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Solvent Effects on Electrophilicity

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Abstract: Continuum solvent effect on the electrophilicity index recently proposed by Parr and co-workers (Parr, R. G.; von Szentpaly, L.; Liu, S. *J. Am. Chem. Soc*. **1999**, *121*, 1922) is discussed in detail. Solvent effect is introduced using the self-consistent isodensity polarized continuum model (SCI-PCM). A linear relationship is found between the change in electrophilicity index and the solvation energy as represented in the frame of the reaction field theory. The effect of a polarizable environment on the global electrophilicity is examined for a series of 18 well-known electrophiles presenting a wide diversity in structure and bonding properties. It is found that solvation enhances the electrophilicity power of neutral electrophilic ligands but attenuates this power in charged and ionic electrophiles.

It has been recently proposed that the electrophilicity power of an atom or molecule may be conveniently represented by the electrophilicity index ω defined by Parr and co-workers[1] by:

$$\omega \equiv \frac{\mu^2}{2\eta} \tag{1}$$

which may be regarded as a quantitative formulation of Maynard et al.'s model.[2] In eq 1 μ and η represent the electronic chemical potential and the chemical hardness of the electrophilic ligand, respectively. In this definition of the ω index, the electronic chemical potential is approached as $\mu = -(I + A)/2$, and the chemical hardness is represented by $\eta = (I - A)$, in terms of the ionization potential I and electron affinity A. Other definitions of electrophilicity are available in the literature,[3−6] but we shall concentrate here on the one defined by eq 1. Even though the electrophile/nucleophile interactions that take place in solution phase are assumed to be preceded by a desolvation step, so that intrinsic in vacuo studies would suffice to describe them accurately, it is expected, however, that this desolvation process may not be complete and similar in charged and neutral ligands. Some partial solvation may affect the electrophile/nucleophile interactions to a different extent.[7] Consider for instance the case of hard electrophiles such as H^+, Li^+, and Na^+, where the desolvation process has to take place in the presence of a quite strong reaction field potential.[8,9] These considerations leave the effect of the solvent on the electrophilicity power of ligands as an open and relevant problem. In this work, we intend to examine the variations in the electrophilicity pattern, as measured by the electrophilicity index defined in eq 1, for a wide variety of well-known ligands that may be induced by solvation effects.

Consider a first-order variation in the electrophilicity index ω, induced for instance by a change from the gas to the solution phase:

$$d\omega = \left(\frac{\mu}{\eta}\right)d\mu - \frac{1}{2}\left(\frac{\mu}{\eta}\right)^2 d\eta \tag{2}$$

A first-order finite variation in ω describing the change of phase from vacuum to a polarizable environment characterized by its dielectric constant ϵ is then given by:

$$\Delta\omega(1\rightarrow\epsilon) = \left(\frac{\mu}{\eta}\right)\Delta\mu - \frac{1}{2}\left(\frac{\mu}{\eta}\right)^2\Delta\eta = \Delta\omega^{(1)} + \Delta\omega^{(2)} \tag{3}$$

where $\Delta\mu$ and $\Delta\eta$ describe the changes in electronic chemical potential and chemical hardness from the gas to solution phase. Note that the shift in electrophilicity may be represented in terms of first- and second-order changes in energy. The first-order contribution may be rearranged to:

$$\Delta\omega^{(1)}(1\rightarrow\epsilon) = \left[\frac{\Delta E}{\Delta N}\right]_{v(\mathbf{r})}\left[\frac{\Delta N}{\Delta\mu}\right]_{v(\mathbf{r})}\Delta\mu \cong \Delta E_{\text{ins}} \tag{4}$$

where $\Delta E_{\text{ins}} = E(\epsilon) - E(1)$ is the insertion energy of the solute

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Table 1. Global Quantities for the Series of Electrophilic Species in Gas and Solution Phases[a]

	$\epsilon = 1.0$				$\epsilon = 78.5$			
	μ (eV)	η (eV)	ω (eV)	ΔN_{max}	μ (eV)	η (eV)	ω (eV)	ΔN_{max}
Li^+	−40.83	70.43	11.84	0.57974	−23.34	48.97	5.56	0.47669
	−39.98	69.28	11.53	0.57706	−22.42	47.78	5.26	0.46934
Na^+	−26.37	41.90	8.30	0.62933	−15.03	29.14	3.88	0.51595
	−25.43	40.98	7.89	0.62064	−13.97	28.20	3.46	0.49553
CH_3^+	−17.70	15.69	9.98	1.12804	−10.20	7.78	6.69	1.31118
	−16.85	15.79	8.99	1.06727	−9.26	7.77	5.51	1.19125
NO_2^+	−16.11	17.20	7.54	0.93660	−9.35	10.41	4.20	0.89804
	−20.75	27.70	7.77	0.74903	−13.40	19.91	4.51	0.67321
$LiCH_3$	−3.87	7.35	1.02	0.52716	−1.88	3.82	0.46	0.49212
	−3.07	6.04	0.78	0.50811	−1.00	2.63	0.19	0.38158
HF	−6.38	19.29	1.06	0.33088	−5.26	12.01	1.15	0.43808
	−5.20	18.29	0.74	0.28434	−4.15	11.23	0.77	0.36958
HCl	−5.35	14.95	0.96	0.35814	−4.70	9.26	1.19	0.50754
	−4.30	14.65	0.63	0.29360	−3.64	8.95	0.74	0.40706
H_2SO_4	−5.44	13.60	1.09	0.40033	−4.81	9.31	1.24	0.51684
	−5.07	15.80	0.81	0.32078	−3.94	10.81	0.72	0.36418
BH_3	−6.38	13.55	1.50	0.47055	−5.80	7.76	2.17	0.74840
	−5.62	13.64	1.16	0.41231	−5.04	7.82	1.63	0.64485
BF_3	−5.86	18.47	0.93	0.31726	−5.40	12.89	1.13	0.41937
	−5.94	20.98	0.84	0.28301	−5.42	15.38	0.96	0.35264
$AlCl_3$	−5.63	11.61	1.37	0.48504	−5.02	7.61	1.65	0.65905
	−5.55	13.08	1.18	0.42468	−4.84	9.12	1.28	0.53058
PCl_3	−5.34	10.80	1.32	0.49469	−4.83	6.57	1.78	0.73533
	−4.51	11.37	0.90	0.39686	−3.92	6.95	1.11	0.56389
PF_3	−5.25	14.17	0.97	0.37037	−4.54	8.72	1.18	0.52081
	−4.41	14.51	0.67	0.30357	−3.51	8.73	0.71	0.40192
CH_3Cl	−4.49	13.77	0.73	0.32619	−4.03	8.96	0.91	0.44981
	−3.39	13.98	0.41	0.24256	−2.89	9.18	0.45	0.31459
CH_3CH_2Cl	−4.33	13.46	0.70	0.32159	−3.93	8.99	0.86	0.43681
	−3.22	13.84	0.37	0.23240	−2.77	9.29	0.41	0.29849
HCOH	−4.51	12.56	0.81	0.35937	−4.16	6.69	1.29	0.62128
	−3.42	12.06	0.49	0.28394	−3.09	6.18	0.77	0.49968
CH_3COCH_3	−3.81	11.52	0.63	0.33090	−3.62	6.89	0.95	0.52530
	−2.68	11.37	0.32	0.23579	−2.55	6.61	0.49	0.38612
SO_3	−6.31	12.75	1.57	0.49558	−5.84	7.54	2.26	0.77406
	−5.80	14.38	1.17	0.40312	−5.24	9.18	1.49	0.57049

[a] First entry: B3P/6-311G** calculations. Second entry: HF/6-311G** calculations.

into the solvent. This quantity is related to the solvation energy ΔE_{solv} within the reaction field theory of solvent effects by:[10−12]

$$\Delta E_{ins} = 2\Delta E_{solv} \tag{5}$$

and eq 4 becomes:

$$\Delta\omega^{(1)}(1\rightarrow\epsilon) \cong 2\Delta E_{solv} \tag{6}$$

We consider now the second contribution in eq 3, which upon a little rearrangement may be rewritten as:

$$\Delta\omega^{(2)}(1\rightarrow\epsilon) = \frac{1}{2}\left(\frac{\mu}{\eta}\right)^2\Delta\eta = \frac{1}{2}\left(\frac{\mu}{\eta}\right)\left(\frac{\mu}{\eta}\frac{\Delta\mu}{\Delta N}\right) = \frac{1}{2}\left(\frac{\mu}{\eta\Delta N}\right)\left(\frac{\mu}{\eta}\Delta\mu\right) = \frac{1}{2}\left(\frac{\mu}{\eta\Delta N}\right)\Delta E_{ins} \tag{7}$$

However, the ratio μ/η has been proposed by Parr et al.[1] to represent the maximum amount of charge transfer from the environment $-\Delta N_{max}$. Use of this result in eq 7, together with relationship 5, leads to:

$$\Delta\omega^{(2)}(1\rightarrow\epsilon) = \frac{1}{2}\left(\frac{\mu}{\eta}\right)^2\Delta\eta \cong -\frac{\Delta N_{max}}{\Delta N}\Delta E_{solv} \tag{8}$$

Substitution of eqs 6 and 8 into eq 3 gives the desired result, namely:

$$\Delta\omega(1\rightarrow\epsilon) = \left(2 + \frac{\Delta N_{max}}{\Delta N}\right)\Delta E_{solv} = \gamma\Delta E_{solv} \tag{9}$$

showing that up to second order in energy variations, the changes in global electrophilicity will show a linear dependence with the solvation energy, with a regression slope:

$$\gamma = \left(2 + \frac{\Delta N_{max}}{\Delta N}\right) \tag{10}$$

To test the predicted linear relationship between the changes in electrophilicity and solvation energy, we considered 18 well-known electrophilic species that are shown in Table 1. This database includes charged and neutral electrophiles displaying quite diverse structure and bonding properties. We first evaluated the electronic chemical potential and hardness using the approximate expressions[13,14]

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$$\mu \cong -\frac{(I+A)}{2} \tag{12a}$$

and

$$\eta \cong \mathrm{I} - A \tag{12b}$$

by approaching the ionization potential I and the electron affinity A by the difference in total energies between the neutral and the corresponding ionic species. The calculation for ions is carried out at the frozen geometry of the neutral parent species. To show that the electrophilicity index as well as the linear relationship between the variations of the electrophilicity index and solvation energy are independent of the level of theory used, Hartree−Fock/6-311G** and B3LYP/6-311G** calculations were performed on all 18 species considered at their ground-state optimized structures using the GAUSSIAN94 package of programs.[15] Solvation energies were evaluated using the self-consistent isodensity polarized continuum model, SCI-PCM,[16,17] for a dielectric constant $\epsilon = 78.5$ (i.e., to mimic water as solvent). In this model, the cavity where the solute system is embedded is defined by an isodensity surface of the molecule, instead of a set of atomic radii. The recommended value of 0.0004e for the isodensity contour was used. With the values of electronic chemical potential and chemical hardness at hand, the electrophilicity index and the $\Delta N_{\max}$ values may be readily computed via eq 1, and using the relationship $\Delta N_{\max} = -\mu/\eta$ for the system in the gas and solution phases. The results obtained at HF/6-311G** and B3LYP/6-311G** are depicted in Table 1. The electronic chemical potential displays negative values in both phases, indicating the ability of the system to accept electrons from the environment. However, this ability to exchange electrons with the environment is smoothly attenuated in the solution phase for the neutral system. This result is in agreement with Pearson's prediction that electronegativity (the negative of the electronic chemical potential) of neutral systems is almost unaffected by solvation.[14] This is approximately true for most of the neutral electrophilic ligands considered in Table 1. Note that the major changes in electronic chemical potential induced by solvation are observed for the charged and ionic species, suggesting that Pearson's result may not hold for charged and ionic species. For instance, the charged electrophiles Li^+, Na^+, CH_3^+, and NO_2^+ show a variation in electronic chemical potential of about 50% upon solvation. The ionic electrophile $LiCH_3$ also displays a similar pattern, yet the also ionic HCl molecule falls in the bigger third group of ligands that marginally modify their electronegativity upon solvation.

Chemical hardness values are also displayed in Table 1 for the gas and solution phases. The most interesting result is that solvation renders the electrophilic ligands softer than in the gas phase. This seems to hold for both neutral and charged species. This result may be rationalized by adopting a simple solvation picture proposed by Komorowski.[18] This model is based on the simplest representation of solvation energy, namely, the reaction field generalized Born equation:[19−21]

$$\Delta E_{\mathrm{solv}} = -\frac{1}{2}\left(1 - \frac{1}{\epsilon}\right)\sum_A \sum_B Q_A Q_B \Gamma_{AB} \tag{13}$$

where Q_k represent the net atomic charge of atom k in the molecule, and Γ_{AB} is a solute−solvent interaction integral.[19−22] Within the present approach, the first derivative of ΔE_{solv} with respect to the charge is proportional to changes in electronic chemical potential $\Delta\mu(1 \rightarrow \epsilon)$, which becomes equal to the reaction field potential.[10−12] To see this, just take the first derivative with respect to the charge Q_k of expression 13 to get:

$$\Delta\mu = \frac{\partial \Delta E_{\mathrm{solv}}}{\partial Q_k} = -\left(1 - \frac{1}{\epsilon}\right)\sum_k Q_k \Gamma_{kk} \tag{14}$$

where Γ_{kk} may represent the inverse of the ionic (or covalent) radius R_k of atom k in the molecule.[20,21] Note that according to this simplified model, the change in electronic chemical potential induced by solvation becomes charge dependent, and therefore it explain well the variation pattern of the electronic chemical potential induced by solvation in the series of molecules considered here: the most significant changes are observed for charged and ionic electrophile species, whereas for neutral ligands this change is in general lower, in agreement again with Pearson's prediction. The charge dependence of the electronic chemical potential of solvation is not surprising, as the electronegativity (the negative of μ) has been shown to depend on the charge for atoms.[23] This result was generalized for molecules later.[24] In the present case, the variations in electronic chemical potential upon solvation appear to be dependent on the polarization charge $Q_k^{\mathrm{pol}}(\epsilon) = -(1 - (1/\epsilon))Q_k^{o}$, within the reaction field model of solvent effects considered here.

To explain the variation pattern in global hardness upon solvation, we just differentiate expression 13 twice with respect to the charge Q_k. There results

$$\Delta\eta \cong \frac{\partial^2 \Delta E_{\mathrm{solv}}}{\partial {Q_k}^2} = \frac{\partial \Delta\mu}{\partial Q_k} = -\left(1 - \frac{1}{\epsilon}\right)\sum_k \Gamma_{kk} \tag{15}$$

This result predicts that independent of the net charge that the electrophilic species may bear, the variation in chemical hardness always will be negative, because the quantities ϵ and Γ_{kk} are both positive definite. In other words, solvation effects render the electrophile ligands softer that in the gas phase. This may be a controversial outcome of the Born model of solvation, yet it correctly explains the trend in the chemical hardness variations upon solvation within the series of electrophiles quoted in Table 1.

Also quoted in Table 1 are the values of the electrophilicity index in both gas and solution phases. According to eq 1 this is a positive definite quantity. It may be seen that upon solvation,

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Table 2. Changes in Electronic Chemical Potential, Chemical Hardness, Electrophilicity, and Solvation Energy for a Series of Electrophilic Ligands[a]

	$\Delta\mu$ (eV)	$\Delta\eta$ (eV)	$\Delta\omega(1\rightarrow\epsilon)$ (eV)	ΔE_{solv} (eV)
Li^+	17.49	−21.46	−6.273	−6.771
	17.55	−21.50	−6.272	−6.820
Na^+	11.34	−12.77	−4.419	−4.971
	11.46	−12.78	−4.431	−5.093
CH_3^+	7.50	−7.91	−3.295	−3.560
	7.59	−8.01	−3.477	−3.599
NO_2	6.76	−6.77	−3.344	−3.435
	7.35	−7.79	−3.259	−3.556
$LiCH_3$	2.00	−3.53	−0.559	−1.654
	2.07	−3.42	−0.589	−1.779
HF	1.12	−7.28	0.097	−0.231
	1.05	−7.06	0.028	−0.261
HCl	0.65	−5.68	0.235	−0.095
	0.66	−5.70	0.110	−0.100
H_2SO_4	0.63	−4.29	0.154	−0.498
	1.13	−4.99	−0.096	−0.628
BH_3	0.57	−5.80	0.672	−0.042
	0.58	−5.81	0.467	−0.051
BF_3	0.46	−5.58	0.203	−0.115
	0.52	−5.60	0.116	−0.186
$AlCl_3$	0.61	−3.99	0.288	−0.193
	0.72	−3.96	0.104	−0.304
PCl_3	0.51	−4.23	0.455	−0.056
	0.59	−4.41	0.210	−0.069
PF_3	0.71	−5.45	0.211	−0.108
	0.89	−5.78	0.037	−0.138
CH_3Cl	0.46	−4.81	0.173	−0.079
	0.50	−4.80	0.043	−0.093
CH_3CH_2Cl	0.40	−4.48	0.161	−0.079
	0.44	−4.55	0.040	−0.093
HCOH	0.36	−5.87	0.480	−0.131
	0.33	−5.88	0.285	−0.184
CH_3COCH_3	0.19	−4.63	0.320	−0.161
	0.13	−4.76	0.177	−0.203
SO_3	0.48	−5.20	0.695	−0.230
	0.56	−5.20	0.325	−0.363

[a] First entry: B3LYP/6-311G** calculations. Second entry: HF/6-311G** calculations.

the charged Li^+, Na^+, CH_3^+, and NO_2^+, as well as the ionic $LiCH_3$ electrophilic ligands, diminish their electrophilic power with respect to the one displayed in the gas phase. This result may be traced to the opposite variation pattern displayed by the quantities μ and η from the gas to solution phase quoted in Table 2: while the hardness diminishes upon solvation, suggesting that the charged and ionic electrophiles will display a lower resistance to exchange electrons with the environment, the electronic chemical potential of these species display the opposite behavior against the charge transfer capability, so that the lowering in the electrophilicity power appears to be mostly controlled by the variations in electronic chemical potential. Within our model condensed in eq 3, the first term contributes a quantity $2\Delta E_{\text{solv}}$ to the lowering in the electrophilicity power $\Delta\omega(1\rightarrow\epsilon)$ induced by solvation. Therefore, strong solvation and the increasing variation pattern of the electronic chemical potential of the charged and ionic species seem to account for the observed lowering of the electrophilicity power upon solvation in charged and ionic electrophiles.

For the series of neutral and more covalent electrophiles, however, the changes in μ upon solvation are markedly lower than the corresponding hardness variations, in agreement with Pearson's results.[14] Therefore, the enhancement in electrophilicity power observed in the neutral ligands almost results form the decrease in the resistance to exchange electrons with the environment on one hand ($\Delta\eta < 0$), and also from the moderate stabilizing solvation effect ($\Delta E_{\text{solv}} < 0$), yielding a slight enhancement in the $\Delta\omega(1\rightarrow\epsilon)$ quantity for these species. In summary, while the strong solvation effect together with a significant increase in electronic chemical potential lower the electrophilicity power in charged and ionic electrophiles, the enhancement in electrophilicity power in neutral ligands appears to be controlled by changes in chemical hardness and the solvation energy, with a marginal contribution from the electronic chemical potential of solvation. Within the crude Born model of solvation adopted here and condensed in eq 15, the chemical hardness variation upon solvation is predicted to be negative and independent of the polarization charge distribution.

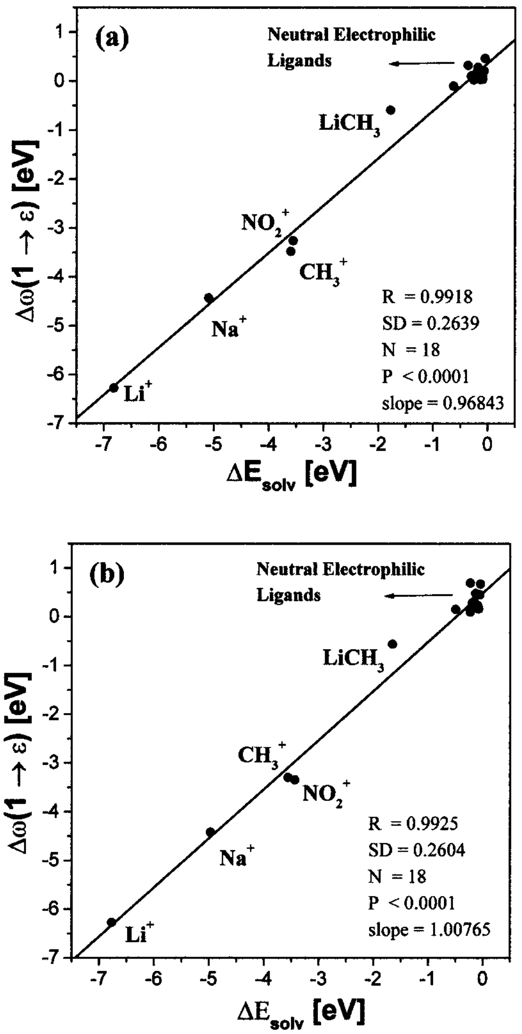

Figure 1. Linear relationship between electrophilicity changes and solvation energy for a series of electrophilic ligands at (a) HF/6-311G** and (b) B3LYP/6-311G** levels of theory. *R* is the regression coefficient, SD is the standard deviation, *N* is the number of points, and *P* is the probability that the observed relationship between the variables was randomly obtained.

The linear relationship between the variation of electrophilic power and solvation energies predicted from our model eq 9 was tested for the whole series of electrophilic ligands considered in the present study. Actual values of the changes in electrophilicity power evaluated as $\Delta\omega(1\rightarrow\epsilon) = \omega(\epsilon) - \omega(1)$ were plotted against the corresponding solvation energy, evaluated within the SCI-PCM model of solvation. The results are depicted in Figure 1, parts a and b, which correspond to HF/6-311G** and B3LYP/6-311G** calculations, respectively. Both quantities show a high linear correlation which seems to be independent of the computational scheme used.

While the variations in the electronic chemical potential upon solvation appear to be dependent on the polarization charges induced in the environment within the reaction field approach, there remains the problem of rigorously establishing the expected variation pattern of the η quantity for a system coupled to an external electric field. The charge dependence of the electronic chemical potential is consistent with the Politzer model,[23] yet the almost invariance of chemical hardness with the charge deserves further study beyond the rather crude Born-like model adopted here and represented in eq 15.

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