Supporting Information for

Anti-corrosion potential of 2-mesityl-1H-imidazo[4,5-f][1,10] phenanthroline on mild steel in sulphuric acid solution: Experimental and theoretical study.

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1. DERIVATION OF THERMODYNAMIC PARAMETERS USING STATISTICAL MODEL.

The inhibition process of an organic compound onto a metal surface can be explained by the formation of metal-inhibitor reaction complex. The adsorption of an inhibitor species, \( I \), on a metal surface, \( M \), can be represented by a simplified equation:

\[
M + I \leftrightarrow M (I)_{\text{ads}}
\]  

(1)

Let \( M \) of the above reaction be the system in the ensemble and the solvent containing inhibitor molecules as donor particles be the medium. The complex-forming process can be regarded as the course of distribution of donor particles to the system. So it is justifiable to extend the model of variable number of particles in statistical physics for the inhibiting process.

According to statistical physics [1], the probability of distribution for such kind of systems of variable number of particles is given by:

\[
\sigma(i, \varepsilon) = A \exp \left( \frac{i\mu - \varepsilon_i}{\theta} \right)
\]  

(2)

where \( A \) is the normalizing coefficient, \( \mu \) the chemical potential which depends upon the temperature and concentration of the donor particles, \( i \) the number of donor particles distributed in each system, \( \theta \) the distribution modulus, \( \varepsilon_i \) the energy of the system containing \( i \) donor particles, being assumed approximately equal for the systems containing the same number \( i \) of donor particles, and \( \varepsilon_i = 0 \) at \( i = 0 \).

The normalizing condition is:

\[
\sum_{i=0}^{n} \sigma(i, \varepsilon) = 1
\]  

(3)

or

\[
A \left\{ 1 + \sum_{i=1}^{n} \exp \left( \frac{i\mu - \varepsilon_i}{\theta} \right) \right\} = 1
\]  

(4)

The average number of donor particles accepted by each system is:
\[ \bar{n} = \sum_{i=1}^{n} i \omega(i, \varepsilon) = \sum_{i=1}^{n} i A \exp \left( \frac{i \mu - \varepsilon_i}{\theta} \right) \]  

(5)

Eliminating \( A \) from Eqs. (4) and (5), we obtain:

\[ \bar{n} = \frac{\sum_{i=1}^{n} i \exp((i \mu - \varepsilon_i) / \theta)}{1 + \sum_{i=1}^{n} \exp((i \mu - \varepsilon_i) / \theta)} \]  

(6)

For inhibiting process, the \( \text{M (I)}_{\text{ads}} \) formation reaction corresponds to the distribution with \( i = 0 \) or 1. The condition for which \( i = 0 \) is taken to correspond to a state of complete corrosion (surface coverage \( \eta = 0 \) and protection efficiency \( %I = 0 \)), \( i = 1 \) to a state of complete inhibition (surface coverage \( \eta = 1 \) and protection efficiency \( %I = 100 \)). The actual corrosion inhibition process is a random distribution between \( i = 0 \) and 1. So the corresponding actual protection efficiency (\( %I \)) is a data between 0 and 100, and the actual surface coverage \( \eta \) is equal to the statistical average value for such a (0, 1) distribution, then for inhibiting process, Eq. (6) is reduced to:

\[ \bar{n} = \eta = \frac{1}{1 + \exp((\varepsilon - \mu) / \theta)} \]  

(7)

Here \( 0 < \bar{n} < 1 \). Considering \( \eta \) is related to the concentration of donor particles and \( \varepsilon \) to the thermodynamic equilibrium constant of the complex-forming reaction, which is correlated to the change of free energy of adsorption \( \Delta G^\circ_{\text{ads}} \), thus the following equation can be derived from Eq. (7) [2, 3]:

\[ \ln \left( \frac{1 - \eta}{\eta} \right) = \frac{\Delta G^\circ_{\text{ads}}}{\theta} - \frac{RT \ln C}{\theta} \]  

(8)

where \( C \) is the concentration of inhibitor particles.
S.2 SOME GLOBAL AND LOCAL REACTIVITY PARAMETERS BASED ON THE DENSITY FUNCTIONAL THEORY.

Density functional theory has been found to be successful in providing insights into the chemical reactivity and selectivity, in terms of global parameters such as electronegativity ($\chi$), hardness ($\eta$) and softness ($\sigma$), and local ones such as the Fukui function ($f(r)$) and local softness ($s(r)$). Thus, for an $N$-electron system with total electronic energy ($E$) and an external potential ($\nu(r)$); chemical potential ($\rho$) known as the negative of electronegativity ($\chi$), has been defined as the first derivative of the $E$ with respect $N$ at $\nu(r)$ [4]:

$$\chi = -\rho = -\left(\frac{\partial E}{\partial N}\right)_{\nu(r)}$$  \hspace{1cm} (9)

Hardness ($\eta$) has been defined within the DFT as the second derivative of the $E$ with respect $N$ at $\nu(r)$ property which measures both the stability and reactivity of a molecule [4]:

$$\eta = \left(\frac{\partial^2 E}{\partial N^2}\right)_{\nu(r)} = \left(\frac{\partial \rho}{\partial N}\right)_{\nu(r)}$$  \hspace{1cm} (10)

where $E$ is the electronic energy, $N$ is the number of electrons, and $\nu(r)$ is the external potential due to the nuclei and $\rho$ is chemical potential.

The number of transferred electrons ($\Delta N$) from the inhibitor molecule to the metal surface can be calculated by using the following equation [5]:

$$\Delta N = \frac{\chi_{Fe} - \chi_{inh}}{2(\eta_{Fe} + \eta_{Fe})}$$  \hspace{1cm} (11)

where $\chi_{Fe}$ and $\chi_{inh}$ denote the absolute electronegativity of iron and the inhibitor molecule, respectively; $\eta_{Fe}$ and $\eta_{inh}$ denote the absolute hardness of iron and the inhibitor molecule, respectively.

$I$ and $A$ are related in turn to $E_{\text{HOMO}}$ and $E_{\text{LUMO}}$ using the equations below [6]:

$$I = -E_{\text{HOMO}}$$  \hspace{1cm} (12)

$$A = -E_{\text{LUMO}}$$  \hspace{1cm} (13)
These quantities are related to electron affinity ($A$) and ionization potential ($I$) using the equation below:

$$
\chi = \frac{I + A}{2}, \quad \chi = -\frac{E_{\text{LUMO}} + E_{\text{HOMO}}}{2} \tag{14}
$$

$$
\eta = \frac{I - A}{2}, \quad \eta = -\frac{E_{\text{LUMO}} - E_{\text{HOMO}}}{2} \tag{15}
$$

Recently, a new global chemical reactivity parameter has been introduced and is called an electrophilicity index ($\omega$). It is defined as [7]:

$$
\omega = \frac{\rho^2}{2\eta} \tag{16}
$$

This was proposed as a measure of the electrophilic power of a molecule. Global softness can also be defined as [7]:

$$
\sigma = \frac{1}{\eta} \tag{17}
$$

It is also important to consider the situation corresponding to a molecule that is going to receive a certain amount of charge at some center and is going to back-donate a certain amount of charge through the same center or another one. To describe the energy change associated with these two processes, the second order simple charge transfer formula was regarded as a two-parameter expression, in which the donation and back-donation processes are differentiated through the use of the values of the chemical potential for each case, while the hardness is fixed to the value of $\eta = (\mu^+ - \mu^-)$ in both situations. Thus, according to the simple charge transfer model for donation and back-donation of charges proposed recently by Gomez et al., [8], when a molecule receives a certain amount of charge, $\Delta N^+$:

$$
\Delta E^+ = \mu^+ \Delta N^+ + \frac{1}{2} \eta (\Delta N^+)^2 \tag{18}
$$

while when a molecule back-donates a certain amount of charge, $\Delta N^-$, then:
\[ \Delta E^+ = \mu^+ \Delta N^+ + \frac{1}{2} \eta (\Delta N^+) \]

If the total energy change is approximated by the sum of the contributions of Eqs. (18) and (19), and assuming that the amount of charge back-donation is equal to the amount of charge received, \( \Delta N^- = -\Delta N^+ \), then;

\[ \Delta E_r = \Delta E^+ + \Delta E^- = (\mu^+ - \mu^-) \Delta N^+ + \eta (\Delta N^+)^2 \]

The most favourable situation corresponds to the case when the total energy change becomes a minimum with respect to \( \Delta N^+ \), which implies that \( \Delta N^+ = -(\mu^+ - \mu^-)/2\eta \) and that;

\[ \Delta E_r = -(\mu^+ - \mu^-)^2 / 4\eta = -\eta / 4 \]

The local reactivity of the ALLOX was analyzed through an evaluation of the Fukui indices [8]. These are measurements of the chemical reactivity, as well as an indicative of the reactive regions and the nucleophilic and electrophilic behavior of the molecule. The regions of a molecule where the Fukui function is large are chemically softer than the regions where the Fukui function is small, and by invoking the HSAB principle in a local sense, one may establish the behavior of the different sites with respect to hard or soft reagents. The Fukui function \( f(r) \) is defined as the first derivative of the electronic density \( \rho(r) \) with respect to the number of electrons \( N \) at a constant external potential \( v(r) \). Thus, using a scheme of finite difference approximations from Mulliken population analysis of atoms in MEIP and depending on the direction of electron transfer we have [9-10]:

\[ f_k^+ = q_k(N+1) - q_k(N) \]

(for nucleophilic attack) \hspace{1cm} (22)

\[ f_k^- = q_k(N) - q_k(N-1) \]

(for electrophilic attack) \hspace{1cm} (23)

\[ f_k^o = \frac{q_k(N+1) - q_k(N-1)}{2} \]

(for radical attack) \hspace{1cm} (24)

where \( q_k \) is the gross charge of atom \( k \) in the molecule i.e. the electron density at a point \( r \) in space around the molecule. The \( N \) corresponds to the number of electrons in the molecule. \( N+1 \) corresponds to an anion, with an electron added to the LUMO of the neutral molecule; \( N-1 \) corresponds to the cation with an electron removed from the HOMO of the
neutral molecule. All calculations were done at the ground-state geometry. These functions can be condensed to the nuclei by using an atomic charge partitioning scheme, such as Mulliken population analysis in Eqs. (22) - (24).
References


