J. Phys. Chem. A **2004,** *108,* 6045−6051

Solvent Effect on Density Functional Reactivity Indexes Applied to Substituted Nickel Phthalocyanines

Claudia A. Caro,[†] José H. Zagal,[†] Fethi Bedioui,[§] Carlo Adamo,[§] and Gloria I. Cárdenas-Jirón*[,‡]

Departamento de Química de los Materiales and Laboratorio de Química Teórica, Departamento de Ciencias Químicas, Facultad de Química y Biología, Universidad de Santiago de Chile, Casilla 40, Correo 33, Santiago, Chile, and Ecole Nationale Supérieure de Chimie de Paris, Laboratoire d'Electrochimie et Chimie Analytique, UMR CNRS-ENSCP No. 7575, 11 rue P. et M. Curie, F-75231 Paris Cedex 0.5, France

Received: February 2, 2004; In Final Form: May 3, 2004

The solvent effect has been studied at the PBE0/CEP-121G level of theory on different intramolecular and intermolecular density functional global reactivity indexes for a set of substituted nickel phthalocyanines ($NiPc(X)_n$; X is the substituent). For all the indexes analyzed, we found that solvent plays a nonnegligible role: in some molecules it induces a stabilization, while in others it has a destabilizing effect. However, we also found along the whole set of $NiPc(X)_n$ molecules that the presence of the solvent leads to the same overall trend obtained in the gas phase. To rationalize the behavior of the set $NiPc(X)_n$, we also did an analysis of the partial energy contributions to the total energy considering the environment variable given by the solvent and the chemical variable given by the substituent.

1. Introduction

The polarizable continuum (PCM) solvation model[1] is widely used to accurately describe the solvent effect on the electronic energy of a given structure. Recently, an effective strategy for the description of chemical systems in solution has been described based on the continuum conductor approach (CPCM).[2] This model can be applied to polar solvents and provides energies and energy gradients with limited computational times. It can make use of a specific procedure to build the solute cavity allowing the calculation of solvation free energies with chemical accuracy for a large number of chemical systems at either the Hartree−Fock (HF) or density functional level of theory.[3] The solvent effect has been studied on the structure, energy, and charge density of different molecules that exist in equilibrium with other species.[4−9] The solvent effect has also been studied on hyperpolarizabilities,[10] on mechanisms,[11,12] and on conformational effects.[13,14]

Metal complexes of N_4 ligands, such as phthalocyanines, are widely studied as biomimetic models for several biological redox processes, but at the same time they are well-known efficient catalysts for oxidative degradation of various types of pollutants and residual wastes.[15] In the past decade these complexes were also reported to be efficient catalysts, and electrodes modified with these metal complexes have been extensively developed since they can act as electrocatalysts, by lowering particularly the overpotential of oxidation or reduction of the target molecules.[16] The redox processes occurring on metallophthalocyanines involve minimal structural changes, due to the relatively large size of these molecules and the large π delocalized system compared to the size of the redox center. Thus reorganizational energies accompanying electron-transfer (ET) processes occurring on these complexes are small and ET processes are expected to be very fast.[17] At the same time, ET reactions strongly depend on the environment since the reduced and oxidized species can be stabilized differently and, consequently, the overall reactivity can dramatically change.

Density functional theory (DFT) is focused on the electron density as the fundamental property describing the ground state of an atomic or molecular system.[18,19] Several global and local reactivity descriptors derived from DFT have been proposed and used in past years.[20−51] Global reactivity descriptors such as molecular hardness and softness[20,25,27] have been useful tools to improve our understanding of the most stable state of a chemical species.[28,29] Local reactivity descriptors[21,23,30,34] such as softness and Fukui functions have been used for understanding at a local level a chemical reaction. However, usually these studies are performed in the gas phase.

In past years we have focused our attention on rationalizing some aspects concerning the electronic structure of transition metal complexes, either as isolated complexes[37−39,42,43,45] or as inserted in an oxidation reduction process.[35,36,40,41,44] Thus, we have used several DFT reactivity descriptors and reactivity principles such as hardness maximum principle[22,25,47] and local HSAB (hard soft acid basis)[47−50] have been verified.[36]

In this work, we will apply a CPCM solvation model to rationalize the solvent effect on DFT-based reactivity descriptors applied to a set of substituted nickel phthalocyanines, namely $NiPc(NH_2)_4$, $NiPc(SO_3H)_4$, $NiPc(NO_2)_4$, $NiPc(C_4H_9O)_8$, $NiPc(C_6H_5O)_4$, $NiPc(C_{15}H_{15}O)_4$, and $NiPc(C_6H_5)_4$ (see Figure 1). We chose this series of molecules in order to understand at a theoretical level of quantum chemistry the differences in activity experimentally observed for such compounds.[52] To this end, the study of the chosen set of molecules $NiPc(X)_n$ should give detailed information about the effects of substituent and environment, given by the presence or not of the solvent, on the reactivity properties. We have applied the notions of

---

* To whom correspondence should be addressed. E-mail: gcardena@lauca.usach.cl.

[†] Departamento de Química de los Materiales, Universidad de Santiago de Chile.

[‡] Departamento de Ciencias Químicas, Univerisdad de Santiago de Chile.

[§] UMR CNRS-ENSCP No. 7575.

10.1021/jp049530y CCC: $27.50

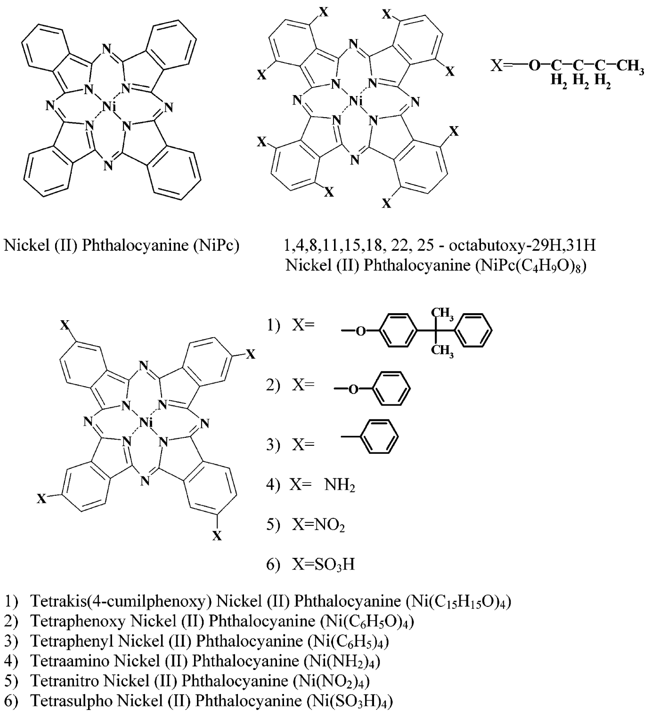

Figure 1. Structure for the set of NiPc$(X)_n$ molecules. X corresponds to the substituent.

hardness and donor−acceptor hardness to better quantify these effects and discriminate among the examined molecular complexes.

2. Theoretical and Computational Details

2.1. DFT Reactivity Descriptors. The molecular hardness (η), a global intramolecular reactivity index, has been defined in the context of density functional theory as the second partial derivative with respect to the number of electrons:[20,23,24,34]

$$\eta = \left(\frac{\partial^2 E}{\partial N^2}\right)_{v(\vec{r})} \tag{1}$$

E is the total energy, N is the number of electrons in the ground state of the system, and $v(\vec{r})$ is the external potential at position $\vec{r}$, i.e., the potential due to the positions of the nuclei plus applied external field, if any. The operational definition of η considering the average frontier properties, that is, the variation in the energy when one electron is added or removed from the system, is given by

$$\eta = I - A \tag{2}$$

which has been obtained using a finite difference approximation. I and A are the first vertical ionization potential and electron affinity, respectively. These energies are calculated using a ΔSCF procedure:

$$I = E(N-1) - E(N_0) \tag{3}$$

$$A = E(N_0) - E(N+1) \tag{4}$$

The terms $E(N_0)$, $E(N+1)$, and $E(N-1)$ correspond to the total energy of the ground state, anion, and cation, respectively.

The reactivity between a donor species and an acceptor species may be determined making use of the global reactivity index as it is the donor−acceptor hardness (η_{DA}). This is an intermolecular reactivity index that involves the participation of two species. It was first defined by Parr and Zhou as the hardness associated with a two-partner electron-transfer chemical reaction[53,54] where a donor (D) species and an acceptor (A) species are present:

$$\eta_{DA} = I_D - A_A \approx -\epsilon_{HOMO,D} + \epsilon_{LUMO,A} \tag{5}$$

Electron transfer from a donor species to an acceptor species is facilitated the closer in energy the HOMO of D is to the LUMO of A (second term, right side of eq 5). Of course, that this is an approximation to the more basic principle that the chemical reaction is favored if the energy required to ionize D, that is, the ionization potential I_D, is completely provided by the energy gained by giving an electron to A, its electron affinity A_A (first term, right side of eq 5).[54] The hardness defined in eq 5 corresponds to the hardness of the donor−acceptor pair before any interaction occurs between D and A.

Chattaraj et al. have applied the definition of hardness η_{DA}, given by the first term on the right side of eq 5, which they called pair hardness, to calculate the free energy changes ΔG_{ET} associated with the electron-transfer process produced by the direct reaction of resonance-stabilized carbonium ions with a variety of organic anions:[55,56]

$$\Delta G_{ET} \approx \Delta H_{ET} = I_D - A_A = \eta_{DA} \tag{6}$$

Equation 6 is true providing that the entropy changes of the electron-transfer processes (ΔS_{ET}) are negligible. From experimental values of heats of heterolysis ΔH_{het} and homolysis ΔH_{homo}, these authors investigated relationships with ΔG_{ET}.[55,56]

η_{DA} was first named as donor−acceptor hardness by the Cárdenas-Jirón group because it was applied to rationalize at a theoretical level different oxidation reduction processes involving transition metal complexes where one donor species and one acceptor species are present.[35,44] Later on, Griveau et al. have used η_{DA} to study the oxidation of 2-mercaptoethanol by cobalt macrocycles.[46] As seen from eq 6, η_{DA} corresponds to the electron-transfer enthalpy change (ΔH_{ET}), and therefore it is a reactivity index for a donor−acceptor pair that gives information about the thermodynamics of the chemical reaction.

2.2. Theoretical Calculations. Solvent effects were evaluated using the polarizable continuum model (CPCM)[58] on a nickel phthalocyanine (NiPc) and on a set of substituted analogues (NiPc$(X)_n$) which are displayed in Figure 1. Solvation energies have been computed by a cavity model, namely the united atoms topological model (UATM),[59] coupled to the conductor-like polarizable continuum model (CPCM).[3] This model presents a continuum description for the solvent where the physical system is represented by a charge distribution which describes the molecule that one has identified as solute.[58] This approach provides results very close to those obtained by the original dielectric model for high dielectric constant solvents, and produces fewer numerical errors arising from the small part of the solute electron cloud lying outside the cavity (escaped charge effects). The main advantage of the CPCM method is its applicability to different levels of quantum mechanical and more complex physical systems.

Hartree−Fock SCF theoretical calculations with full geometry optimization for the set of NiPc$(X)_n$, NO and NO_2^-, were performed at the semiempirical level of theory named PM3(tm) (tm, transition metal) using the TITAN package.[60] Then, the optimized geometries were used in single-point DFT calculations using a recent hybrid Kohn−Sham/Hartree−Fock (KS/HF) model referred to as PBE0.[61] This approach is obtained casting the PBE exchange and correlation functional[62,63] in a

TABLE 1: Differences between Properties (P) Obtained in Gas Phase (g) and in Solution Phase (l): $\Delta P = P(\mathrm{l}) - P(\mathrm{g})$[a]

molecule	ΔE	ΔT	ΔV_{ne}	ΔV_{ee}	$\Delta \rho_{Ni}$
$NiPc(C_{15}H_{15}O)_4$	−29.9	59.9	−2206.9	2117.1	7.5×10^{-4}
$NiPc(SO_3H)_4$	−54.2	−77.3	747.3	−724.2	-4.4×10^{-2}
$NiPc(NO_2)_4$	−21.7	−29.3	1011.7	−1004.0	-3.9×10^{-2}
$NiPc(C_6H_5)_4$	−16.0	54.4	−1646.2	1575.7	4.1×10^{-4}
$NiPc(NH_2)_4$	−11.8	23.1	−2306.3	2271.4	2.1×10^{-2}
$NiPc(C_6H_5O)_4$	−20.4	53.9	−1734.1	1659.9	1.9×10^{-3}
NiPc	−9.7	42.3	−1333.3	1278.5	2.6×10^{-3}
$NiPc(C_4H_9O)_8$	−19.1	44.4	−2922.2	2858.7	1.1×10^{-1}

[a] Resulting values (in kcal/mol) of total energy change (ΔE), electronic kinetic energy change (ΔT), nucleus−electron potential energy change (ΔV_{ne}), and electron−electron potential energy change (ΔV_{ee}). The electronic population of the nickel atom ($\Delta \rho_{Ni}$) is also included.

hybrid scheme HF/DFT, where the HF exchange ratio (1/4) is fixed a priori.[64] All the DFT calculations were carried out with a modified version of the Gaussian98 code.[65] These calculations were performed in gas phase and in solution phase using water as solvent. The CEP-121G pseudopotential with the corresponding basis set (contraction [8s8p6d/4s4p3d]) for the nickel atom was used. For all the other atoms, that is, C, N, O, S, and H, a 6-31G(d) basis set was considered. The same basis set was used for NO and NO_2^-. The set of substituted nickel phthalocyanines corresponds to $NiPc(NH_2)_4$, $NiPc(SO_3H)_4$, $NiPc(NO_2)_4$, $NiPc(C_4H_9O)_8$, $NiPc(C_6H_5O)_4$, $NiPc(C_{15}H_{15}O)_4$, and $NiPc(C_6H_5)_4$. In all the complexes we used Ni(II); therefore, for each complex a singlet multiplicity and a charge equal to zero were used.

3. Results and Discussion

3.1. Total Energy Decomposition. The solvent effect was also analyzed for the total energy (E) and for the different electronic energy contributions of the NiPc(X)$_n$ molecules. Thus, we studied the electronic kinetic energy (T), the nuclear−electron attraction potential energy (V_{ne}), and the electron−electron repulsion energy (V_{ee}). Table 1 presents the differences between the obtained values for these properties (P) in gas phase (g) and in solution phase (l): $\Delta P = P(\mathrm{l}) - P(\mathrm{g})$.

As can be seen in Table 1, in all cases we obtained negative values for ΔE, indicating that the total energy in the presence of the solvent decreases with respect to the gas phase, which means that the solvation process stabilizes each of the molecules. In relation to the partial energetic contributions to the total energy, we found that all the molecules, with the exception of $NiPc(SO_3H)_4$ and $NiPc(NO_2)_4$, present an increase in the electronic kinetic energy when the solvent is included in the calculation; $T(\mathrm{l}) > T(\mathrm{g})$. Positive values for ΔT are obtained. This fact supposes that the electronic density ($\rho(r)$) in solution phase is more diffuse toward the central region of the macrocycle. The Mulliken electronic population analysis evaluated on the nickel atom (see Table 1) shows that $\rho_{Ni}(\mathrm{l}) > \rho_{Ni}(\mathrm{g})$, $\Delta \rho_{Ni}$ is positive, confirming an increase of $\rho(r)$ in that region that justifies the increase in $T(\mathrm{l})$ with respect to $T(\mathrm{g})$. The solvent effect increases the electron donor character of the substituents. In the case of $NiPc(SO_3H)_4$ and $NiPc(NO_2)_4$, the presence of the solvent produces a decrease in T with respect to the gas phase; $T(\mathrm{l}) < T(\mathrm{g})$. Negative values for ΔT are obtained. In analogy to the above discussion, we can suppose that in solution phase $\rho(r)$ is more concentrated on the periphery of the macrocycle. The values obtained for ρ_{Ni} indicate that in these molecules $\rho_{Ni}(\mathrm{l}) < \rho_{Ni}(\mathrm{g})$; that is, $\Delta \rho_{Ni}$ is negative (see Table 1). These results show that the solvent effect on the substituents produces an increase in the electron-withdrawing character of them.

In relation to the nuclear−electron potential energy, we found that, with the exception of $NiPc(SO_3H)_4$ and $NiPc(NO_2)_4$, the values obtained of ΔV_{ne} are always negative, indicating that $V_{ne}(\mathrm{l}) > V_{ne}(\mathrm{g})$. Values of V_{ne} are negative because the nuclear−electron interaction is attractive. A highest numerical value for V_{ne} implies a highest interaction between the nucleus and the electrons. The highest value for $V_{ne}(\mathrm{l})$ is explained with the same arguments given for the kinetic energy: $\rho(r)$ is more diffuse, which leads to an increase in V_{ne}. For $NiPc(SO_3H)_4$ and $NiPc(NO_2)_4$ is found that $V_{ne}(\mathrm{l}) < V_{ne}(\mathrm{g})$. As $\rho(r)$ is more concentrated on the substituents, it leads to a decrease in the nucleus−electron interaction.

The results of ΔV_{ee} displayed in Table 1 show that in all the molecules, with the exception of $NiPc(SO_3H)_4$ and $NiPc(NO_2)_4$, $V_{ee}(\mathrm{l}) > V_{ee}(\mathrm{g})$. Absolute values of V_{ee} are positive because the electron−electron interaction is repulsive. These results are explained on the same basis of the above discussion for T and V_{ne}. The increase of $V_{ee}(\mathrm{l})$ is produced by a highest $\rho(r)$ in that region. In the case of $NiPc(SO_3H)_4$ and $NiPc(NO_2)_4$, we found that an opposite solvent effect is observed: here ΔV_{ee} is negative; that is, $V_{ee}(\mathrm{l}) < V_{ee}(\mathrm{g})$. The repulsive interaction between the electrons decreases because a set of them is concentrated on the periphery of the macrocycle.

Finally, we can say that the total energy shows for all the molecules a stabilizing effect by the solvent denoted by a lowest total energy obtained. The above discussion on the energy decomposition has been done by rationalizing the solvent effect of this kind of compounds, making use of an electronic picture of the ground state, and it is valid to explain only the behavior in this electronic state. It is interesting to note that the analysis on the energy decomposition clearly shows a different behavior for the electron-withdrawing substituents with respect to the electron-donor substituents. Obviously, the analysis done cannot be taken in an isolated way and must be complemented by the analysis of other electronic properties which we will see in the following.

3.2. Ionization Potential (I) and Electron Affinity (A). The solvent effect was investigated on energetic properties such as the ionization potential and the electron affinity. Figure 2 shows the results obtained for I (Figure 2a) and A (Figure 2b) of NiPc(X)$_n$ in gas and solution phases. We found that two regions clearly appear in Figure 2 as identifying two different groups of NiPc(X)$_n$. One group, which we name "A", is composed of the $NiPc(NH_2)_4$, $NiPc(C_6H_5)_4$, $NiPc(NO_2)_4$, $NiPc(SO_3H)_4$, and $NiPc(C_{15}H_{15}O)_4$ molecules. The second one, which we name "B", corresponds to the $NiPc(C_4H_9O)_8$, NiPc, and $NiPc(C_6H_5O)_4$ molecules. Figure 2a shows that the groups A and B present an ionization potential which is not favored thermodynamically because their values are positive. Group A presents values for I with higher energies than group B. These results indicate that the lack of the first electron in these systems is not favored in both groups. The reason for these results may be understood as that the stabilization of a positive charge in this kind of molecules is not possible. We also observe in Figure 2a that for the molecules of group A the ionization potential increases

TABLE 2: Differences between Properties (P) Obtained in Gas Phase (g) and in Solution Phase (l): $\Delta P = P(\mathrm{l}) - P(\mathrm{g})$ (eV)[a]

molecule	ΔI	ΔA	Δh	$\Delta\eta_{DA}^{NO}$	$\Delta\eta_{DA}^{NO_2^-}$
$NiPc(C_{15}H_{15}O)_4$	0.72	1.27	−0.55	−4.79	1.70
$NiPc(SO_3H)_4$	1.25	0.40	0.86	−3.91	2.58
$NiPc(NO_2)_4$	0.77	0.64	0.12	−4.16	2.33
$NiPc(C_6H_5)_4$	0.86	1.45	−0.59	−4.96	1.53
$NiPc(NH_2)_4$	1.52	2.35	−0.82	−5.86	0.63
$NiPc(C_6H_5O)_4$	−0.86	1.48	−2.34	−4.99	1.50
NiPc	−1.06	1.56	−2.62	−5.08	1.42
$NiPc(C_4H_9O)_8$	−1.61	1.59	−3.20	−5.11	1.39
NO	−3.52				
NO_2^-	2.98				

[a] Resulting values of ionization potential change (ΔI), electronic affinity change (ΔA), molecular hardness change ($\Delta\eta$), and donor−acceptor hardness change ($\Delta\eta_{DA}$) evaluated for the oxidation of nitric oxide (NO) and for the oxidation of nitrite ion (NO_2^-).

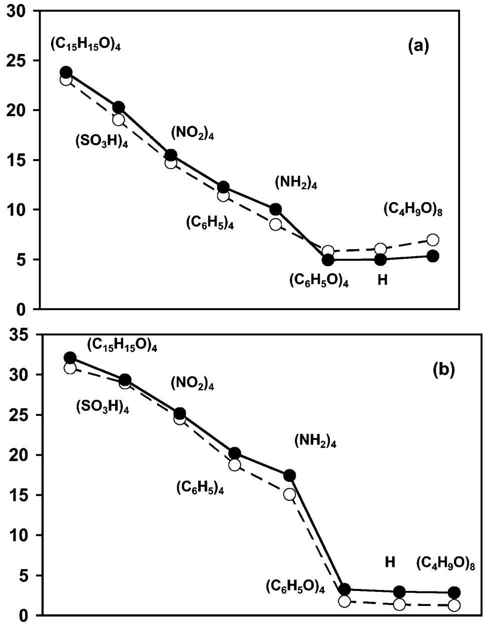

Figure 2. (a) Ionization potential (eV) and (b) electron affinity (eV) for the set of $NiPc(X)_n$ molecules calculated at the PBE0/CEP-121G level of theory. —, solution phase; — —, gas phase.

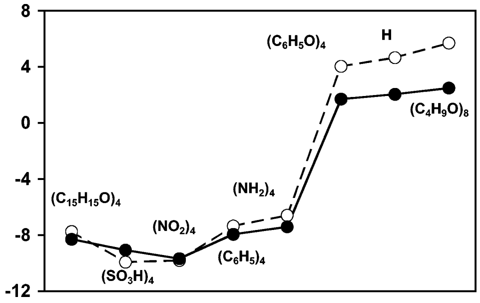

Figure 3. Molecular hardness (eV) for the set of $NiPc(X)_n$ molecules determined at the PBE0/CEP-121G level of theory. —, solution phase; — —, gas phase.

when the solvent is included, thus making the process of ionization more endothermic. An opposite behavior is found for the molecules of group B: the solvent decreases the value of I, predicting a less endothermic process. The solvent effect on the ionization process may be quantified by calculation of the differences between the ionization potential obtained in solution phase with that obtained in gas phase. These values are $\Delta I = I(\mathrm{l}) - I(\mathrm{g})$, and they are shown in Table 2. The minimum value for ΔI is found for $NiPc(C_{15}H_{15}O)_4$ and corresponds to 0.72 eV. The maximum value for ΔI is for $NiPc(C_4H_9O)_8$ with a value of 1.61 eV. As may be seen, the minimum and maximum values are not negligible.

Figure 2b shows that all of the molecules present positive values of the electron affinity but those corresponding to group A have higher values, and those belonging to group B present small values near zero. These results suggest that the molecules of group A stabilize very well the negative charge, hence they present strongly positive electron affinities. Here we also found a difference between the values obtained of A for both phases, but in this case the electron affinities predicted in the calculation with solvent are higher than those obtained in gas phase. These results indicate that the process of electron gain by each of the molecules is thermodynamically favored in the presence of the solvent. Thus, the solvent effect constitutes a stabilizing effect on the electronic affinity. The maximum value of $\Delta A = A(\mathrm{l}) - A(\mathrm{g})$, also included in Table 2, is observed for $NiPc(NH_2)_4$ with a value of 2.35 eV, and the minimum value of ΔA is found for $NiPc(SO_3H)_4$ with a value of 0.40 eV. It is important to note that $NiPc(C_6H_5O)_4$ and $NiPc(C_4H_9O)_8$ present very similar values of ΔA with NiPc, denoting that the size of the substituents $(C_6H_5O)_4$ and $(C_4H_9O)_8$ does not have an important effect on the property A and they have an effect comparable to that of the hydrogen atom in NiPc. The minor solvent effect occurring on $NiPc(SO_3H)_4$ may be understood in terms of the effect produced by the continuum reaction field on the solute ($NiPc(SO_3H)_4$). The solvent polarizes the solute, but in this molecule $\rho(r)$ is already polarized toward the groups SO_3H because it is an electron-withdrawing substituent. Therefore, the presence of the solvent increases the polarization of $\rho(r)$, leading to a minor amount of regions with ability to receive one electron. In the case of $NiPc(NH_2)_4$, the larger solvent effect is obtained because $\rho(r)$ is more distributed along the molecule. The higher dispersion of $\rho(r)$ leads to more regions with the ability to add one electron than in $NiPc(SO_3H)_4$. The result more interesting in this study is that, although it is shown that the solvent produces an effect on each of these properties, I and A, the trend along the set of molecules is the same in both phases. The main conclusion in this section is that the solvent is a variable that may be avoided in a quantum chemistry theoretical study on a family of similar molecules, such as those reported in the present study.

3.3. Molecular Hardness (η).

Figure 3 shows the results of molecular hardness obtained in gas phase and in solution phase. As observed for I and A, two regions appear in both phases. Molecules of group A present the lowest molecular hardness, and molecules of group B present the highest molecular hardness. The results of η predict the same behavior as the electronic affinity; i.e., molecules of group A are softer, and therefore they are more reactive, in this case stabilizing a negative charge, as explained by the electronic affinity. The solvent effect on the molecular hardness may be quantified by calculating the parameter $\Delta\eta$. Resulting values of $\Delta\eta$ are presented in Table 2. It is interesting to note that the opposite

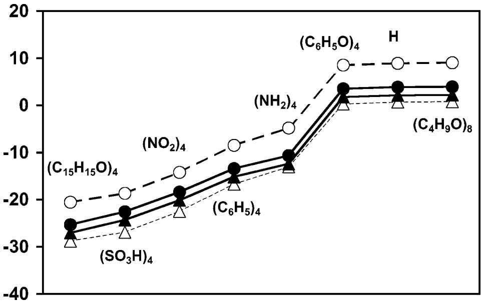

Figure 4. Donor−acceptor hardness (eV) for the set of NiPc(X)$_n$ molecules determined at the PBE0/CEP-121G level of theory. Reactivities toward NO (○) and NO_2^- (△) are shown in gas phase (− −) and in solution phase (—).

behavior (change of sign) obtained in the compounds NiPc(SO$_3$H)$_4$ and NiPc(NO$_2$)$_4$ for ΔT, ΔV_{ne}, and ΔV_{ee} discussed above with respect to the other molecules is also observed for the molecular hardness. Positive values for $\Delta\eta = \eta(l) - \eta(g)$ are obtained in NiPc(SO$_3$H)$_4$ and NiPc(NO$_2$)$_4$, and negative values for $\Delta\eta$ are found for the other molecules studied here. The molecular hardness calculated by eq 2 is a measure of the ability to stabilize a positive charge and a negative charge. As seen above, all the molecules studied here only can stabilize a negative charge and thus η is reflecting the possibility that this fact occurs. For NiPc(SO$_3$H)$_4$ and NiPc(NO$_2$)$_4$, a concentration of $\rho(r)$ already exists on the substituents SO$_3$H and NO$_2$, which is highest in solution phase. Then any nucleophilic attack on these molecules will not be successful, and hence the molecular hardness increases in solution phase. On the contrary, for the remaining molecules the major concentration of $\rho(r)$ is localized in the central region of the macrocycle. In consequence, there will be more sites with the ability to undergo a nucleophilic attack and hence the hardness decreases in the solution phase. A greater difference between the molecular hardness obtained for both phases is observed for NiPc(C$_4$H$_9$O)$_8$ with a value of 3.20 eV. The minor solvent effect is observed for NiPc(NO$_2$)$_4$ with a value of 0.12 eV. Although the differences for η calculated for both phases are not insignificant, it may be seen in Figure 3 that the trend predicted for η in gas phase is the same as that obtained in solution phase. Finally, it is important to note that, although there is no agreement of the solvent effect on the total energy, in all the molecules it decreases with the solvent, and no agreement on the molecular hardness along the series of molecules, the obtained results for η in the Gaussian98 framework are well explained in terms of a set of properties such as the energy decomposition properties (T, V_{ne}, V_{ee}) and the frontier electronic properties (I, A).

3.4. Donor−Acceptor Hardness (η_{DA}). In the context of an oxidation−reduction process where a donor−acceptor pair is present, the solvent effect was investigated on the donor−acceptor hardness. In particular, we studied the two oxidation reactions, from NO to get NO$^+$ and from NO_2^- to get NO$_2$, and we rationalize the reactivity of these reactions through η_{DA}. This index was determined using the definition given in eq 5 for the set of NiPc(X)$_n$ molecules. First we will analyze by separating the reactivity characteristics of each substrate in gas phase and in solution phase. Figure 4 includes the results obtained of η_{DA} for NO and NO_2^- calculated in gas phase and in solution phase. We found, as shown in Figure 4, that for both substrates (NO and NO_2^-) the same trend occurs when the results in gas phase are compared with the ones in solution phase. Because η_{DA} represents the reactivity of a donor−acceptor pair measured through their frontier properties such as the ionization potential of the donor and the electron affinity of the acceptor, a low value of η_{DA} implies that both donor−acceptor species of the pair have similar frontier properties and therefore present a good reactivity between them. A comparison along the set of NiPc(X)$_n$ molecules shows that in both phases the lowest values for η_{DA} are obtained by the molecules of group A, thus suggesting that these molecules would present a higher reactivity upon NO oxidation. In the case of the NO_2^- oxidation reaction a similar result is observed in Figure 4, with the molecules of group A having the lowest η_{DA} value in both phases. As for NO, this set of molecules presents a higher reactivity toward NO_2^- than group B. We also observed in this figure that in the case of NO the inclusion of the solvent in the calculations produces lower values of η_{DA} than in gas phase. These results indicate that the presence of the solvent favors the interaction between the donor and acceptor species. Then the solvent effect in the NO oxidation reaction represents a stabilizing effect on the donor−acceptor interaction. For NO_2^-, we can observe in Figure 4 that the inclusion of the solvent in the calculations predicts higher values of η_{DA} than in gas phase. These results suggest that the solvent does not favor the donor−acceptor interaction. Thus, the solvent effect in the NO_2^- oxidation reaction constitutes a destabilizing effect.

The reason why NO_2^- and NO present opposite behaviors can be explained in terms of the values of ionization potential obtained for these substrates that are included in Table 2 as $\Delta I = I(l) - I(g)$. NO presents a negative value for ΔI, that is, $I(l) < I(g)$. This means that the oxidation process to remove one electron is more favored in solution phase, and hence that the full process, that is, oxidation of the substrate (NO) and reduction of NiPc(X)$_n$, presents the lowest η_{DA} in that phase. However, NO_2^- has a positive value for ΔI, that is, $I(l) > I(g)$. Here the oxidation process of NO_2^- is more difficult in solution phase because this substrate is an anion and probably the effect that the continuum reaction field of the solvent produces on the charge of the anion leads to a delocalization of it. This effect would decrease the ability of NO_2^- in solution phase to be oxidized with respect to the gas phase. Thus, the highest values for η_{DA} evaluated in solution phase with respect to the gas phase are obtained. On the other hand, we also compared the reactivity order obtained in this work for the NO oxidation by the set of NiPc(X)$_n$ molecules with the activity order obtained experimentally by Caro et al.[52] for the same family of compounds. We found that there is good agreement between the theoretical and experimental results for only the substituents SO$_3$H and C$_4$H$_9$O, with the former having the highest reactivity toward NO and the latter the lowest reactivity toward NO. It is important to mention that the obtention of a good correlation between theoretical and experimental results in the sense to get the same reactivity order is not easy because at the experimental level there are many variables holding the experiment that may not always be taken into account in a theoretical calculation. In particular, the experimental results of activity provided by Caro et al.[52] are obtained from Tafel plots where the log of the kinetic current, at constant potential, is plotted versus the redox potential of the substituted nickel phthalocyanine adsorbed on vitreous carbon electrode.

On the other hand, when we compared the solvent effect for each molecule, we noted for both oxidation reactions an important difference between η_{DA} determined in gas phase and that determined in solution phase. The values of $\Delta\eta_{DA} = \eta_{DA}(l) - \eta_{DA}(g)$ for each molecule are shown in Table 2. The maximum value of $\Delta\eta_{DA}$ is 5.86 eV for NiPc(NH$_2$)$_4$ upon NO reactivity and 2.58 eV for NiPc(SO$_3$H)$_4$ upon NO_2^- reactivity. The minimum value of $\Delta\eta_{DA}$ for NO reactivity corresponds to

3.91 eV for $NiPc(SO_3H)_4$, and that for NO_2^- reactivity is 0.63 eV corresponding to $NiPc(NH_2)_4$. An explanation very similar to that presented in the electronic affinity section for the minimum and maximum solvent effects may be given here as that those effects are again seen for the same substituents. The results of $\Delta\eta_{DA}$ suggest that a minor solvent effect occurs for NO_2^-, because it presents the lowest values of $\Delta\eta_{DA}$ for each molecule. In contrast, a larger solvent effect occurs for NO because this oxidation reaction presents the highest values of $\Delta\eta_{DA}$. The interesting point to mention here is that, although the values of $\Delta\eta_{DA}$ are numerically important, the trend of η_{DA} along the set of $NiPc(X)_n$ molecules in the presence of the solvent is the same.

4. Conclusions

We have presented a study of the solvent effect on global reactivity indexes of a set of substituted nickel phthalocyanines. We found for all the indexes analyzed that the presence of the solvent produces an effect either stabilizing or destabilizing the molecular system. The results of ionization potential and electron affinity showed that the molecules studied stabilize a negative charge and not a positive charge. Both behaviors are enhanced in the presence of the solvent. In molecular hardness, we found that the solvent produces in some molecules a stabilizing effect on the molecular system, increasing the value of η. In other molecules it has a destabilizing effect, with values of η decreased. The donor−acceptor hardness showed that the solvent increases the reactivity of NO toward $NiPc(X)_n$, presenting a decrease in the values of η_{DA}. In contrast, the solvent decreases the reactivity of NO_2^- toward $NiPc(X)_n$, increasing the values of η_{DA}. We also did an analysis of the different contributions to the total energy which were useful in the discussion about the behavior of these molecules with respect to the environment variable given by the solvent and with respect to the chemical variable given by the substituent. Although all the properties analyzed here showed an important solvent effect in absolute terms for each $NiPc(X)_n$ molecule, it is interesting to note that in general the trend found along the set of molecules is constant. Thus, our results suggest that the inclusion of the solvent may be avoided when a theoretical study is carried out in a family of molecules like those studied here.

Acknowledgment. J.H.Z., F.B., and C.A. thank Project ECOS (France)−CONICYT (Chile) C99E03 for financial support for travel expenses. J.H.Z. and G.I.C.-J. are grateful to Project FONDECYT Lineas Complementarias No. 8010006. G.I.C.-J. also thanks Vicerrectoría de Investigación y Desarrollo (USACH) for a Research Associate position. C.A.C. is grateful to CONICYT for a Doctoral Fellowship and a Doctorate Terminal Thesis Fellowship.

References and Notes

(1) Miertus, S.; Scrocco, E.; Tomasi, J. *J. Chem. Phys.* **1981**, *55*, 117.

(2) Cossi, M.; Barone, V.; Mennucci, B.; Tomasi, J. *Chem. Phys. Lett.* **1998**, *286*, 253.

(3) Barone, V.; Cossi, M.; Tomasi, J. *J. Chem. Phys.* **1997**, *107*, 3210.

(4) Gontrani, L.; Mennucci, B.; Tomasi, J. *J. Mol. Struct. (THEOCHEM)* **2000**, *500*, 113.

(5) Wong, M. W.; Wiberg, K. B.; Frisch, M. J. *J. Am. Chem. Soc.* **1992**, *114*, 523.

(6) Wong, M. W.; Wiberg, K. B.; Frisch, M. J. *J. Am. Chem. Soc.* **1992**, *114*, 1645.

(7) Kasaab, E.; Langlet, J.; Evleth, E.; Akacem, Y. *J. Mol. Struct. (THEOCHEM)* **2000**, *531*, 267.

(8) Ciofini, I.; Adamo, C. *J. Phys Chem. A* **2001**, *105*, 1086.

(9) Adamo, C.; Heitzman, M.; Meilleur, F.; Rega, N.; Grand, A.; Cadet, J.; Barone, V. *J. Am. Chem. Soc.* **2001**, *123*, 7113.

(10) Yamaguchi, Y.; Yohomichi, Y.; Yokoyama, S.; Mashiko, S. *J. Mol. Struct. (THEOCHEM)* **2002**, *578*, 35.

(11) Domingo, L. R.; Picher, M. T.; Andrés, J.; Moliner, V.; Safont, V. S. *Tetrahedron* **1996**, *52* (32), 10693.

(12) Barone, V.; Cossi, M.; Adamo, C. *J. Comput. Chem.* **1993**, *18*, 1997.

(13) Seluki, C.; Aviyente, V.; Varnali, T.; López Rodríguez, R. *J. Mol. Struct. (THEOCHEM)* **1997**, *418*, 41.

(14) Adamo, C.; Dillet, V.; Barone, V. *Chem. Phys. Lett.* **1996**, *264*, 113.

(15) Meunier, B.; Robert, A.; Pratviel, G.; Bernadou, J. In *The Porphyrin Handbook*; Kadish, K. M., Smith K. M., Guilard, R., Eds.; Academic Press: San Diego, 2000; Vol. 4.

(16) Zagal, J. H. *Coord. Chem. Rev.* **1992**, *119*, 89.

(17) Astruc, D. *Electron Transfer and Radical Processes in Transition Metal Chemistry*, VCH Publishers Inc.: New York, 1995. Kuznetsov, A. M.; Ultrup, J. *Electron Transfer in Chemistry and Biology. An Introduction to Theory*; John Wiley & Sons: New York, 1998.

(18) Parr, R. G.; Yang, W. *Density Functional Theory of Atoms and Molecules*; Oxford University Press: New York, 1989.

(19) Adamo, C.; di Matteo, A.; Barone, V. *Adv. Quantum Chem.* **1999**, *36*, 4.

(20) Parr, R. G.; Pearson, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 7512.

(21) Parr, R. G.; Yang, W. *J. Am. Chem. Soc.* **1984**, *106*, 4049.

(22) Pearson, R. G. *J. Chem. Educ.* **1987**, *64*, 561.

(23) Chermette, H. *J. Comput. Chem.* **1999**, *20*, 128.

(24) Geerlings, P.; De Proft, F.; Langenaeker, W. *Chem. Rev.* **2003**, *103*, 1793.

(25) Pearson, R. G. In *Chemical Hardness, Structure and Bonding*; Sen, K. D., Mingos, D. M. P., Eds.; Spinger-Verlag: Berlin, Heidelberg, 1993; Vol. 80, pp 1−10.

(26) Chattaraj, P. K.; Parr, R. G. In *Chemical Hardness, Structure and Bonding*; Sen, K. D., Mingos, D. M. P., Eds.; Spinger-Verlag: Berlin, Heidelberg, 1993; Vol. 80, pp 11−25.

(27) Gázquez, J. L. In *Chemical Hardness, Structure and Bonding*; Sen, K. D., Mingos, D. M. P., Eds.; Spinger-Verlag: Berlin, Heidelberg, 1993; Vol. 80, pp 27−43.

(28) Chattaraj, P. K.; Lee, H.; Parr, R. G. *J. Am. Chem. Soc.* **1991**, *113*, 1855.

(29) Datta, D. *J. Phys. Chem. A* **1992**, *96*, 2409.

(30) Ghosh, S. K.; Berkowitz, M. *J. Chem. Phys.* **1981**, *55*, 117.

(31) Yang, W.; Parr, R. G. *Proc. Natl. Acad. Sci. U.S.A.* **1985**, *83*, 2976.

(32) Geerlings, P.; De Proft, F.; Langenaeker, W. *Adv. Quantum Chem.* **1999**, *33*, 303.

(33) Geerlings, P.; De Proft, F.; Martin, J. L. M. *Theor. Comput. Chem.* **1996**, *4*, 773.

(34) De Proft, F.; Geerlings, P. *Chem. Rev.* **2001**, *101*, 1451.

(35) (a) Zagal, J. H.; Gulppi, M.; Isaacs, M.; Cárdenas-Jirón, G. I.; Aguirre, M. J. *Electrochim. Acta* **1998**, *44*, 1349. (b) Zagal, J. H.; Cárdenas-Jirón, G. I. *J. Electroanal. Chem.* **2000**, *489*, 96. (c) Cárdenas-Jirón, G. I.; Zagal, J. H. *J. Electroanal. Chem.* **2001**, *497*, 55. (d) Cárdenas-Jirón, G. I.; Gulppi, M. A.; Caro, C. A.; del Río, R.; Páez, M.; Zagal, J. H. *Electrochim. Acta* **2001**, *46*, 3227.

(36) Cárdenas-Jirón, G. I.; Caro, C. A.; Venegas-Yazigi, D.; Zagal, J. H. *J. Mol. Struct. (THEOCHEM)* **2002**, *580*, 193.

(37) Ríos-Escudero, A.; Costamagna, J.; Cárdenas-Jirón, G. I. Submitted for publication in *J. Phys. Chem. A*.

(38) Cárdenas-Jirón, G. I. *Int. J. Quantum Chem.* **2003**, *91*, 389.

(39) Cárdenas-Jirón, G. I.; Parra-Villalobos, E. *J. Phys. Chem. A* **2003**, *107*, 11483.

(40) Cárdenas-Jirón, G. I.; Venegas-Yazigi, D. A. *J. Phys. Chem. A* **2002**, *106*, 11938.

(41) Venegas-Yazigi, D. A.; Cárdenas-Jirón, G. I.; Zagal, J. H. *J. Coord. Chem.* **2003**, *56*, 1269.

(42) Cárdenas-Jirón, G. I. *J. Phys. Chem. A* **2002**, *106* 3202.

(43) Ríos-Escudero, A.; Estiú, G.; Costamagna, J.; Cárdenas-Jirón, G. I. *J. Coord. Chem.* **2003**, *56*, 1257.

(44) Caro, C. A.; Zagal, J. H.; Cárdenas-Jirón, G. I. *J. Phys. Chem. A*, in preparation.

(45) Caro, C. A.; Bedioui, F.; Páez, M. A.; Cárdenas-Jirón, G. I.; Zagal, J. H. *J. Electrochem. Soc.* **2004**, *151*, E32.

(46) Griveau, S.; Bedioui, F.; Adamo, C. *J. Phys. Chem. A* **2001**, *105*, 11304.

(47) Pearson, R. G. *Acc. Chem. Res.* **1993**, *26*, 250.

(48) Pearson, R. G. *J. Am. Chem. Soc.* **1963**, *85*, 3533.

(49) Pearson, R. G. *Science* **1966**, *151*, 172.

(50) *Hard and Soft Acids and Bases*; Pearson, R. G., Ed.; Hutchinson and Ross: Stroudsburg, PA, 1973.

(51) Padmanabhan, J.; Parthasarathi, R.; Sarkar, U.; Subramanian, V.; Chattaraj, P. K. *Chem. Phys. Lett.* **2004**, *383*, 122.

(52) Caro, C. A.; Zagal, J. H.; Bedioui, F. *J. Electrochem. Soc.* **2003**, *150*, E95.

(53) Parr, R. G.; Zhou, Z. *Acc. Chem. Res.* **1993**, *26*, 256.

(54) Zhou, Z.; Parr, R. G. *J. Am. Chem. Soc.* **1990**, *112*, 5720.

(55) Chattaraj, P. K.; Cedillo, A.; Arnett, E. M.; Parr, R. G. *J. Org. Chem.* **1995**, *60*, 4707.

(56) Chattaraj, P. K. *Proc. Indian Natl. Sci. Acad.* **1996**, *62*, 513.

(57) Yang, W.; Mortier, W. *J. Am. Chem. Soc.* **1986**, *108*, 5708.

(58) Tomasi, J.; Persico, M. *Chem. Rev.* **1994**, *94*, 2027.

(59) Barone, V.; Cossi, M.; Tomasi, J. *J. Comput. Chem.* **1998**, *19*, 407.

(60) *TITAN 1.0.7*; Wavefunction, Inc. and Schrodinger Inc., 18401 Von Karman Avenue, Suite 370, Irvine, CA 92612.

(61) Adamo, C.; Barone, V. *J. Chem. Phys.* **1999**, *110*, 6158.

(62) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *77*, 3865.

(63) Perdew, J. P.; Ernzerhof, M. *J. Chem. Phys.* **1996**, *105* 9982.

(64) Adamo, C.; Barone, V. *Chem. Phys. Lett.* **1997**, *274*, 242.

(65) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian98*, revision A.7; Gaussian, Inc.: Pittsburgh, PA, 1998.