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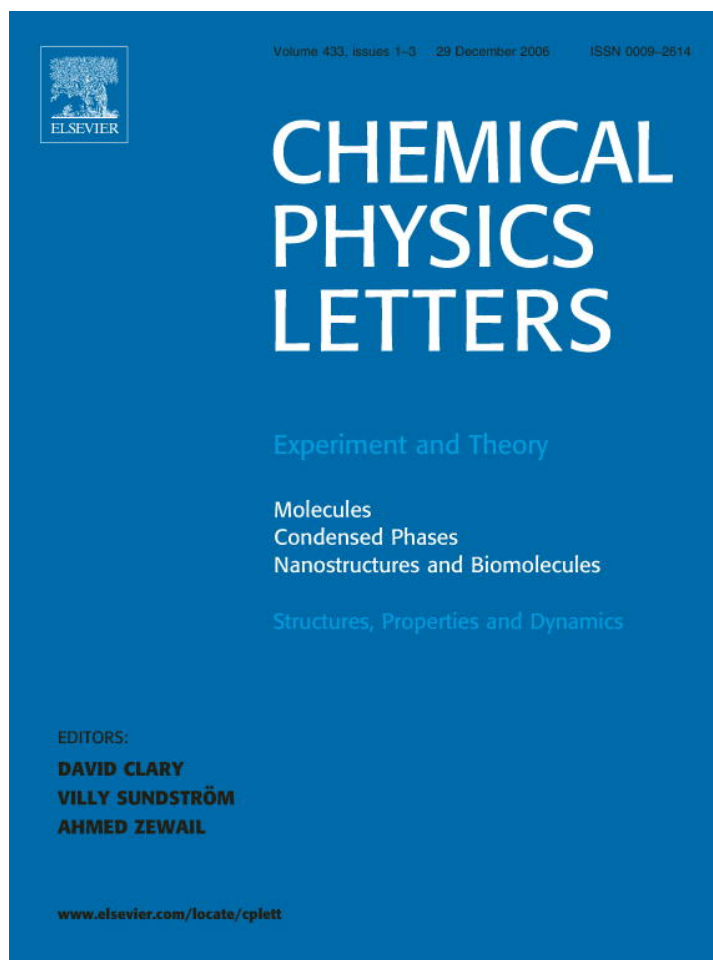


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On the variations of electronic chemical potential and chemical hardness induced by solvent effects

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Abstract

The effects that a polarizable medium exerts on the electronic chemical potential and the chemical hardness of neutral and charged molecules are discussed in detail, using the continuum approach based on the polarizable charge model. The variations in electronic chemical potential result from charge transfer between the solute and the solvent, a result which is confirmed by supermolecule calculations. Both models predict that chemical hardness diminishes in solution phase due to the decrease in electrostatic potential that result from the increase of the effective radii of neutral and charged solutes.

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1. Introduction

The development of global and local reactivity indexes defined in the context of the empirical density functional theory [1,2] has significantly helped in the study of reactivity and selectivity for a wide number of systems [3–12]. An excellent review that illustrates well this fact may be found in Ref. [13]. However, most of these studies are performed for the ground state of isolated molecules, neglecting the medium effects induced by the solvent. Whether or not such an approximation is valid still remains an open problem. Previous works in this field have provided partial information without giving a definitive response about the variation pattern of the electronic chemical potential (the negative of electronegativity) and chemical hardness induced by solvation. Within a finite difference approach, the electronic chemical potential $\mu \equiv -(I + A)/2$ and the chemical hardness $\eta \equiv (I - A)/2$ are both expressed in terms of the vertical ionization potential I and electron affinity A [1,2]. Using these approximate expressions, Pearson obtained the effective

electronic chemical potential and chemical hardness in solution by estimating solution ionization potentials and electron affinities I' and A' , respectively [14]. These values were obtained by combining gas phase proton affinities, aqueous pK_a values and hydration energies. The main results reported by this author were that the solution phase electronic chemical potentials (i.e. electronegativities) for neutral systems display marginal changes with reference to the gas values, and he concluded that the solvent had no effects on this property. Chemical hardness in solution on the other hand becomes very small, and in general, neutral species in solution were predicted to be very much softer than in the gas phase. As a result, this author recommended that gas phase calculations sufficed to estimate both quantities in neutral systems. However, there remains to establish if these results are still valid for charged species. The answer is not trivial because the electronic chemical potential must show a dependence on the net charge of the atomic or molecular ions. This statement was proved by Huheey some time ago [15]. In fact, the valence state electronegativity of an atom in a molecule differs from the isolated value in an amount which is proportional to the charge capacity of the system [15]. The dependence of the chemical hardness change

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induced by solvation is less obvious, and it is one of the aspects of the problem we shall address in this work.

Previous theoretical efforts to elucidate the variation patterns of electronegativity and chemical hardness induced by solvation in neutral and charged species have been reported. De Luca et al. [16] have studied the influence of the water on the hardness values using the polarizable continuum model (PCM). They have found differences between gas and solvent phase only when they worked in the finite difference approach. The changes in the chemical hardness from the gas phase to solution $\Delta\eta$ are negatives in both, neutral and charged systems, in agreement with the conclusions reported by Pearson [14]. On the other hand, Geerlings et al. [17,18] have reported the effect of the solvent on the chemical potential, the hardness and some selectivity index using the effective fragment potential model (EFP). The changes in the chemical potential are positives for cationic and neutral ionic species, while they are negatives for all anionic and neutral covalent species. The charged species exhibit a significant change in chemical potential. The chemical hardness, however, show positive and negative changes when passing from the gas phase to solution, in contradiction with Pearson's results.

Another pertinent work concerned the solvent effects on the electrophilicity index ω [19], which is defined in terms of μ and η as $\omega = \mu^2/2\eta$ [20]. However the changes in the electrophilicity index encompasses the variation of both μ and η quantities, so that it may leads to a confusing situation where the invariance of ω may be traced to compensating effects coming from the individual variations of each quantities from the gas to solution phase.

In this work we shall revisit this problem by analyzing previous theoretical results based on the continuum approach to solvent effects and by incorporating new results obtained from the supermolecule approach.

2. Discussion

One of the key aspects of this problem refers to the model used to represent the free energy of solvation. Within the continuum models based on the polarization charge model, this quantity is approximated using the Born's model. The resulting expression is:

$$\Delta E_{\text{solv}} = -\left(1 - \frac{1}{\varepsilon}\right) \frac{Q^2}{2a} \quad (1)$$

Where ε is the macroscopic dielectric constant of the solvent, Q is the net charge of the ion, and a its ionic radius [21]. The solvation energy, as expressed by Eq. (1) encompasses two main contributions, namely, the insertion energy $\Delta E_{\text{ins}} = E(\varepsilon) - E(1)$, where $E(\varepsilon)$ and $E(1)$ are the self energies of the ion in the presence and in the absence of the dielectric medium, and a polarization term $\Delta E_{\text{pol}} = -1/2\Delta E_{\text{ins}}$ accounting for the entropic contributions related

to the solvent re-organization [21]. Eq. (1) has been generalized to molecular systems [21] and also implemented to compute solvation energies of extended systems [22]. The generalized Born's formula becomes [21]:

$$\Delta E_{\text{solv}} = -\frac{1}{2} \left(1 - \frac{1}{\varepsilon}\right) \sum_A \sum_B Q_A Q_B \Gamma_{AB} \quad (2)$$

where Q_A and Q_B are the net charges of atoms A and B in the molecule and Γ_{AB} is a solute–solvent Coulomb integral [21].

For the sake of simplicity and without lost of generality, we continue our reasoning based on the simpler expression (1). If we differentiate once the solvation energy with respect to net charge we obtain:

$$\frac{\partial \Delta E_{\text{solv}}}{\partial Q} = -\left(1 - \frac{1}{\varepsilon}\right) \frac{Q}{a} = -\Delta\mu_{\text{solv}}; \quad (3)$$

which may be rearranged to

$$\Delta\mu_{\text{solv}} = \left(1 - \frac{1}{\varepsilon}\right) \frac{Q}{a}, \quad (4)$$

if we remind that in general the net charge may be expressed as $Q_A = Z_A - N_A$, where Z_A and N_A are the number of electrons of atom A in the isolated and valence states, respectively, then $\frac{\partial Q_A}{\partial N_A} = -\frac{\partial}{\partial N_A}$. Using the definition $\mu = \left[\frac{\partial E}{\partial N}\right]_{v(r)}$, Eq. (4) follows.

Eq. (4) indicates that if the external potential $v(r)$ is kept fixed in the process of inserting the molecule in the dielectric medium, the change in the electronic chemical potential will depend on both, the sign and magnitude of the net charge. That is, for neutral systems, this variation in electronic chemical potential induced by solvation will approximately vanish, in agreement with Pearson's result [14]. However, the result for charged species is different. For instance, Eq. (4) predicts that for cations the change in electronic chemical potential from gas to solution phase will be positive and for anions negative. The interpretation of this result may be as follows. For cations, the increase of the electronic chemical potential entails a decrease in electronegativity which may be explained by a saturation effect coming from an amount of charge transfer from the solvent molecules to the cation. Note that the coordination of water to the cation is oriented towards the electron donating oxygen atom. The coordination of water molecules to anions is trough a hydrogen bond, in which the solute acts as a proton acceptor, and therefore it release an amount of electronic charge to the solvent, thereby increasing its effective electronegativity. The generalized expression for molecular systems is:

$$\Delta\mu_{\text{solv}} = \left(1 - \frac{1}{\varepsilon}\right) \sum_A Q_A \Gamma_{AA}; \quad (5)$$

and the net results obtained above remain valid.

In order to obtain an estimation about the changes in chemical hardness upon solvation we differentiate Eq. (1) twice with respect to the net charge. There results:

$$\Delta\eta_{\text{solv}} = -\left(1 - \frac{1}{\varepsilon}\right) \frac{1}{a}; \quad (6)$$

The corresponding generalized expression is:

$$\Delta\eta_{\text{solv}} = -\left(1 - \frac{1}{\varepsilon}\right) \sum_A F_{AA} \quad (7)$$

Note that in both cases, and independent of the sign of the net charges, the changes in chemical hardness induced by solvation is predicted to be negative within the continuum model of solvent effects. Note also that this result is again in agreement with Pearson's results for neutral systems: they are consistently predicted to be softer in solution than in the gas phase. For charged species however this result is less clear, as molecular cations and anions are both predicted to decrease their chemical hardness when they are transferred from the gas to the solution phase, keeping their geometry frozen. Unfortunately in this case, there is not any previous theoretical result that could illuminate on whether or not the chemical hardness is dependent on the global charge of the system, as it was the case of the electronegativity using Huheey's result [15].

In order to obtain more insight into the dependence on the sign and magnitude in hardness variation upon solvation we have chosen a different approach using the supermolecule technique. The results are displayed in Table 1. They were obtained by taking a solvation layer formed by eight water molecules around the positively and negatively charged solutes shown in Table 1. All the quantities quoted in Table 1 were obtained at the B3LYP level of theory using the Gaussian98 [23] package of programs with the 6-31G* basis set. The values of the electronic chemical potential and the chemical hardness were obtained from the expressions $\mu = (\varepsilon_{\text{H}} + \varepsilon_{\text{L}})/2$ and $\eta = (\varepsilon_{\text{L}} - \varepsilon_{\text{H}})$, in terms of the one electron energies of the HOMO and LUMO frontier molecular orbitals, ε_{H} and ε_{L} , respectively, by performing single point calculations for the substrate surrounded by its solvation layer. Note that the variations in electronic chemical potential (or electronegativity) consistently reproduce the trends predicted by the Born model: while cations increase their electronic chemical potential

and therefore decrease their electronegativity in the solution phase, anions consistently show the opposite trend. Taking a closer look at the third column of Table 1 we notice that the intrinsic electronic chemical potential of water is greater than the corresponding electronic chemical potential of the three cations quoted in Table 1, thereby confirming that the charge transfer takes place from water to the cations, a result also anticipated by the Born formula that explains the decrease in electronegativity. A similar analysis is also true for the two anions quoted in Table 1. In this case, the intrinsic electronic chemical potential of water is less than NH_2^- and OH^- , thereby suggesting that the charge transfer will take place towards the water solvating molecules, causing an increase in the corresponding effective electronegativities. Note however that for anions, the absolute electronic chemical potentials are predicted to be positive quantities which may be traced to the fact that in the gas phase both species are thermodynamically unstable. The problem here is essentially the accurate calculation of the vertical electron affinity of negatively charged species. However, the overall result based on the difference in electronic chemical potential from gas to solution phase consistently predict the expected increase in electronegativity of the solvated anions.

The variations in chemical hardness may be more easily explained by considering the fact that both anions and cations (as well as neutral species) increase their effective radii in solution phase. This means that independent of the sign of the charge that the ion may bear, the electrostatic potential q/r will always diminish and therefore the solvated species, cations neutrals and anions will decrease their effective hardness and will therefore become softer in the solution phase. This result demonstrated by Pearson [14] for neutral species may be generalized here on the basis of this simple electrostatic argument and it is again consistent with the Born-like Eqs. (6) and (7). An additional comment regarding the solvent effects evaluated using the supermolecule approach is worth making. As an increasing number n of explicit solvent molecules are incorporated, the frontier molecular orbitals of the system may in some cases shift from the isolated solute limit ($n = 0$) to the bulk solvent region, and therefore the evaluation of the vertical ioniza-

Table 1
Chemical hardness and electronic chemical potential values for neutral and charged species in the gas (g) and solution (s) phases^a

Molecule	$\eta_{(\text{g})}$ (eV)	$\mu_{(\text{g})}$ (eV)	$\eta_{(\text{s})}$ (eV)	$\mu_{(\text{s})}$ (eV)	$\Delta\eta$ (eV)	$\Delta\mu$ (eV)	Occupied state localized on the solute	Unoccupied state localized on the solute
CH_3NH_3^+	11.98	-11.13	4.54	-5.94	-7.44	5.19	H	L
NH_4^+	16.75	-14.11	6.62	-7.31	-10.13	6.80	H-4	L
H_3O^+	12.33	-13.40	2.40	-5.41	-9.93	7.99	H	L
CH_3NH_2	8.52	-1.96	1.44	-0.08	-7.08	1.88	H	L
NH_3	9.01	-2.36	1.61	-1.13	-7.40	1.23	H	L
H_2O	9.63	-3.11	3.70	-2.18	-5.93	0.93	H-1	L
NH_2^-	5.87	7.38	0.17	4.92	-5.70	-2.46	H	L
OH^-	6.87	7.81	1.49	4.54	-5.39	-3.27	H	L

^a The solution phase values were obtained from the supermolecule approach incorporating eight water molecules. The two last columns report the molecular orbital on which the solute is localized. H = HOMO of the whole system; L = LUMO of the whole system.

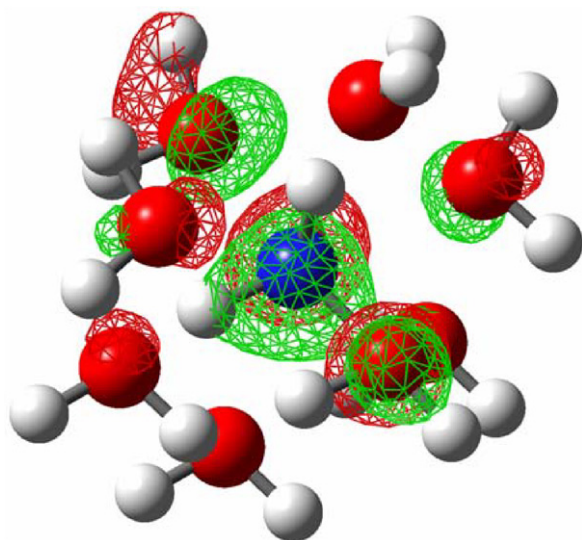


Fig. 1. Plot of the HOMO-4 state localized on the solute.

tion potential I and electron affinity A not longer represent a property of the solute. This is the case for instance of NH_4^+ and water. In the first case, the state localized on the solute whose eigenvalue is used to calculate electronic chemical potential and hardness reported in Table 1 is the HOMO-4 state and the HOMO-1 state for water. A plot of the HOMO-4 state of NH_4^+ is shown in Fig. 1 to illustrate this fact.

3. Concluding remarks

The solvent effects on two main global descriptors of reactivity, namely the electronic chemical potential (the negative of electronegativity) and the chemical hardness have been revisited. The following general conclusions may be drawn from the present study. The electronic potential of cations increases by solvation, and therefore their solution phase electronegativity decreases as a consequence of charge transfer from the solvent to the solute. For anions, the electronic chemical potential decreases by solvation and therefore their electronegativity increases as a consequence of charge transfer from the solute to the solvent (mediated by hydrogen bond). Independent of the sign and magnitude of the charge, the chemical hardness always decreases upon solvation because the electrostatic potential decreases as the effective radius (solute radius plus a solva-

tion layer) of the solute increases. Unfortunately it is very difficult to give an order of decreasing pattern in hardness for cations vs anions because this quantity is strongly dependent of the actual structure of the charged solutes plus its solvation layer

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