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The solvent effect on the electronegativity and hardness of bonded atoms

Józef Lipiński, Ludwik Komorowski

Institute of Physical and Theoretical Chemistry, Technical University of Wrocław, Wyb. Wyspiańskiego 27, 50-370 Wrocław, Poland

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Abstract

The role of solvent interactions in modifying the electronegativity (χ) and hardness (η) of bonded atoms has been studied. The simple virtual charge model of a homogeneous polar medium was chosen for the description of the solvent properties. Molecular χ and η indices show minor dependences on the solvent polarity. The hardness of ions decreases with increasing solvent polarity whereas the electronegativity index decreases for cations and increases for anions.

1. Introduction

Electronegativity has been a classical and empirical parameter quantifying the tendency of atoms to attract electrons; it has recently found theoretical justification and support from density functional theory [1]. Electronegativity was proved to be identical to the negative chemical potential of the electronic gas and the first derivative of the energy functional by the electron density function. The second derivative has been identified with the hardness property, first introduced by Pearson in his hard and soft acids and bases rule (HSAB or Pearson principle) [2]. Quantum chemical calculations of electronegativity and hardness indices for bonded atoms have recently been proposed [3,4]; the method has also been extended to produce indices for chemical groups [5]. This present study is focused on the analysis of atomic electronegativity and hardness indices for molecules in a homogeneous polar medium – a solvent. Quantum chemical procedures that include the solvent effect have been well known (see e.g. Refs. [6–29]). Most of them follow from the model of a continuous dielectric by Onsager and Kirkwood [30–32]. Formally, these models introduce an energy operator $\mathbf{F}$ as

$$\mathbf{F} = \mathbf{F}^0 + \mathbf{V}, \tag{1}$$

where $\mathbf{F}^0$ stands for the energy operator for a free molecule, and $\mathbf{V}$ is the electrostatic potential produced by the solvent molecules. Calculation techniques differ only in the choice of form for $\mathbf{V}$. This present work employs the simple virtual charge model (VCM) of Constanciel and co-workers [17–19]. In this approach, the solvent is represented by a set of polarization charges (q^{pol}) characteristic of a respective atomic center as follows:

$$q_{\mathrm{A}}^{\mathrm{pol}} = -(1 - f_{\mathrm{A}})\, q_{\mathrm{A}}\, f(\epsilon), \tag{2}$$

where the dielectric function $f(\epsilon)$ is related to the dielectric constant by

$$f(\epsilon) = 1 - \epsilon^{-1/2}. \tag{3}$$

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q_A is the net charge on the atom A, ϵ denotes the permittivity of the solvent and f_A is the screening factor of atom A that characterizes steric inhibition to solvation due to the specific neighbourhood at atomic center A [33].

2. Electronegativity and hardness from the Hartree–Fock–Roothaan model

The electronic energy for a closed shell system, given the energy operator $\mathbf{F}^0 = \mathbf{H}^0 + \mathbf{G}$ and the disturbing potential $\mathbf{V}$ is

$$E = \sum_k \sum_l P_{kl}\left(H^0_{kl} + 0.5G_{kl} + V_{kl}\right). \tag{4}$$

The procedure developed in earlier works [3–5] leads to the following energy derivatives:

$$X_{kl} = \partial E/\partial P_{kl} = F^0_{kl} + W_{kl},$$

where

$$W_{kl} = \sum_m \sum_n \partial(P_{mn}V_{mn})/\partial P_{kl}. \tag{5}$$

Then the electronegativity of a bonded atom becomes

$$\chi_A = K_A^{-1} \sum_{k\in A} \sum_l X_{kl}a_{kl} = \chi_A(F^0) + \Delta\chi_A(V), \tag{6}$$

where

$$\chi_A(F^0) = -K_A^{-1} \sum_{k\in A} \sum_l F^0_{kl}a_{kl}$$

and

$$\Delta\chi_A(V) = -K_A^{-1} \sum_{k\in A} \sum_l W_{kl}a_{kl}.$$

The physically relevant part of the hardness, the valence hardness, becomes

$$\eta_A^{val} = \eta_A^{val}(F^0) + \Delta\eta_A(V), \tag{7}$$

where

$$\eta_A^{val}(F^0) = -K_A^{-1} \sum_{k\in A} \sum_l F^0_{kl}b_{kl}$$

and

$$\Delta\eta_A(V) = -K_A^{-1} \sum_{k\in A} \sum_l (W_{kl}b_{kl} + W'_{kl}a_{kl}),$$

$$W'_{kl} = \partial W_{kl}/\partial N.$$

When the disturbing potential $\mathbf{V}$ is due to the solvent, the terms $\Delta\chi(V)$ and $\Delta\eta(V)$ represent the primary solvent effect on electronegativity and hardness, respectively. Important parameters a_{kl} and b_{kl} may be found under Koopmans' theorem as [3,4]

$$a_{kl} = \tfrac{1}{2}\left(C_k^{LUMO}C_l^{LUMO} + C_k^{HOMO}C_l^{HOMO}\right), \tag{8}$$

$$b_{kl} = \tfrac{1}{2}\left(C_k^{LUMO}C_l^{LUMO} - C_k^{HOMO}C_l^{HOMO}\right), \tag{9}$$

$K_A = \partial N_A/\partial N$ correspond to the Fukui indices and may be found from

$$K_A = \sum_{k\in A} \sum_l S_{kl}a_{kl}, \tag{10}$$

where S_{kl} is the overlap integral.

χ_A and η_A^{val} can be combined to give molecular electronegativity and valence hardness:

$$\chi_M = \sum_A K_A\,\chi_A, \quad \eta_M^{val} = \sum_A K_A\eta_A^{val}. \tag{11}$$

Expressions for χ_A and η_A derived above (Eqs. (6) and (7)) contain the effect of the external potential under $\mathbf{V}$. The energy operator $\mathbf{F}^0$ is formally identical to that of a free molecule; its matrix elements, however, are different, inasmuch as the wavefunction departs from the one of a noninteracting molecule. Therefore, the corresponding electronegativity and hardness $\chi_A(F^0)$ and $\eta_A(F^0)$ are not necesssarily identical to those for atoms in a free molecule (secondary solvent effect).

3. Primary solvent effects

The solvent effect may be directly introduced by including the dielectric function $f(\epsilon)$ into two terms related to the external potential in Eqs. (6) and (7): $\Delta\chi(V)$ and $\Delta\eta(V)$ according to the adopted VCM model.

$$\Delta\chi_A(V) = -f(\epsilon)\sum_B (q_B - N_B)\gamma_{AB}, \tag{12}$$

$$\Delta\eta_A(V) = f(\epsilon)K_A^{-1}D_A\sum_B (q_B - N_B)\gamma_{AB} - 2f(\epsilon)\sum_B K_B\gamma_{AB}, \tag{13}$$

where $D_A = \Sigma_{k\in A}b_{kk}$ and γ_{AB} is the Coulomb integral. Two additional effects must be included into the energy of a molecule in a polar medium (Eq. (4)):

the charge–medium (c
(m–m) interactions. Re
the following form (see

$$E^{c-m} = -f(\epsilon)\sum_A \sum_B Z_A$$

$$E^{m-m} = 0.5\,f^2(\epsilon)\sum_A \sum_B$$

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and hardness of the bon

Table 1
Calculated values for electrone
are shown for bonded atom in
effects (Eqs. (16) and (17)) are

Molecule	Atom
LiH	Li
	H
NaH	Na
	H
BeH_2	Be
BH_3	B
NH_3	N
PH_3	P
H_2O	O
H_2S	S
HF	F
HCl	Cl
HCN	N
	C
	H
LiF	Li
	F
NaF	Na
	F
CO	C
	O
H_2CO	O
	C
OH^-	O
CN^-	C
	N
SH^-	S
H_3O^+	O
CH_3^+	C

the charge–medium (c–m) and medium–medium (m–m) interactions. Respective energy terms have the following form (see Refs. [17–19]):

$$E^{c-m} = -f(\epsilon) \sum_A \sum_B Z_A q_B \gamma_{AB}, \tag{14}$$

$$E^{m-m} = 0.5\, f^2(\epsilon) \sum_A \sum_B q_A q_B \gamma_{AB}. \tag{15}$$

The primary solvent effect of the electronegativity and hardness of the bonded atom is now contained in the explicit expressions for $\Delta\chi_A$ and $\Delta\eta_A$ (cf. Eqs. (6) and (7)):

$$\Delta\chi_A = f(\epsilon)[f(\epsilon) - 2] \sum_B q_B \gamma_{AB}, \tag{16}$$

$$\Delta\eta_A = f(\epsilon)[f(\epsilon) - 2] \times \left(K_A^{-1} D_A \sum_B q_B \gamma_{AB} + \sum_B K_B \gamma_{AB} \right). \tag{17}$$

For a monatomic ion, the change in electronegativity and hardness becomes attractively simple and re-

Table 1
Calculated values for electronegativity and hardness in a polar solvent ($f(\epsilon) = 0.88$, water). Electronegativity ($\chi_{(gas)}$) and hardness ($\eta^{val}_{(gas)}$) are shown for bonded atom in a free molecule, the secondary changes are shown as $\chi(F^0)$ and $\eta(F^0)$, respectively. The sole primary effects (Eqs. (16) and (17)) are shown as $\Delta\chi$ and $\Delta\eta$

Molecule	Atom	Electronegativity (V)			Hardness (V/e)		
		$\chi_{(gas)}$	$\chi(F^0)$	$\Delta\chi$	$\eta^{val}_{(gas)}$	$\eta^{val}(F^0)$	$\Delta\eta$
LiH	Li	2.40	1.55	1.27	0.71	0.27	−3.04
	H	8.42	6.85	6.58	8.38	6.93	2.25
NaH	Na	1.13	0.51	0.70	0.58	0.04	−2.63
	H	6.71	6.40	8.07	6.70	5.42	3.86
BeH_2	Be	5.87	5.47	0.50	5.46	4.56	−3.03
BH_3	B	5.27	5.25	−0.13	3.65	3.59	−3.74
NH_3	N	7.75	7.45	1.47	9.00	8.41	−4.86
PH_3	P	6.68	6.62	−0.42	7.46	7.17	3.97
H_2O	O	8.99	8.61	2.41	10.46	10.86	−4.73
H_2S	S	7.10	7.05	0.57	7.80	7.54	−4.28
HF	F	11.81	11.68	2.62	13.32	13.94	−5.30
HCl	Cl	9.18	9.24	1.06	9.71	10.39	−4.44
HCN	N	8.35	7.30	2.50	9.22	9.42	−4.04
	C	0.56	1.57	−0.87	2.76	2.10	−3.66
	H	13.48	15.85	−1.85	13.48	15.84	−5.38
LiF	Li	−0.05	−0.19	2.03	0.25	0.27	−4.18
	F	10.26	9.50	9.68	10.27	9.61	4.24
NaF	Na	−0.18	−0.22	1.19	0.31	0.23	−3.18
	F	8.50	8.28	10.99	8.50	8.32	5.80
CO	C	5.93	6.23	−0.48	6.36	6.26	−4.18
	O	4.88	3.42	1.81	5.38	5.05	−4.32
H_2CO	O	8.81	7.05	3.92	8.65	8.51	−2.73
	C	0.88	2.90	−1.22	0.34	0.51	−3.46
OH^-	O	−2.72	−2.88	14.16	6.12	5.58	1.34
CN^-	C	−3.51	−2.99	8.41	5.64	5.69	−4.05
	N	4.73	6.23	7.74	6.44	6.61	−6.02
SH^-	S	−1.51	−1.44	9.99	4.98	4.89	−0.18
H_3O^+	O	21.23	21.24	−8.77	17.25	17.27	−10.60
CH_3^+	C	15.60	15.69	−9.09	1.46	1.12	−1.44

Table 2
Calculated solvent effect on the electronegativity and hardness of molecules and bonded atoms. Ph = phenyl ring, *o*-C, *m*-C and *p*-C denote ortho-, meta- and para-carbon, respectively (Pearson's [35] experimentally found data are given in parentheses)

Molecule	Atom	Electronegativity (V)		Hardness (V/e)	
		$\chi_{(\text{free molecule})}$	$\chi\ (f(\epsilon)=0.88)$	$\eta_{(\text{free molecule})}$	$\eta\ (f(\epsilon)=0.88)$
$PhCH_3$		5.81	5.69	5.46	2.22
	o-C	3.45	3.34	2.96	−0.27
	m-C	2.76	2.44	2.23	−1.18
	p-C	11.12	11.12	11.10	7.90
PhF		6.09	5.68	5.38	2.20
	F	11.48	11.51	11.48	8.88
	o-C	3.96	3.75	2.98	0.09
	m-C	2.91	2.48	1.79	−1.23
	p-C	11.48	11.08	11.98	7.84
PhCl		6.03	5.67	5.35	2.20
	Cl	11.38	11.29	11.38	8.94
	o-C	3.59	3.54	2.60	−0.08
	m-C	2.52	2.40	1.38	−2.26
	p-C	11.38	11.07	11.38	7.88
PhOH		5.82	5.66	5.36	2.15
	O	11.20	11.37	11.20	8.80
	o-C	3.68	3.74	3.06	0.08
	m-C	2.55	2.40	1.84	−1.21
	p-C	11.20	11.04	11.20	7.81
$PhNH_2$		5.30 (3.30)	5.44 (3.28)	5.02 (4.40)	2.14 (1.68)
	N	10.32	10.73	10.32	7.94
	o-C	3.43	3.81	3.04	0.20
	m-C	1.27	1.58	0.76	−2.02
	p-C	10.32	10.58	10.32	7.52
PhCN		6.27	6.06	5.20	2.18
	C	5.25	0.94	3.96	−3.54
	N	7.12	6.55	6.23	2.76
	o-C	5.60	4.90	4.40	0.88
	m-C	6.77	7.70	5.80	4.27
	p-C	6.23	6.43	5.16	2.63
$PhNO_2$		7.19	6.22	5.14	2.11
	N	2.05	0.84	−2.05	−3.96
	o-C	9.53	8.45	8.42	4.66
	m-C	11.58	10.70	11.29	7.63
	p-C	2.05	1.21	−2.05	3.99
benzene		5.86 (4.02)	5.78 (4.03)	5.54 (5.22)	2.20(2.53)
	C	5.86	5.78	5.54	2.20
pyridine		5.87 (4.33)	5.95 (4.31)	5.47 (4.94)	1.96 (2.61)
	N	8.40	0.89	8.12	−4.31
	o-C	2.75	6.78	1.98	2.92
	m-C	4.07	9.74	3.38	6.29
	p-C	0.73	0.57	−0.29	−3.88
pyridine oxide		5.86	5.75	4.50	1.88
	O	8.26	10.11	7.63	6.42
	N	2.62	5.08	0.30	0.76
	o-C	6.92	5.46	5.89	1.74
	m-C	3.12	5.21	0.90	1.74
	p-C	4.98	4.96	3.36	1.29

flects the electrostatic model, upon which this analysis is founded:

$$\Delta\chi_A = f(\epsilon)[f(\epsilon) - 2]q_A\gamma_{AA} = -(1 - 1/\epsilon)q_A\gamma_{AA}, \quad (18)$$

$$\Delta\eta_A = f(\epsilon)[f(\epsilon) - 2]\gamma_{AA} = -(1 - 1/\epsilon)\gamma_{AA} \leqslant 0. \quad (19)$$

The electronegativity and hardness of the entire molecule in a polar solvent may be obtained by appropriate summation, according to Eq. (11).

4. Results and discussion

Calculations of the electronegativity and hardness were based on the semi-empirical GRINDOL method as previously described [3,5,34]. Solvent dependent terms were added according to Eqs. (16) and (17). Results are presented in Table 1 for a set of simple molecules, and in Table 2 for a set of benzene derivatives selected as a convenient reference group. The range of $f(\epsilon)$ function chosen for calculation was 0.0–0.88; this covers the realistic range of common solvents including water. Electronegativity and hardness values found for $f(\epsilon) = 0.88$ (water) represent extreme, physically achievable values of χ and η for atoms and molecules in focus.

Results collected in Table 1 indicate that secondary effects (change in the wavefunction and in $\chi(F^0)$ and $\eta(F^0)$) rather weakly contribute to the solvent effect, which is dominated by the primary, electrostatic effect included in $\Delta\chi_A$ and $\Delta\eta_A$ (Eqs. (16) and (17)). In general, only a minor effect of the solvent on the electronegativity of atoms in neutral molecules was found, in contrast to typical ionic compounds (alkali salts), where the electronegativity of the anion increases significantly with $f(\epsilon)$: the primary and secondary effects equally contribute to that change. For free monatomic ions the change in hardness is always negative while the electronegativity increases for anions and decreases for cations (Eqs. (18) and (19)). A similar strong effect was found for polyatomic ions (OH^-, CN^-, SH^-, H_3O^+, CH_3^+).

The impact of solvent on χ and η has been studied in more detail for benzene derivatives. As demonstrated by the data in Table 2, the electronegativity varies slightly with solvent polarity and the atomic hardness decreases uniformly by 2–3 eV/e for most ring carbons, except for more polar molecules: nitrobenzene, pyridine and pyridine oxide. The polar solvent effect on ring atoms in pyridine is impressive: nitrogen becomes much less electronegative and considerably softer, while the electronegativity of meta-carbon increases and the atom also becomes harder.

Qualitative conclusions of this work agree perfectly with the work by Pearson [35]. This author studied changes in ionization energy (I) and electron affinity (A) due to hydration. The author notes that neutral molecules do not change their electronegativity in water while their hardness decreases. Anions become poorer electron donors (here more electronegative), cations become poorer electron acceptors (here less electronegative). However, as noticed by the author, all the results were derived from experimental values of the free enthalpy of solvation which invariably contain the entropy contribution. This makes the resulting I and A values for solution (hence χ and η) impractical for predicting the direction and possibly the amount of electron transfer when two molecules (atoms, ions) interact.

The shortcomings of the latter work have been overcome by the calculation method proposed in this present study. All the results for χ and η are based on free energies, hence their predicting power is as good as those for free molecules. Direct confrontation between the results of the two approaches is possible for aniline, pyridine and benzene as shown in Table 2. While the values of χ are systematically higher here by ≈ 2.0 eV, the η values differ by less than 1.0 eV and the changes from the gas to solution values of χ and η are close in the two works.

The key issue of directly adopting the available χ and η parameters in reproducing experimentally accessible data still remains to be resolved. DFT theory, despite its spectacular successes in understanding atomic and molecular systems has not yet been allowed to reach much further beyond the early Pauling result on the relation between the ionic bonding energy and electronegativity difference. The Pearson HSAB principle has never been quantified so far (see Ref. [4] for a discussion of that subject). It has been suggested [3,4] that not the χ and η values themselves but rather the interaction energy of two

electronic systems derived therefrom (charge transfer affinity) is the proper parameter for experimental correlations; successful relation to the Hammett substituent constants has then been demonstrated [5]. The progress in such studies is crucially dependent on the development of procedures that open access to a body of data (e.g. χ and η), now rooted in the DFT, whose practical utility is yet to be discovered. This Letter is a step in this direction.

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