

Cluster/Polarized Continuum Models for Density Functional Theory Investigations of Benzimidazole Corrosion Inhibitors at Metal/Solution Interface

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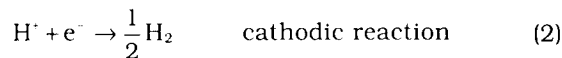
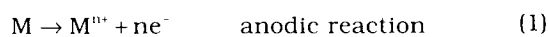
ABSTRACT

The molecular behavior of some benzimidazole (C₇H₈N₂) derivatives as corrosion inhibitors of iron in hydrochloric acid (HCl) solution was investigated quantum electrochemically via the inhibitors' chemical potential (μ), molecular softness (σ), and the extent of charge transfer from the inhibitor to the metal (ΔN). These quantities were obtained from density functional theory (DFT) calculations for three models, i.e., isolated inhibitors (in vacuo), inhibitors in solution, and, finally, inhibitors in electrical double layer (EDL). In these models, the effects of solvent, substrate, and electric field were considered using a polarized continuum model, iron Fe₁₃(9.4) cluster, and a finite-normal-homogeneous electric field. The investigations show that at the metal/solution interphase, the desolvation of benzimidazole takes place more easily than in the bulk of solution. Moreover, as the molecule enters EDL, an abrupt increase in μ and σ is observed. The calculations of interaction energies show that among the various possible adsorption modes of the inhibitor molecule on the iron surface, the vertical adsorption via a nitrogen lone pair is predominant. Finally, a relatively good correlation is observed between inhibitor efficiency and individual quantities of μ , σ , and ΔN . Moreover, it is observed that these correlations are improved as the model changes from a simple-ideal form (isolated inhibitor) to a more sophisticated-realistic one (inhibitors at metal/solution interphase).

KEY WORDS: benzimidazole corrosion inhibitors, cluster model, electric double layer, iron/solution interface, polarized continuum model based on integral equation formalism

INTRODUCTION

Corrosion is the destructive attack of a metal through chemical or electrochemical reactions with its environment.¹ The electrochemical reactions involved in the corrosion of metals in deaerated acid solution are:²



It is possible to reduce the rate of corrosion by suppressing one or both of these reactions. The addition of some specific organic compounds to the metal-environment system can suppress either or both of these electrochemical reactions. These specific compounds are known as corrosion inhibitors and most often contain hetero atoms (e.g., O, N, P, ...), aromatic rings, or π -electrons.^{3,4}

The experimental works on chemical compounds serving as inhibitor molecules have been going on for a long time and a number of compounds have been designed and applied.^{5,6} However, the theoretical works are relatively new and are mostly based on the isolated inhibitor model,⁷⁻¹¹ i.e., the substrate and environmental factors (e.g., substrate, solvent, and electric field in electric double layer [EDL], Figure 1) have been totally ignored.

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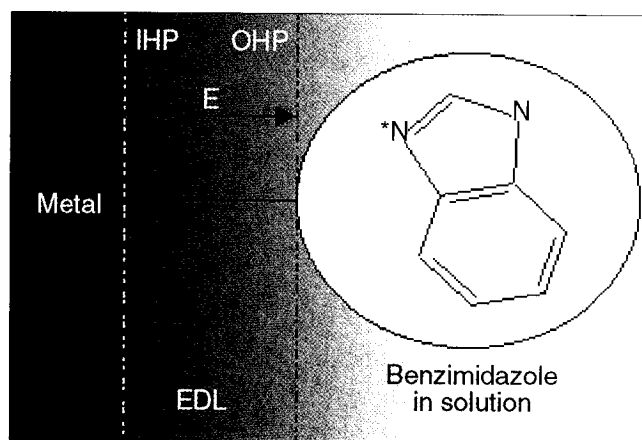


FIGURE 1. Schematic representation of the benzimidazole molecule, as it enters into the EDL.

Although the inhibitory action taking place is normally complex, it is generally accepted that two processes are involved. The first step is the diffusion of the inhibitor molecule to the metal/solution interphase (EDL), and the second is its adsorption on the metal surface. Both of these have been taken into account in our previous theoretical work.¹² In that work, the inhibition behavior of a series of pyridine derivatives as a corrosion inhibitor for iron and aluminum in acid media were investigated quantum electrochemically by some models, based on density functional theory (DFT), cluster model (CM), polarized continuum model (PCM), and EDL.¹³⁻¹⁶

In the present work, the authors have extended their investigations to a series of larger molecules with several adsorbing centers.

THEORETICAL MODELS

The study of substrate, solvent, and electric field effects has been performed via CM, PCM, and by applying a finite electric field, respectively, as given previously.^{12,14-15,17}

In general, fundamental studies of surface and interfacial phenomena (such as corrosion, catalysis, etc.) can be performed using two computational strategies, namely, CM and slab model (SM).¹⁸⁻¹⁹ In CM, the adsorbate-surface interactions are regarded locally, and standard quantum chemical calculations are performed on the portion of the metal surface under consideration.¹⁴ While in SM, the long range forces are also taken into account, and thus, calculations are made for multi-layer structures with two-dimensional periodicity.¹⁸ Although each of these models has its own merits, SM is more favorable for physical systems for the analysis of ordered over-layers, while CM is well suited for chemical systems with low symmetry adsorption.^{14,18-19} Considering these facts in the present work, CM has been preferred over SM (and

its related affairs such as the relaxation of atoms in metal lattice). Therefore, our theoretical works have been performed accordingly.^{12,17,20} In PCM, the interaction of inhibitor molecules and solvent are accounted for by considering inhibitor molecules trapped in a cavity surrounded by a continuum dielectric media.¹² However, since solvent molecules behave anisotropically adjacent to the metal/solution interface, the application of a special version of PCM based on integral equation formalism, IEFPCM, seems to be more appropriate.²¹⁻²² Moreover, the effect of the electric field present in EDL (Figure 1) is taken into account with a perturbation term included in the Hamiltonian of the system.^{12,23}

CALCULATION METHODS

Transition metal systems are electron-rich and their quantum chemical investigations at ab initio levels are very time-consuming and huge. Furthermore, they usually encounter some computational difficulties with convergence problems. Among quantum chemical methods, DFT has some merits in this regard and has been used successfully for theoretical investigations of surface-related phenomena on iron²⁴⁻²⁵ and other transition metals.²⁶⁻²⁸ Recently, a hybrid version of DFT and Hartree-Fock (DFT/HF) methods, i.e., B3LYP, has been recognized and widely used for transition metals^{17,27-28} with much fewer convergence problems than those commonly found for pure DFT methods.²⁹⁻³⁰ Briefly, B3LYP uses a Becke's three-parameter functional (B3) and includes a mixture of HF with DFT exchange terms associated with the gradient-corrected correlation functional of Lee, Yang, and Parr (LYP).³¹⁻³² Since core electrons of surface atoms have fewer effects on chemical bond formation between inhibitor molecules and the metal surface, these electrons are commonly treated by means of pseudo-potential methods, and the remaining electrons of metal are described by a double zeta (DZ) basis set.^{27,33} Thus, in the present work, the iron atoms were described by LANL1DZ in which the 18 inner shell electrons of iron ($1s^2 2s^2 2p^6 3s^2 3p^6$) were substituted with an effective core potential of Hay and Wadt,³⁴ and the other remaining electrons at the valence layer ($3d^6 4s^2$) were described explicitly with DZ. Using this basis set, computational time and convergence difficulties were considerably reduced.

As we mentioned in the previous work,¹² the surface effect on corrosion inhibition studies of iron metal can be taken into account by using a two-layer cluster of 9 and 4 atoms of body-centered cubic (bcc) iron with orientation (100), i.e., $Fe_{13}(9,4)$, which is depicted in Figure 2. In order to keep this cluster with bulk metal characteristics for iron atoms, the naturally optimized structure was used. In this cluster the locus of atoms was determined from experimental crystallographic data,³⁵ namely, the distance of the closest ad-

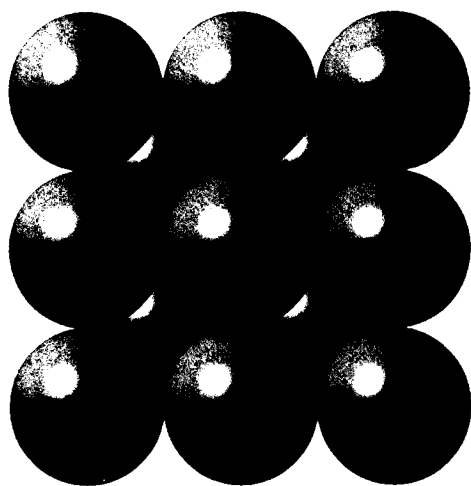


FIGURE 2. Top view of the $Fe_{13}(9,4)$ cluster selected from (100) crystal planes of bcc iron.

acent atoms was fixed at 2.8664 Å and the two layers were separated by 1.4332 Å.¹⁷ Moreover, since at the metal/solution interface, the inhibitor molecules are located in the solution part of the interface (Figure 1), their equilibrium structures were kept as an imposed structure by this region rather than in vacuo. The geometry optimization of inhibitor molecules through various models applied here used the standard basis set 3-21G.²³

All of the calculations in this work were performed with the aid of Gaussian98 computer codes³⁶ working on 1.800-MHz dual processors.

RESULTS AND DISCUSSION

The corrosion inhibitors investigated here are given in Table 1. These are four substituted benzimidazole ($C_7H_6N_2$) molecules with noncyclic functional groups. The experimental data of relative inhibition efficiencies were taken from Khaled's work.¹¹ The structures given in this table were geometrically optimized using the B3LYP/3-21G method.

Electronic chemical potential (μ) and molecular softness (σ) are two important factors, through which the inhibitory action can be investigated.^{12,37,38} These quantities are defined as follows:

$$\mu = \frac{\partial E}{\partial n} \approx -\frac{1}{2}(IP + EA) \quad (3)$$

$$\sigma = \frac{1}{IP - EA} \quad (4)$$

In these relations, IP and EA are ionization potential and electron affinity, respectively, and their values can be approximately equal to negative values of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels:

TABLE 1
Relative Inhibition Efficiencies
of Some Benzimidazole Derivatives
as Corrosion Inhibitors of Iron in Acidic Media at 25°C

B 51.07 ^(A)	HB 58.05
MB 68.24	AB 78.28

^(A) Experimental data taken from Khaled.¹¹

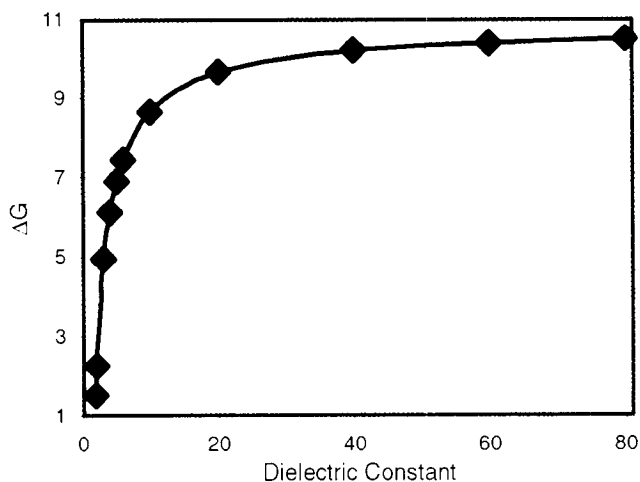


FIGURE 3. Variation of benzimidazole desolvation free energy (in kcal/mol) as a function of the dielectric constant of media.

$$IP = -E_{\text{HOMO}} \quad (5)$$

$$EA = -E_{\text{LUMO}} \quad (6)$$

The chemical interaction of inhibitor molecules with the metal surface is possible only after the migration of the molecules from the bulk of solution to the metal/solution interface (Figure 1). Thus, desolvation free energy (ΔG), chemical potential (μ), and molecular softness (σ) of benzimidazole were calculated using the IEFPCM method via the 6-311G** standard basis set, and graphed as a function of solvent dielectric constant (Figures 3 and 4). Figure 3 shows that ΔG

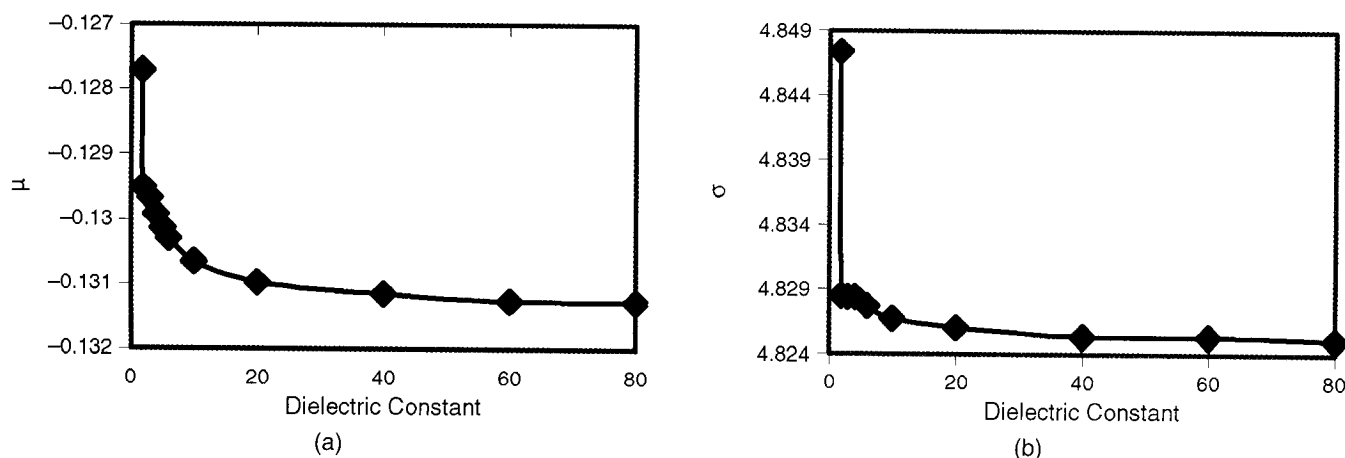


FIGURE 4. Variation of the benzimidazole electronic chemical potential (μ) and molecular softness (σ), in atomic units, during migration from the bulk of solution toward EDL.

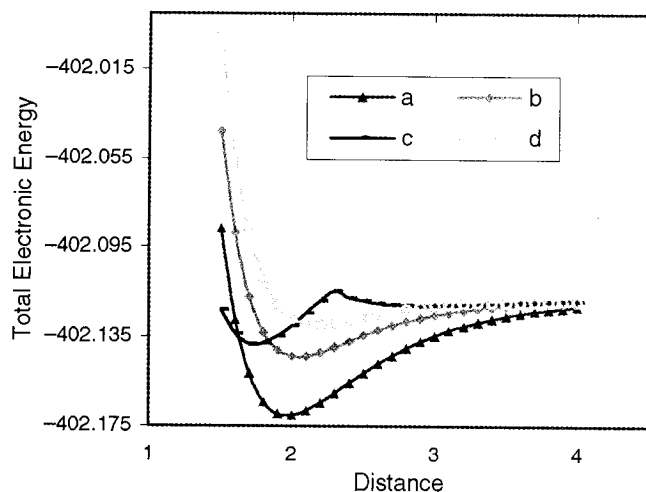


FIGURE 5. Total electronic energies of benzimidazole-iron system (atomic units) as a function of distance (Å) through (a) the lone pair of N^* , (b) π -electrons of N^* , (c) π -electrons of benzene aromatic ring, and (d) π -electrons of N (see Figure 1).

is varied smoothly until the molecule enters EDL. At this region ΔG is decreased abruptly, which could be interpreted to mean that the desolvation is more feasible in the field of EDL. Similarly, when the benzimidazole molecule enters EDL, both μ and σ are increased sharply (Figure 4). This is due to the fact that the inhibitor molecule becomes more activated (less stable and more susceptible to change²⁶) as it enters EDL, and this fact can be related to the presence of a giant electric field inside EDL (about 10^7 V/cm), which causes the media dielectric constant to decrease, and the inhibitor molecule becomes polarized (a small charge separation in molecule due to the effect of the electric field, resulting in an increase in the tendencies of the molecule to donate or accept electrons).^{12,39}

As benzimidazole can be adsorbed on the metal surface through several centers, the total electronic

TABLE 2
Interaction of Benzimidazole
with Iron Through Various Centers^(A)

Site	Equilibrium Distance (Å)	Interaction Energy (kcal/mol)
a	2.0	-34.0
b	2.0	-17.5
c	1.7	-13.8
d	2.2	-8.8

^(A) a: Lone pair of N^* ; b: π -electrons of N^* ; c: π -electrons of benzene aromatic ring; and d: π -electrons of N (Figure 1).

energy of the system (benzimidazole-iron) has been calculated for adsorptions through (a) the lone pair electron of pyridine-like nitrogen atom, N^* , (b) π -electrons of N^* , (c) π -electrons of the benzene ring, and (d) π -electrons of pyrrole-like nitrogen atom, N. These energies are plotted as a function of the distance of molecule from the iron surface (Figure 5). The interaction energies of the inhibitor molecule with the iron atom¹⁷ are also calculated and given in Table 2. As can be seen from this table, the maximum interaction occurs when the benzimidazole molecule approaches iron vertically and it is adsorbed via the lone pair of N^* . The minimum interaction occurs when adsorption is via π -electrons of N. This can be attributed to the fact that the adsorption through the pyridine-like nitrogen atom involves a pair of nonbonding electrons, while the adsorption through pyrrole-like nitrogen is through a pair of π -electrons, a phenomenon which is already involved in the aromatic ring.

When the benzimidazole molecule approaches iron to be adsorbed via π -electrons of the benzene ring (Figure 5[c]), at distance 2.3 Å, a repulsive interaction is observed. This is probably due to the repulsive interaction of electrons in d-orbitals of iron with π -electrons of the aromatic ring. A similar observation is not witnessed for the adsorption of benzimidazole on Al, a nontransition metal.⁴⁰

TABLE 3

IP and EA of Benzimidazole Derivatives (Table 1) Obtained from (B) In Vacuo Optimized Structure, (C) in Solution-Optimized Structure, and (D) and (E) in EDL Structure (the Case of [2] with Applying of an External-Normal Electric Field) when Adsorption is Vertical and Parallel, Respectively

Inhibitors ^(A)	B	HB	MB	AB
IP (eV)	8.35 ^(B)	8.00	7.98	7.33
	8.34 ^(C)	7.96	7.88	7.29
	8.40 ^(D)	8.03	7.95	7.37
	8.33 ^(E)	7.95	7.88	7.29
EA (eV)	-1.22 ^(B)	-1.59	-1.22	-1.79
	-1.22 ^(C)	-1.57	-1.25	-1.71
	-1.15 ^(D)	-1.49	-1.20	-1.68
	-1.22 ^(E)	-1.57	-1.25	-1.71

^(A) See Table 1.

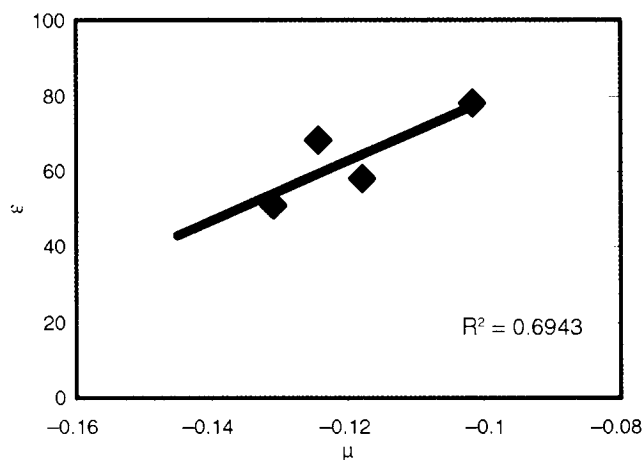
^{(B)-(E)} Corresponding data with models (1) through (4), respectively.

Although the Kohn-Sham orbitals and energies involved in DFT are artifacts with no real physical significance, they are being used frequently and it seems that they are quite close to the Hartree-Fock orbitals.¹¹ This route was used successfully in our previous work.¹² However, based on theorems involved in DFT (e.g., Hohenberg and Kohn¹²), it is more reliable to calculate IP and EA using the following Equations (7) and (8):²⁶

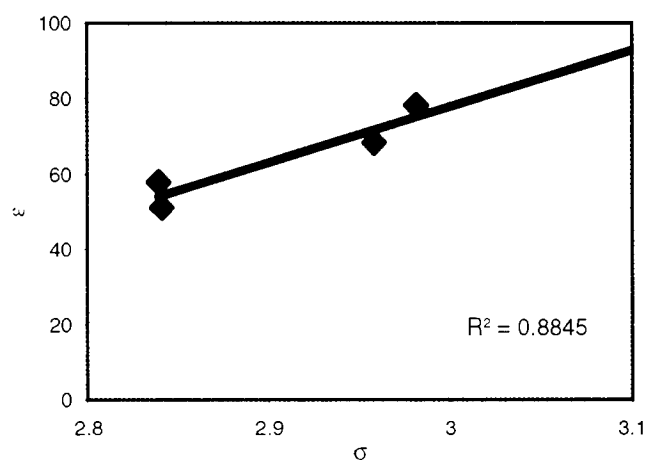
$$I^{\circ} \rightarrow I^{\bullet} + e^{-}; \quad IP = E^{\bullet} - E^{\circ} \quad (7)$$

$$I^{\circ} \rightarrow I^{-} + e^{-}; \quad EA = E^{\circ} - E^{-} \quad (8)$$

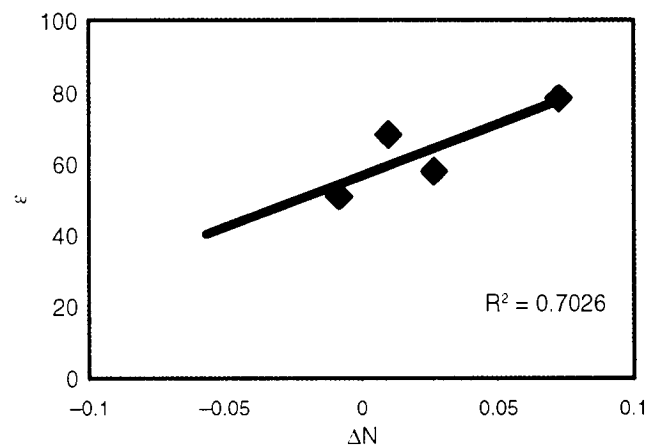
In these formulas, E^{\bullet} , E° , and E^{-} correspond to the total electronic energy of cationic, neutral, and anionic forms of inhibitor molecules (rather than interaction energies reported in Table 2). Moreover, it has been assumed that the electron transfer is adiabatic and thus the geometry of molecules remains as a neutral form. From Equations (7) and (8), IP and EA were obtained via the B3LYP/6-311G** method by four models, namely, (1) in vacuo optimized structure, (2) in solution-optimized structure (with dielectric constant of six), and (3) and (4) in EDL structure (the case of [2] with the application of a finite-external-normal-homogeneous electric field of about 10^7 V/cm) when the adsorption is taking place vertically and horizontally (relative to the metal surface), respectively. These values were calculated for inhibitor molecules in Table 1 and are given in Table 3. As can be seen, the results of models (2) and (4) are similar. It means that when the benzimidazole molecules are adsorbed horizontally, the presence or absence of the electric field has no considerable effect on the values of IP and EA. This behavior is a result of the low polarizability of the benzimidazole ring under the external-normal electric field. A similar behavior was formerly observed by our group for pyridine corrosion inhibitors.¹²



(a)



(b)



(c)

FIGURE 6. Corrosion inhibition efficiencies of benzimidazole derivatives for iron as a function of electronic chemical potential (μ), molecular softness (σ), and extent of charge transfer (ΔN). Data (in atomic units) were obtained from the in-vacuo optimized structure.

The inhibition efficiencies of the compounds given in Table 1 are plotted as functions of the inhibitor chemical potential (μ), molecular softness (σ), and charge transfer to the metal surface (ΔN) for the three

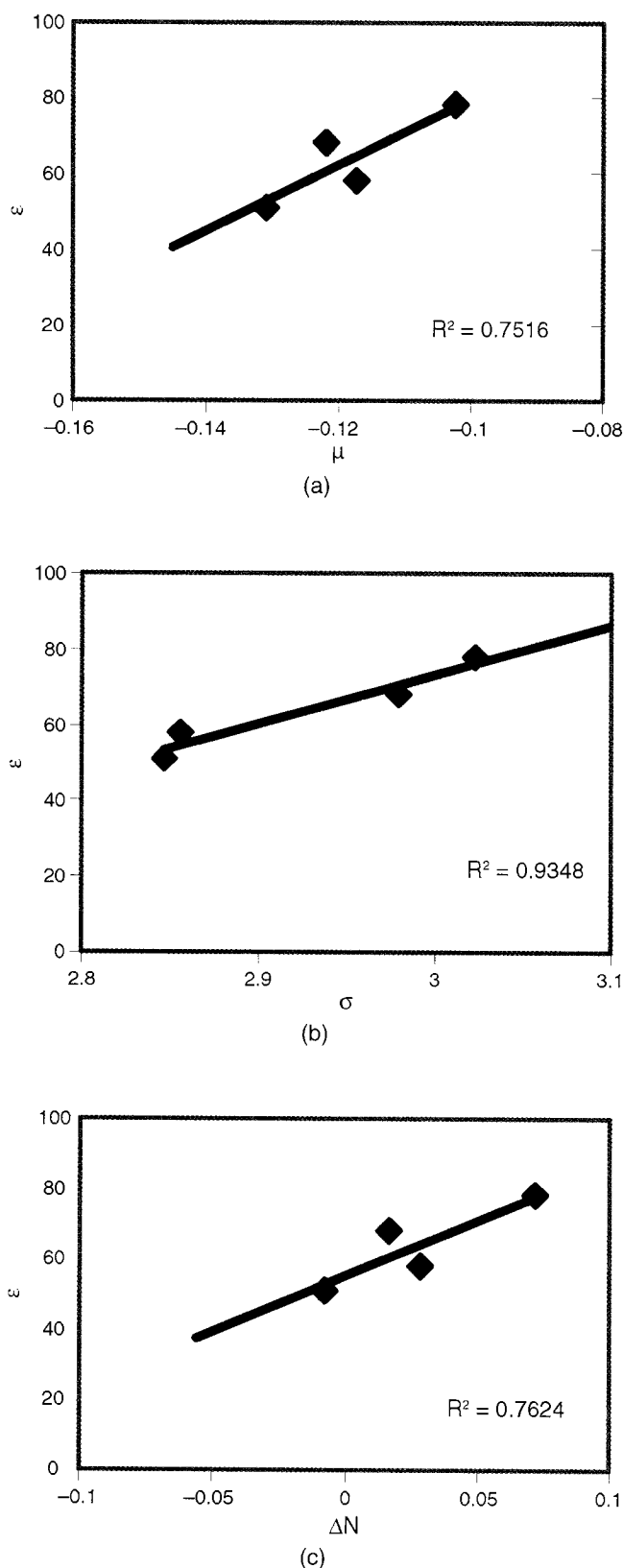


FIGURE 7. Corrosion inhibition efficiencies of benzimidazole derivatives for iron as a function of electronic chemical potential (μ), molecular softness (σ), and extent of charge transfer (ΔN). Data (in atomic units) were obtained from the in-solution optimized structure with a dielectric constant of six.

models mentioned above. The values of μ and σ are calculated from Equations (3) and (4) and ΔN by the following equation:^{37,2}

$$\Delta N = \frac{\mu_I - \mu_M}{2(\eta_I + \eta_M)} \quad (9)$$

where the indices I and M refer to inhibitor molecule and metal cluster, respectively. η is molecular hardness and is equal to $(2\sigma)^{-1}$.²⁶ The respective plots are given in Figures 6 through 8. As can be seen and has been explained previously,^{12,37} there are relatively good correlations between the experimental values of inhibition efficiencies (ϵ) and each of the theoretically obtained quantities of μ , σ , and ΔN . Moreover, the correlations are improved as models change from a simple-ideal case (isolated inhibitor) to relatively more sophisticated-realistic ones, i.e., inhibitors in EDL. Furthermore, the sensitivity of inhibition efficiency to μ , σ , and ΔN are represented in Table 4 as the slopes of respective lines of Figures 6 through 8. As can be seen from this table, the sensitivity of inhibition efficiency is more affected by μ than σ and ΔN . Thus, it can be predicted that a variation in chemical potential caused by a change in molecular structure will affect the inhibition efficiency the most. This fact can be very helpful in designing inhibitor molecules.

CONCLUSIONS

- ❖ The quantum electrochemical investigation of corrosion inhibitors based on DFT has some merits relative to semi-empirical methods such as PM3, AM1, etc. The most important one is that the latter methods are only applicable to certain parameterized atoms while the former does not involve this restriction.^{17,23} Moreover, in comparison with other methods based on ab initio, DFT involves fewer calculation tasks; thus it requires less computational time and fewer efforts.
- ❖ Although the theoretical evaluation of corrosion inhibitors is a complex interdisciplinary problem in the field of theoretical electrochemistry, there are some challenging aspects involved, worthy of further persuasion.
- ❖ The corrosion inhibition behavior of organic molecules can be correlated with molecular parameters such as electronic chemical potential, molecular softness, and the amount of charge transfer to the metal.
- ❖ When the inhibitor molecule crosses into the Helmholtz Outer Plane (OHP) and enters the EDL, an abrupt change will occur in its electronic structures, which leads to an increase in electronic chemical potential and molecular softness, and a decrease in desolvation free energy.
- ❖ Among various centers present in the benzimidazole molecule, the adsorption through nonbonding electrons of a pyridine-like nitrogen atom is most predominant.

TABLE 4

Sensitivity of Inhibition Efficiency to μ , ΔN , and σ

Sensitivity	In Vacuo	In Solution	In EDL
$\partial\epsilon/\partial\mu$	790.73	867.5	869.88
$\partial\epsilon/\partial(\Delta N)$	288.17	312.77	314.91
$\partial\epsilon/\partial\sigma$	148.32	130.13	142.72

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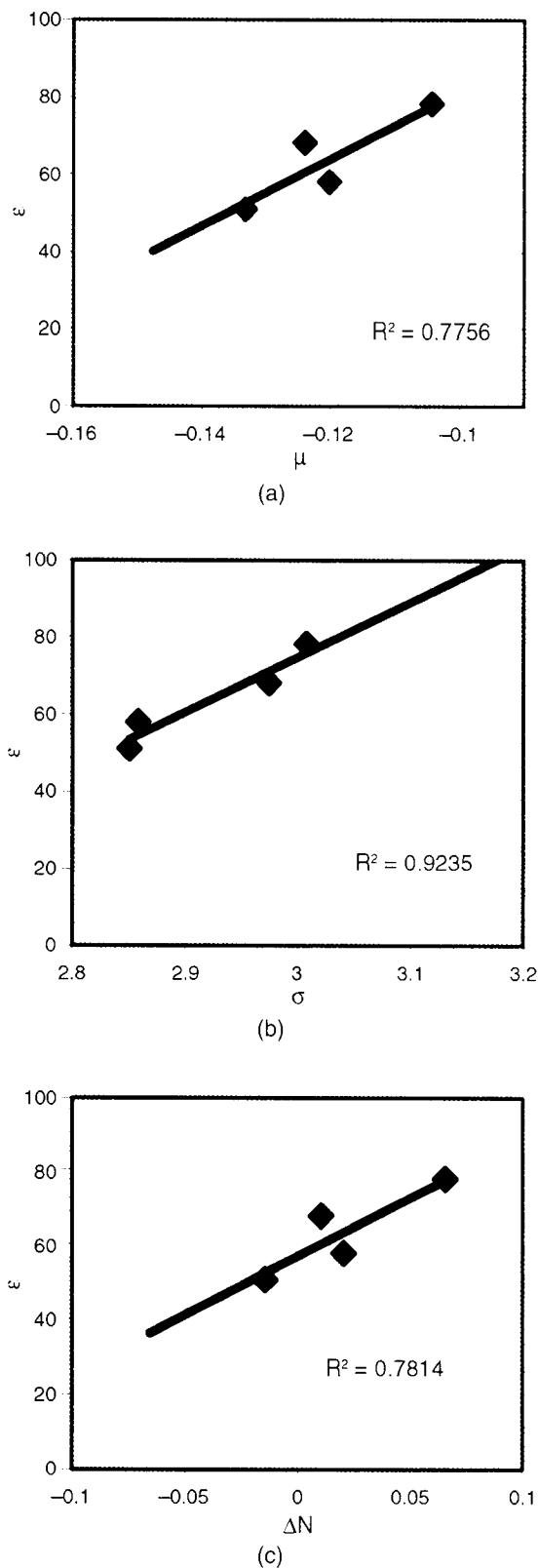


FIGURE 8. Corrosion inhibition efficiencies of benzimidazole derivatives for iron as a function of electronic chemical potential (μ), molecular softness (σ), and extent of charge transfer (ΔN). Data (in atomic units) were obtained from the EDL optimized structure (via PCM model with $D = 6$ and field = 10^7 V/cm); vertical adsorption through N^* (see Figure 1).

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* **March 12-17—CORROSION/2006—San Diego, CA;** Contact NACE, Phone: +1 281/228-6223; E-mail: firstservice@nace.org.

March 14-16—Offshore West Africa Conference and Exhibition—Abuja, Nigeria; Contact Samantha Malcolm, Phone: +44 (0) 1992 656 619; E-mail: owaconference@pennwell.com; Web site: www.offshorewestafrica.com.

March 28-30—Water Chemistry and Corrosion Control and Failure Prevention in Steam Systems—Calgary, AB, Canada; Contact Otakar Jonas, Phone: +1 302/478-1375; E-mail: jonasinc@steamcycle.com; Web site: www.steamcycle.com.

March 29-31—Water and Membrane China (Shanghai) 2006—Shanghai, China; Contact Lucia Gao, Phone: 0086-10-85323275; E-mail: Lucia5201@hotmail.com/Lucia1025@126.com; Web site: www.sino-expo.net.

* **April 3-5—Weld Integrity Corrosion, Inspection, and Assessment—Manchester, United Kingdom;** Contact James Marrow, Phone: +44 (0) 161 306 3611; E-mail: james.marrow@manchester.ac.uk.

April 23-26—3rd International Brazing and Soldering Conference—San Antonio, TX; Contact Customer Service, Phone: +1 440/338-5151, ext. 6; E-mail: cust-srv@asminternational.org; Web site: www.asminternational.org/ibsc.

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April 25-27—American Petroleum Institute (API) Pipeline Conference and Cybernetics Symposium—Fort Worth, TX; Contact Madeleine Sellouk, Phone: +1 202/682-8332; E-mail: sellouk@api.org; Web site: www.api.org.

* **May 2-4—40th Annual Western States Corrosion Seminar—Pomona, CA;** Contact Sylvia Hall, Phone: +1 323/564-6626; E-mail: info@westernstatescorrosion.org; Web site: www.westernstatescorrosion.org.

May 7-11—International Conference on Shape Memory and Superelastic Technologies—Pacific Grove, CA; Contact ASM Customer Service, Phone: +1 440/338-5151, ext. 6; E-mail: cust-srv@asminternational.org; Web site: www.asminternational.org.

* **May 10-11—Israeli 7th Conference on Corrosion and Electrochemistry—Ramat Gan, Israel;** Contact Alec Groysman, Phone: +972 4 8788623; E-mail: galec@orl.co.il; Web site: www.engineers.org.il/Index.asp?CategoryID=1122.

* **May 10-11—NACE Pipeline Seminar Series: Internal Corrosion: Tools, Technologies, and Case Studies—Houston, TX;** Contact Helena Seelinger, Phone: +1 281/228-6220; E-mail: helena.seelinger@nace.org.

May 10-12—5th International Conference on NDE in Relation to Structural Integrity for Nuclear and Pressurized Components—San Diego, CA; Contact Brent Lancaster, Phone: +1 704/547-6017; E-mail: blancast@epri.com; Web site: www.epri.com.

* **May 10-12—Pipeline Integrity Management Seminar (PIMS)—New Orleans, LA;** Contact NACE, Phone: +1 281/228-6223; E-mail: firstservice@nace.org.

May 15-18—International Thermal Spray Conference and Exposition (ITSC)—Seattle, WA; Contact ASM Customer Service, Phone: +1 440/338-5151, ext. 6; E-mail: cust-srv@asminternational.org; Web site: www.asminternational.org.

* **May 21-26—LATINCORR 2006—Fortaleza, Ceara, Brazil;** Contact ABRACO, Phone: +55 21 2516 1962; E-mail: eventos@abraco.org.br; Web site: www.abraco.org.br/latincorr2006.

May 30-June 2—7th Congress of CEOCOR—Mondorf-les-Bains, Luxembourg; Contact Congress Secretariat, Phone: +352 31 05 02 201/202; Web site: www.ceocor.lu/luxembourg.

June 5-9—International Gas Union, 23rd World Gas Conference—Amsterdam, Netherlands; Contact WGC2006 Conference and Exhibition Secretariat, Phone: +31 20 6793411; E-mail: wgc2006@eurocongres.com.

July 17-20—International Materials Technology Conference and Exhibition (IMTCE 2006)—Kuala Lumpur, Malaysia; Contact Conference Secretariat, Phone: +603 51218228/512191411/512 19412; E-mail: iomm@po.jaring.my; Web site: www.iomm.org.my.

* **September 10-14—NACE Corrosion Technology Week/2006—Orlando, FL;** Contact NACE, Phone: +1 281/228-6223; E-mail: firstservice@nace.org.