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Solvatochromism and electrophilicity

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ABSTRACT

Solvatochromic dyes that exhibit a negative or a positive behaviour may be distinguished and their solvatochromism predicted with the aid of DFT-based indices, such as their electrophilicity ω , hardness η and by the Fukui electrophilic functions f_C^+ of the donor and acceptor moieties of the molecule, calculated in the gas-phase and in solvents treated as polarised continua. The protocol was successfully applied to 10 examples of phenolate betaines from the literature, five of them exhibiting a negative and five a positive solvatochromism.

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1. Introduction

Among organic compounds, solvatochromic dyes comprise a wide variety of molecules that have in common a donor and an acceptor fragment joined together so that an internal charge-transfer (CT) transition takes place, which is dependent on the solvating medium [1].

If the CT transition leads to a bathochromic shift of its solvatochromic band with the increasing polarity of the medium, the dye is said to exhibit a positive solvatochromism. A negative solvatochromism is observed if hypsochromic shifts occur with the increasing solvent polarity.

The solvatochromic behaviour of a dye is rationalised in terms of the relative polarities of its ground and excited states. If the ground state is more polar than the excited state, increasing the medium polarity will stabilize the former more than the latter, leading to larger transition energies, and a negative solvatochromic behaviour. The opposite occurs if the ground state is less polar than the excited state, leading to a positive solvatochromic behaviour in media of increased polarity [1,2].

The solvatochromic behaviour of a dye is generally defined *a posteriori*, after recording its spectra in a variety of solvents of distinct polarity. We have recently contended that it should be an intrinsic property of the molecule, that could be derived from theoretical considerations even in the absence of a solvent [3].

However strange this proposition may appear – to derive a solvent-dependent property of a molecule in the absence of any solvent – the notion is not original nor new. Other groups have tried to interpret the solvatochromic behaviour of dyes with theoretical tools, by characterising their charge-transfer properties [4–7].

In continuation of a previous approach to relate solvatochromism with DFT-based frontier-molecular-orbital indices [3], in the present communication we show that the electrophilicity index ω and the electrophilic Fukui functions of the two molecular moieties involved in the internal charge-transfer process may be used to distinguish and predict the behaviour of solvatochromic dyes. The general protocol was applied to one thiolium- and nine iminium-phenolate betaine dyes, a family of compounds with a well characterised behaviour, allowing reliable associations between their structure and the type of solvatochromism they exhibit. They are formed when a phenolate fragment is conjugated with a positively charged heterocyclic group [8–17].

In the following analysis, it is shown that analogous dyes exhibiting a positive or a negative solvatochromism are clearly distinguished by their global and group electrophilicities, and by how these and other DFT-based indices, such as their hardness and chemical potential, vary with the medium polarity. Ten examples from the literature, five negative and five positive, are presented to substantiate the general conclusions, which are observed for all studied compounds.

2. Computational procedures

All calculations were performed with the GAUSSIAN03 package [18]. Molecular structures were optimised with the B3LYP/6-31G* method, in the gas-phase and in the presence of a polarised continuum (PCM option) that mimicked the appropriate solvent by introduction of its relative permittivity in the calculations. The list of solvents included trichloromethane ($\epsilon(r) = 4.7$), chlorobenzene (5.7), tetrahydrofuran (7.4), propanone (20.5), acetonitrile (35.7), dimethylsulphoxide (46.8) and water (78.4). Solvation energies were estimated as the difference between the total energy of the optimised molecule in the continuum and its energy in the gas-phase.

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Scheme 1. Zwitterionic and non-polar canonical contributors to the resonance hybrid of a generic donor–acceptor solvatochromic pair composed of moieties X and Y.

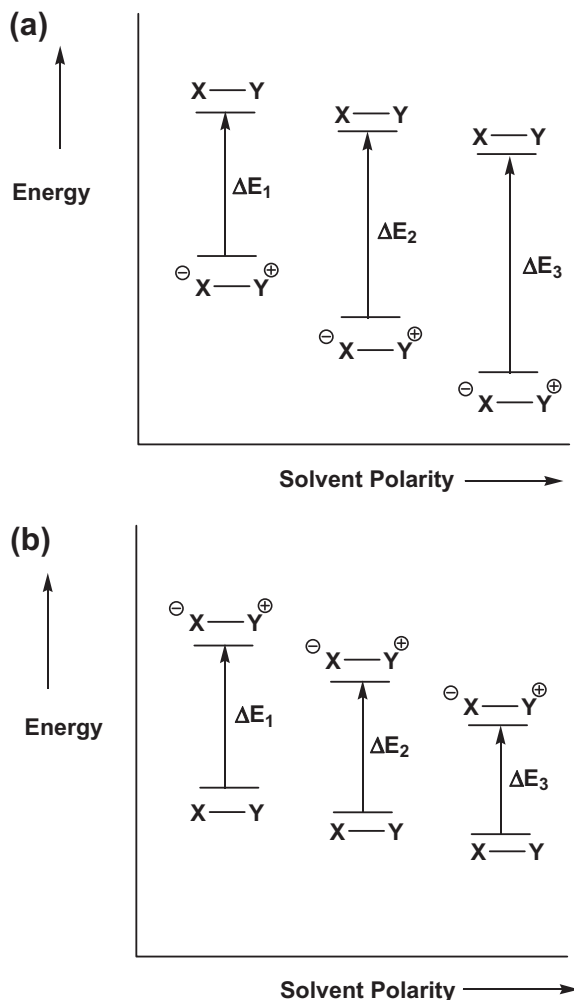


Figure 1. Schematic representation of the variations of the charge-transfer transition energy ΔE with the medium polarity in the case of a negative (a) and positive (b) solvatochromism. The ground and excited states are represented by their major canonical contributors.

The global electrophilicity of each molecule was calculated from its chemical potential μ and its hardness η , according to Eq. (1). The chemical potential μ and its hardness η were obtained from the HOMO and LUMO energies of the molecule, E_{HOMO} and E_{LUMO} , with the aid of Eqs. (2) and (3). The group Fukui electrophilic function for the molecular fragments (f_G^+) was obtained by summation of the condensed-to-atom Fukui functions f_k^+ of all atoms belonging to group G. These atom functions were calculated by a described procedure [19,20] which involved a single-point calculation, or by the method of Yang and Mortier [21]. The first procedure calculates the condensed-to-atom Fukui electrophilic function f_k^+ from the LUMO coefficients and the overlap matrix, by means of a short routine that reads the output of a Gaussian94 optimisation [19]. Alternatively, and especially in the case of larger molecules, the method of Yang and Mortier [21] was used, which expresses the Fukui electrophilic function of an atom k as the difference q_k

$(N+1) - q_k(N)$ between the charges of atom k , obtained by two single-point calculations of the molecule with N and $N+1$ electrons.

3. Results and discussion

The electrophilicity index ω was originally proposed by Parr et al. [22] as a measure of the electrophilic power of an atom, an ion or a molecule. It is associated with the energy gained by a system immersed in a sea of free electron gas, after an amount of charge ΔN flows from the sea to the system. The index ω is defined as

$$\omega = \mu^2 / 2\eta \quad (1)$$

where μ is the chemical potential and η is the hardness of a chemical system, obtained from the HOMO and LUMO energies of a system as [23]

$$\mu = (E_{\text{HOMO}} + E_{\text{LUMO}}) / 2 \quad (2)$$

$$\eta = E_{\text{LUMO}} - E_{\text{HOMO}} \quad (3)$$

From the global electrophilicity of a molecule we may obtain the local electrophilicity ω_k of an atom k by the product of the global index by the Fukui function for nucleophilic attack (f_k^+) at that particular site.

$$\omega_k = \omega f_k^+ \quad (4)$$

A group electrophilicity may be obtained by summing up the local electrophilicities of all of its atoms. A Fukui electrophilic function f_G^+ is defined for group G as the summation of the condensed-to-atom Fukui functions f_k^+ taking place over all atoms belonging to G.

$$\omega_G = \omega \cdot f_G^+ = \omega \sum f_k^+ \quad (5)$$

Let XY be a solvatochromic dye, where charge is transferred from one of the moieties to the other, in an internal charge-transfer process with a solvent-dependent transition energy. The dye structure is a hybrid of two major canonical formulae, a zwitterionic ($^-\text{X}-\text{Y}^+$) and a non-polar structure (X–Y): (Scheme 1).

If the ground-state of the dye has the zwitterionic formula as its major contributor, negative charge will flow from X[−] to Y⁺ upon excitation; the converse will happen if its major contributor is the neutral formula X–Y: charge will flow from Y to X upon excitation. The direction of the charge flow may be obtained by comparing the group electrophilicities of X and Y: if Y is more electrophilic than X in the ground state, negative charge is transferred from X to Y, X acts as a donor and Y as an acceptor. The converse will happen if X is less electrophilic than Y.

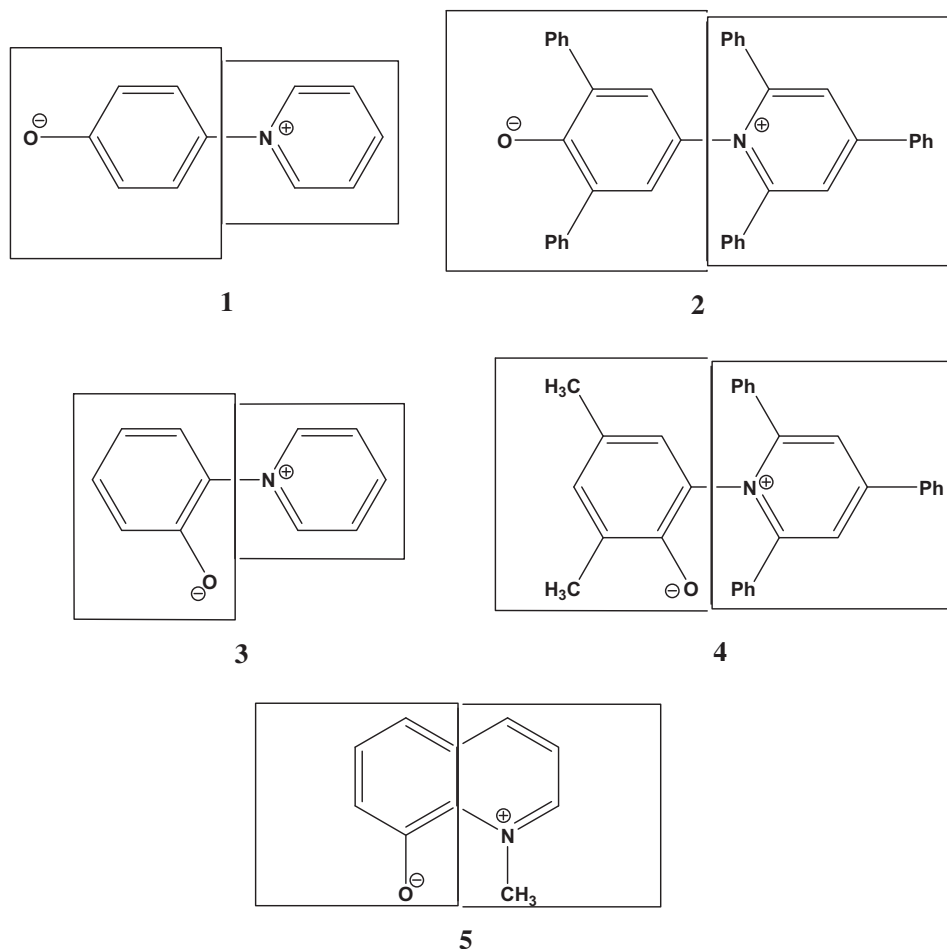
If the electrophilicity of Y is larger than that of X ($\omega_Y \gg \omega_X$) in any solvent, the ground state structure of the dye will have the zwitterionic formula $^-\text{X}-\text{Y}^+$ as the major contributor. This situation is depicted in Figure 1a, where the ground state is always more polar than the excited state, and the dye presents negative solvatochromism.

If $\omega_Y \ll \omega_X$ in any solvent, the neutral or non-polar formula X–Y will be the major contributor to the ground state of the dye. This situation corresponds to Figure 1b, where the ground state is always less polar than the excited state, and the dye presents positive solvatochromism.

Thus, calculation of the electrophilicities ω_X and ω_Y of the two moieties X and Y involved in the internal charge-transfer process of a dye, in the gas phase and in solvents of increasing polarity, will determine the direction of electron flow in the ground state in the various media, and the nature of the dye solvatochromism.

This protocol was applied to the solvatochromic betaines **1–10**, which are represented below with their zwitterionic canonical

Negative Solvatochromism



Scheme 2. Structures of the negatively solvatochromic dyes studied in this work, represented with their zwitterionic canonical formulae. For the calculation of their group electrophilic Fukui functions f_X^+ and f_Y^+ , moieties X and Y are indicated, phenolate moieties being always designated as X.

structures. Their solvatochromic behaviour has been described in the literature, in a wide range of solvent polarities. Compounds **1** [16] and **2** [2] share a common pyridiniophenolate backbone, similarly to the pair **3** [16] and **4** [10]. The *N*-methyl-8-oxidoquinolinium betaine **5** was originally described by Ueda and Schelly [24]. A sequential QM/MM study of its solvatochromism has been recently published [25]. Compound **6** [9] is a stable analogue of merocyanines like **7** [17], formed in a photochromic equilibrium with spiro derivatives. Azo merocyanines **8** and **9** have been described by Buncel and Rajagopal [26] who suggested them and some analogous derivatives as the basis of a π_{azo}^+ polarity scale. The structure of Phenol Blue **10** departs somewhat from the general scheme of a phenolate moiety conjugated with a heterocyclic cation, followed by dyes **1–9**. Replacing the latter fragment (Y), a *N,N*-dimethylanilinium group is joined to a phenolate moiety through a nitrogen atom. A classic example of positive solvatochromism, its solvatochromic shift in water has been studied recently by a hybrid QM/MM approach [27].

Compounds **1–5** (Scheme 2) exhibit negative solvatochromism, compounds **6–10** (Scheme 3) show a positive solvatochromic behaviour.

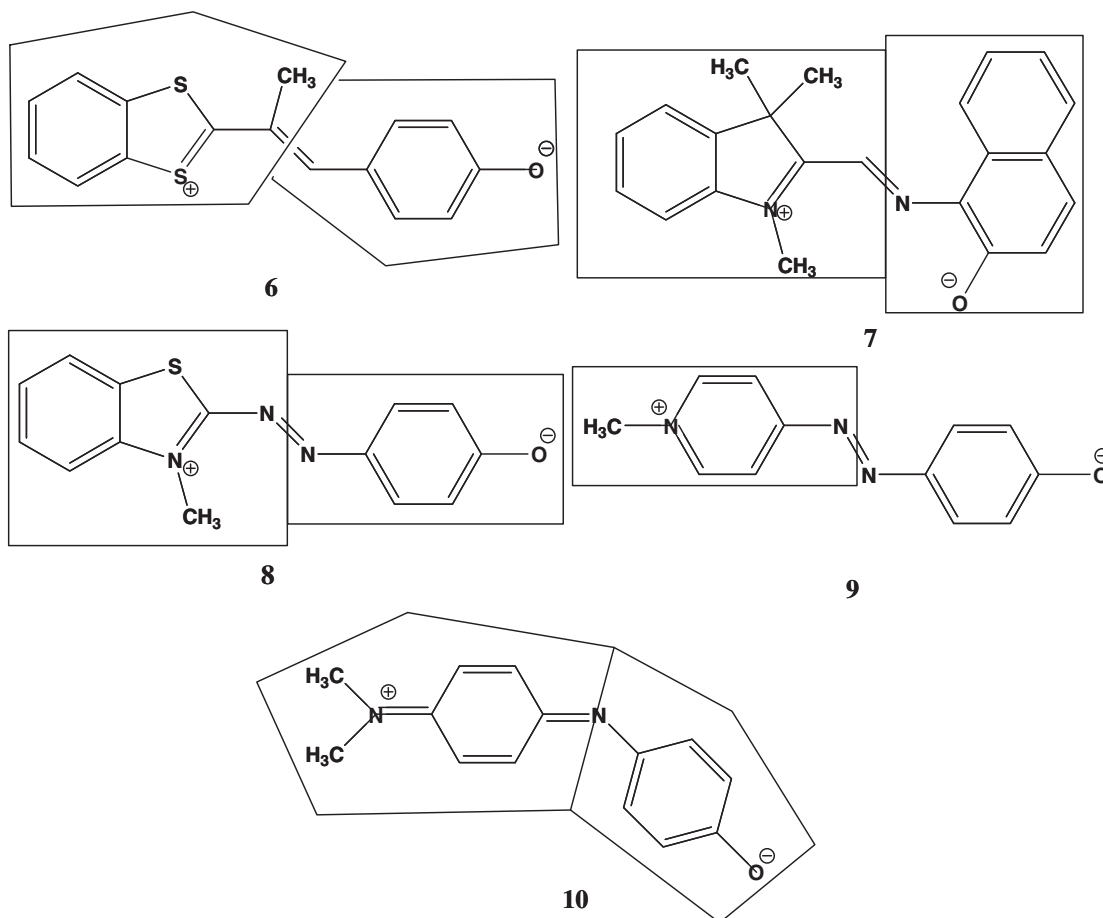
In the following analysis, each molecule, represented in its zwitterionic canonical formula, was halved into two moieties, as indicated in the Schemes. The direction of the electron flow in the ground state is determined by the relative electrophilicities of the two moieties. Compounds **1–10** had in common a phenolate/

quinone moiety that was always represented by X. If the phenolate/quinone moiety acts as an electron-donor, charge is transferred internally from it to a heterocyclic cation, and the solvatochromic transitions take place according to Figure 1a. If X acts as an electron-accepting group, charge is transferred from the neutral heterocyclic to the quinone moiety, and the transitions take place according to Figure 1b.

The global and group electrophilicities of each betaine were calculated in the gas-phase and in media of increasing polarities, treating the solvent as a continuum, and adopting the corresponding values of relative permittivity: $\epsilon(r) = 1$ (gas phase), 4.9 (trichloromethane), 5.7 (chlorobenzene), 7.58 (tetrahydrofuran), 20.7 (propanone), 36.64 (acetonitrile), 46.7 (dimethylsulphoxide), 78.4 (water).

According to Eq. (5), the group electrophilicity ω_G is obtained as the product of the global electrophilicity ω by the group electrophilic Fukui function f_G^+ . Thus, in order to decide on the relative electrophilicities of the two moieties X and Y, it suffices to calculate for each moiety the corresponding function f_G^+ , in the gas-phase or in the polarising continuum. The larger value of f_G^+ corresponds to the more electrophilic group. Note that, in general, $f_X^+ + f_Y^+$ equalled 1, with the exception of compounds **5** and **10**. In the former, the donor and acceptor rings share a common bond, in the latter the two moieties share a common nitrogen atom. As common atoms to the donor and acceptor moieties, these elements were not included in the calculations of the group Fukui functions.

Positive Solvatochromism



Scheme 3. Structures of the positively solvatochromic dyes studied in this work, represented with their zwitterionic canonical formulae. For the calculation of their group electrophilic Fukui functions f_X^+ and f_Y^+ , moieties X and Y are indicated, phenolate moieties being always designated as X.

Tables 1 and 2 list the calculated group Fukui electrophilic functions for the phenolate (f_X^+) and the heterocyclic (f_Y^+) moieties in various media, characterised by their relative permittivities $\epsilon(r)$. Betaines showing a negative solvatochromic behaviour are grouped in Table 1, those with a positive solvatochromism in Table 2. Group Fukui electrophilic functions were calculated by the method of Contreras et al. [19] or by the method of Yang and Mortier [21]. As can be seen from one particular case (compound 3) where the two methods were employed and compared, though they differed in the absolute values, the group Fukui functions calculated by the two methods followed the same trends. The hardness η , chemical potential μ and global electrophilicity ω of each molecule are also given, all of them calculated in the different media.

At this stage it is interesting to relate the above results with the general conclusions reached by Contreras et al. in a study of solvent effects on the electrophilicity of 18 small chemical species [28]. The authors employed two methods of calculation (B3P/6-311G** and HF/6-311G**) and a continuum model to mimic the solvent, in the gas-phase ($\epsilon(r) = 1$) and in water ($\epsilon(r) = 78.5$). The observed trends were the same for both methods and could be summarised in two major conclusions:

1. A linear relationship was found between the change in the electrophilicity index $\Delta\omega$ and the corresponding change in the solvation energy ΔE_{solv} of a chemical species. This relationship is expressed by (6)

$$\Delta\omega = \gamma \cdot \Delta E_{\text{solv}} \quad (6)$$

2. Solvation by a polar solvent increased the global electrophilicity of a neutral species (v.g. HF, HCl, CH_3Cl , SO_3 etc.), and decreased the electrophilicity of charged or ionic species (v.g. Li^+ , Na^+ , CH_3Li).

These conclusions will be compared with the results of Tables 1 and 2.

The first important observation that arises from a comparison between the Tables is the clear distinction made by the relative group electrophilic Fukui functions f_X^+ and f_Y^+ , between the negatively (compounds 1–5) (Table 1) and positively (6–10) (Table 2) solvatochromic compounds. In the former set, the phenolate moiety is always less electrophilic than the heterocyclic one ($f_X^+ \ll f_Y^+$) in all solvents. The opposite occurs for the latter set, $f_X^+ \gg f_Y^+$ in all solvents. Thus, for all betaines 1–5 in solvents of increasing polarity, charge is always transferred from the phenolate to the pyridinium moiety, reproducing the situation depicted in Figure 1a. The converse happens for dyes 6–10: in all solvents, the quinonoid fragment acts as the accepting moiety in the internal charge-transfer process, reproducing the trends of Figure 1b.

A second major difference between the two sets lies in the variation of their electrophilic power with the increasing medium polarity. The electrophilicity ω decreases for dyes 1–5, as the solvent becomes more polar, increasing for betaines 6–10 under the same conditions. Variations of their hardness values also differ for the two sets. Hardness η increases with the increasing polarity, in the case of betaines 1–5, and decreases in more polar media, in the case of compounds 6–10.

Table 1

Variations, in media of increasing polarity, of the global hardness η , chemical potential μ , electrophilicity ω and group Fukui electrophilic functions for the donor (f_X^+) and acceptor (f_Y^+) moieties of negatively solvatochromic betaines **1–5**.

Cpd	ϵ^a	f_X^+	f_Y^+	η^b	μ^b	ω^b	E_{solv}^c	$\gamma(r)^d$
1^e	1	0.28	0.72	52.96	−80.66	61.42	0	0.51
	4.9	0.20	0.80	57.28	−79.25	54.82	−14.18	(0.996)
	5.7	0.19	0.81	57.42	−79.15	54.55	−14.88	
	7.58	0.18	0.82	58.30	−79.09	53.65	−16.47	
	20.7	0.17	0.83	60.52	−79.04	51.61	−19.72	
	36.64	0.16	0.84	61.20	−78.93	50.90	−20.77	
	46.7	0.16	0.84	61.30	−79.03	50.94	−20.86	
2^f	78.4	0.14	0.86	61.92	−78.88	50.24	−21.58	
	1	0.31	0.69	35.74	−78.33	85.84	0	0.74
	4.9	0.19	0.81	40.60	−78.23	75.37	−16.34	(0.994)
	5.7	0.19	0.81	41.00	−78.30	74.77	−17.04	
	7.58	0.18	0.82	42.20	−78.38	72.79	−19.20	
	20.7	0.15	0.85	44.74	−78.26	68.45	−23.84	
	36.64	0.14	0.86	45.78	−78.43	67.18	−25.50	
3^g	46.7	0.14	0.86	45.70	−78.26	67.01	−25.32	
	1	0.21 (0.39)	0.79 (0.61)	57.70	−78.70	53.67	0	0.41
	4.9	0.16 (0.30)	0.84 (0.70)	62.06	−78.28	49.37	−10.30	(0.999)
	46.7	0.14 (0.26)	0.86 (0.74)	65.16	−78.69	47.51	−15.11	
4^f	78.4	0.13 (0.26)	0.87 (0.74)	65.46	−78.72	47.34	−15.62	
	1	0.12	0.88	32.60	−72.93	81.58	0	1.1
	46.7	0.09	0.91	47.08	−76.12	61.54	−17.47	(0.998)
5^f	78.4	0.08	0.92	48.46	−76.97	61.13	−19.28	
	1	0.37	0.59	56.76	−75.59	50.33	0	0.27
	4.9	0.33	0.60	61.54	−76.70	47.80	−8.48	(0.997)
	46.7	0.32	0.61	64.00	−77.54	46.97	−12.31	
	78.4	0.31	0.61	64.28	−77.65	46.90	−12.74	

^a Solvent relative permittivities $\epsilon(r)$ correspond to gas phase ($\epsilon(r)=1$), trichloromethane (4.9), chlorobenzene (5.7), tetrahydrofuran (7.58), propanone (20.7), acetonitrile (36.64), dimethylsulphoxide (46.7) and water (78.4).

^b In kcal.mol^{−1} (1 kcal mol^{−1} = 4.18 kJ mol^{−1}).

^c Calculated solvation energy, in kcal mol^{−1}.

^d Slope γ of the linear relationship between $\Delta\omega$ and E_{solv} (Eq. (6)), with the corresponding correlation coefficient r given in brackets.

^e Fukui functions calculated according to [19].

^f Fukui functions calculated according to [21].

^g Fukui functions calculated according to [19] and [21] (values in brackets).

These trends reflect the essentially opposite nature of the two sets of solvatochromic dyes. This is illustrated in more details with two examples of each set.

Figure 3 plots the variations of the electrophilic power ω of compounds **1** (Figure 3a) and **2** (Figure 3b) with the calculated solvation energy of the betaine in solvents of increasing polarity. Straight lines were obtained in both cases, in agreement with the linear dependence anticipated by Eq. (6) between $\Delta\omega$ and E_{solv} . Linear plots, with very good correlations ($r > 0.99$) were obtained for all compounds in the Table, as illustrated in Figures 2 and 3. They differed however in the sign of their slopes γ , since ω decreases for negative dyes **1–5** (Figure 2), and increases for positive compounds **6–10** (Figure 3).

Negatively solvatochromic compounds **1–5** thus correspond to the group of charged or ionic electrophiles described by Contreras and co-workers [28]. Their electrophilic power decreases with the increasing medium polarity. However, contrary to the ‘controversial outcome’ those authors observed for those species, by comparing their hardnesses in two different media (gas phase and water), the data of Table 1 show that solvation by more polar environments renders dyes **1–5** harder than in the gas phase. This is in agreement with the situation depicted in Figure 1a. The zwitterionic contribution to the hybrid $-X - Y^+ \leftrightarrow X - Y$ in the ground state increases with the medium polarity, thus making the dye harder.

By contrast, compounds **6–10** show the opposite behaviour of Figure 3, illustrated for betaines **6** and **7** by the plots of Figure 3.

This set of positively solvatochromic dyes behave like the group of neutral electrophiles (HF, HCl, BF₃, CH₃CH₂Cl, HCOH etc.) studied

Table 2

Variations, in media of increasing polarity, of the global hardness η , chemical potential μ , electrophilicity ω and group Fukui electrophilic functions for the donor (f_X^+) and acceptor (f_Y^+) moieties of positively solvatochromic betaines **6–10**.

Cpd	ϵ^a	f_X^+	f_Y^+	η^b	μ^b	ω^b	E_{solv}^c	$\gamma(r)^d$
6^e	1	0.70	0.30	65.66	−90.19	61.94	0	−0.41
	4.9	0.68	0.32	62.92	−90.78	65.49	−8.60	(0.995)
	7.58	0.68	0.32	62.52	−90.94	66.14	−9.92	
	20.7	0.67	0.33	61.98	−91.10	66.95	−11.73	
	36.64	0.67	0.33	61.84	−91.10	67.10	−12.28	
	46.7	0.67	0.33	61.82	−91.18	67.24	−12.34	
	78.4	0.66	0.34	61.72	−90.91	66.95	−12.94	
7^e	1	0.74	0.26	63.54	−83.02	54.24	0	−0.59
	4.9	0.73	0.27	61.70	−84.94	58.47	−7.97	(0.996)
	5.7	0.73	0.27	61.66	−85.10	58.73	−8.40	
	7.58	0.73	0.27	61.46	−85.29	59.18	−9.19	
	20.7	0.72	0.28	61.04	−85.99	60.57	−11.04	
	36.64	0.72	0.28	60.98	−86.28	61.04	−11.73	
	46.7	0.72	0.28	60.94	−86.27	61.06	−11.73	
8^f	78.4	0.71	0.29	60.68	−86.47	61.61	−12.39	
	1	0.63	0.37	68.00	−93.24	63.92	0	0.55
	4.9	0.66	0.34	65.34	−94.45	68.26	−8.28	(0.999)
	46.7	0.67	0.33	64.32	−95.27	70.56	−11.83	
9^f	78.4	0.67	0.33	64.24	−95.33	70.73	−12.46	
	1	0.58	0.42	65.58	−85.59	55.85	0	0.50
	4.9	0.60	0.40	63.28	−88.64	62.08	−12.37	(0.999)
	46.7	0.60	0.40	62.84	−90.18	64.71	−17.77	
10^f	78.4	0.60	0.40	62.82	−90.50	65.19	−18.55	
	1	0.56	0.35	58.34	−90.63	70.40	0	−1.00
	4.9	0.58	0.33	54.46	−92.19	78.03	−7.60	(0.999)
	46.7	0.57	0.34	53.04	−92.94	81.43	−10.80	
	78.4	0.57	0.34	52.94	−92.94	81.58	−11.25	

^a Solvent relative permittivities $\epsilon(r)$ correspond to gas phase ($\epsilon(r)=1$), trichloromethane(4.9), chlorobenzene (5.7), tetrahydrofuran (7.58), propanone (20.7), acetonitrile (36.64), dimethylsulphoxide (46.7) and water (78.4).

^b In kcal mol^{−1} (1 kcal mol^{−1} = 4.18 kJ mol^{−1}).

^c Calculated solvation energy, in kcal mol^{−1}.

^d Slope γ of the linear relationship between $\Delta\omega$ and E_{solv} (Eq. (6)), with the corresponding correlation coefficient r given in brackets.

^e Fukui functions calculated according to [19].

^f Fukui functions calculated according to [21].

by Contreras and co-workers [28]. The electrophilicity of neutral, softer species increases with the medium polarity. Their hardness η decreases with solvation by more polar environments, in agreement with the situation depicted in Figure 1b: the zwitterionic contribution to the hybrid $-X - Y^+ \leftrightarrow X - Y$ increases in the excited state but decreases in the ground state with the medium polarity, with the result that the dye becomes softer in more polar media. The data of Table 1 show that this effect is compensated by a parallel increase of the absolute value of the chemical potential μ of these compounds, resulting in the observed enhancement of their electrophilic power ω .

4. Conclusions

An analysis of the DFT-based electrophilicity (ω) and hardness (η) indices of phenolate betaines exhibiting negative or positive solvatochromism allowed a clear distinction between these two types of solvatochromic behaviour. Fragment electrophilicities that are proportional to the corresponding group electrophilic Fukui functions for these dyes may be calculated in various media, assuming a continuum model for the solvent effects. Negatively solvatochromic betaines were characterised as highly polar, zwitterionic compounds, in which the phenolate moiety acts as a donor group: in the gas phase and in all solvents, its group Fukui electrophilic function f_X^+ is smaller than the corresponding acceptor function f_Y^+ . Their zwitterionic nature and global hardness increase, while their global electrophilicity decreases with the medium

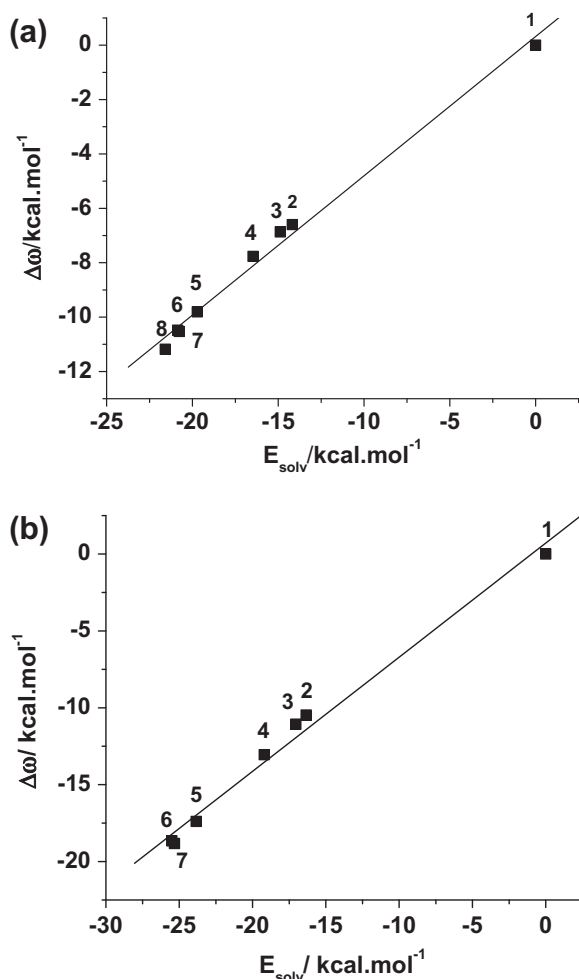


Figure 2. (a) Linear dependence of $\Delta\omega$ on E_{solv} for dye 1 in various media. Data points refer to gas phase (1), CHCl₃ (2), PhCl (3), THF (4), Me₂CO (5), MeCN (6), DMSO (7), and water (8). Correlation coefficient $r = 0.996$; (b) linear dependence of $\Delta\omega$ on E_{solv} for dye 2 in various media. Data points refer to gas phase (1), CHCl₃ (2), PhCl (3), THF (4), Me₂CO (5), MeCN (6) and DMSO (7). Correlation coefficient $r = 0.994$.

polarity. A linear dependence was observed between their electrophilicity power and their solvation energy, the former decreasing with the increased solvation by the medium. Thus, betaine phenolates exhibiting a negative solvatochromism behave similarly to charged and ionic electrophiles, as regards the effect of solvents on their electrophilicity [28].

Positively solvatochromic betaines were characterised as relatively non-polar compounds, in which the phenolate fragment really acts as an electron-accepting quinonoid moiety in all media: in the gas phase and in all solvents, its group Fukui electrophilic function f_X^+ is larger than that of the corresponding donor heterocycle (f_V^+). Their zwitterionic nature and global hardness decrease, while their global electrophilicity increases with the medium polarity. A linear dependence was observed between their electrophilicity power and their solvation energy, the former increasing with the increased solvation by the medium. Thus, betaine phenolates exhibiting a positive solvatochromism behave similarly to neutral electrophiles, as regards the effect of solvents on their electrophilicity [28].

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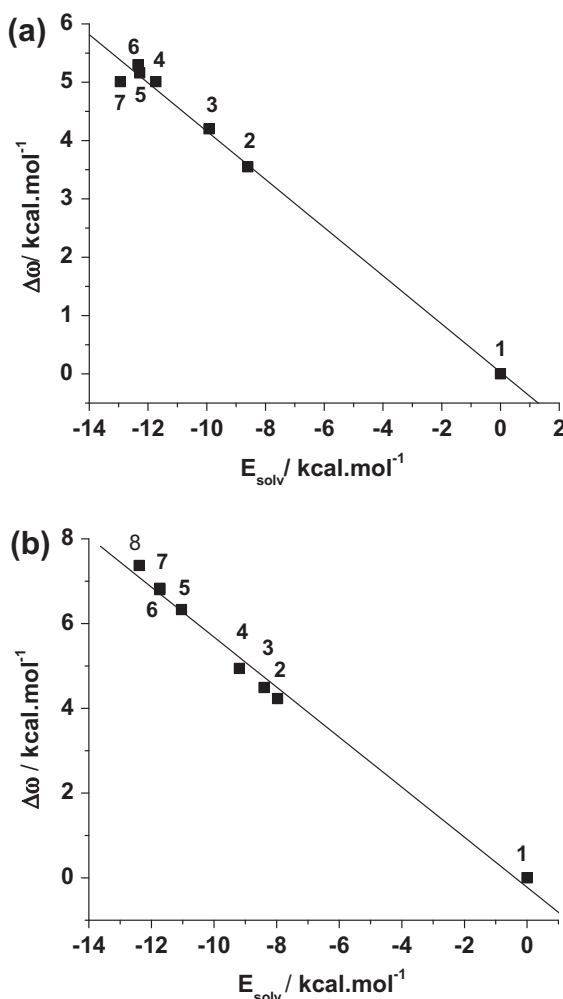


Figure 3. (a) Linear dependence of $\Delta\omega$ on E_{solv} for dye 6 in various media. Data points refer to gas phase (1), CHCl₃ (2), THF (3), Me₂CO (4), MeCN (5), DMSO (6) and water (7). Correlation coefficient $r = 0.995$; (b) linear dependence of $\Delta\omega$ on E_{solv} for dye 7 in various media. Data points refer to gas phase (1), CHCl₃ (2), PhCl (3), THF (4), Me₂CO (5), MeCN (6), DMSO (7) and water (8). Correlation coefficient $r = 0.996$.

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