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Electrophilicity and solvatochromic reversal of pyridinium phenolate betaine dyes

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ABSTRACT

The solvatochromic reversal of phenolate betaine dyes may be theoretically rationalized and predicted by determining the flow direction of their internal charge-transfer in media of increasing polarity, with the aid of the electrophilicities of the donor and acceptor moieties, or of the corresponding electrophilic Fukui functions. The protocol was applied to ten examples from the literature.

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1. Introduction

The solvatochromic behavior of phenolate betaine dyes may be classified as positive, reverse or negative. A positively solvatochromic behavior corresponds to bathochromic shifts of the solvent-dependent UV/Vis absorption band with an increase of the solvent polarity, whereas negatively solvatochromic dyes exhibit hypsochromic band shifts under the same solvent change. Dyes that exhibit a reverse solvatochromism invert their response from a positive to a negative solvatochromism at a certain solvent polarity value [1].

The phenomenon of solvatochromic reversal has been a subject of controversy over the past decades, since it was first described and theoretically rationalized [2] with an emblematic compound, Brooker's merocyanine (compound **1** in Scheme 1).

A literature search reveals the permanent interest in rationalizing the solvatochromic behavior of this compound, often subject to conflicting interpretations. [3–8].

Its solvatochromic reversal in solvents of low polarity has been denied, and attributed to self-aggregation [9–11]. A recent paper, with the purpose of 'demystifying the solvatochromic reversal in Brooker's merocyanine dye' [7] by means of hybrid QM/MM simulation techniques, arrived at the conclusion that compound **1** may not self-aggregate in non-polar solvents. Theoretical studies on structural variations of this compound in different media have arrived at contradictory conclusions [4,5]. Deciding between a zwitterionic or a quinoid structure for this and other phenolate betaines is admittedly a 'tricky task' [12] because pieces of information regarding these compounds are often inconsistent: the observed negative solvatochromism exhibited by them in solvents of medium to high polarity is at variance with the expectations of a positive behavior originating from their quinoid structure [12].

In searching for theoretical descriptors capable of distinguishing the positive, negative and reverse behavior of solvatochromic dyes, we have argued that it should be possible to derive information about the behavior of a dye from purely theoretical and structural considerations, independently of empirical factors, such as their solubility or their tendency to aggregate [13].

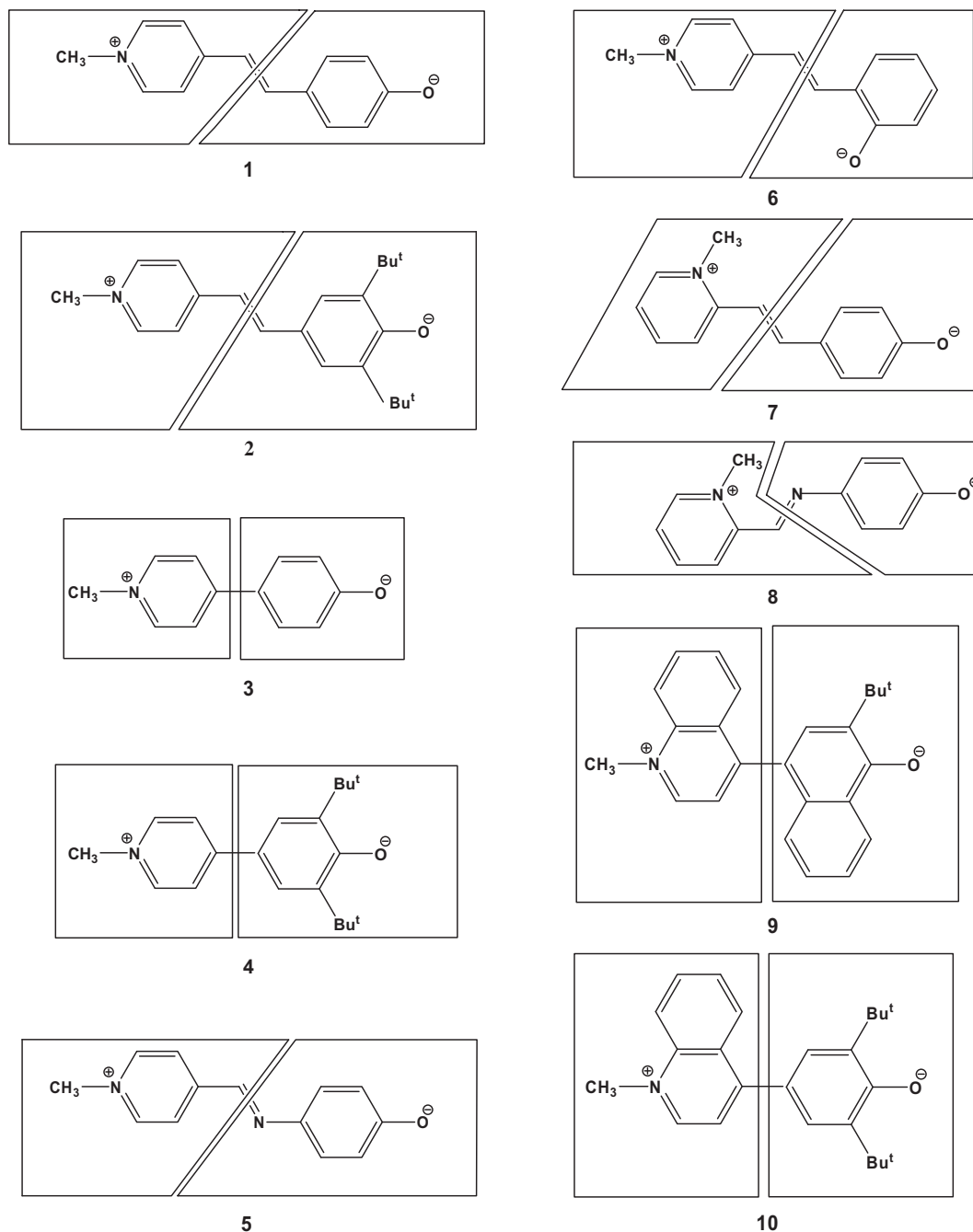
We also rejected the rationalization of their solvatochromic reversal as arising from structural changes brought about by solvent polarity changes [1], because solvation of positively or negatively solvatochromic dyes also affects their molecular structure, without changing their behavior.

In a preceding letter [14] our contention was supported by establishing a clear distinction between positively and negatively solvatochromic dyes. We employed a protocol based on DFT-based indices and, in particular, on Parr's electrophilicity ω [15], to various phenolate betaines reported in the literature.

In the present communication we extended our protocol to the more controversial case of the reverse solvatochromism of phenolate betaines. Compared with the study of positive or negative solvatochromism, relatively straightforward, because they constitute extreme cases, the study of solvatochromic reversal poses more difficulties. A major problem arises from the lack of clearcut experimental evidence for their reversal, because of solubility problems. Sometimes, the range of investigated solvent polarities is not wide enough to establish a clear reversal. Low solubility drastically restricts the number of solvents for which reliable data are available [12]. A second, theoretical difficulty has to do with a proper simulation of solvent effects. When comparing the solvatochromic behavior of different dyes in a variety of solvents, a protocol must be adopted for simulating solvent effects that should be simple enough and common to all compounds and media. Continuum models satisfy these requirements, but ignore specific solute–solvent interactions that are very important, for example, in protic solvents. The conclusions obtained from the application of these models may therefore reproduce experimental trends only qualitatively.

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Scheme 1. Molecular structures of the ten phenolate betaine dyes X–Y studied in this work. All molecules are represented with their zwitterionic canonical formulae, with an indication of how they were split into moieties X and Y, X being always a phenolate group.

In spite of these difficulties, in the present letter we show that the solvatochromic reversal of phenolate betaines is a theoretically predictable phenomenon. DFT-based descriptors, in particular Parr's electrophilicity, may be used to characterize the behavior of these dyes based on their molecular structures, without considerations of their solubility or eventual aggregation in certain media.

2. Computational details

All calculations were performed with the GAUSSIAN03 package [16]. Molecular structures were optimized with the B3LYP/6-31G* or with the HF/6-31G* method, in the gas-phase and in the presence of a polarized continuum (PCM option) that mimicked

the appropriate solvent by introduction of its relative permittivity ϵ_r in the calculations. The list of solvents included trichloromethane ($\epsilon_r = 4.9$), tetrahydrofuran (7.6), propanone (20.7), acetonitrile (36.6), dimethylsulfoxide (46.7) and water (78.4). Solvation energies were estimated as the difference between the total energy of the optimized molecule in the continuum and its energy in the gas-phase.

The global electrophilicity of each molecule was calculated from its chemical potential μ and its hardness η , according to Eq. (1).

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

where μ is the chemical potential and η is the hardness of a chemical system.[15]

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) [17]

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

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

The group Fukui electrophilic function for the molecular fragments (f_k^+) 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 the method of Yang and Mortier [18], which expresses the Fukui electrofilic 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

We applied our theoretical protocol to 10 phenolate betaine dyes described in the literature. Their structures are shown in

Table 1

Calculated group Fukui electrophilic functions f_X^+ and f_Y^+ for moieties X and Y of compounds **1–10** in media of increasing polarity, characterized by their relative permittivities ϵ_r in a continuum model.

Cpd ^a		Gas	CHCl ₃ ^b	THF ^c	Me ₂ CO ^d	MeCN ^e	DMSO ^f	H ₂ O ^g
1	f_X^+	0.69	0.62	0.57	0.48	0.45	0.45	0.43
	f_Y^+	0.31	0.38	0.43	0.52	0.55	0.55	0.57
1	f_X^{+h}	0.53	0.51	0.50	0.49	0.48	0.48	0.48
	f_Y^{+h}	0.47	0.49	0.50	0.51	0.52	0.52	0.52
2	f_X^+	0.73	0.67	0.66	0.61	–	0.59	0.56
	f_Y^+	0.27	0.32	0.34	0.39	–	0.41	0.44
3	f_X^+	0.53	0.42	–	0.36	0.35	0.35	0.34
	f_Y^+	0.47	0.58	–	0.64	0.65	0.65	0.66
3	f_X^{+h}	0.48	0.45	–	0.42	0.42	0.42	0.41
	f_Y^{+h}	0.52	0.55	–	0.58	0.58	0.58	0.59
4	f_X^+	0.57	0.47	–	0.42	–	0.41	0.39
	f_Y^+	0.43	0.53	–	0.58	–	0.59	0.61
5	f_X^+	0.71	0.66	0.50	0.27	–	0.24	0.23
	f_Y^+	0.29	0.34	0.50	0.73	–	0.76	0.77
6	f_X^+	0.67	0.54	0.49	0.42	–	0.40	0.39
	f_Y^+	0.33	0.46	0.51	0.58	–	0.60	0.61
7	f_X^+	0.69	0.62	0.58	0.52	–	0.49	0.48
	f_Y^+	0.31	0.38	0.41	0.48	–	0.51	0.52
8	f_X^+	0.69	0.58	0.39	0.26	–	0.23	0.22
	f_Y^+	0.31	0.42	0.61	0.74	–	0.77	0.78
9	f_X^+	0.58	0.49	–	0.42	0.40	0.40	0.38
	f_Y^+	0.42	0.51	–	0.58	0.60	0.60	0.62
10	f_X^+	0.58	0.51	0.47	0.39	–	0.37	0.34
	f_Y^+	0.42	0.49	0.53	0.61	–	0.63	0.66

^a Optimised with the HF/6–31G* method, unless otherwise stated

^b $\epsilon_r = 4.9$

^c $\epsilon_r = 7.6$

^d $\epsilon_r = 20.7$

^e $\epsilon_r = 36.6$

^f $\epsilon_r = 46.7$

^g $\epsilon_r = 78.4$

^h Optimized with the B3LYP/6–31G* method.

Scheme 1, with an indication of how they were split into an X and Y moiety, X being always the phenolate/quinoid fragment.

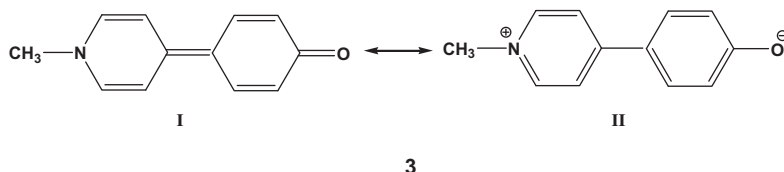
Like compound **1**, the solvatochromic behavior of some of these betaine dyes has been interpreted in different ways. Dye **2** was first described by Catalán et al. [10], who denied any solvatochromic reversal in the zone of low polarity. The same data published by these authors and analyzed in a later paper by another group [19], yielded a graph with a shallow but discernibly concave curve, indicative of a reverse solvatochromism. Compound **3** showed a negative behavior in polar solvents, but its low solubility in non-polar solvents precluded its evaluation in media less polar than propanone. Its negative behavior puzzled the authors, because of their expectation of a positive behavior due to the quinoid structure suggested by NMR data [14]. Its more lipophilic analog **4** showed a negative behavior in polar media, with an incipient reversal in THF and 1,4-dioxane [20]. A plot of its transition wave-numbers ν_{max} against the solvent polarity E_T^N (a scale based on the negatively solvatochromic $E_T(30)$ betaine) presented a curvature in non-polar solvents, suggesting a borderline situation [19]. Compounds **9** and **10** exhibited a more clearly defined solvatochromic reversal in solvents of medium polarity (propanone, dichloromethane) [20].

Compounds **5** and its isomer **8** exhibited a solvatochromic reversal in non-polar solvents [21]. The solvatochromism of compounds **6** [22] and its isomer **7** [23] was described as negative, but their spectral behavior was investigated in only a few solvents, most of which were protic and polar.

The general protocol calculated, for each of these molecules X–Y, resulting from the conjugation of a phenolate/quinoid fragment X with a heterocyclic moiety Y, the electrophilicities of the X and Y fragments in media of different polarity. The relative values of the X and Y electrophilicities, or of their electrophilic Fukui functions f_X^+ and f_Y^+ , determined the flow direction of their internal charge-transfer in these media, and consequently the dye response to the changes in the medium polarity. For negatively solvatochromic dyes $f_X^+ < f_Y^+$ in the gas phase and in all solvents, so that charge always flows from the phenolate donor to the heterocyclic acceptor moiety. For positively solvatochromic dyes the opposite occurs: $f_X^+ > f_Y^+$ in the gas phase and in all solvents, so that charge always flows from the heterocyclic donor to the quinoid acceptor moiety.

We have applied this protocol to compounds **1–10** in the gas phase and in solvents of increasing polarity, characterized by their relative permittivities ϵ_r with a PCM continuum model. The corresponding Fukui functions f_X^+ and f_Y^+ calculated in the gas phase and in all solvents are given in **Table 1**. Two optimisation methods were initially employed, a hybrid DFT B3LYP/6–31G* and an HF/6–31G* method, and their results compared for compounds **1** and **3**. For all other compounds, optimisations employed the HF/6–31G* method.

As can be seen in **Table 1**, varying the medium polarity leads to a perturbation of the relative values of f_X^+ and f_Y^+ , and to an eventual reversal of these relative values at some more polar environment. The only exception to this was compound **2**, for which $f_X^+ > f_Y^+$ in all media. The reversal of the relative values of f_X^+ and f_Y^+ indicates a reversal of the flow direction of the internal charge-transfer and a change from a positive ($f_X^+ > f_Y^+$) to a negative



Scheme 2. Quinoid (I) and zwitterionic (II) canonical formulae that contribute to the resonance hybrid of **3**.

Table 2

Dipole moments (μ) and C–O bond distances of **1** and **3** calculated in the gas phase with an HF/6-31G* and a DFT B3LYP/6-31G* method

μ /D	C–O bond/pm			
	HF/6-31G*		B3LYP/6-31G*	
Compound	HF/6-31G*	B3LYP/6-31G*	HF/6-31G*	B3LYP/6-31G*
1	13.80	15.20	120	124
3	12.98	13.14	121	124

Table 3

Variations of the global hardness (η), chemical potential (μ), electrophilicity (ω) and solvation energy (E_{solv}) of phenolate betaines **1–10**, calculated with the HF/6-31G* method and the PCM option, in media of increasing polarity.

Cpd	ϵ_r^a	η^b	μ^b	ω^b	E_{solv}^b
1	1	180.6	–56.7	8.9	0.0
	4.9	172.7	–58.1	9.8	–14.3
	7.6	171.6	–58.6	10.0	–17.0
	20.7	171.9	–59.2	10.2	–21.0
	36.6	172.6	–59.3	10.2	–22.3
	46.7	172.7	–59.4	10.2	–22.6
1 ^c	78.4	173.4	–59.5	10.2	–23.5
	1	58.9	–75.8	48.8	0.0
	4.9	58.3	–77.0	50.9	–14.1
	7.6	58.5	–77.3	51.1	–16.5
	20.7	58.9	–77.7	51.2	–19.7
	36.6	59.1	–77.8	51.1	–20.7
2	46.7	59.2	–77.8	51.2	–20.9
	78.4	59.3	–77.8	51.0	–21.6
	1	178.9	–54.6	8.3	0.0
	4.9	173.2	–54.6	8.6	–8.4
	7.6	172.1	–54.7	8.7	–9.8
	20.7	170.6	–54.7	8.8	–12.3
3	46.7	170.1	–54.8	8.8	–13.0
	78.4	169.7	–54.7	8.8	–14.7
	1	191.2	–55.6	8.1	0.0
	4.9	189.5	–58.0	8.9	–15.2
	20.7	191.6	–59.4	9.2	–21.5
	36.6	192.1	–59.6	9.3	–22.6
3 ^c	46.7	192.3	–59.7	9.3	–22.8
	78.4	192.7	–59.7	9.3	–23.7
	1	67.6	–74.5	41.1	0.0
	4.9	68.9	–76.2	42.1	–13.7
	20.7	70.2	–77.0	42.3	–19.0
	36.6	70.4	–77.2	42.3	–19.9
4	46.7	70.5	–77.2	42.3	–20.0
	78.4	70.7	–77.2	42.2	–20.8
	1	188.2	–53.7	15.3	0.0
	4.9	186.6	–53.5	15.4	–8.5
	20.7	186.8	–54.0	15.6	–12.3
	46.7	186.9	–54.1	15.6	–13.1
5	78.4	187.2	–54.4	15.8	–14.2
	1	175.1	–60.0	10.3	0.0
	4.9	165.1	–61.5	11.5	–11.3
	7.6	160.1	–61.7	11.9	–13.5
	20.7	163.2	–62.8	12.1	–18.2
	46.7	165.3	–63.2	12.1	–19.9
6	78.4	166.5	–63.4	12.1	–21.3
	1	179.8	–56.1	8.7	0.0
	4.9	174.3	–59.6	10.2	–14.0
	7.6	174.3	–60.3	10.4	–17.9
	20.7	175.9	–61.4	10.7	–20.3
	46.7	176.8	–61.8	10.8	–21.7
7	78.4	177.6	–61.9	10.8	–22.9
	1	185.4	–56.2	8.5	0.0
	4.9	179.0	–57.4	9.2	–13.5
	7.6	178.4	–57.8	9.4	–15.9
	20.7	178.6	–58.3	9.5	–19.5
	46.7	179.1	–58.6	9.6	–20.8
8	78.4	179.5	–58.5	9.5	–21.8
	1	175.0	–61.0	10.6	0.0
	4.9	165.3	–61.1	11.3	–10.5
	7.6	162.8	–61.3	11.5	–12.8
	20.7	166.9	–62.0	11.5	–17.1
	46.7	168.8	–62.3	11.5	–18.8

Table 3 (continued)

Cpd	ϵ_r^a	η^b	μ^b	ω^b	E_{solv}^b
9	78.4	169.9	–62.4	11.5	–19.8
	1	178.9	–57.5	9.2	0.0
	4.9	172.6	–58.4	9.9	–9.8
	20.7	169.5	–59.0	10.3	–14.2
	36.6	169.3	–59.2	10.4	–15.1
	46.7	169.3	–59.2	10.4	–15.2
10	78.4	169.2	–59.3	10.4	–16.0
	1	184.5	–60.0	9.8	0.0
	4.9	178.3	–59.8	10.0	–10.3
	7.6	177.5	–59.9	10.1	–11.6
	20.7	175.7	–60.1	10.3	–13.5
	46.7	175.4	–60.1	10.3	–14.2
	78.4	175.0	–60.5	10.5	–15.4

^a Relative permittivities ϵ_r correspond to gas-phase (1), trichloromethane (4.9), tetrahydrofuran (7.6), propanone (20.7), acetonitrile (36.6), dimethylsulfoxide (46.7) and water (78.4).

^b In kcal.mol^{–1}, 1 kcal.mol^{–1} = 4.18 kJ.mol^{–1}.

^c Calculations performed with the B3LYP/6-31G* method.

behavior ($f_X^+ < f_Y^+$). The theoretical prediction of the solvent polarity where this reversal takes place must be made with caution. There are two reasons for this, the first one related with the employed method of calculation, the second with the use of a continuum model for simulating solvent effects.

Different methods of calculation may lead to different reversal points, as can be seen by a comparison of the Fukui constants of **1** and **3**, calculated by an HF and a hybrid DFT method. This is due to the fact that geometry optimisations by the two methods yield molecular structures with different charge distributions and zwitterionic character. The molecular structure of compound **3**, for example, may be described as a hybrid of a quinoid and a zwitterionic canonical formulae, as shown in Scheme 2.

The dipole moment μ and the C–O bond length of the betaine increase with an increased contribution of the zwitterionic formula to the hybrid.

The dipole moments and C–O bond lengths of **1** and **3** in the gas phase, calculated with the two methods, are compared in Table 2.

It is seen that the DFT method yielded ground-state structures with a greater zwitterionic character than the HF method. Even in the gas phase, its structures were more polarized than those by the HF method. Additional polarization by a PCM option had the effect of increasing their zwitterionic character, in agreement with a negative solvatochromic behavior. Accordingly, both methods predict a negative behavior for these compounds in polar media, in agreement with what is observed experimentally. In addition, they predict a reversal for compound **1** in propanone ($\epsilon_r = 20.7$). For compound **3** however, a reversal is predicted by the HF method in non-polar medium ($\epsilon_r = 4.9$), but not by the DFT method. With this method, the reversal is not observed even in the gas phase, though a limit situation is attained, since the electrophilicities and the corresponding Fukui electrophilic functions of the two moieties become practically equal ($0.48 \approx 0.52$).

A second important limitation stems from the failure of the PCM method to reproduce the effect of more polar solvents on the dye molecular structure. As a result of the permittivity term $(\epsilon_r - 1)/4\pi\epsilon_r$ that affects the apparent surface charge distribution in the method [24], the effect of the polarizing medium tends to level off as ϵ_r increases. This poorer sensitivity of the method to variations of ϵ_r in polar media is reflected in Table 1, where results of f_X^+ and f_Y^+ do not differ appreciably in widely different solvents like acetonitrile, dimethylsulfoxide or water. As a consequence, the method is not reliable in reproducing electrophilicity inversions in more polar solvents. This may account for the fact that calculations for compound **2** predicted a positive behavior in these

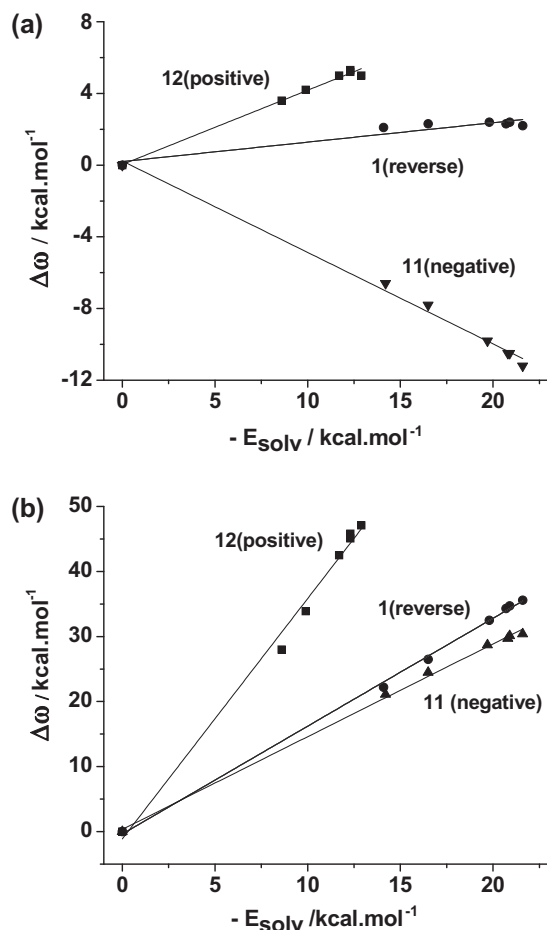


Figure 1. Variation of the electrophilicity difference $\Delta\omega = \omega - \omega_{\text{gas-phase}}$ with the calculated solvation energy E_{solv} , in media of increasing permittivity values ϵ_r (4.9, 7.6, 20.7, 36.6, 46.7, 78.4), for three solvatochromic phenolate betaines showing a negative (compound **11**), a reverse (compound **1**) and a positive behavior (compound **12**). All calculations were performed with the B3LYP/6-31G* method. (a) Electrophilicity values calculated with Eqs. (1), $\eta = E_{\text{LUMO}} - E_{\text{HOMO}}$ (2) and $\mu = (E_{\text{HOMO}} + E_{\text{LUMO}})/2$ (3); (b) electrophilicity values calculated with Eqs. (1), $\eta = I - A$ (4) and $\mu = -(I + A)/2$ (5).

solvents, corresponding to a dye molecular structure with little zwitterionic character, in contrast with the experimental evidence.

Table 3 lists the chemical potential μ , hardness η , electrophilicity ω and the solvation energy E_{solv} calculated for all compounds in the gas phase and in the six media of increasing polarity. For the sake of comparison, results from calculations with the B3LYP/6-31G* and the HF/6-31G* methods for compounds **1** and **3** are included. In all other cases, calculations were performed with the HF/6-31G* method.

The two methods yielded different absolute values for all indices in the Table. However, they reproduced the same qualitative trends with the increasing medium polarity.

We compare graphs of $\Delta\omega$ vs E_{solv} for a negative, a reverse and a positive behavior in Figure 1, where $\Delta\omega$ is the difference between

Table 4

Values of η , μ and ω for compounds **1**, **11** and **12**, calculated in media of different relative permittivities ϵ_r from Eqs. (4) and (5), and with Koopmans' approximation (Eqs. (2) and (3)), with the B3LYP/6-31G* method.

Cpd	ϵ_r	η^a	μ^a	ω^a	E_{solv}^a
1	1	126.0 (58.9)	−75.6 (−75.8)	22.7 (48.8)	0.0
	4.9	65.7 (58.3)	−76.8 (−77.0)	44.8 (50.9)	−14.1
	7.6	60.3 (58.5)	−77.0 (−77.3)	49.2 (51.1)	−16.5
	20.7	54.2 (58.9)	−77.4 (−77.7)	55.2 (51.2)	−19.7
	36.6	52.7 (59.1)	−77.4 (−77.8)	56.9 (51.1)	−20.7
	46.7	52.3 (59.2)	−77.5 (−77.8)	57.4 (51.2)	−20.9
11^b	78.4	51.5 (59.3)	−77.5 (−77.8)	58.2 (51.0)	−21.6
	1	128.4 (53.0)	−80.1 (−80.7)	25.0 (61.4)	0
	4.9	67.2 (57.3)	−78.7 (−79.3)	46.1 (54.8)	−14.2
	7.6	62.6 (58.3)	−78.7 (−79.1)	46.5 (53.7)	−16.5
	20.7	57.6 (60.5)	−78.6 (−79.0)	53.7 (51.6)	−19.7
	36.6	56.3 (61.2)	−78.5 (−78.9)	54.7 (50.9)	−20.8
12^b	46.7	56.2 (61.3)	−78.6 (−79.0)	55.1 (50.9)	−20.9
	78.4	55.6 (61.9)	−78.5 (−78.9)	55.4 (50.2)	−21.6
	1	131.2 (65.7)	−89.2 (−90.2)	30.3 (61.9)	0
	4.9	70.1 (62.9)	−90.4 (−90.8)	58.4 (65.5)	−8.6
	7.6	64.1 (62.5)	−90.7 (−90.9)	64.2 (66.1)	−9.9
	20.7	56.8 (62.0)	−91.0 (−91.1)	72.8 (67.0)	−11.7
	36.6	54.9 (61.8)	−91.0 (−91.1)	75.4 (67.1)	−12.3
	46.7	54.5 (61.8)	−91.1 (−91.2)	76.2 (67.2)	−12.3
	78.4	53.3 (61.7)	−90.9 (−90.9)	77.4 (67.0)	−12.9

^a In kcal.mol^{−1} (1 kcal.mol^{−1} = 4.18 kJ.mol^{−1}). Values between brackets were obtained from Eqs. (2) and (3), assuming Koopmans' approximation.

^b Values between brackets of η , μ , ω and values of E_{solv} for **11** and **12** were taken from reference [13].

the electrophilicity values in a certain medium and in the gas-phase. Data for the negative and the positive compounds were taken from reference [14], for the 4-(pyridinium-1-yl)phenolate **11** and the benzodithiolium derivative **12**, respectively (Scheme 3).

Following a suggestion by one referee, we performed an additional calculation of η , μ and ω for the three compounds **1**, **11** and **12**, employing the same method B3LYP/6-31G*, but utilizing Eqs. (4) and (5) for the calculation of η and μ , where I and A are the ionization potential and the electronic affinity of the molecule, respectively.

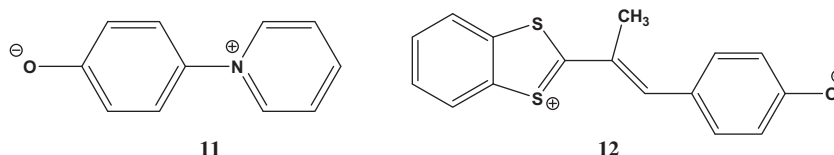
$$\eta = I - A \quad (4)$$

$$\mu = -(I + A)/2 \quad (5)$$

Values of I and A were calculated from the energies of the ionic states M^+ and M^- of each system M using the geometry of the neutral system optimized at the B3LYP/6-31G* level.

The values of η , μ and ω obtained from Eqs. (4) and (5) are compared in Table 4 with the same values from Koopmans' approximation (Eqs. (2) and (3)).

Values of hardness η from Eqs. (4) and (5) are seen to decrease for all compounds, as the polarity of the medium increases. This is in contrast with the trend observed from Koopmans' approximation for the reverse dye **1** and the negatively solvatochromic betaine **11**, for which η increases with ϵ_r . On the other hand, agreement between values of μ from both methods is quite good. These observations are in line with a previous report on η and χ ($= -\mu$) values for 52 atoms or molecules, calculated with DFT methods, employing Eqs. (4)/(5) or Koopmans' theorem [25]. Calculated



Scheme 3. Examples of a negatively (**11**) and a positively (**12**) solvatochromic dye, compared in Figure 1 with compound **1**, a dye showing a reverse behavior.

electronegativities χ based on Eqs. (4)/(5) and (2)/(3) were rather similar, whereas η values from the two approaches were different. This was ascribed to the poor agreement of Koopmans' approximation – $E_{\text{LUMO}} \approx A$. Negative values for the LUMO energies were systematically larger than the corresponding experimental or calculated electronic affinities.

As a consequence of the different trends exhibited by η , electrophilicity values in Table 4 also follow different trends: they increase with the medium polarity for all types of solvatochromic behavior, when calculations are based on the ionization potential and electronic affinity of the molecules, while decreasing with ϵ_r , in the case of the negatively solvatochromic dye **11**, when Koopmans' approximations are adopted.

Figure 1 depicts variations of $\Delta\omega$ vs E_{solv} for a negative (compound **11**), a reverse (compound **1**) and a positive behavior (compound **12**), employing Koopmans' approximation (Figure 1a), or Eqs. (4)/(5) (Figure 1b). In all cases, a linear dependence of $\Delta\omega$ on E_{solv} was observed. Notice that, although variations of $\Delta\omega$ with the medium depend on the employed method of calculation of η and μ , the three types of solvatochromism are distinguished by the response of the global electrophilicity of the dye to polarity variations of the medium. Slope values for the straight lines of $\Delta\omega$ vs E_{solv} increase in the order negative < reverse < positive, an indication that a reverse solvatochromism is a transition from a purely negative to a positive behavior.

4. Conclusions

The present communication described a theoretical protocol, based on global and group electrophilicities, and on the corresponding electrophilic Fukui functions, that allows the distinction and prediction of the solvatochromic behavior of phenolate betaine dyes. The protocol provides a theoretical way of distinguishing and rationalizing the three types of solvatochromism. The controversial and hitherto poorly rationalized solvatochromic reversal of many of these dyes arises from a reversal of the flow direction of their internal charge-transfer at some polarity value, theoretically predicted by calculations of their group Fukui electrophilic functions. Although the protocol is capable of reproducing the solvatochromic reversal of these compounds, caution should be exercised in the prediction of the polarity value where such reversal takes place, due to the limitations of the employed continuum model for the simulation of solvent effects.

Variations of the global electrophilicity of the dye, $\Delta\omega$, with its calculated solvation energy E_{solv} in media of increasing permittivities ϵ_r , yield straight lines with slope values that may be used to distinguish the three types of solvatochromism. Although these slope values depend on the method of calculating η and μ , they increase in the order negative < reverse < positive. A reverse response is thus a transition from a purely negative to a positive solvatochromic behavior.

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