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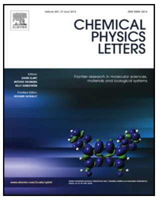

Reactivity trends of Fe phthalocyanines confined on graphite electrodes in terms of donor–acceptor intermolecular hardness: Linear versus volcano correlations

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ABSTRACT

In this work, we have studied the interaction between the hydrazine N_2H_4 molecule with several FeN4 macrocyclic complexes (FePc's). In order to modulate the electron density located on the metal center using iron-phthalocyanine (FePc) as the reference, we used substituted iron-phthalocyanines with different types of substituents electron-donating groups such as iron-tetraamino-phthalocyanine ($4\beta(NH_2)$FePc) and iron-octamethoxyphthalocyanine ($8\beta(OCH_3)$FePc), and with electron-withdrawing groups such as iron-tetranitrophthalocyanine($4\beta(NO_2)$FePc) and iron-hexadecachlorophthalocyanine (16(Cl)FePc), respectively.

We have found that the energy of interaction between hydrazine and the Fe center in the macrocycle increases as the electron-withdrawing power of the substituents increases. When rate constants instead of currents are compared in a semilog plot versus $\Delta\varepsilon_{\text{D-A}}$, a linear correlation is found where log *k* increases as the intermolecular hardness of the systems decreases.

1. Introduction

In electrocatalysis, one of the main fundamental challenges is to establish theoretical models or reactivity guidelines for designing new and more active catalysts for a given reaction [1,2]. However, apart from the exponential dependence of electrochemical reaction rates on the potential predicted by empirical correlations such as the Butler–Vollmer and Tafel equations, the focus is made on the electrode potentials (as the driving force of the reaction) and the role of the electrode surface does not appear explicitly in the correlations and it is hiding in the exchange current. Several theoretical treatments have been proposed by Hush [3], Marcus [4] and Levich and Dogonadze [5]; but these approaches are applicable to simple solution electron transfers processes without the formation or rupture of bonds. So, essentially, the electrode mainly plays the role of a source or sink of electrons. In electrocatalysis, interactions between reactants, intermediates or products with the electrode surface are involved. Moreover, important contributions have been made by several groups on the theory of electrocatalysis but these models have been mainly focused on metallic surfaces [1,2,6,7]. Non-metallic catalytic surfaces, and especially MN4 macrocyclic catalysts represent a challenge for developing theoretical models since in contrast to metals they have discrete energy levels and have properties that can be tailored for a given reaction by modifying their electronic structure and ability to bind extra-planar ligands.

On the other hand, the study of the reactivity of chemically modified electrodes containing immobilized MN4 macrocyclic complexes with specific activities for a given reaction is important because of the great variety of applications of these systems in electrocatalysis in sensors [8–14]. Metal phthalocyanines (M-Pc's) when confined on electrode surfaces are very active and versatile catalysts for a great variety of ET reactions [11]. In previous work the catalytic activity of the different FePc's in the electro-oxidation of hydrazine were examined using the complexes adsorbed on graphite electrodes. A plot of the log *i* (current density at constant potential) versus de Fe(II)/(I) formal potential gives a typical volcano curve. These volcano type correlations have also been observed in the electro-oxidation of thiocyanate, thiols, glucose and hydrazine with modified electrodes with different substituted macrocyclic complexes [15,16,20,21]. Volcano correlations are well-known in heterogeneous catalysis, where the

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catalytic activity is compared against some parameter that indicates the degree of interaction of a reactants or intermediates with the active sites present on the surface [18,19]. For explaining the volcano correlations, the so-called Sabatier principle is invoked that essentially states that the most active catalyst in a series of them for a given reaction is the one that binds the key intermediate not too weakly, not too strongly [18]. In previous studies, the relationship between the catalytic activity with structural and thermodynamic parameters of the phthalocyanines has been established [15,20–27]. These parameters include the formal potential of the M(II)/(I) redox couple in the metal complex [11,21], the role of the substituents in the ligand system [15,20], the magnetic moment [28], and the catalytic activity in other processes [11,15–21,28–37]. This type of correlations shows that the redox potential of the catalysts needs to have an intermediate value to achieve maximum activity, and somehow resembles the Sabatier principle. In other words, the redox potential of the catalyst can be 'tuned' for maximum activity and this parameter in the phthalocyanine molecule can be modulated by placing suitable substituents on the ligand to withdraw or donate electron density to the metal center [35]. The shifting of the redox potential or processes located on the central metal also reflects shifts in the energies of the frontier orbitals with *d*-character [35]. In the catalytic process of hydrazine electro-oxidation on an electrode surface, the crucial step is the formation of a bond between the hydrazine molecule and an active site on the electrode surface [20]. The metal center represents the active site in the phthalocyanine. In recent experimental work, we discussed two possible reaction mechanisms for the electro-oxidation of hydrazine, catalyzed by FePc's. One mechanism (see mechanism A, Ref. [22]) involved the adduct formation between the Fe and the hydrazine molecule before the rate determining step. In the other mechanisms (see mechanism B, Ref. [22]) we proposed that electron transfer could also occur in a concerted fashion with direct bond forming [21,22,38].

In this letter we have analyzed the electronic and geometrical parameters obtained for the interaction of the hydrazine molecule with the Fe centers. Also, we explore the correlation between the adduct stability against the experimental catalytic activity of the Fe-Pc's confined on graphite electrode surfaces for the hydrazine oxidation reaction. Furthermore, we discuss a theoretical analysis using density functional theory (DFT) to analyze two different hydrazine oxidation mechanisms previously reported by us.

2. Computational details

All geometries and properties were calculated using the ADF 2008.01 code [40] at the relativistic level incorporating scalar and spin-orbit (SO) corrections via the ZORA Hamiltonian (ZORA + SO) [41,42]. For the calculations we employed a triple-ζ Slater basis set plus polarization function (STO-TZP). Geometry optimizations were carried out considering the full symmetry, via an analytical energy gradient method implemented by Verluis and Ziegler [43]. Non-local corrections of exchange and correlations (XC) were incorporated via a general gradient approximation (GGA), within the functional PW91 [44]. In all cases, frequency analysis was performed after each geometry optimization, where we obtained only positive frequencies verifying in this fashion the local minima.

3. Results and discussion

In this work we studied iron-tetraamino-phthalocyanine ($4\beta(NH_2)FePc$), iron-phthalocyanine (FePc), iron-octamethoxy-phthalocyanine ($8\beta(OCH_3)FePc$), iron-tetranitrophthalocyanine ($4\beta(NO_2)FePc$) and iron-hexadecachlorophthalocyanine (16(Cl)FePc), respectively. The structures are shown in Figure 1.

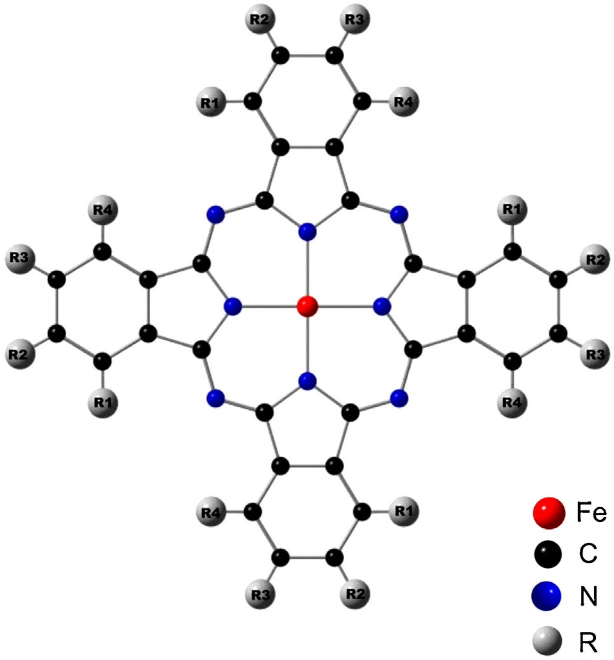

Figure 1. Structure of iron phthalocyanines used in this work. $4\beta(NH_2)FePc$: $R_1 = R_4 = —H$, R_2 or $R_3 = —NH_2$; $8\beta(OCH_3)FePc$: $R_1 = R_4 = —H$, $R_2 = R_3 = —OCH_3$; FePc: $R_1 = R_2 = R_3 = R_4 = —H$; $4\beta(NO_2)FePc$: $R_1 = R_4 = —H$, R_2 or $R_3 = —NO_2$; 16(Cl)FePc: $R_1 = R_2 = R_3 = R_4 = —Cl$

The substituents are symbolized as R1, R2, R3, and R4 for each phthalocyanine respectively. The molecular structures of eight substituted FePc's were obtained through geometries optimization at the GGA level and the ground-states of all systems were characterized as triplet. These results show good agreement with the available experimental and calculated data (Table 1).

The interaction of the hydrazine molecule with the iron phthalocyanines is described in Figure 1. Figure 2 shows the possible conformations of hydrazine. Hydrazine can take two conformations namely: conformation C_{2h} which is 1.0 eV more stable than the energy of the D_{2h} flat conformation. This indicates that a π^*

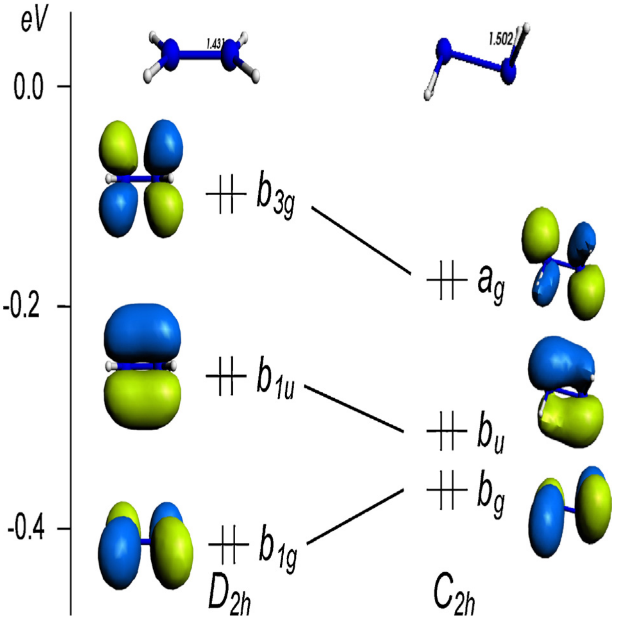

Figure 2. Molecular orbital diagram of D2h and C2h conformations of the hydrazine molecule. C2h–D2h = relative binding energy = 1 eV.