Pyridinium *N*-phenolate betaine dyes as empirical indicators of solvent polarity: Some new findings*,‡

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Abstract: Solutions of the zwitterionic betaine dye 4-(2,4,6-triphenylpyridinium-1-yl)-2,6-diphenylphenolate are solvatochromic, thermochromic, piezochromic, and halochromic. That means the position of its longest-wavelength intramolecular charge-transfer absorption band depends on solvent polarity, solution temperature, external pressure, and the nature and concentration of added salts. The extraordinarily large negative solvatochromism of this standard betaine dye has been used to establish UV/vis spectroscopically an empirical scale of solvent polarity, called $E_T(30)$, respectively E_T^N scale, meanwhile known for many organic solvents and solvent mixtures. In this review, the solvatochromic properties of some new hydrophilic and lipophilic betaine dyes with better solubility in water (respectively, nonpolar solvents), as well as some recent applications of these betaine dyes in various fields of interest [e.g., microheterogeneous (micellar) and polymer solutions, chemical sensors, as well as surface polarity of silicas, aluminas, and cellulose derivatives] are described.

INTRODUCTION

Most chemical reactions are carried out in solution. That means the selection of a proper solvent, suitable for the reaction under study, is of paramount importance for the success of this reaction.

Nowadays, it is well known that solvents can have a strong influence on the position of chemical equilibria, reaction rates, and the position and intensity of spectral absorptions (e.g., UV/vis, IR, ESR, NMR). For example, the enol content of acetylacetone increases from 62 to 95 % when acetonitrile is substituted with *n*-hexane [2]. The rate of solvolysis of 2-chloro-2-methylpropane increases ca. 10^{11}-fold by changing the solvent from benzene to water, which corresponds to a decrease of the Gibbs activation energy by ca. 14 kcal/mol [3]. The C=O stretching absorption band in the IR spectrum of camphor is shifted by $\Delta\tilde{v} = 1752 - 1723 = 29$ cm^{-1} in going from *n*-heptane to hexafluoro-2-propanol as solvent [4]. For further examples of solvent effects, see ref. [5].

Usually, chemists attempt to understand such solvent influences on chemical reactivity in terms of the so-called "solvent polarity". But what does solvent polarity really mean? Already in 1965, the author tried to give a rather simple, pragmatic definition of this term [6], which was accepted in 1994 by the IUPAC committee responsible for the edition of "Glossary of terms used in physical organic chemistry" [7]. Accordingly, solvent polarity is simply defined as the "overall solvation capability (or solvation power) for (i) *educts* and *products*, which influences chemical equilibria; (ii) *reactants* and

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activated complexes, which determines reaction rates; and (iii) *ions* or *molecules in their ground and first excited state*, which are responsible for light absorptions in the various wavelength regions. This overall solvation capability depends on the action of *all* possible, nonspecific and specific, inter-molecular solute/solvent interactions, however, excluding such interactions which lead to definite chemical alterations of the ions or molecules of the solute" [7].
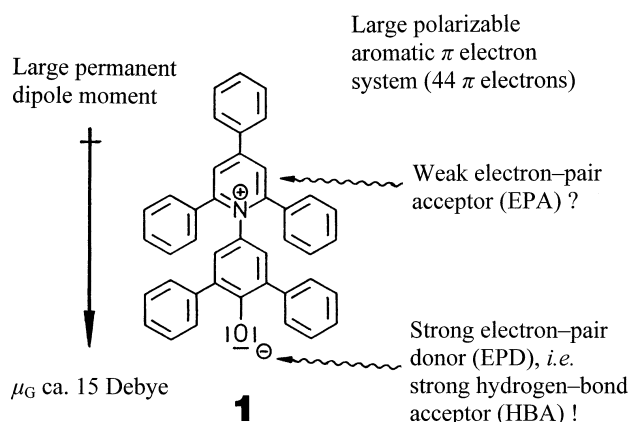
Solvent polarity defined in this way cannot be measured by single macroscopic physical bulk solvent parameters such as relative permittivity (ε_r), refractive index (n_D), or functions thereof, considering solvents simplistic as a nonstructured homogeneous continuum. Solvent polarity is much better described by molecular–microscopic empirical solvent parameters derived from suitable solvent-dependent reference processes, with individual solvent molecules surrounding the ions or dipoles of the reference solute, leading to a loose or tight solvation shell. Carefully selected, well-understood, sufficiently solvent-sensitive reference processes, and the empirical parameters derived therefrom, reflect the multitude of possible solute/solvent interactions such as ion/dipole, dipole/dipole, dipole/induced dipole, induced dipole/induced dipole (dispersion), hydrogen-bond donor (HBD)/hydrogen-bond acceptor (HBA), and electron-pair donor (EPD)/electron-pair acceptor (EPA) interactions much better than single physical constants of the solvent. In this approach, solvents are considered as a discontinuous, more or less structured medium, consisting of individual, mutually interacting solvent molecules.

The first empirical parameter of solvent polarity was introduced in 1948 by Winstein et al. using the S_N1 solvolysis of 2-chloro-2-methylpropane ("*t*-butyl chloride") as solvent-dependent reference process [8]. However, instead of laborious kinetic measurements, it is much easier to use solvent-dependent UV/vis absorptions of solvatochromic indicator dyes for the empirical determination of solvent polarity; see ref. [9] for a review. The first suggestion that solvatochromic dyes can serve as empirical indicators of solvent polarity was made by Brooker et al. in 1951 [10], but Kosower was the first to set up a real UV/vis spectroscopic solvent polarity scale in 1958, called *Z* scale, using the intermolecular charge-transfer (CT) absorption of 1-ethyl-4-(methoxycarbonyl)pyridinium iodide as solvent-sensitive absorption process [11].
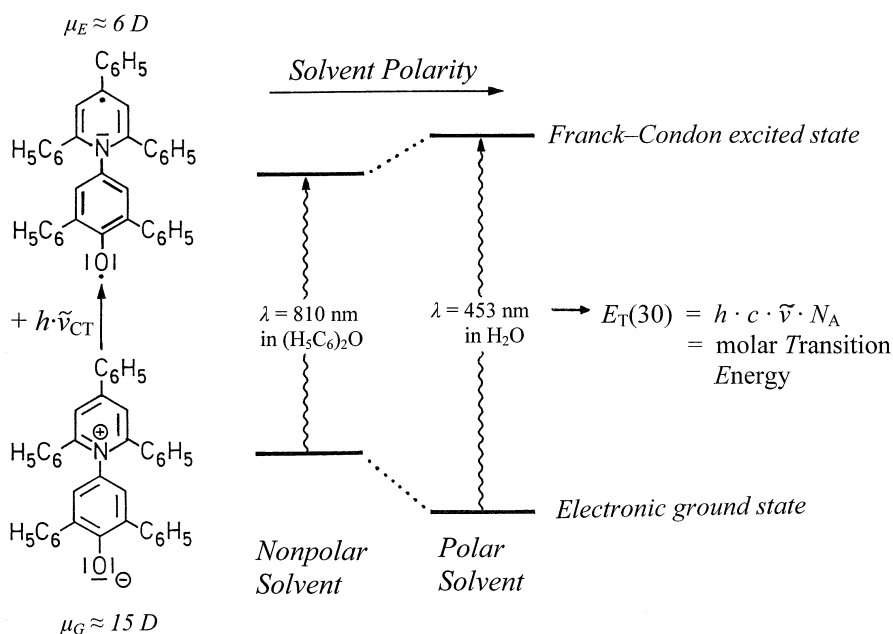
By virtue of their exceptionally large negative solvatochromism, zwitterionic pyridinium *N*-phenolate betaine dyes were introduced by us in 1963 as new solvent polarity indicators, which overcome some practical limitations of other solvatochromic dyes [12]. Since their long-wavelength solvatochromic absorption band lies within the visible region of the spectrum, even a visual estimate of solvent polarity can often be made with these betaine dyes: e.g., the solution color of betaine dye **1** (Scheme 1) is red in methanol, violet in ethanol, blue in 2-propanol, green in acetone, and yellowish-green in methoxybenzene [13]. A variety of convenient and versatile experiments to demonstrate visually the different polarity of organic solvents in classrooms by means of betaine dye **1** (which is commercially available), using test tubes or overhead projectors, have been recently described in the *Journal of Chemical Education* [14–18].

The extraordinarily large negative solvatochromism of **1** stems from differential solvation of its highly dipolar electronic ground state ($\mu_G \approx 15$ D) [19a] and its considerably less dipolar first excited state ($\mu_E \approx 6$ D) [19b]; see Fig. 1. With increasing solvent polarity, the dipolar ground state is more stabilized by solvation than the less dipolar Franck–Condon excited state, which may even be somewhat destabilized because its solvation shell is still equal to that of the ground state according to the Franck–Condon principle. As result, the long-wavelength, solvatochromic, intramolecular CT band is hypsochromically shifted from $\lambda_{max} = 810$ nm in diphenyl ether to $\lambda_{max} = 453$ nm in water as solvent, corresponding to a solvent-induced band shift of $\Delta\lambda = -357$ nm (i.e., $\Delta\tilde{v} = 9730$ cm^{-1} resp. $\Delta E_T = 28$ kcal/mol = 117 kJ/mol = 1.2 eV).

The inherent properties of betaine dye **1** (Scheme 1) make this zwitterionic dye particularly appropriate to measure simultaneously a variety of solute/solvent interactions: it exhibits (a) a large permanent dipole moment, suitable for the registration of nonspecific dipole/dipole and dipole/induced dipole interactions between solute and solvent; (b) a large polarizable aromatic π system, consisting of

Large permanent
dipole moment

Large polarizable
aromatic π electron
system (44 π electrons)

Weak electron–pair
acceptor (EPA) ?

Strong electron–pair
donor (EPD), *i.e.*
strong hydrogen–bond
acceptor (HBA) !

μ_G ca. 15 Debye

1

Scheme 1 Molecular structure with some inherent properties of the standard pyridinium *N*-phenolate betaine dye **1**, used to establish the solvent polarity scales $E_T(30)$ resp. E_T^N.

$\mu_E \approx 6\,D$

C_6H_5

H_5C_6 C_6H_5

H_5C_6 C_6H_5

$+ h \cdot \tilde{\nu}_{CT}$

C_6H_5

H_5C_6 C_6H_5

H_5C_6 C_6H_5

$\mu_G \approx 15\,D$

Solvent Polarity

Franck–Condon excited state

$\lambda = 810$ nm
in $(H_5C_6)_2O$

$\lambda = 453$ nm
in H_2O

$E_T(30) = h \cdot c \cdot \tilde{\nu} \cdot N_A$
$\quad\quad\quad = $ molar *T*ransition
$\quad\quad\quad\quad$ Energy

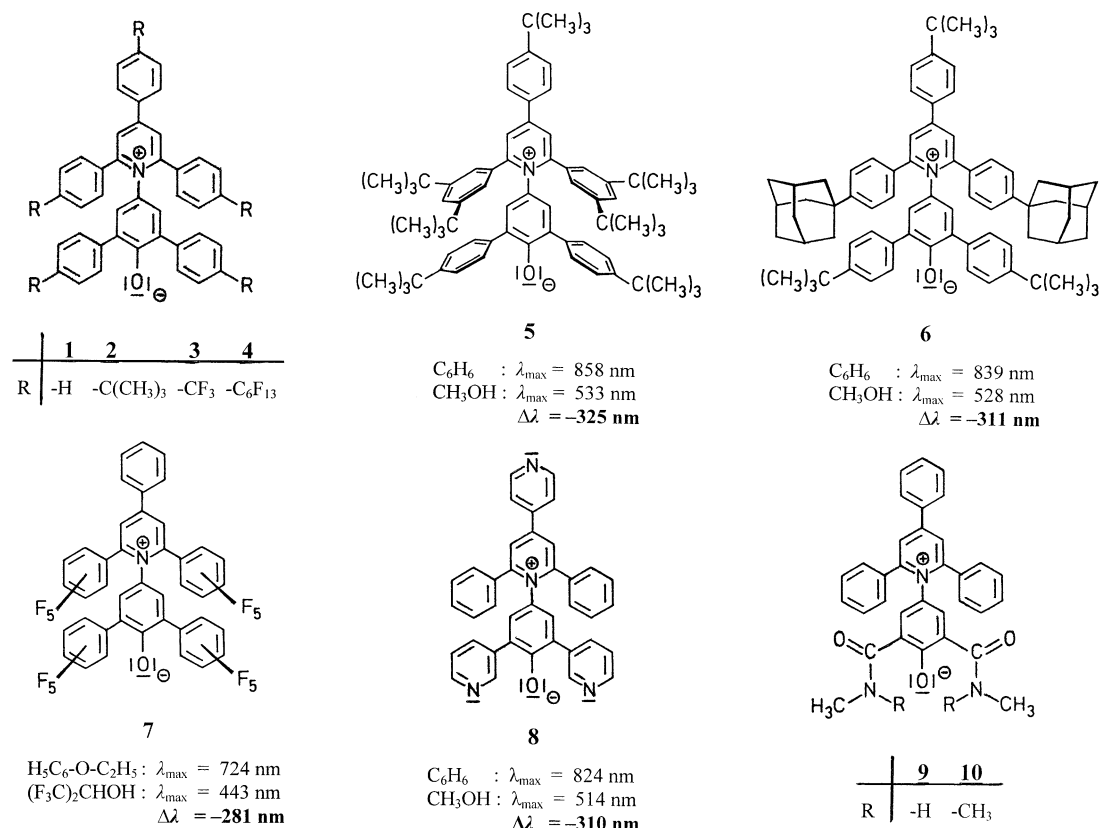*Electronic ground state*

Nonpolar
Solvent

Polar
Solvent

Fig. 1 Simplified qualitative illustration of the solvent influence on the intramolecular CT absorption of standard betaine dye **1** ($\mu_G > \mu_E$) and definition of $E_T(30)$ values as molar transition energies of **1**.

altogether 44 π electrons, suitable for the registration of nonspecific dispersion interactions; and (c) with the phenolate oxygen a strong electron-pair donor (EPD) or hydrogen-bond acceptor (HBA) center, suitable for specific hydrogen-bond interactions with HBD ("protic") solvents. The positive charge of the pyridinium moiety is delocalized and somewhat shielded by the three 2,4,6-phenyl groups and the pyridinium ring does not act as an electron-pair acceptor (EPA). Therefore, the EPD properties (Lewis basicity) of solvents are practically not registered by this betaine dye.

This more qualitative explanation of the extreme solvatochromism of betaine dye **1** has been quantitatively confirmed by a variety of recent quantum-chemical calculations at various levels of theory [20–30]. All calculations are in agreement with an $S_0 \rightarrow S_1$ intramolecular CT transition and they reveal valuable details on the geometrical structure of the S_1 state and the excited-state dynamics.

Of particular interest in this respect is the direct experimental proof for the light(laser)-induced intramolecular charge transfer within the betaine molecule **1**: the electromagnetic radiation that is emitted from betaine molecules, oriented by an external electric field (ca. 10 kV/cm), on photoexcitation has been directly measured [31]. The light-induced charge transfer is accompanied by the movement of the electron's charge from the phenolate to the pyridinium moiety and undergoes acceleration in an electric field. The acceleration of charge generates an electromagnetic transient emission which was directly measured in the terahertz (10^{12} Hz) region. The dipole moment decreases and *changes its direction* upon photoexcitation from ca. 15 D in the ground state to ca. –6 D in the excited state. That is, the excited-state dipole moment of dye **1** is antiparallel to the ground-state dipole moment and the dipole flip on photoexcitation amounts up to 15 – (–6) = 21 D!

In this review, some further, more recent applications of solvatochromic pyridinium *N*-phenolate betaine dyes **2–10** (Scheme 2) to measure the polarity of solvents and solvent mixtures as well as of various other media (polymers, surfaces) from our and other research groups are compiled. Two reviews on earlier applications of solvatochromic betaine dyes have already been published in this journal [32,33].

	1	**2**	**3**	**4**
R	-H	-C(CH₃)₃	-CF₃	-C₆F₁₃

C₆H₆ : λ_{max} = 858 nm
CH₃OH : λ_{max} = 533 nm
$\Delta\lambda$ = **–325 nm**

C₆H₆ : λ_{max} = 839 nm
CH₃OH : λ_{max} = 528 nm
$\Delta\lambda$ = **–311 nm**

H₅C₆-O-C₂H₅ : λ_{max} = 724 nm
(F₃C)₂CHOH : λ_{max} = 443 nm
$\Delta\lambda$ = **–281 nm**

C₆H₆ : λ_{max} = 824 nm
CH₃OH : λ_{max} = 514 nm
$\Delta\lambda$ = **–310 nm**

	9	**10**
R	-H	-CH₃

Scheme 2 Molecular structures and some solvatochromic ranges of further negatively solvatochromic pyridinium *N*-phenolate betaine dyes **2–10**.

THE $E_T(30)$ OR E_T^N SOLVENT POLARITY SCALE

The $E_T(30)$ values, empirically derived from solvatochromic measurements (see Fig. 1), are simply defined as the molar *t*ransition *e*nergies (in kcal/mol; 1 kcal = 4.184 kJ) of the standard betaine dye **1**,

measured in solvents of different polarity at room temperature (25 °C) and normal pressure (1 bar), according to eq. 1,

$$E_T(30) \text{ (kcal/mol)} = h \cdot c \cdot \tilde{\nu}_{max} \cdot N_A = (2.8591 \cdot 10^{-3}) \, \tilde{\nu}_{max} \text{ (cm}^{-1}) = 28591/\lambda_{max} \text{ (nm)} \qquad (1)$$

where $\tilde{\nu}_{max}$ is the wavenumber and λ_{max} the wavelength of the maximum of the long-wavelength solvatochromic, intramolecular CT absorption band of betaine dye **1**, and h, c, and N_A are Planck's constant, the speed of light, and Avogadro's constant, respectively. According to Fig. 1, high $E_T(30)$ values correspond to high solvent polarity. As in the first publication [12], the betaine dye **1** had accidentally the formula number **30**, the number 30 was added later on to avoid confusion with E_T, used as abbreviation for *t*riplet excitation *e*nergy in photochemistry.

The indicator dye **1** is not soluble in nonpolar solvents such as aliphatic hydrocarbons, perfluorohydrocarbons, and tetramethylsilane (TMS) and, therefore, it is impossible to determine their $E_T(30)$ values directly. For this reason, the more lipophilic penta-*t*-butylsubstituted betaine dye **2** (Scheme 2) has been synthesized and used as a secondary solvatochromic probe dye [34].

The excellent linear correlation between the E_T values of dyes **1** and **2** for those solvents in which both dyes are soluble, allows the calculation of $E_T(30)$ values for such nonpolar solvents in which the primary probe dye **1** is not soluble enough for UV/vis–spectroscopic measurements.

The $E_T(30)$ solvent polarity scale ranges from 63.1 kcal/mol for water, the most polar solvent, to 30.7 kcal/mol for TMS, the least polar solvent for which an $E_T(30)$ value could be experimentally determined. In order to avoid the non-SI unit "kcal/mol" and the recalculation into the SI unit "kJ/mol", in 1983 the dimensionless normalized E_T^N scale was introduced, using water ($E_T^N = 1.00$) and TMS ($E_T^N = 0.00$) as reference solvents to fix the scale, according to eq. 2 [34].

$$E_T^N = [E_T(\text{solvent}) - E_T(\text{TMS})]/[E_T(\text{water}) - E_T(\text{TMS})] = [E_T(\text{solvent}) - 30.7]/32.4 \qquad (2)$$

$E_T(30)$ and E_T^N values are known for more than 360 solvents and for many binary and even ternary solvent mixtures; for compilations, see refs. [5,9]. These and other empirical solvent polarity parameters have been successfully used in the correlation analysis of solvent influences on chemical equilibria, reaction rates, and spectral absorptions [5,9,33,37] within the framework of so-called linear free-energy relationships [5,9,35–37].

A graphical representation of the E_T^N solvent polarity scale is given in Fig. 2, together with the location of 22 solvents on this scale: 14 common organic solvents above the line and 8 more exotic solvents below the line. Unfortunately, due to the negligible volatility of betaine dye **1**, an $E_T(30)$ resp. E_T^N value for the gas phase could not be directly determined; the value given in Fig. 2 ($E_T^N = -0.11$) is an extrapolated value of unknown accuracy, which, therefore, could not be used as a point to fix the polarity scale.

In going from left to right above the line, with increasing solvent polarity, one can first find the *apolar non-HBD ("aprotic") solvents* (cyclohexane, benzene, THF, dichloromethane), followed by the *dipolar non-HBD ("aprotic") solvents* (acetone, DMF, DMSO), and eventually the group of *dipolar HBD ("protic") solvents* (alcohols). This quantitative classification of organic solvents is in good agreement with the qualitative classification of Parker [38], which has been adopted by most textbooks of organic chemistry.

Below the line from left to right, one can find supercritical carbon dioxide, the solvent polarity of which is similar to that of hydrocarbons [39], tetraethylsulfamide (TES), a substitute for HMPT and ethers as solvents in some organometallic reactions [40], 3-methylsydnone, a zwitterionic solvent (m.p. 36 °C) with a rather large dipole moment ($\mu = 7.3$ D [41a]) and high relative permittivity ($\varepsilon_r = 144$ at 40 °C [41b]), and a selection of five ionic liquids, some of which recently have gained interest as "green" solvents [42].

Amongst the ionic liquids shown in the lower part of Fig. 2, the HBD solvents ethylammonium nitrate ($E_T^N = 0.95$ [43,44]), dimethylammonium chloride ($E_T^N = 0.91$ [45]), and dimethylammonium di-
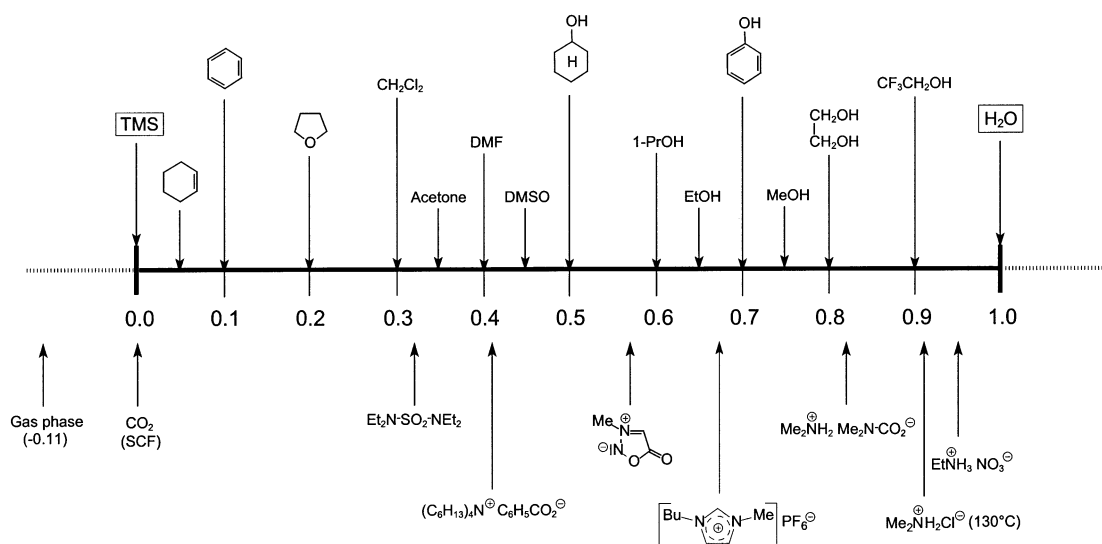
Fig. 2 Dimensionless solvent polarity scale E_T^N (cf. eq. 2 for definition) with $E_T^N = 0.00$ for tetramethylsilane (TMS) and $E_T^N = 1.00$ for water as arbitrarily fixed points [34], with ordering of 22 selected solvents on this scale.

methylcarbamate (Dimcarb; $E_T^N = 0.82$ [46]) are found in the polarity range of other dipolar HBD solvents such as the alcohols, whereas fully alkylated ammonium salts like tetra-n-hexylammonium benzoate ($E_T^N = 0.41$ [45,47]) exhibit as non-HBD solvents a solvent polarity similar to that of other dipolar aprotic solvents such as DMF. For many room-temperature ionic liquids (RTILs) of the 1,3-dialkylimidazolium salt type, such as 1-(1-butyl)-3-methylimidazolium hexafluorophosphate, [bmim]$^+$PF$_6^-$ ($E_T^N = 0.67$ at 30 °C [49a,50,51a,52]), many empirical solvent polarity parameters, particularly $E_T(30)$ resp. E_T^N values, were recently determined [44,48–53]. Depending on the nature of the 1,3-alkylsubstituents and the anion, these RTILs exhibit E_T^N values between ca. 0.5 and 0.7. Increasing the length of the alkyl substituents cause a small decrease in E_T^N values; alternation of the anion has only very little effect on the E_T^N value. In comparison with conventional organic solvents, it can generally be said that such RTILs are more polar than acetonitrile but less polar than methanol [46a], their polarities correspond to that of short-chain primary and secondary alcohols [49]. The C2–H bond of the positively charged imidazolium ion can act as a weak hydrogen-bond donor with suitable HBA solutes. That is, the polarity of RTILs does not show any spectacular behavior; they behave as normal liquids, with some desirable new properties, e.g., negligible vapor pressure. Each solvent ion is surrounded by a sphere of oppositely charged solvent ions with complete dissociation, because an imaginary ion pair lacks stability as the electrostatic attractive force between the ions of the pair is nullified by the equal interactions of each ion with all its surrounding ions.

For extensive compilations of available $E_T(30)$ and E_T^N values, see refs. [5] and [9].

FURTHER SECONDARY SOLVATOCHROMIC STANDARD BETAINE DYES

For most UV/vis spectroscopic determinations of $E_T(30)$ resp. E_T^N values, the primary solvatochromic indicator dye **1** (Scheme 2) is sufficiently soluble in organic solvents and solvent mixtures. However, betaine dye **1** has also some disadvantages: (a) as a zwitterionic inner salt, it is not or only sparingly soluble in nonpolar solvents such as aliphatic hydrocarbons, perfluorohydrocarbons, and TMS; (b) its solubility in water and highly aqueous mixtures is very low due to the core of five hydrophobic phenyl groups around the betaine chromophore. The solubility in water is only about 2×10^{-6} mol/l [54], just

enough to determine its $E_T(30)$ value directly; (c) $E_T(30)$ resp. E_T^N values are not directly available for acidic solvents such as carboxylic acids because in such solvents the phenolate oxygen atom is protonated and the long-wavelength CT absorption band disappears. Fortunately, the excellent linear correlation between the $E_T(30)$ values for nonacidic solvents and Kosower's Z values [11], which are available for acidic solvents, allows the calculation of $E_T(30)$ resp. E_T^N values for such solvents; (d) for its low volatility, it was not possible to measure the UV/vis absorption maximum of **1** in the gas phase; the gas-phase value given in Fig. 2 ($E_T^N = -0.11$) is the result of extrapolations and calculations.

To overcome at least some of these disadvantages, particularly the solubility problem, a number of further, structurally somewhat modified pyridinium *N*-phenolate betaine dyes **2–10** (Scheme 2) have been recently synthesized and their negative solvatochromism has been studied.

The use of the more lipophilic penta-*t*-butylsubstituted betaine dye **2** (Scheme 2) for the extension of the E_T^N scale to nonpolar solvents has already been mentioned [34]. The introduction of altogether seven peripheral *t*-butyl groups (as in dye **5**) as well as three *t*-butyl and two 1-adamantyl groups (as in dye **6**) increases the solubility in nonpolar solvents considerably [55], but, to our regret, both dyes were still insoluble in perfluorohydrocarbons, the least nonpolar solvents, for which E_T values would be desirable. Unfortunately, also the introduction of five peripheral trifluoromethyl or five perfluoro-*n*-hexyl substituents (as in dyes **3** and **4**) as well as the replacement of four peripheral phenyl groups by four pentafluorophenyl groups (as in dye **7**) did not result in the desired solubility of **3**, **4**, and **7** in perfluorohydrocarbons [56]. However, the introduction of such strongly electron-withdrawing substituents into the betaine dye reduces somewhat the basicity of its phenolate part and makes these chromophores less sensible to more acidic solvents. For example, the $E_T(30)$ value of rather acidic hexafluoro-2-propanol (pKa = 9.3) could be determined by means of dye **7** [56]. Replacement of the two *o,o′*-phenyl groups in the phenolate part of standard betaine dye **1** by two chlorine atoms leads also to a less easily protonated betaine dye (formula not shown), suitable for measurements in more acidic solutions [57].

In order to get better water-soluble betaine dyes, a hydrophilic sodium carboxylate group, $-CO_2^-Na^+$ [58], or some hydrophilic methanesulfonyl substituents, $-SO_2-CH_3$ [59], were introduced into the peripheral phenyl groups of **1**, however, with limited success. However, replacement of at least three of the five peripheral phenyl groups of dye **1** by 1-, 2-, or 3-pyridyl groups (as in dye **8**; Scheme 2) leads to a considerably increase in water solubility, which now allows studies of the polarity of aqueous electrolyte solutions [60a] and highly aqueous binary solvent mixtures [60b] by means of **8** and other pyridyl-substituted betaine dyes [60]. Without changing the basic zwitterionic chromophore of dye **1**, the additional peripheral nitrogen atoms of **8** are prone to form intermolecular hydrogen bonds with the surrounding water molecules, thus pulling the whole betaine molecule into the aqueous solution. Another way to increase the water solubility of **1** is the replacement of the two *o,o′*-phenyl groups in its phenolate part by two hydrophilic carbamoyl substituents as in dyes **9** and **10** (Scheme 2) [1]. However, only betaine **10** is well water-soluble; betaine dye **9** is not, presumably because of the preferred formation of *intra*molecular hydrogen bonds between the two *N*-methylaminocarbonyl groups and the phenolate oxygen atom, instead of forming *inter*molecular hydrogen bonds with the solvent [1].

With the pyridinium *N*-phenolate betaine dyes shown in Scheme 2 (and some others not mentioned here), a whole series of solvatochromic dyes are now available, suitable for the empirical determination of the polarity of not only a great variety of nonpolar and polar solvents, but also of solid materials (e.g., polymers), solid surfaces, interfaces, and microheterogeneous solutions (e.g., micelles); see later. In all cases, the $E_T(X)$ values of the betaine dyes **X = 2–10** correlate linearly with the $E_T(30)$ values of dye **1** for those solvents in which both dyes **X** and **1** are soluble, thus allowing the recalculation of $E_T(30)$ resp. E_T^N values for such media in which dye **1** is not soluble or applicable.

Some of the solvatochromic betaine dyes given in Scheme 2 have found remarkable other practical applications, for which a few examples will be mentioned here.

The internal polarity of solid transparent polymer films (e.g., polystyrene PS, polycaprolacton PCL, polyvinyl alcohol PVA) has been directly measured by embedding dye **1** into the polymers using a special technique [61]. As expected, the internal polarity increases in the order PS (hydrocarbon) < PCL (ester) < PVA (alcohol).

The lipophilic betaine dyes **2** or **6** have been dissolved in thin layers of a plasticized poly(ethylene vinyl acetate) copolymer, which were then coated with PTFE [62]. These polymer membranes respond to surrounding aqueous ethanol mixtures with a color change from green to blue with increasing ethanol content and have been used to develop an optical ethanol sensor. This sensor, using reflectance measurements in a flow-through cell, allows the continuous monitoring of the ethanol content of alcoholic beverages such as white wine, beer, and vodka [62].

Betaine dye **1** dispersed in a poly(methyl methacrylate) (PMMA) film has been used to fabricate on optical humidity sensor [63a]. The optical intensity and the wavelength of absorption observed at $\lambda \approx 780$ nm for the dye **1**/polymer composite is sensitive to the humidity of the surrounding more or less humid air. The water sorption of further dye **1**/polymer films has been measured for a variety of other polymers [63b]

Six betaine dye-doped polymer films have been exposed to a series of vapors from organic solvents of different polarity. Reversible and reproducible changes in the long-wavelength CT absorption maximum of dye **1** were observed [64]. This makes these dye **1**/polymer composites potential devices for the development of real-time chemical sensors for remote detection of volatile organic compounds (VOCs) [64].

A solvatochromic betaine dye-doped polymer (PMMA) has been developed for the detection of polar additives (e.g., methanol, *t*-butanol, *t*-butyl methyl ether, MTBE) in hydrocarbon blends [65a]. Such betaine dye **1**/PMMA spin-coated films can detect repeatedly down to 0.1 % (v/v) methanol and *t*-butanol as well as 1 % (v/v) TBME in hydrocarbon blends, making them useful candidates for a chemical sensor for in situ monitoring of octane improvers in gasoline [65a].

A covalently polymer-bound betaine dye **1** has been synthesized step by step (five steps) on an insoluble Merrifield peptide resin (i.e., a functionalized polystyrene) [65b]. The strong negative solvatochromism of dye **1** persists in the solid polymer-bound betaine when solvent molecules are allowed to diffuse into the polymer network. This solvatochromic polymer (a green insoluble powder) can be possibly used as chemical detector in solvatochromic sensors for organic solvents. Methanol contents as low as 10^{-2} % (v/v) in commercial hydrocarbon blends have been detected with this polymer-bound betaine dye [65b]. Another covalently immobilized betaine dye was prepared by addition of a 4-amino-substituted dye **1** to an isothiocyanatopropyl-substituted silica as polymer substrate [66]. The internal polarity of organic/inorganic polymer hybrids has been estimated by means of solvatochromic polymers prepared by incorporating betaine dye **1** covalently in the side chain of poly(2-methyl-2-oxazoline) [67].

Eventually, betaine dye **1** was also successfully entrapped into organically modified silica (ormosil) sol-gel matrices, while retaining its sensitivity to changes in the environment polarity [68]. The variations in the cage interfacial polarity of such ormosils, suitable as alcohol sensors, could be measured this way.
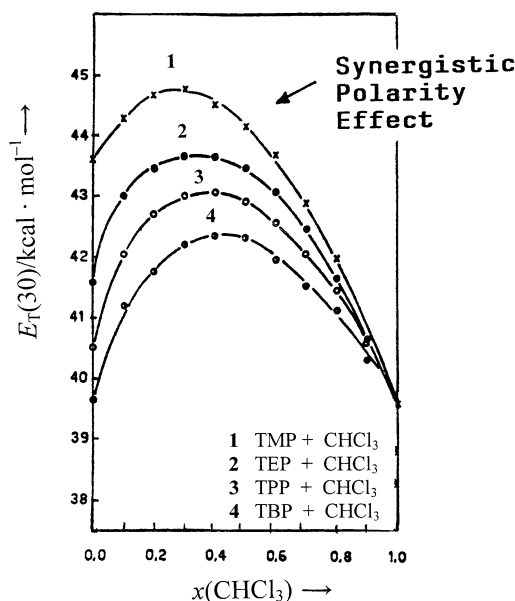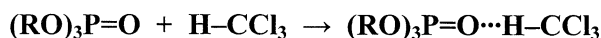
POLARITY OF SOLVENT MIXTURES

Solvent mixtures possess often a better solvency for solutes than pure organic solvents and are, therefore, preferably used as reaction media in many synthetic reactions [5]. $E_T(30)$ resp. E_T^N values for a great variety of binary solvent mixtures have been determined; see refs. [9,69–77] for some compilations. Even for some ternary solvent mixtures $E_T(30)$ values are meanwhile available (i.e., MeOH/EtOH/acetone [78,110], MeOH/CH$_3$CN/1-PrOH [79]).

The $E_T(30)$ values (and other solvent parameters) of binary and ternary solvent mixtures are not related to their composition in a simple linear manner [80]. Most solvent mixtures behave as more or less nonideal mixtures. The addition of a small amount of a polar solvent to a solution of betaine dye **1** in a nonpolar solvent causes a disproportionally large hypsochromic band shift, corresponding to an excessively large increase in $E_T(30)$. This behavior can easily be explained with the strong *selective* or *preferential solvation* of the dipolar betaine dye by the more polar component of the binary solvent mixture. That is, the molecular–microscopic solvation shell of the betaine dye has a composition which is different from that of the bulk mixture. This selective solvation has been extensively studied during the last years [69–80] and a useful general equation has been derived, relating the E_T^N values of a binary solvent mixture to the E_T^N values of the two pure solvents, the so-called preferential solvation parameters, and the solvent mixture composition, using a simple two-step solvent exchange model for the selective solvation of the indicator dye **1** [70,71].

The strong dependence of the $E_T(30)$ resp. E_T^N values on the composition of binary solvent mixtures of *solvents with different polarity* can be used for the quantitative UV/vis spectroscopic determination of water (or other polar components) in less polar organic solvents [17,18,69,81].

A particularly interesting so-called *synergistic solvent effect* was found for solutions of dye **1** in some binary solvent mixtures composed of HBD and HBA solvents. An example is given in Fig. 3, showing surprisingly a maximum in the $E_T(30)$/composition graph for mixtures of trialkyl phosphates (HBA solvent) and trichloromethane (HBD solvent) [82].

$$(RO)_3P{=}O \; + \; H{-}CCl_3 \; \rightarrow \; (RO)_3P{=}O{\cdots}H{-}CCl_3$$

Fig. 3 $E_T(30)$ values of four binary trialkyl phosphate/trichloromethane mixtures, $(RO)_3P{=}O/CHCl_3$, with R = Me (TMP), Et (TEP), 1-Pr (TPP), and 1-Bu (TBP); $E_T(30) = 39.1$ for $CHCl_3$ and 39.6 kcal/mol for TBP [82].

That means, this binary solvent mixture behaves somewhat more polar than either of their two co-solvents! The behavior of such synergistic binary solvent systems was explained by the formation of hydrogen-bonded 1:1 HBD/HBA solvent complexes, which create a third new, more polar solvent [82]. Another, related explanation would be a cooperative solvation of the betaine solute by the two pure co-solvents, that is, synergistic solvation effects of both the HBD and the HBA solvent [77]. An extreme other case of such a cooperative solvation effect is the solubility behavior of a chloro-oxalato-tripyri-

dine-rhodium(III) complex, which dissolves in a 1:1 mixture of pyridine (HBA) and water (HBD), but neither in pure water nor in pyridine [83].

POLARITY OF MICROHETEROGENEOUS SOLUTIONS

The extreme sensitivity to small changes in the surrounding medium has made betaine dye **1** and some of its derivatives useful molecular probes for the study of the internal polarity of micellar systems [84], microemulsions, phospholipid bilayers, model liquid membranes, vesicles [85], oil/water interfaces [86], etc.; see ref. [84] and Table 5 in ref. [9] for earlier work in this field. For more recent work, see refs. [87–89]. Only one example will be outlined here [90].

Figure 4 demonstrates that betaine dye **1** can be used as internal probe for the micellar aggregation behavior of surfactants such as homologous tetraalkylammonium betaines (molecular structure given as insert) in aqueous solution. The micellisation with increasing surfactant concentration can easily be followed UV/vis spectroscopically by means of dye **1**: the $E_T(30)$ values strongly decrease after reaching the critical micelle concentration (*cmc*) due to the transfer of dye molecules from an aqueous into a micellar microenvironment [90]. Even mean aggregation numbers of such homologous tetraalkylammonium betaines in aqueous solution could be determined by means of the $E_T(30)$ values [90]. For another recent determination of *cmc* values for sodium *n*-dodecyl sulfate (SDS) in aqueous buffer solutions see ref. [91].
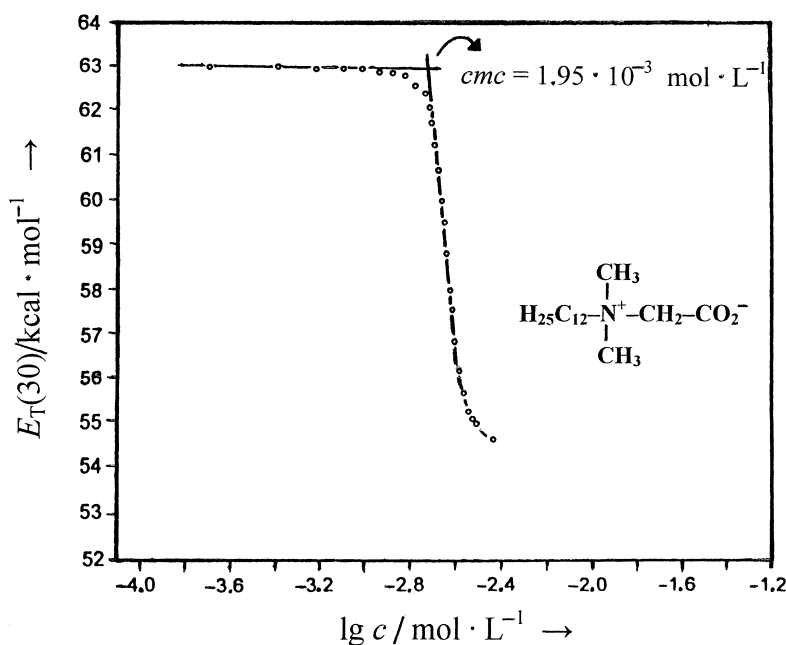
Fig. 4 $E_T(30)$ values of solutions of dye **1** and a zwitterionic C_{12}-tetraalkylammonium betaine in an aqueous buffer vs. lg c of the surfactant concentration [90].
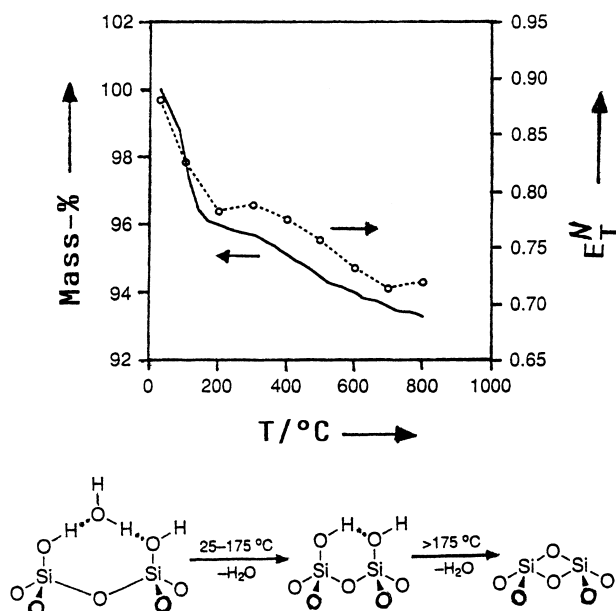
POLARITY OF SURFACES

X-ray amorphous pyrogenic silica (e.g., Aerosil®), prepared by flame hydrolysis from tetrachlorosilane ($SiCl_4 + 2H_2 + O_2 \rightarrow SiO_2 + 4 HCl$), consists of fine spherical particles with diameters of ca. 10–20 nm, a volume of ca. 15 ml/g, and a high specific surface of 100–400 m²/g, covered by silanol ($\equiv$Si–OH) groups which determine its surface polarity. Such pyrogenic silicas have found many practical applica-

tions, e.g., as dental materials, in toners, as fillers in silicon rubber, as thixotropic thickeners, etc. [92]. Their surface polarity can be determined by means of solvatochromic probes such as betaine dye **1** [93]. On addition of dye **1** to a suspension of pyrogenic silica in 1,2-dichloroethane, the dye is completely adsorbed at the silica surface, accompanied by a color change from green to orange red, and its UV/vis spectrum can be measured in transmission by means of a diving cuvet. For example, dried Aerosil® 300 has an $E_T(30)$ value of 57.8 kcal/mol ($E_T^N = 0.84$), which is close to that of 2,2,2-trifluoroethanol [$E_T(30) = 59.8$ kcal/mol; $E_T^N = 0.90$].

Chemical modification of the silica surface by reaction of the silanol groups with trimethoxy- or trichloro-alkylsilanes, $(RO)_3Si–R$ or $Cl_3Si–R$, reduces the surface polarity significantly up to $\Delta E_T(30) \approx -8$ kcal/mol [93]. Thus, solvatochromic indicator dyes like betaine **1** can be used to characterize quantitatively the surface polarity of bare and chemically modified silicas, which is of distinct practical value [93–95].

Another remarkable example is the variation in surface polarity of *thermally* treated, mesoporous, commercially available silica (e.g., "Kieselgel 60", Merck/Darmstadt) as shown in Fig. 5 [95,96]. Initial heating of "Kieselgel 60" causes a rapid loss of mass due to the removal of loose hydrogen-bonded water. Further heating results in a loss of silanol groups by a condensation reaction producing more and more less dipolar siloxane bridges (2 ≡Si–OH → ≡Si–O–Si≡ + H_2O). The loss of surface water corresponds well with the simultaneous decrease of surface polarity as shown by the E_T^N values, determined by diffuse reflectance UV/vis spectroscopy of betaine dye **1** adsorbed on the silica surface. The E_T^N value drops from 0.88 for wet "Kieselgel 60" to a final value of 0.72 for the dehydrated probe [95,96]. Chemical modification of these silicas by trimethoxy-phenylsilane exhibits a reverse linear correlation between the degree of functionalization and the surface polarity as measured by the E_T^N values [95,96]. The surface polarity of various materials with adsorbed betaine dye **1** can even be estimated by eye: very polar surfaces such as untreated silicas are red, changing to purple and blue for organically modified silicas, and eventually to green for nonpolar surfaces such as macroporous polystyrene [95,96].

Fig. 5 Thermogravimetric analysis (left ordinate) and the influence of thermal treatment on the surface polarity, E_T^N (right ordinate), of silica "Kieselgel 60" (Merck/Darmstadt), and the corresponding dehydration process at the silica surface [95,96].

The surface polarity of microporous, neutral, chromatographic grade alumina (surface area ca. 150 m^2/g; Aluminum Company of America/Pittsburgh) has been determined as a function of thermal activation and water deactivation by means of adsorbed betaine dye **1**, using diffuse reflectance UV/vis spectroscopy [97]. The alumina surface consists mainly of hydrogen-bonded aluminol groups (=Al–OH) and adsorbed hydrogen-bonded water. Alumina of activity grade I (according to the Brockmann scale I–V that of highest activity) exhibits an $E_T(30)$ value of 68.4 kcal/mol ($E_T^N = 1.16$) [97], corresponding to a higher polarity than water [$E_T(30) = 63.1$; $E_T^N = 1.00$] [9]. As the amount of water added to the thermally activated alumina increases, the $E_T(30)$ value decreases by $\Delta E_T(30) \approx -2$ kcal/mol in the range of 0 to 15 % (w/w) added water. Obviously, the empirical determination of surface polarity with solvatochromic dyes such as **1** is a convenient means to estimate the activity of aluminas in a single UV/vis spectroscopic measurement [97].

Since in adsorption liquid chromatography done on alumina, the retention of solutes is related to the activity of the alumina stationary phases, the empirical determination of surface activities by means of solvatochromic dyes is also very useful for the classification of all kinds of stationary phases [97]. For complementary solvatochromic studies of stationary phases used in thin-layer [98] and reversed-phase chromatography [99–102] see refs. [98–102].

Eventually, the application of betaine dye **1** and other solvatochromic dyes for the empirical determination of surface polarity of zeolite cages [103], of solid poly(α-amino acids) [104], as well as of native polysaccharides (e.g., cellulose, glycogene, amylopectin, amylose, starch, cellobiose, etc.) [105a] and various cellulose derivatives (e.g., carboxymethylcellulose, cellulose tosylate, etc.) [105b,c] should be mentioned. For example, microcrystalline celluloses of different provenance have $E_T(30)$ values of 49–53 kcal/mol ($E_T^N = 0.56-0.69$), that is, not unexpectedly, in the polarity region of short-chain primary and secondary alcohols [105]; see particularly Scheme 3 in ref. [105b].

The applications of pyridinium N-phenolate betaine dye **1** as a versatile empirical indicator of surface polarity has been recently reviewed [96].

MULTIPARAMETER CORRELATION EQUATIONS

The application of a single empirical polarity parameter such as $E_T(30)$ resp. E_T^N in correlation analyses, i.e., in the (mostly linear) correlation of other solvent-dependent processes, was unexpectedly rather successful [5,33]. However, in many cases, satisfactory correlations between $E_T(30)$ resp. E_T^N and other solvent-dependent quantities such as equilibrium or rate constants, absorption maxima, etc., were not obtained. In applying $E_T(30)$ and E_T^N, it is tacitly assumed that the intermolecular solute/solvent interactions of the reference indicator dye (i.e., betaine dye **1**; see Scheme 1) are similar to those in the system under investigation the prediction of whose solvent effects is being raised. This is obviously true only for closely related solvent-dependent processes. Nevertheless, the special combination of intermolecular solute/solvent interactions registered by betaine dye **1** can be met very often—as their successful application to countless other solvent-dependent processes demonstrates. According to its molecular structure (Scheme 1), betaine dye **1** is not prone to register the Lewis basicity resp. electron–pair donor (EPD) and hydrogen-bond acceptor (HBA) properties of solvents and surfaces. This drawback can be overcome by using two-parameter eq. 3 for correlation analysis, including the donor number (DN) of Gutmann et al. [106] as a second parameter for the registration of the EPD properties of the surrounding medium [107]:

$$XYZ = (XYZ)_0 + \alpha \cdot E_T(30) + \beta \cdot DN \tag{3}$$

XYZ and $(XYZ)_0$ stand for the solute property under investigation (e.g., lg K, lg k, $\tilde{\nu}_{max}$, etc.), determined in solvents of different polarity and in a reference solvent (or gas phase), respectively. This equation has been successfully applied for many further solvent-dependent processes for which $\beta \neq 0$ [107]; for successful one-parameter $E_T(30)$ correlations β has to be zero.

A more detailed analysis of the medium influence on solvent-dependent processes can be made by using multiparameter correlation equations such as eq. 4, introduced by Kamlet, Abboud, and Taft (KAT), in which π^* stands for the solvent's

$$XYZ = (XYZ)_0 + s \cdot \pi^* + a \cdot a + b \cdot \beta \tag{4}$$

dipolarity/polarizability, and α and β are measures of the solvent's HBD acidity and HBA basicity, respectively; all solvent parameters were determined UV/vis spectroscopically by means of carefully selected reference compounds [108]. In application of eq. 4, the solvent-dependent process under consideration has to be studied in a variety of solvents differing in their π^*, α, and β values.

It is interesting to analyze the $E_T(30)$ resp. E_T^N values by means of the KAT eq. 4. This was done by Marcus for 166 organic solvents [109], leading to correlation eqs. 5a and 5b ($n = 166$, $r = 0.979$), respectively:

$$E_T(30)/(\text{kcal} \cdot \text{mol}^{-1}) = 31.2 + 11.5 \cdot \pi^* + 15.2 \cdot \alpha \tag{5a}$$

$$E_T^N = 0.01 + 0.36 \cdot \pi^* + 0.47 \cdot \alpha \tag{5b}$$

These multiparameter correlations clearly show that the $E_T(30)$ resp. E_T^N values measure preferably the solvent's dipolarity/polarizability (given by π^*) and HBD acidity (given by α). In HBD solvents, the HBD acidity can even be the dominant solvent property: the quotient a/s of the corresponding regression coefficients (see eq. 4) amounts to 1.3 for eqs. 5a and 5b. For non-HBD solvents, for which α is equal to zero, the $E_T(30)$ resp. E_T^N values essentially reflect only a blend of the solvent's dipolarity ($\rightarrow$ dipole/dipole, dipole/induced dipole interactions) and polarizability ($\rightarrow$ dispersion interactions). In conclusion, the correlation eqs. 5a and 5b are in full agreement with the molecular structure of the pyridinium *N*-phenolate betaine dye **1** (Scheme 1), which has no functional groups capable of intermolecular interactions with HBA resp. EPD solvents.

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