OH-terminated surfaces.

Dahmani et al.⁵⁷ determined which of the compounds present in the cinnamon essential oil (CiO) is responsible for its experimental CI performance on bare Cu and CuO₂(110) surfaces. Using the major constituents compounds of CiO: trans-cinnamaldehyde (P46), δ -cadinene (P8), and β -Cubebene (P5), and through MD simulations with classical potentials, they found that P8 is interacting most favorably with the CuO₂(110) surface, adopting a parallel adsorption configuration that covers the surface. Their experimental results, particularly using scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDS), suggested that the presence of the inhibitor protected the metal since the surface was smooth and exempted from all corrosion products. Since their simulations show the molecules are adsorbed to the surface (via MD trajectory analysis), they conclude that it protects the surface. They also analyzed the inhibitors through DFT calculations to determine the molecular properties usually associated with the CI efficiency: HOMO-LUMO energies, electronegativity, and ionization potentials, among others. Their DFT results suggested that P8 and P46 are the compounds with higher CI efficacy. However, both conclusions about the DFT and MD results and the CI efficiency are weak arguments similar to the other ones found in the corrosion literature, attributing the corrosion protection only to the ability of the molecule to stick to the surface and their value of specific molecular properties calculated in the isolated inhibitors.

Many authors report on Monte Carlo simulations in combination with experimental techniques to predict CI performance^{141–148}. Quadri et al.¹⁴³

Fig. 2 | Inhibitor adsorption sketch considering the isolated and monolayer cases. The blue surface illustrates the metallic slab of the same size in both cases, showing that more molecules are needed to investigate the self-assembled monolayer (SAM) case. The green arrows indicate the empty lateral space, preventing the molecules from interacting with their images in simulations that apply periodic boundary conditions (PBC), for the case of low coverage adsorption.



evaluated the CI performance of three N-hydrospiro-chromeno-carbonitriles (INH-1, INH-2, INH-3) on mild steel in acidic solutions performing electrochemical measurements together with DFT and Monte Carlo simulations. The authors found the highest CI performance for INH-3, followed by the INH-2 and INH-1 compounds, which were evaluated through electrochemical impedance spectroscopy. Their Monte Carlo simulations showed that the adsorption energies of the corrosion inhibitors followed the same trend as the CI performance. The adsorption configuration mode for the molecules on the surface was found to be nearly parallel to the surface, using their π -electron-rich centers.

Madkour et al.¹⁴⁶ showed the CI performance for some arylazo-triazoles (AATRs) on Cu using electrochemical measurements and Monte Carlo simulations. Their simulations showed that the AATRs adsorbed on the surface with a parallel configuration due to the donation of π -electrons from the aromatic rings, as well as the lone pair electrons from the heteroatoms to the unfilled d -orbitals of the Cu surface. This configuration maximizes surface contact and enhances surface coverage. The experimental results showed that AATRs are good inhibitors for Cu, with an increased CI performance at higher concentrations but decreased with rising temperatures.

The coverage ratio is one of the most important aspects of investigating inhibitors' adsorption mechanisms on metallic surfaces. From the modeling point of view, that can be addressed by either increasing the number of molecules in a simulation box of fixed size or decreasing the box dimensions for a fixed number of adsorbed molecules. In this manner, the adsorption of a given inhibitor on a metallic surface can be investigated as a function of the surface coverage, ranging from low to high concentrations, and potentially leading to the SAM's formation. However, increasing the inhibitor's concentration in experiments does not necessarily guarantee the formation of an ordered SAM layer, but often leads to disordered SAMs. For the SAM case, the lateral interactions between the inhibitors can stabilize the adsorption on the surface. For a given surface with a fixed simulation box size, Fig. 2 sketches those two adsorption scenarios.

Several works using isolated and monolayer adsorption cases are reported in the literature. For example, ref. 132 investigated the adsorption of 2-mercaptobenzimidazole (MBT) and 2-mercaptobenzimidazole (MBI) on Cu(111) surface via DFT calculations. Using different surface coverages until reaching the SAM formation, they found the most stable adsorption modes (2-atom bonded) of both MBI and MBT on the Cu(111) surface, where the MBI adsorbs more strongly than the MBT due to better lateral interactions in the SAM. The more stable adsorption of MBI would increase its CI performance compared to MBT.

Guo et al.¹⁴⁹ investigated the CI properties of three thiourea derivatives (1-(4-methoxyphenyl)-3-(4-phenylthiazol-2-yl)thiourea, 1-benzyl-3-(4-phenylthiazol-2-yl) thiourea, and 1-(2-hydroxyethyl)-3-(4-phenylthiazol-2-yl)thiourea, named Inh1, Inh2, and Inh3 in Fig. 3, respectively, from ref. 149) on Fe surfaces by means of MD simulations with classical potentials to compute adsorption energies. Using this approach, they found that the Inh1 derivative presented strong adsorption for the varying coverages, followed by Inh2 and Inh3, as shown in Fig. 3. Their findings show the effect of the coverage in the adsorption energies, where the interactions between the inhibitors are maximized at a certain coverage, increasing its stability on the surface.

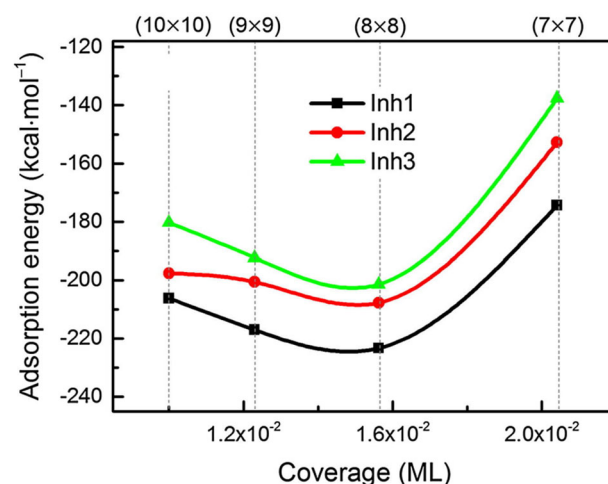


Fig. 3 | Variation of the adsorption energy with the surface coverage. The number of molecules per surface Fe atom is considered as the coverage unit (ML). The size of the supercell is shown at the top of the graphic. Adapted from ref. 149 with authorization.

Chiter et al.¹⁵⁰ provide more insights about the CI properties of MBT monolayers adsorbed on Cu(110) via DFT calculations. Their findings showed that the thione and thiolate MBT are chemisorbed on the surface. The chemisorption leads to a stable and dense monolayer on the surface, which saturates all the Cu surface atoms at a concentration of 3.68 mol nm⁻². The CI performance of the MBT monolayers was evaluated by calculating the Cu vacancy formation energy (the energy cost of creating one Cu vacancy) on the surface, both in the presence and in the absence of the inhibitor. A higher vacancy formation energy suggests a reduced probability of metal dissolution. In this study, their higher Cu vacancy energy for the thiolate case compared with the thione indicates that the thiolate form mitigates the metal dissolution.

In the same regard, ref. 151 investigated the formation of MBT monolayers on Cu₂O/Cu surfaces using DFT simulations combined with x-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ions mass spectrometry (ToF-SIMS). Their results showed MBT multilayer formation on the Cu oxide surface, which inhibits the oxide layer growth, as shown in Fig. 4. The figure depicts the MBT layers' adsorption mechanism on the surface, illustrating the adsorption on both Cu₂O oxide and bare Cu. In the latter case, the adsorption of the MBT multilayers would inhibit the growth of the Cu₂O and the metal redissolution. Their DFT results showed that MBT molecules are strongly bonded to the surface through both S atoms, covered by a weakly bonded multilayer. They also found coadsorbed water between the MBT layers, interacting with the N(H) group via H bonds. Moreover, the adsorption of MBT on the surface inhibits the coadsorption of Cl⁻, besides preventing Cu dissolution.

The electronic properties can also be used to analyze the adsorption of inhibitors on the metallic surface. One can use the system's electronic density to obtain other quantities such as work functions, the total (DOS) and local (LDOS) density of states, electrostatic potentials, and the electronic

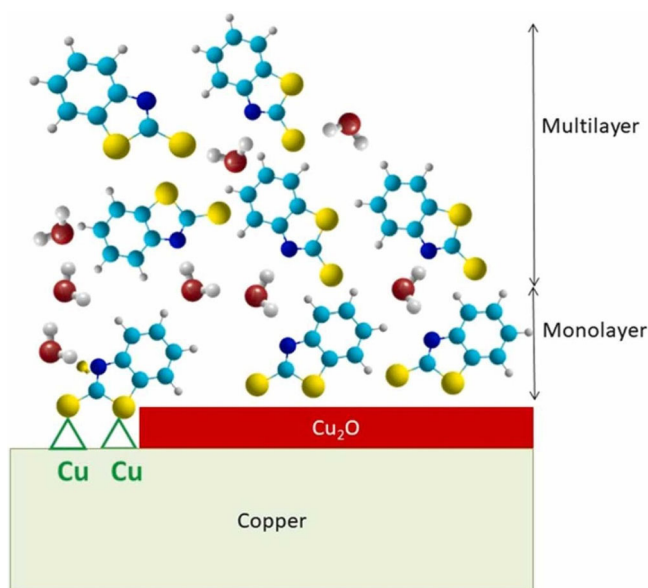


Fig. 4 | Sketch of the adsorption of 2-mercaptobenzothiazole (MBT) layers on the $\text{Cu}_2\text{O}/\text{Cu}$ surfaces, where the adsorption is taking place on both the Cu_2O oxide and the metallic zones. The MBT layers contain water molecules trapped between them. Adapted from¹⁵¹ with authorization.

density distribution. The work function of a metallic surface is the minimum energy required to remove an electron from the solid surface to a point in the vacuum just outside the surface. It relates to the electronic energy level and thus with the electrode potential¹⁵². When the corrosion inhibitor is adsorbed on the metallic surface, there could be a change in the work function related to the adsorption process and intermolecular interactions (e.g., dipole moment) between inhibitors. The modified work function could affect the adsorption of ions on the surface and make less favorable the electron charge transfer to the metal from any of the chemical species present. In this case, when the adsorbate reduces the work function of the system, the adsorption of anions that donate electrons to the metal becomes less favorable. This affects the anodic reaction of the system, and this could be used to evaluate the CI process^{128,153–157}.

The DOS allows for understanding how the states of a given atom (or other entity, such as the orbitals) are distributed in terms of energy. It can also provide hints about atoms interacting with each other. LDOS is the space-resolved density of states. This quantity is commonly used in scanning tunneling microscope analysis as it is directly related to the measured current as a function of the applied voltage and the tip position¹⁵⁸. One can also assess the interaction between the corrosion inhibitor and the surface by analyzing the DOS⁸⁴. When the corrosion inhibitor is being adsorbed on the surface, the electronic states of the inhibitor start to broaden because of the inhibitor-surface interaction¹²⁸.

Several authors have used the DOS to extract information about the CI process^{114,128,132,133,135,139,156,159–161}. Chiter et al.¹³³, for instance, studied the adsorption of MBI on Cu interfaces ($\text{Cu}_2\text{O}/\text{Cu}$). The strong adsorption of MBI on the $\text{Cu}_2\text{O}/\text{Cu}$ surface and the formation of chemical bonds were confirmed by the electronic analysis in terms of the DOS and the LDOS. The authors observed drastic changes in both quantities before and after the adsorption process, suggesting the formation of strong bonds between the MBI and the surface. For the isolated MBI, in the thione form, the alignment of the HOMO and LUMO orbitals with respect to the slab's Fermi level suggests an electron donor behavior during the adsorption process. In contrast, the radical thiolate presents both electron donor and electron acceptor behavior. For each form, the DOS showed that sulfur orbitals were the dominant ones for the states close to the Fermi level, suggesting that the sulfur atom is the most reactive site on the MBI. Once the MBI in both forms is adsorbed on the surface, the strong molecule-surface interactions change

the molecule's DOS. These strong changes suggest the formation of covalent bonds between the inhibitor and the surface.

The molecular electrostatic potential (MEP) analysis, defined as the interaction energy between the charge distribution and a test positive charge, provides insights into the charge distribution of the molecule by mapping its value onto the molecule surface, typically the van der Waals volume¹⁶². The MEP can offer information about how the molecule interacts with the surface, revealing the electron-rich and electron-poor sites. These details allow us to predict potential reactions between the inhibitor and the surface of the molecule charge distribution, leading to a favorable interaction with the surface charges and enhancing its adsorption. Moreover, the molecule's charge distribution, as shown by the MEP analysis, can influence the position of ions in the electrolyte solution and then modify the EDL^{155,163}. For instance, ref. 164 investigated the interaction of hydrazone derivatives with the Fe surface using the electrostatic potential maps and Mulliken atomic charges, and the nucleophilic and electrophilic regions of the hydrazone derivatives could be identified with both quantities. The nucleophilic regions are responsible for interactions with the Fe surface due to their electron-rich properties.

Investigating the interaction between the inhibitors and the metallic surface is an indisputable improvement to QSAR and MEPTIC approaches. That allows for evaluating several properties that offer insights into the molecule's ability to bind to the surface. However, many works use unrealistic surface models or neglect to include crucial ingredients, such as solvent effects. We discuss these issues in the following.

Surface models

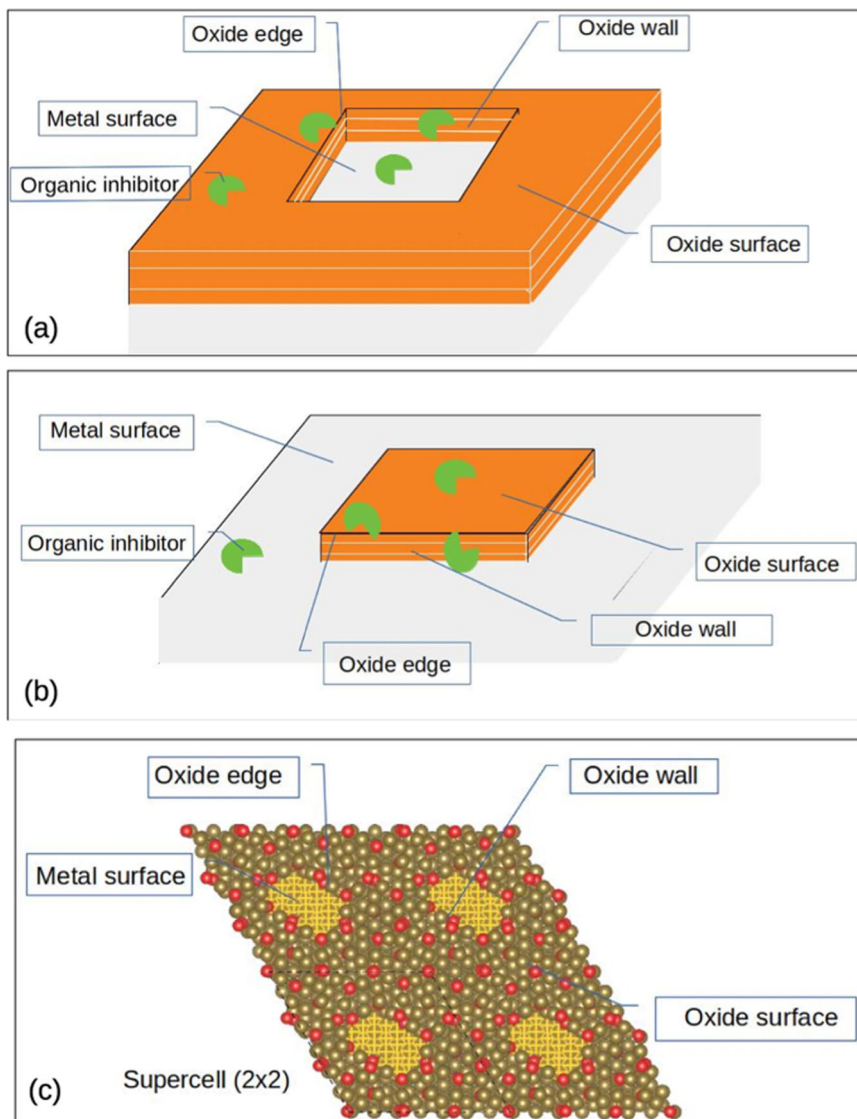
The models used to simulate the metallic surface play a pivotal role in CI modeling. Simple surface models typically consist of bare crystalline metallic surfaces oriented according to specific Miller indices, where the inhibitor molecule binds to the surface according to the different adsorption sites on the surface. Simple surface models neglect essential features of the surface, such as surface crystalline structure, grain boundaries or defects, or are present when the material is in dissolution, such as the formation of oxide layers and other adsorbates on the surface. In all cases, depending on the pH of the media, a native oxide layer (or the corresponding hydroxide) can be formed on the surface, forming a passivated surface. In that case, the surface might become less reactive, increasing its corrosion resistance. Therefore, it is essential to consider more complex metallic surfaces in molecular modeling works to have more realistic models^{132,157,165,166}.

However, modeling the passivated surface is not straightforward due to the more complicated structural and electronic properties than bare metal surface¹⁶¹. Passivated surfaces are often disordered, or present different terminations, and their lattice vectors can have a mismatch with the ones of the metallic surface. That requires using larger supercells to minimize the strain, which increases the computational cost. Furthermore, the inhibitor may have more adsorption modes for passivated surfaces than for bare metals.

A few articles dealing with oxidized surface models are reported in the literature^{5,114,133,135,155,161,167–170}. Chiter et al.¹³³ investigated the formation of MBI monolayers on Cu(111) surfaces covered by an ultra thin Cu_2O (111) film. Both thione and thiolate MBI species formed the monolayers. The SAM formation is favored at high coverages, where the molecules adopt a perpendicular orientation to the surface, enhancing the $\pi - \pi$ interactions between the molecules. Their findings showed that the thiolate monolayer interacts more strongly with the surface than the thione due to the added Cu-C bond. The authors suggested that the MBI-thiolate can replace the H_2O and OH at the oxidized Cu surface due to its higher affinity with the surface, evaluated through its higher adsorption energy than the water/OH adsorption energy.

Chiter et al.¹⁶¹ studied MBT inhibitors on oxidized copper surfaces: Cu(111) surfaces covered by a layer of Cu_2O (111), where a dense and ordered monolayer perpendicular to the surface was obtained at full coverage, favored over single molecular adsorption at low coverage. They found that the adsorption induces a reconstruction of the oxide surface's

Fig. 5 | Model of the partially depassivated Cu surface. **a** Local depassivation model. The different parts on the surface are also depicted: Cu_2O surface, walls, and edges, as well as the metal surface and the corrosion inhibitor. **b** Incomplete depassivation situation. **c** Locally depassivated surface model, where the different parts on the surface will influence the inhibitors' adsorption. Adapted from ref. 138 with authorization.



outermost layer, and the results also suggest that both thione and thiolate forms of MBT might substitute H_2O and OH at the $\text{Cu}_2\text{O}(111)$ surface, forming a protective layer on the surface in an aqueous environment.

Later, ref. 138 also investigated the adsorption of MBT on locally depassivated Cu surfaces using DFT calculations. The surface model consisted of a $\text{Cu}(111)$ surface covered partially with an ultra thin layer of $\text{Cu}_2\text{O}(111)$. The authors were able to simulate different adsorption zones on the surfaces used: oxide and metallic surfaces, edges, and walls, as shown in Fig. 5. Their results show how the inhibitor interacts with different surfaces to form an organic film strongly adsorbed on it. Due to the interfacial barrier properties, the organic film can prevent the initiation of localized corrosion. In the different surfaces studied, the most reactive sites were found to be the exposed Cu atoms and the single and doubly unsaturated O atoms of the oxide. The reactive sites for MBT were the S (exo or endo) and N (N or NH) atoms.

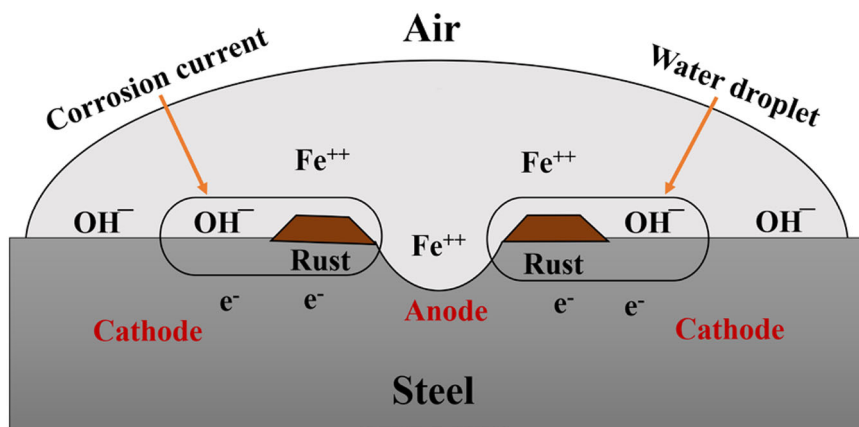
Another aspect studied by ref. 138 was the adsorption energy of MBT. They observed that the MBT adsorption changes with respect to the different zones along the surface. The strength of the adsorption decreases in the following order: oxide edges > oxide surface > metal surface > oxide walls. The adsorption trend was similar for the thione and thiolate species, except for the oxide walls in the latter one. The authors also found that the molecule blocks the most reactive sites, which are the most susceptible to interacting with ions that promote corrosion.

Wang et al.¹¹⁴ also evaluated the effect of surface morphology, investigating the adsorption energy of imidazole (IMD), benzotriazole (BTAH), and 2-mercaptobenzoxazole (MBO) on the grain boundary of $\text{Cu}(100)$ surface. They found that the corrosion inhibitors prefer to adsorb on the grain boundary of the surface, with perpendicular and parallel adsorption modes. In the perpendicular adsorption, the molecules bond to the surface through the azole group. In the parallel one, the bonding occurs through the benzene ring and the azole group.

Other corrosion products such as Cl, H, and other counterions can also be adsorbed on the surface, and their presence might modify the surface reactivity¹⁰⁹. The coadsorbed products can also modify the thermodynamics and kinetics of some stand-alone reactions, block the surface's reactive sites, or modify the surface electronic structure¹⁷¹. Taylor et al.¹⁷², for instance, investigated how the adsorption of Cl is influenced by the coadsorption of H_2O , OH , and O on the bare surface of some metallic systems: $\text{Ni}(111)$, $\text{Fe}(110)$, $\text{Mg}(0001)$, $\text{Zr}(0001)$, and $\text{Al}(111)$. The adsorption of Cl is related to its role in interfering with processes such as the re-passivation or metal dissolution, which can either inhibit corrosion by the growth of passivating oxide phases or accelerate corrosion.

Dlouhy et al.¹⁷³ systematically investigated how the co-adsorption of O, OH, H, and Cl affect the adsorption of imidazole on $\text{Cu}(111)$ using high-throughput DFT calculations, covering over 400 different adsorption configurations, evaluating the coverage effects, and the distance between

Fig. 6 | Sketch of the corrosion mechanism of steel caused by exposure to water. The anodic and cathodic sites are adjacent, and at the pit's edge, the rust is formed by different oxidized Fe compounds. Adapted from ref. 227 with authorization.



imidazole and the co-adsorbates. Their findings revealed an enhancement in the imidazole adsorption in the presence of O and Cl. At the same time, H and OH have negligible impact on the adsorption, even if OH can also diminish it. Furthermore, the higher co-adsorbate concentration on the surface played a stabilizing role in the imidazole adsorption through the formation of hydrogen bonds between the imidazole and the co-adsorbate and the change in the induced work function due to the co-adsorption. The contrary effect was investigated by ref. 174, where the layers of corrosion inhibitors, long chain *n*-alkyl carboxylic acids, play a role of protecting a metallic Al surface from the penetration of Cl[−]. Their DFT calculations showed that the energy barrier for the Cl[−] penetration increases with the thickness of the inhibitor layers and Cl[−] concentration.

Effect of anodic and cathodic zones

During the adsorption process of the corrosion inhibitor on the metallic surface, some chemical transformations, such as the making/breaking of bonds, or physical aspects, such as conformational rearrangements, can occur. Some of these chemical transformations are electrochemical reactions. During the corrosion process, there are two different electrochemical zones on the metallic surface exposed to the solvent media where two electrochemical reactions occur: oxidation (anodic reaction) and reduction (cathodic reaction), which are linked together to form a corrosion cell. In the oxidation process, the electrons lost travel to the cathodic site. The anodic reaction is the dissolution of the metal, while the cathodic one depends on what reducible species are in solution but usually is the reduction of the dissolved oxygen gas.

The metal dissolution produces metal cations that can react with the electrolytes and form soluble compounds or insoluble ones (rust) like metal oxide or hydroxide, depending on the electrode potential and pH conditions. In turn, the metal dissolution leads to a mass loss in the material, which can affect its structural resistance. This process is illustrated for steel in Fig. 6. The Fe dissolution occurs in the anodic site, surrounded by the cathodic site, leading to the rust formation at the pit's edge. Different oxidized Fe compounds form the rust that gets deposited on the material surface.

Understanding these fundamental reactions and their kinetics at the nanoscale through molecular modeling might help in proposing inhibitors or even comprehending better the underlying mechanisms of the inhibitors currently used¹⁷⁵. Some authors have explored these reactions using molecular modeling^{90,114,167,169,170,176,177}. Kokalj et al.¹⁵⁵ investigated the adsorption of benzotriazole on Cu₂O and Cu surfaces using DFT, finding that benzotriazole passivates the under-coordinated surface sites, which suffers the corrosion attack. In this case, the adsorption of benzotriazole significantly reduces the metal work function. They also suggested that this effect might potentially result in a reduction of the anodic corrosion reaction, as it is reported in the experiments¹⁵⁵.

To model these processes properly, it is necessary to consider some key aspects, such as the solvent structure rearrangement due to the dissolution

process. Typically, the time scale of these processes is longer than that provided by molecular modeling, especially QM simulations. Some chemical reactions occur on time scales ranging from nanoseconds to milliseconds, while QM simulations are generally limited to tens of hundreds of picoseconds. It is also important to consider the metal-solvent interface, as its characteristics will affect the reactions.

Solvent effects

Solvents play a central role in the corrosion process. Many chemical and physical properties of CI, such as reaction rates, solubility, acidic-basic properties, hydrogen bonds, etc., depend on the solvent media. Thus, it must be considered in CI modeling if one wants to perform simulations as realistically as possible¹⁷⁸. The most direct way of including the solvent effects is by explicitly adding solvent molecules. Nonetheless, the high computational cost needed for that in QM simulations, not only in terms of the increased number of atoms but also the time scale that should be reached to sample the configurational space satisfactorily (e.g., in MD simulations), is the main reason why the majority of the QM simulations do not explicitly consider solvent molecules. Moreover, when the solvent effects are included in simulations, most of the works only consider pure water, which is not ideal for simulating the actual aqueous solution with electrolytes present in corrosive media. Some authors do go beyond and consider solvents other than pure water^{52,53,61,64,67,73,76,80,81,115,142,179–185}.

A widely used method to include the solvent effect in QM simulations is through continuum/implicit solvent methods, where the solvent is considered a continuum dielectric¹⁸⁶. This approach can also be used to estimate solvation free energies (The solvation free energy estimates the energy involved in taking a solute from a gas phase and inserting it into a liquid/solvated media.) in chemical reactions^{187,188}. In that manner, quantities such as adsorption energies or descriptors used in MEPTIC/QSAR can be obtained, now including the solvent effects^{79,97,99,102,127}. This sort of method, such as the polarizable continuum method¹⁸⁹, usually includes only the electrostatic contribution (Some continuum solvation models such as the Solvation Model based on Density¹⁹⁰ considers dispersion interactions.) to the solvation energy.

Using this continuum approach to model the solvent, some authors have calculated the adsorption energies of corrosion inhibitors^{79,127}. For instance, ref. 127 investigated the influence of solvent polarity in the adsorption of SAMs on Cu surfaces, incorporating the solvent effects via the Conductor-like Screening MOdel (COSMO)¹⁹¹. By simulating various solvents with different polarities, using their respective dielectric constants, they found that the solvent polarity plays a significant role in the formation of dissociated *n*-octadecanethiol (C18S) SAMs compared to the non-dissociated case (C18SH). Their findings indicated that as the solvent polarity increases, the adsorption energy becomes more negative, making the adsorption stronger¹²⁷.

Laggoun et al.⁷⁹ reported on the adsorption energy of *p*-toluenesulfonylhydrazide on the Cu surface computed with DFT, including the solvent effects also using COSMO. The authors considered the HCl solution by choosing the dielectric constant accordingly. In that case, all geometries were optimized in the presence of the continuum solvent. They obtained a negative value for the adsorption energy, suggesting that the inhibitor would attach to the surface under the solvation conditions considered.

Some authors compare the inhibitor's solvation free energy with its adsorption energy on a given surface to evaluate if it is likely to be adsorbed on a metallic surface or prefers to be surrounded by the solvent. Gustincic et al.¹³⁵, for instance, evaluated that effect using the COSMO model. Although not many details are given, the authors found that the deprotonated forms of the molecules investigated interact more strongly with the solvent (solvation free energies of about -3 eV) than with the surface (adsorption energies of about -2 eV) for the coordinatively saturated site studied. This analysis can provide some initial insights into the solvent effects, and conducting a more comprehensive analysis will allow a deeper understanding of the solvent's role.

Reactivity indices of corrosion inhibitors have also been evaluated under solvent effects via implicit models^{54,69,76,79,81,82,149,192}. For instance, ref. 149 investigated the experimental and theoretical CI performance of thiourea derivatives on carbon steel using COSMO to analyze the solvent effects on some reactive descriptors, such as Fukui indices. The authors found small changes in the charge distribution of the inhibitors compared with the case in vacuum. They concluded that the inhibitors with more negative solvation free energies, i.e., those interacting more strongly with the solvent, will perform worse than those with lower solvation free energies. The solvation free energy trend obtained also follows the adsorption energies trend (computed from MD simulations with classical potentials) for the varying coverages.

Implicit solvent methods could be valuable in understanding the solvent effects on the inhibitor's CI mechanism. Nonetheless, non-electrostatic interactions like the dispersion forces and the explicit interaction between the solvent molecules and the corrosion inhibitor must be included to have a complete description of these effects. In that sense, both QM and MM simulations could describe those effects and interactions. However, to our knowledge, no articles have addressed QM simulations with explicit solvent so far in the CI modeling. Since the computational cost of MM simulations is generally low compared to QM simulations, the inclusion of explicit solvent molecules is commonly reported in works using MM simulations.

For MM simulations, the interactions between the inhibitor, surface, and solvent are typically governed by well-established FF such as the SPC¹⁹³, TIP3P, and TIP4P¹⁹⁴ models. Several authors^{52,53,57,61,62,64,67,68,73,80,111,115,117,137,142,179–185,195,196} reported on MD simulations with classical potentials including explicit water molecules to address some specific aspect of CI. Oukhrif et al.⁵³, for instance, investigated the CI performance of five pirazolylnucleosides on Cu(111) surfaces in acidic media, using MD with classical potentials, DFT, and Monte Carlo simulations. Their MD results showed that all the molecules adopted a parallel adsorption configuration on the surface. They attributed this adsorption configuration to the enhancement of the bond formation between the inhibitor and the Cu surface due to the electron donation between the *p*-orbitals from the active sites of the inhibitor to the vacant *d*-orbitals on the Cu surface.

Gao et al.⁶⁸ employed weight loss experiments, electrochemical measurements such as electrochemical impedance spectroscopy, and microscope techniques such as atomic force and scanning electron microscopy to evaluate the CI performance of the Papain freeze-dried (PFD) compound. Then, using MD simulations with classical potentials, including 1000 water molecules in the COMPASS FF framework, they proposed that the protonated PFD (PFDH⁺) can be adsorbed on the Cu(111) surface on a parallel pattern. This parallel adsorption configuration can provide maximum coverage on the surface, protecting the Cu surface from the corrosive media.

The structural features of polyaspartic acid (PASP), polyepoxysuccinic acid (PESA), oxidized starch (OS), and carboxymethyl cellulose inhibitors for CaCO₃ and CaSO₄ were evaluated by ref. 56 using MD simulations with classical potentials and analyzing the coordinates through radial distribution function. The radial distribution functions showed peaks below 3 Å, which represents ionic bonds (chemisorption) between the inhibitor and the surface. When the solvent was included in the simulations, the peak intensity for the radial distribution function decreased. This showed that the water molecules weaken the interaction between the inhibitor and the surface.

As one can see, including the solvent effects is challenging, as a cost-effective and accurate method is needed. A purely QM approach is too computationally expensive, while a purely MM approach might not be accurate enough to account for all the occurring phenomena. To overcome this problem, one can use a hybrid methodology that combines the low computational effort of MM and the high accuracy of QM, the so-called Quantum Mechanics/Molecular Mechanics (QM/MM) method. In that case, the system is split into two subsystems: one described with QM and the rest with MM. The solvent atoms, usually comprising a large number of atoms, can be included in the MM subsystem. The QM system is chosen to be the part of the system that requires a higher accuracy (e.g., where the charge transfer occurs). With that, fewer atoms are considered in the QM subsystem, which is the most computationally expensive. Thus, larger time scales, as well as a realistic amount of atoms, can be reached. This method is widely applied in biological systems and the area of biosensors^{197–204}. However, it is yet to be explored in the context of CI.

Electrodes' potential effects

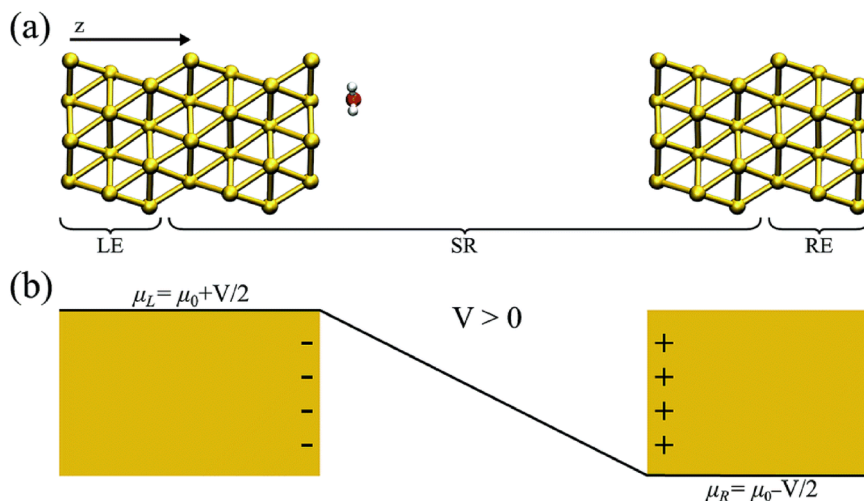
The last aspect we highlight when investigating the corrosion process is the electrodes' potential effect. Including the electrode potential is essential to describe the electrochemical reactions that take place during the CI process. Moreover, the electrode potential also affects the adsorption of the inhibitor, changing its alignment with the surface. This could change the inhibitor's ability to bond to the metallic surface and the inhibitor-inhibitor interactions that lead to the formation of the subsequent layers adsorbed on the material¹⁷⁵.

When the voltage is applied to metallic electrodes (the working and the reference electrodes in a typical electrochemical cell), we observe the charging of the metal and, consequently, the formation of an electric field between the electrodes, which will induce polarization in the system. The inhibitor's charge distribution will be affected by this polarization, inducing its accumulation and depletion in certain areas. This induced charge distribution has an impact on the structure of the system's EDL, which remains a challenging aspect to characterize correctly in molecular modeling.

Different methodologies are available in the literature for including the electrode's potential in molecular modeling. These approaches involve changing the charges of the electrodes by adding or removing electrons, introducing constant electrical potentials, employing Grand Canonical formulations, or shifting the chemical potential of the electrodes. However, each of these methods comes with some challenges and limitations, which we will discuss in the following^{205,206}.

In MM simulations, a common approach to account for the electrode potential involves modeling the induced charges on the metal atoms by external charges in the electrolyte. Gaussian functions centered on the surface atoms represent the induced charge density on the metal surface atoms. Then, the induced charges are evolved at each simulation step using an extended Lagrangian technique^{207,208}. In that way, the MM simulation can account for the charge in the slab, allowing us to evaluate the response of the electrolyte under those conditions. This approach is able to model applied external voltage differences between different electrodes²⁰⁹. It can qualitatively predict the structure of water monolayers on different metal substrates (Cu, Ni, Ag, and Pt) when compared with experiments. However, some adjustments or generalizations are necessary when dealing, for example, with the presence of adsorbates on the surface, or the reconstruction of the metal surface induced by the voltage^{209–213}.

Fig. 7 | Illustrations of the metal-water system and the capacitor voltage effect. **a** A diagram illustrating the metal-water system studied via the non-equilibrium Green's functions formalism employed by ref. 205. The left (LE) and right (RE) electrodes, as well as the scattering region (SR), are denoted. **b** A sketch illustrating the effect of a positive voltage on a parallel plate capacitor. The accumulated charge in each plate, as well as the voltage ramp, are shown. Adapted from ref. 205 with authorization.



Reed et al.²¹³ proposed a similar methodology that uses variable charges to introduce the applied voltage. The model, based on the ref. 209 formulation, adjusts the magnitudes of the variable charges on each step of the MD simulation with classical potentials using a variational procedure to keep the potential constant. It has been applied to describe the interfacial structure between two ionic liquids conformed by binary mixtures of molten salts, accurately reproducing the charge distribution within the electrode.

Petersen et al.²¹⁰ developed an efficient approach where the electrode polarization by the electrolyte is considered using the image charges method. In this method, the net fluctuating charge is distributed on the surface atoms of each electrode, and an additional charge is added to maintain constant the potential difference. This approach has been applied within the Marcus Theory framework to determine the probability for oxidation and reduction of reactants.

As one recent application of these methodologies, ref. 212 performed MD simulations with classical potentials of water at electrified graphene interfaces to analyze its structuring, dynamics, and spectroscopic properties. They found that the applied voltage in the simulations dramatically affects the structure and dynamics of water, where positive voltages slow down water's reorientation and translational dynamics. In contrast, an increasingly negative voltage first accelerates the interfacial water dynamics before being reduced at large negative voltages. They attributed these dynamics to the hydrogen bond exchange.

While all these methodologies offer important insights into the effect of the electrode's potential, the use of empirical models restricts the scope of the results. Ideally, using QM approaches would provide a more accurate understanding of these effects. One of the first attempts to describe the electrodes' potential effects using QM simulations was done by ref. 214 and ref. 215 introducing a net surface charge density in the electrodes and maintaining the charge neutrality in the electrochemical cell with a background charge. The induced electric field due to the charged surface at the interface leads to a potential drop in the system, which can be quantified by comparing the Fermi level of the system with a reference electrode far from the interface. This method is called double reference in the corrosion literature. Some other works^{216,217} applied DFT calculations with *a posteriori* corrections to introduce the thermodynamics effects due to the applied voltage. In this last case, even if their findings could be useful to elaborate catalytic mechanisms, the effects of the induced electric field at the interface are still missing²¹⁸.

The electrodes' potential effects have also been included in QM methodologies that consider an implicit solvent model. In this regard, ref. 219 included the voltage through an external potentiostat added to the system. The electronic charge at the metallic surface was controlled by varying the solvent dielectric constant, as proposed by ref. 220. Grand canonical approaches are also reported in the literature to include the voltage

in the simulations^{221–224}. Within these approaches, a remarkable example was carried out by ref. 223, where a thermopotentiostat approach was developed to compute the dielectric constant of nanoconfined water at constant temperature and electrode potential. Their findings agreed with the experimental observed anisotropic dielectric response in nanoconfined water.

A recent work from ref. 218 investigated the effect of the applied voltage on water-gold interfaces using QM simulations. They used a hybrid explicit-implicit approach to describe the solvent and fixed charges on the Au surface to modulate the electrode potential. Their results showed that the applied voltage affects the structural properties of water and its orientation. Their results suggested that the water forms at least one structural layer with a higher density than bulk water adjacent to the Au(111) electrode.

One method that can explicitly account for the electrodes' potential is the non-equilibrium Green's functions (NEGF) formalism. In this approach, an open system is considered, and the electrodes can be kept under different chemical potentials. An electric field is naturally established in the system, and the charge accumulation/depletion on the metallic atoms is fully described. Pedroza et al.²⁰⁵ have recently applied the NEGF approach to investigate the dynamics of a single water molecule under a voltage applied to Au electrodes, as depicted in Fig. 7. Their findings showed that the water molecule tends to align its dipole moment with the generated electric field in the device. Depending on the sign and magnitude of the applied voltage, either the molecule is attracted or repelled in an asymmetric trend.

Later, ref. 225 extended Pedroza et al.'s work to liquid water by considering Au electrodes in contact with 40 water molecules, demonstrating the feasibility of the method to describe solid-water electrified interfaces. The NEGF can provide a realistic picture of the electrified solid-liquid interfaces, but the computational cost can become prohibitive. A full description of the system (solvent molecules, counter-ions, electrodes, and inhibitors) could require hundreds to thousands of atoms. Multiscale approaches like the QM/MM methods could also overcome those limitations²²⁶. However, those methods are yet to be applied in the context of CI.

As discussed in the introduction to the advanced simulation of CI it is vital that processes A4–A6 are included in simulations and a major contribution of this review is to highlight methods and strategies to do so. As outlined in “Effect of anodic and cathodic zones” the effect of anodic and cathodic zones is critical as it determines the nature of surface charge, surface potential, and the efficiency and nature of inhibitor adsorption. However, the effect of such zones cannot be properly simulated without simulation of both solvent effects (A5) and potential effects (A6). In “Solvent effects” we review papers that outline how solvent effects may both affect the competition between inhibitor solvation and surface absorption and also the strength of such absorption. The section also outlines the complexity of modeling the solvent effects and the relative advantages of QM and MM

methods highlighting the need particularly for MM simulations of selecting appropriate modeling structures and in particular FFs. “Electrodes’ potential effects” highlighted that potential effects can affect the adsorption and alignment of the inhibitor on the metal surface but also the formation of subsequent inhibitor layers. A variety of approaches are outlined but many of these methods have limitations and cannot freely evolve, an emerging approach using NEGF formalism is presented that does permit charges to freely re-arrange. Thus, the review highlights how these complex processes can be integrated into the simulation of CI.

In conclusion, a critical review of the main approaches used in CI modeling was presented, focusing on gaps found in the literature that need to be addressed to perform more realistic simulations. We highlight six important aspects (A) that a model might consider in order to describe the CI process realistically: (A1) the electronic properties of the isolated inhibitors, (A2) the interaction of the inhibitor with the surface, (A3) the surface model, (A4) the effect of anodic and cathodic zones on the surface, (A5) the solvent effects, and (A6) the electrodes’ potential effects and how it shapes the inhibitor-inhibitor interactions and the monolayer and subsequent inhibitor layers. In this sense, we found that A1-A3 are regularly considered in the reported CI simulation literature, while A4-A6, as well as some more complex surface models in A3, are not.

Most of the CI modeling reported in the literature is mainly intended to support experimental observations. The most common approach for these works is to cover A1 and correlate these properties with experimental CI performance using several correlation techniques. However, the lack of interaction with the surface might not accurately describe the CI processes. To overcome that, some works include explicit interaction between the inhibitor and the surface, using either bare metallic or more complex oxidized surface models, thus addressing A2-A3. The more complete surface models allow us to better represent the interactions between the inhibitor and the surface but also increase the simulation’s complexity and computational cost, restricting their use in CI modeling.

As for the solvent effects, the most common approach found was the implicit solvent models, whether the inhibitor is investigated isolated or adsorbed on the surface. The implicit methods can provide a good insight into the solvation process, but they do not consider the explicit interaction between the solvent molecules, inhibitor, and the surface, which is important for the CI process since the inhibitor has to remove some solvent molecules from the interface to get adsorbed on the surface. Explicit solvent methods fit better for this adsorption process, but it makes QM modeling too expensive. In MM methods, such as the MD simulations with classical potentials, the inclusion of explicit water molecules is more common.

Lastly, in terms of the electrodes’ potential effects, which are essential to describe the induced surface charges, the polarization of the solvent and electrolytes, as well as the inhibitor-inhibitor interaction to form monolayers and subsequent layers, the reported methods available in the literature usually control the voltage by adding charges to the metallic atoms or using Gran Canonical approaches. In this regard, the NEGF formalism promises to provide an alternative to those approaches, allowing for controlling the voltage explicitly in the simulations, as it is usually done in experiments. However, those methods are yet to be applied in CI modeling.

In summary, a realistic model to describe the CI process should consider the aforementioned A1-A6 key aspects. Including all these effects will lead to a more detailed description of the CI process from the atomistic point of view, which will be determinant in designing corrosion inhibitors. Some of the results that can be obtained from these simulations might be used to feed artificial intelligence (AI) methods and multiscale models to construct the bridge between the nanoscale CI modeling and the continuum scale of the CI processes.

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Competing interests

The authors declare no competing interests.

Additional information

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