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Cluster approach to corrosion inhibition problems: interaction studies

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Abstract

The interaction energies of 3,5 di-methyl pyridine (A) and 2,4 di-methyl pyridine (B) on the (1 0 0) surface of body-centered cubic (bcc) iron were determined via a cluster model and ab initio quantum chemical calculations at density functional theory level. The obtained energies were used to compare the inhibition behavior of these molecules for iron corrosion in hydrochloric acid solution. The iron surface and its adsorption sites (on-top, bridge, hollow) were considered as some clusters taken from two-layered ⟨1 0 0⟩ planes, i.e. $Fe_1(1)$, $Fe_4(2,2)$, and $Fe_5(4,1)$. So, the process for which quantum chemical calculations was carried out consists of adsorption of molecule A (B) on these clusters. Also for these molecules, two adsorption modes (planar adsorption (P) via pyridine ring and vertical adsorption (V) through nitrogen atom) with three azimuthal angles (0, 45, and 90°) were applied. Comparison of the theoretical and previous experimental results shows a reasonably good correlation which, in turn, supports the reliability of the method employed here.

Keywords: Corrosion inhibitors; Pyridine derivatives; Density functional theory; Iron cluster model

1. Introduction

Corrosion is an electrochemical process by which the metallic structures are destroyed gradually through anodic dissolution [1]. Therefore, various attempts must be employed to prevent or retard this destructive process among methods under taken, application of inhibitors is one of the most practical and economical ones. Inhibitors are chemical compounds containing hetero-atoms (O, N, P, S, . . .) or a de-localized pair of π electrons, through which the molecules are adsorbed on metallic surfaces and retard their degradation [2]. Therefore, the knowledge of the inhibition mechanism is important both from industrial and scientific points of view. In the last few decades, many experimental and theoretical investigations have been undertaken with the common goal of revealing of inhibitive action of various series of chemical compounds [3–8]. Eventually, experimental studies are straightforward, but they are often time-consuming, expensive, and wearisome. Theoretical work based on quantum chemical calculations have been proposed [3,8–10] which can predict some molecular parameters directly related to the corrosion inhibition behavior of the chemical compounds. Thus, after the prediction of these parameters, a correlation between those quantities and the corrosion behavior of similar chemical compounds can be made. This work attempts to establish such a correlation for pyridine derivative.

Pyridine derivatives have shown inhibition effects for corrosion of Armco iron in HCl aqueous solution [5]. In a previous work, the present authors have made some comparative prediction on inhibition efficiencies of molecules of 3, 5 di-methyl pyridine and 2,4 di-methyl pyridine using the isolated inhibitor model [11]. In the present work, we try to extend this work and develop a method which enables us to the direct prediction of inhibition behavior through the calculation of interaction energies of these two pyridine derivatives (Fig. 1) with the metal (iron) surface. We will apply the cluster model and ab initio quantum chemical calculations at density functional theory (DFT) level to the interacting pyridine derivative–iron metal surface system. The cluster model has been applied, previously, to the adsorption of molecules on the surface of catalysts [12,13]. In the present calculations, two extreme orientations of the inhibitor molecule relative to the iron surface are considered. These are the planar adsorption through the de-localized π electrons of the ring and vertical adsorption through the lone pair electron of the nitrogen atom. These orientations were first considered by Ayers and Hackerman [5] and then observed experimentally by others [14–16].

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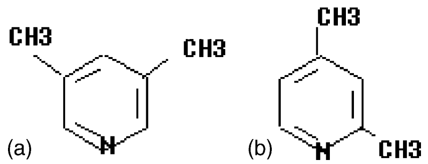

Fig. 1. Structural formula of molecules 3,5 di-methyl pyridine (a) and 2,4 di-methyl pyridine (b).

2. Theoretical studies

2.1. Cluster model

According to the cluster model, the interaction of the corrosion inhibitor molecule with the metal surface is considered locally. Thus, the quantum chemical study is restricted to the calculation of interaction energies between the molecule and metallic atoms upon which the adsorption is directly taking place. As this model has been applied to (1 0 0) planes of body-centered cubic (bcc) iron crystal lattice [8–10], the selected clusters, here, also involve fractures of (1 0 0). Fig. 2 illustrates schematically the distribution of iron atoms in the bcc crystal lattice through two layers of (1 0 0) planes. The distance of the closest adjacent atoms is 2.8664 Å and the two planes are separated by 1.4332 Å [17]. From Fig. 2, it is observed that three different adsorption sites can be imagined as:

1. O: on-top adsorption site; the inhibitor lies directly on top of the iron atom and interacts with it.
2. B: two-fold bridge adsorption site; the adsorption occurs via the center of two adjacent atoms and the inhibitor bridges them. This center has a C_{2V} symmetry.
3. H: four-fold hollow adsorption site; the adsorption site with C_{4V} symmetry. The inhibitor is adsorbed on the center of the four-adjacent atom square on the iron surface. In this case, the position of inhibitors relative to the second (1 0 0) layer is on top.

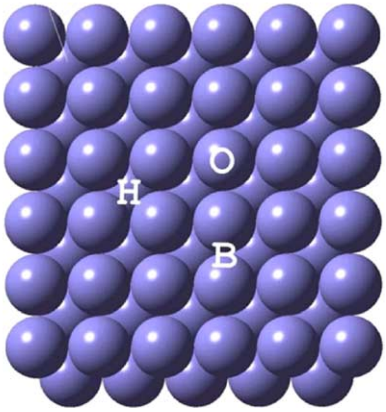

Fig. 2. On-top view of iron atoms in the bcc crystal lattice with O, B, and H sites.

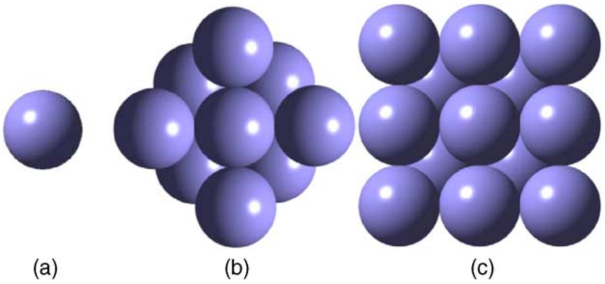

Fig. 3. Schematic diagrams of iron clusters for the on-top adsorption model: (a) Fe_1(1); (b) Fe_9(5,4); (c) Fe_{13}(9,4) iron clusters.

Beyond these, although, it is expected that larger clusters give better results, in practice computational hardware restricts us in cluster size selection.

Regardless to above restriction, the clusters can be constructed systematically as follows. For on-top adsorption site (Fig. 3):

1. Fe_1(1); single atom cluster (the simplest possible form for a cluster).
2. Fe_9(5,4); two-layered nine-atom cluster, the first layer has five and the second layer has four atoms.
3. Fe_{13}(9,4); two-layered 13-atom cluster, the first layer has 9 and the second layer has 4 atoms.

Similarly, the imagined clusters for B and H adsorption sites are, respectively, Fe_2(2), Fe_4(2,2), Fe_{14}(8,6), ... and Fe_5(4,1), Fe_9(4,5), and Fe_{21}(14,9), ...

2.2. Calculation method

As transition metal systems are electron-rich, their quantum chemical calculations at ab initio level are very time-consuming and huge. Furthermore, they encounter some difficulties with convergence problems. Among quantum chemical methods, the DFT has some merit (one of which is the inclusion of the relativistic effect as an electron correlation terms). Recently, a hybrid version of DFT and Hartree–Fock (HF) methods, i.e. B3LYP, has been introduced [18,19]. Briefly, this method uses a Becke's 3-parameter functional (B3) and includes a mixture of HF with DFT exchange terms associated with the gradient-corrected correlation functional of Lee et al. [20]. Although the three semi-empirical parameters are fitted to produce thermo-chemistry of a set of small organic molecules, but it has been shown that performs exceptionally well on transition metal systems as well, and has much less convergence problems than those commonly found for pure DFT methods.

For reducing of computational efforts, here, only valance electrons of iron were considered and the others treated by means of the pseudo-potential method. So, for iron atoms, the eighteen inner shell electrons which are less effect on the chemical bond formation ($1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$ core

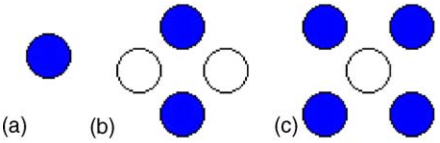

Fig. 4. Applied iron clusters for the evaluation of on-top (a), bridge (b), and hollow (c) sites.

electrons) were substituted by an effective core potential of Hay and Wadt [21]. In this paper, the LANL1 version of this which includes the scalar, mass velocity and Darwin relativistic effects [22] is used. The eight remaining electrons of iron in the valance layer ($3d^6$, $4s^2$ shell electrons) are described explicitly with a single-exponent minimal basis set. Other atoms in iron–inhibitor systems were treated by a STO-3G basis set [23].

All calculations were performed with the aid of Gaussian98 computer codes [24] working on 1800 MHz dual processors.

3. Results and discussion

The geometry of inhibitor molecules A and B were optimized via the B3LYP/ 6-31G** method. The calculation of the interaction energies between these molecules and surface sites were based on the clusters $Fe_1(1)$, $Fe_4(2,2)$, and $Fe_5(4,1)$ represented in Fig. 4. The electronic energies of these isolated iron clusters as well as molecules A and B ($E_{\text{iso, iron cluster}}$ and $E_{\text{iso, inhibitor molecule}}$, respectively) were obtained via the B3LYP/LANL1MB method. By a similar method, the total interaction energies of the inhibitor molecule–cluster model were calculated as a function of inhibitor distance from the iron surface. These energies were explored for both adsorption modes (P and V) with three azimuthal angles (0, 45, and 90°) [25] and the minimum energy values are given in Table 1.

Table 2
The adsorption energy differences (ΔE in a.u.) of molecules B and A for modes P and V; adsorption centers O, B and H; azimuthal angles 0, 45 and 90°

Mode	ΔE				
	O	B		H	
	0°	0°	90°	0°	45°
V	0.00137	0.02158	−0.01237	−0.00049	0.00339
P	−0.00187	−0.00423	−0.00383	−0.00125	−0.05032

From the data presented in Table 1, it can be deduced that the interaction energies have more negative values and the minimum distances of the adsorbed molecule are smaller for vertical adsorption. Such results can be contributed to the fact that the V mode is more likely to have a chemical nature, i.e. some kind of electron sharing is involved in this case. The values of ΔE, the difference between adsorption energies of molecules B and A are given in Table 2 for two adsorption modes (V and P) and three adsorption sites (O, B, and H). Negative signs of the ΔE values indicate that molecule B interacts stronger with the iron surface, thus B is expected to protect the surface better than A against corrosion. Furthermore, from the results of Table 2, the following points can be deduced:

1. In all cases given in this table, the P adsorption mode is more favorable for molecule B, i.e. $\Delta E = E_{\text{int}}(\text{B}) - E_{\text{int}}(\text{A})$ is negative.
2. In most cases studied, molecule B is a better inhibitor than A, i.e. B has a more negative E_{int} value, which is in accord with the experimental observation [5]. In three cases, however, namely, vertical adsorption on-top site, bridge site with azimuthal angle of zero, and hollow site with an azimuthal angle of 45, the opposite behavior is observed. It is probable that the steric effect, due to the presence of a methyl group at ortho position, plays a part

Table 1
Quantum chemical data for iron cluster–corrosion inhibitor systems

System[a]	r_{min}	E_{min}[b]	E_{int}[b]	System[a]	r_{min}	E_{min}[b]	E_{int}[b]
$OAVFe_1$	1.9	−345.29341	−0.09423	$OAPFe_1$	2.6	−345.22161	−0.02243
$OBVFe_1$	1.9	−345.29332	−0.09286	$OBPFe_1$	2.6	−345.22476	−0.02430
$BAVFe_4(2,2)d0$	2.0	−412.34426	−0.06002	$BAPFe_4(2,2)d0$	2.3	−412.32216	−0.03792
$BBVFe_4(2,2)d0$	2.6	−412.32396	−0.03844	$BBPFe_4(2,2)d0$	2.4	−412.32767	−0.04215
$BAVFe_4(2,2)d90$	1.8	−412.35771	−0.07347	$BAPFe_4(2,2)d90$	2.4	−412.31128	−0.02704
$BBVFe_4(2,2)d90$	1.7	−412.37136	−0.08584	$BBPFe_4(2,2)d90$	2.4	−412.31639	−0.03087
$HAVFe_5(4,1)d0$	2.6	−434.51671	−0.03548	$HAPFe_5(4,1)d0$	3.2	−434.51625	−0.03502
$HBVFe_5(4,1)d0$	2.9	−434.51848	−0.03597	$HBPFe_5(4,1)d0$	3.2	−434.51878	−0.03627
$HAVFe_5(4,1)d45$	2.6	−434.51906	−0.03783	$HAPFe_5(4,1)d45$	2.9	−434.45582	0.02541
$HBVFe_5(4,1)d45$	2.9	−434.51695	−0.03444	$HBPFe_5(4,1)d45$	3.3	−434.50742	−0.02491

[a] The first, second, and third letters, i.e. (O, B, H), (A, B), and (P, V), stand for adsorption center, molecules identification, and adsorption modes, respectively. Also, the term $Fe_{m+n}(m+n)$ indicates the used iron clusters and, finally, dθ represents the selected value for azimuthal angle ($\theta = 0$, 45, and 90°).

[b] E_{min} is the energy of the iron–inhibitor system at equilibrium distance of the inhibitor molecule from the metal surface, r_{min}. The interaction of the inhibitor molecule with the iron surface is known as E_{int} and equals to $E_{\text{min}} - (E_{\text{inhibitor}} + E_{\text{iron cluster}})$. The quantities are given in atomic units except the distance in Ångström.

in these observations. Specially, the $r_{\min}$ values given in Table 1 confirm this fact.

4. Conclusions

Through ab initio quantum chemical calculations and a cluster model, the interaction energies of 3,5 di-methyl pyridine (A) and 2,4 di-methyl pyridine (B) on the (1 0 0) iron surface were determined. These energies were utilized to compare the corrosion inhibition behavior of these two pyridine derivatives. The results obtained indicate that the vertical orientation in which the organic molecule is adsorbed through lone pair electrons of the nitrogen atom is more likely to have some kind of chemical nature in comparison to the parallel adsorption of the molecule which involves the π electrons of the aromatic ring. Comparison of the total energies of the two compounds studied (A and B) reveals that the molecule B is a better corrosion inhibitor for iron than A. Furthermore, some steric effects are observed through methyl groups in ortho positions of molecule B when this molecule is adsorbed on the iron surface in vertical orientation.

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