Solvatochromism, Thermochromism, Piezochromism, Halochromism, and Chiro-Solvatochromism of Pyridinium *N*-Phenoxide Betaine Dyes

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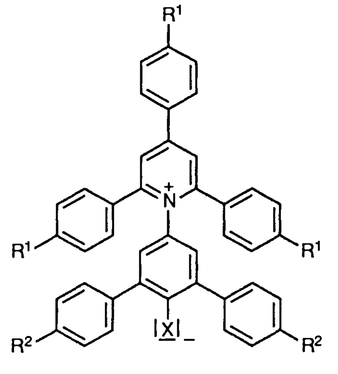
1 Introduction

Whenever a chemist wishes to carry out a given chemical reaction, not only has he to decide which reaction partners, reaction vessel, reaction temperature, and reaction time should be applied – he also has to select carefully the appropriate solvent for the planned reaction. As a result of the pioneering work of Berthelot and Saint-Gilles in Paris in 1862 (discovery of the solvent influence on the esterification of acetic acid by ethanol) and Menschutkin in St. Petersburg in 1890 (solvent dependence of the alkylation of triethylamine by iodoethane), and the host of papers on solvent effects published since then, every chemist is nowadays well aware of the fact that solvents can have a strong influence on reaction rates and chemical equilibria as well as on the position of spectral absorption maxima.[1] At present, there exists a supply of about 300 common organic solvents, apart from the infinite number of solvent mixtures. A chemist therefore needs, in addition to his experience and intuition, some guidelines for the selection of the proper solvent. In principle, there are two main objectives: (a) the prediction of rate or equilibrium constants as well as absorption maxima in other solvents, and (b) to reach some understanding of the various solute–solvent interactions that might effect rate and equilibrium constants as well as absorption spectra.

Usually, chemists have tried to understand solvent effects in terms of the so-called solvent polarity, which is not easy to define precisely or to express quantitatively. Seduced by the simplicity of electrostatic solvation models, attempts at expressing solvent polarity quantitatively involve mostly physical solvent parameters such as dielectric constant, dipole moment, refractive index, or functions thereof. However, this procedure is often inadequate because it does not take into account specific solute–solvent interactions such as hydrogen-bonding, electron-pair donor (EPD) – electron-pair acceptor (EPA), and solvophobic interactions. Hence, from a more practical point of view, it seems reasonable to understand solvent polarity in terms of the *overall solvation capability* of a solvent for reactants and activated complexes as well as for molecules in the ground and excited states, excluding solute–solvent interactions such as protonation, oxidation, reduction, complexation, *etc*., which may lead to a chemical change of the solute.[1] This overall solvation capability depends on *all* possible – specific and non-specific – intermolecular forces between solute and solvent. Obviously, solvent polarity thus defined cannot be described by a single physical solvent parameter. The lack of comprehensive theoretical expressions for the calculation of solvent effects, and the inadequacy of defining solvent polarity in terms of simple physical characteristics, has led to the introduction of empirical parameters of solvent polarity.[1,2]

Based on the assumption that particular, carefully selected and well understood solvent-dependent chemical reactions or spectral absorptions may serve as suitable model processes, various empirical solvent polarity scales have been developed.[1,2] The first empirical parameter of 'solvent ionizing power' was the *Y*-scale introduced by Winstein in 1948 and derived from the S_N1 solvolysis of t-butylchloride.[2c] The first to suggest that solvatochromic dyes might be used as indicators of solvent polarity was Brooker in 1951, but Kosower was the first to set up a real spectroscopic solvent polarity scale in 1958. This was called the *Z*-scale and used the intermolecular charge-transfer absorption of 1-ethyl-4-methoxycarbonylpyridinium iodide as solvent-sensitive reference process.[1,2] The pyridinium *N*-phenoxide betaine dye (1) was proposed by Dimroth, Reichardt, *et al.*[1,3] in 1963 as a new UV/Vis-spectroscopic indicator of solvent polarity which, by virtue of its exceptionally large negative solvatochromism (*i.e.* a hypsochromic shift of the UV/Vis absorption band with increasing solvent polarity), overcame some practical limitations of other solvatochromic reference molecules.[1,2]



(1) $R^1 = R^2 = H$; X = O
(2) $R^1 = R^2 = CMe_2$; X = O
(3) $R^1 = SO_2Me$; $R^2 = H$; X = O
(4) $R^1 = R^2 = H$; X = S

In applying solvent polarity scales based on a single empirical parameter, it is tacitly assumed that the combination of solute–solvent interactions between the reference solute and the solvent is the same as with the particular substrate under consideration. It turns out that, in many cases, this is an oversimplification. Therefore, multiparameter correlation equations have been introduced, which consist of up to four single empirical parameters, each of them measuring a certain aspect of the overall solvation capability of a given solvent (*e.g.* polarizability, dipolarity, Lewis acidity, Lewis basicity).[1,2a]

This kind of procedure, *i.e.* the use of standard or reference compounds in order to establish empirical solvent parameters, is quite common in chemistry. For example, the well-known

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Hammett equation, used to estimate substituent effects on rates, equilibria, and absorptions, is likewise based on an empirical reference process – the ionization of substituted benzoic acids in water at 25 °C. The correlations between these empirical substituent or solvent parameters and the substituent- or solvent-dependent processes under study take usually the form of a linear free-energy (LFE) relationship.[1]

2 Solvatochromism of Betaine (1) and the $E_T(30)$ Scale

The negatively solvatochromic pyridinium *N*-phenoxide betaine dye (1) exhibits one of the largest solvatochromic shifts ever observed: its longest-wavelength intramolecular charge-transfer (CT) absorption band is hypsochromically shifted by 9730 cm^{-1} (375 nm) on going from diphenyl ether (λ_{max} = 810 nm) to water (λ_{max} = 453 nm). Solutions of (1) are red-coloured in methanol, violet in ethanol, blue in isoamyl alcohol, green in acetone, and yellowish-green in ethyl acetate, thus covering the whole visible region and allowing even a visual estimate of the solvent polarity (Figure 1).

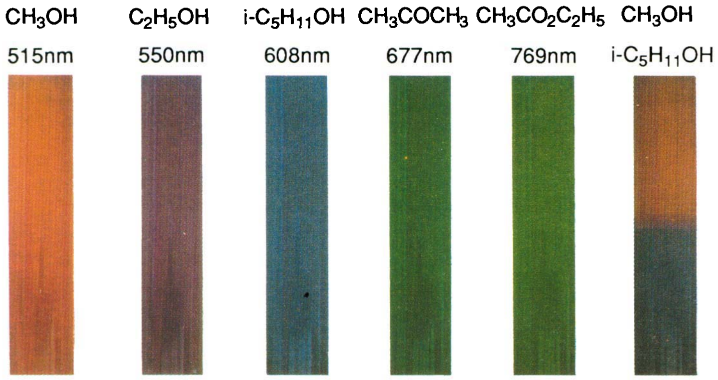
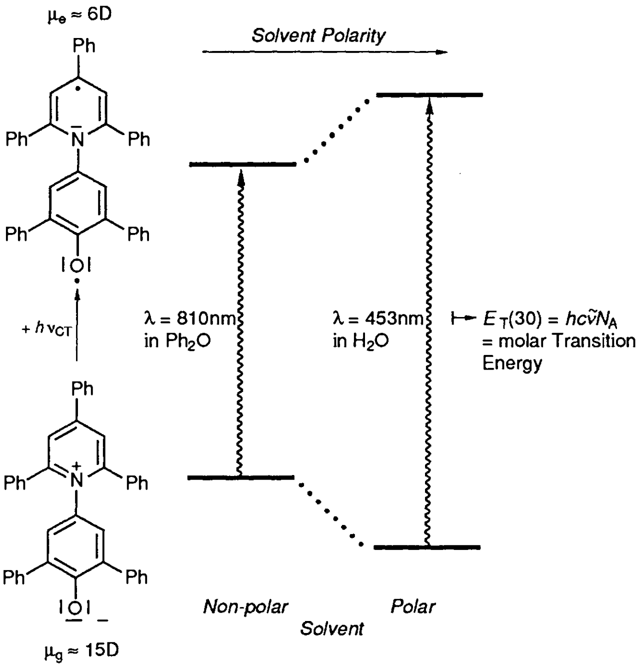


Figure 1 Solution colours of the negatively solvatochromic pyridinium *N*-phenoxide betain dye (1) in five solvents of different polarity and in the two-phase solvent system methanol/isoamyl alcohol (red/blue).

This outstanding negative solvatochromism stems from the unequal, differential solvation of the electronic ground and excited state of (1) with increasing solvent polarity (Scheme 1). The solvent-mediated stabilization of the highly dipolar, zwitterionic ground state of (1), relative to its less dipolar excited state, results from the following properties of the betaine molecule: (a) it exhibits a large permanent dipole moment, suitable for the registration of dipole–dipole and dipole–induced dipole interactions; (b) it possesses a large polarizable π-electron system, suitable for the registration of dispersion interactions; and (c) with the phenoxide oxygen atom it has a highly basic EPD centre, suitable for interactions with Brønsted acids (through H-bonding) and Lewis acids (through EPD–EPA bonding). The positive charge of the pyridinium moiety is delocalized and sterically shielded. Therefore, the CT absorption of (1) depends strongly on the electrophilic solvation power of the solvents, *i.e.* on their hydrogen-bond donor (HBD) ability and Lewis acidity (= EPA behaviour), rather than on their nucleophilic solvation capability (= EPD behaviour). In stronger acidic solvents, (1) is protonated and the solvatochromic CT absorption band disappears (reversibly).[1,3]

$$E_T(30)/(\text{kcal mol}^{-1}) = hc\tilde{\nu}N_A = 2.8591\times10^{-3}\tilde{\nu}_{max}/\text{cm}^{-1} = \frac{28591}{\lambda_{max}/\text{nm}} \qquad (1)$$

In analogy to the *Z*-values of Kosower, the empirical solvent polarity parameter $E_T(30)$ is simply defined as the molar electronic transition energy of dissolved (1), measured in kcal/mol^{-1}, according to equation 1.[5] A high $E_T(30)$ value corresponds to high solvent polarity. In order to avoid the dimension kcal/mol^{-1}, normalized E_T^N values can be used instead of $E_T(30)$.[3b] They are defined according to equation 2, using water and tetramethylsilane (TMS) as, respectively, extreme polar and non-polar reference solvents. Hence, the E_T^N-scale ranges from 0.0 for TMS, the least polar solvent, to 1.0 for water, the most polar solvent.



Scheme 1

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

Since betaine (1) is insoluble in aliphatic hydrocarbons and only sparingly soluble in water, the more lipophilic penta(t-butyl)-substituted dye (2)[3b] as well as the tris(methanesulfonyl)-substituted dye (3)[6b] have been used as secondary standard betaine dyes, the E_T values of which correlate linearly with the $E_T(30)$ values of (1). In that way, $E_T(30)$ values are presently known for more than 300 organic solvents[1,3,4] and for numerous binary solvent mixtures.[1,7–10] In addition, $E_T(30)$ values have been determined for room-temperature liquid salts,[11] supercritical-fluid (SCF) solvents,[12] as well as polymers [13a] and aqueous polymer solutions.[13b] Only for perfluorohydrocarbons [insolubility of (1) and (2)] and acidic solvents [protonation of (1) and (2)] are $E_T(30)$ values not directly measurable. The border between acidic and less acidic solvents for which $E_T(30)$ values are available is determined by the acidity constant of the corresponding acid of (1): the pK_A of protonated (1) is 8.65 ± 0.05,[14] 8.63 ± 0.03[18c] in H_2O. The synthesis of the standard betaine dye (1) has been simplified recently,[15a–c] and the dyes (1) and (2) are now commercially available.[15d]

In addition to the characterization of solvent polarities, the $E_T(30)$ values have found many other applications, *e.g.* (a) LFE correlations with other solvent-dependent reactions and absorptions;[1,16] (b) quantitative analysis of binary mixtures of solvents with different polarity;[1,7–10] (c) characterization of mobile phase polarities in reversed-phase liquid chromatography (RPLC)[17a] and counter-current chromatography (CCC);[17b] (d) determination of the polarity of alumina surfaces in adsorption liquid chromatography (ALC);[17c] and (e) description of the interfacial microenvironment of micro-heterogeneous solutions (*e.g.* microemulsions, micelles, vesicles, phospholipid bilayers, surfactants, tensides).[18] Applications of $E_{\mathrm{T}}(30)$ values in analytical chemistry have been reviewed.[15a] For example, they can be used for rapid UV/Vis-spectroscopic determination of water in organic solvents.[8b] Zwitterionic betaine dyes of type (1) have been used to construct a molecular battery (utilizing reversible one-electron redox reactions of a certain betaine dye),[19] and as potential materials with non-linear optical properties for frequency doubling of laser radiation.[20]

In order to unravel the combination of specific and non-specific betaine–solvent interactions, the pyridinium *N*-thiophenoxide betaine dye (4) (see p.147) has been synthesized recently.[21] Since sulfur is known to be a much poorer hydrogen-bond acceptor than oxygen, the homomorphic thiobetaine (4) should be less sensitive (or even insensitive) to specific hydrogen-bond interactions with HBD solvents. Therefore, a correlation line between $E_{\mathrm{T}}(30)$ of (1) and $E_{\mathrm{T}}^{\mathrm{S}}(30)$ of (4) should be linear for non-HBD solvents, but non-linear with deviations for HBD solvents. Surprisingly enough, there is an excellent linear correlation between $E_{\mathrm{T}}(30)$ of the oxygenbetaine (1) and $E_{\mathrm{T}}^{\mathrm{S}}(30)$ of the thiobetaine (4) including *both* HBD and non-HBD solvents, as shown in equation 3 (number of solvents $n = 60$; correlation coefficient $r = 0.993$). The reasons for this unexpected behaviour of (4) in comparison with (1) have been discussed.[21] The slope of equation 3 is larger than unity. That means that thiobetaine (4) is more strongly solvatochromic than (1) and could serve as a new, more sensitive solvent polarity indicator. Unfortunately, solutions of (4) are rather unstable because the thiobetaine is easily oxidized to the corresponding, sparingly soluble disulfide.[21]

$$E_{\mathrm{T}}^{\mathrm{S}}(30)/(\mathrm{kcal\,mol^{-1}}) = 1.25\,E_{\mathrm{T}}(30)/(\mathrm{kcal\,mol^{-1}}) - 10.81 \tag{3}$$

A recent analysis of the $E_{\mathrm{T}}(30)$ values of (1) for 100 solvents by means of the multiparametric Kamlet–Taft equation[2a] had led to equation 4 ($n = 100$; $r = 0.984$),[22] in which π^* is an index of solvent dipolarity/polarizability, α a measure of the solvent HBD ability and δ a polarizability correction term for the solvent being aromatic ($\delta = 1.0$), polyhalogenated aliphatic ($\delta = 0.5$), or neither ($\delta = 0.0$). Equation 4 clearly shows that $E_{\mathrm{T}}(30)$ values represent a combination of non-specific (π^*) and specific (α) solute–solvent interactions. The ratio of the coefficients of α and π^* is 1.1, hence the sensitivity of $E_{\mathrm{T}}(30)$ to α is slightly larger than to π^* for HBD solvents[22] (*cf.* also reference 4*c*).

$$E_{\mathrm{T}}(30)/(\mathrm{kcal\,mol^{-1}}) = 13.68\,(\pi^* - 3.45\delta) + 14.51\alpha + 30.8 \tag{4}$$

The position of the long-wavelength UV/Vis absorption band of dissolved (1) depends not only on the solvent polarity (solvatochromism), but also on the solution temperature (thermochromism), on external pressure (piezochromism), and on the type and concentration of added salts (halochromism).

3 Thermochromism of Betaine (1)

A solution of (1) in ethanol is blue-violet ($\lambda_{\max} = 568$ nm) at + 78 °C and red-coloured ($\lambda_{\max} = 513$ nm) at − 78 °C. This corresponds to a hypsochromic shift of the CT band of (1) by − 55 nm with decreasing temperature ($\Delta T = 156\,^{\circ}\mathrm{C}$).[23a] This temperature-dependent behaviour of solutions of (1) represents a new type of thermochromism ('negative thermo-solvatochromism'). It is obviously caused by the increased differential stabilization of the dipolar electronic betaine ground state, relative to its less dipolar excited state, with decreasing solution temperature (*cf.* Scheme 1). At low temperatures, the specific and non-specific intermolecular interactions between betaine and solvent molecules are strengthened, without any alterations of the chemical structure of (1). This is in contrast with already known types of thermochromism, which in most cases result simply from the temperature-dependent shift of a chemical equilibrium between a coloured and non-coloured species.

In conclusion, the lower the solution temperature, the higher the corresponding $E_{\mathrm{T}}(30)$ values, and the better the solvation capability of the solvent. That is, solvent polarity is temperature-dependent. This is a rather trivial statement, but thermochromic solutions of (1) allow a simple quantitative determination of this temperature dependence. Recently, the thermochromism of solutions of (1) in some binary solvent mixtures has been studied.[23b] In addition, the thiobetaine dye (4) exhibits an even larger thermochromic range than (1).[21] Since the thermochromic (and solvatochromic) UV/Vis absorption band of (4) [and (1)] lies within the visible range, the thermochromism of (4) [and (1)] can be easily visualized by means of simple test-tube experiments.[21,23]

4 Piezochromism of Betaine (1)

Application of external pressure to solutions of betaines (1) and (2) produces in all solvents used a hypsochromic shift of their long-wavelength CT absorption band.[24] For example, the UV/Vis absorption maximum of (1) in ethanol is shifted hypsochromically by − 27 nm (from $\lambda_{\max} = 547$ to 520 nm) by increasing the external pressure up to 10 kbar (9869 atm).[24c] This corresponds to an increase in the $E_{\mathrm{T}}(30)$-value of ethanol by 2.7 kcal mol^{-1}. Thus, solvent polarity is pressure dependent. The reason for this new type of piezochromism ('negative piezo-solvatochromism') lies again in the differential solvent-mediated stabilization of the dipolar electronic betaine ground state, relative to its less dipolar excited state (*cf.* Scheme 1), with increasing external pressure. The range of piezochromism is different from solvent to solvent. The pressure-dependent absorption energies of (1) and (2), dissolved in one solvent under study, correlate well with the dielectric function $(\epsilon - 1)/(\epsilon + 2)$ of this solvent, which also increases with compression.[26c] This seems to indicate that only non-specific betaine–solvent interactions contribute to the observed piezochromism, whereas any specific betaine–solvent interactions that occur are, to first order, constant with pressure – at least for the alcoholic HBD solvents used.[24c]

5 Halochromism of Betaine (1) and its Crown Ether Substituted Derivatives

Addition of salts (electrolytes, ionophores) to solutions of betaine dye (1) leads in most cases to a hypsochromic shift of its long-wavelength CT absorption band, depending on the nature and concentration of the salt added.[1,6,25] For example, the addition of KI, NaI, LiI, $\mathrm{BaI_2}$, $\mathrm{Ca(SCN)_2}$, and $\mathrm{Mg(ClO_4)_2}$ in excess to solutions of (1) in acetonitrile causes a differential hypsochromic band shift.[25b] This shift increases with this electrolyte order, that is with the increasing effective cation charge (*i.e.* ion charge/ion radius),[19,25b] whereas the anions seem to have little or no influence on this halochromism.[26] There exists even an almost linear correlation between the salt-induced hypsochromic shifts of (1) and the effective charge of the cations of the added alkali and alkaline earth salts, as shown in Figure 2.[19]

Generally, a CT absorption [as that of (1)] depends on the electron affinity of the electron-acceptor part (here the pyridinium moiety) and on the ionization energy of the electron-donor part (here the phenoxide group) of the light-absorbing molecule. Ion-pair association between the phenoxide group of (1) and the cations of the salts added increases the ionization energy of the electron-donor part for electrostatic reasons. This corresponds to an increase in CT excitation energy and is in agreement with the observed salt-induced hypsochromic shifts. A particularly strong betaine–ion association is to be expected with the lithium cation, the alkali ion with the highest effective charge. This is indeed the case, as has been shown recently by addition of $\mathrm{LiClO_4}$ to solutions of (1) in diethyl ether or tetrahydrofuran.[25d] The lithium ions act like Lewis acids towards betaine dye (1), making its CT absorption extremely sensitive to low concentrations of lithium ion. Because of this strong betaine–$\mathrm{Li^+}$

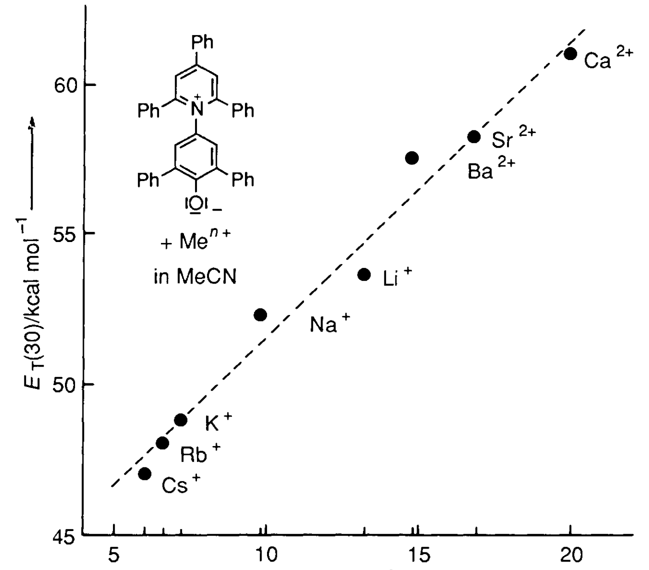


Figure 2 Correlation between the salt-induced change in the molar transition energy $E_T(30)$ of betaine dye (1), dissolved in acetonitrile at 25 °C, and the effective cation charge (= ion charge/Pauling radius) of the added alkali and alkaline earth salts (*i.e.* LiI, NaI, KI, RbI, and CsI, as well as CaI_2, SrI_2, and BaI_2).[19,29b] Effective cation radii: R. D. Shannon, *Acta Crystallogr., Sect. A*, 1976, **32**, 751. Correlation equation: $E_T(30) = 0.992[(n^+/r_{Me^{n+}}) \times 10^3] + 41.6$; pairs of values $n = 8$; correlation coefficient $r = 0.989$; standard deviation of the estimate $s = 0.85$.

interaction in non-polar solvents, one can consider the lithium ion essentially titrating the betaine dye, similar to its behaviour against Brønsted acids.[25d]

Are aqueous salt solutions more polar than pure water? The availability of the more hydrophilic, better water-soluble betaine dye (3) makes investigations of such aqueous electrolyte solutions possible.[6b] Addition of up to one mole salt to an aqueous solution of (3) results in small hypsochromic CT band shifts of 8—28 nm, which correspond to an increase in the $E_T(30)$ values of 0.8—3.9 kcal mol^{-1}, as shown in Figure 3. Obviously aqueous electrolyte solutions behave as more polar solvents than water against betaine dye (3). From the limited data shown in Figure 3, it is at present difficult to draw general conclusions about the influence of the various cations and anions on the extent of halochromism found in aqueous solution. It seems that in aqueous solution, cations with higher effective charges such as Mg^{2+} induce larger hypsochromic shifts than cations of lower charge density. Unfortunately, it is not possible to investigate aqueous solutions of (3) with salt concentrations higher than 1 M because the betaine dye is salted out. Better water-soluble pyridinium *N*-phenoxide betaine dyes are therefore needed.

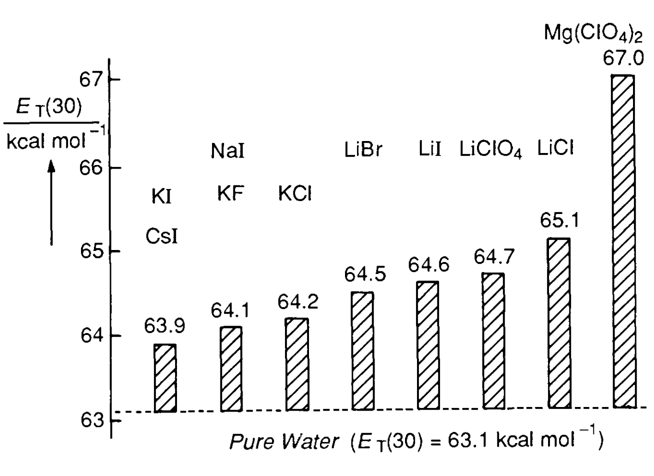


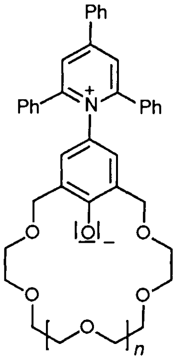
Figure 3 Increase in $E_T(30)$ of (1) for 1 M aqueous salt solutions, relative to the $E_T(30)$-value of pure water, determined by means of the secondary standard betaine dye (3).[6b]

Plots of $E_T(30)$ values for binary solvent mixtures as a function of their composition are mostly not linear – in some cases they exhibit even maxima and minima.[7—10] For the whole concentration range, the two-parameter equation 5 has been developed, describing the entire $E_T(30)$/concentration curve in closed form.[8] $E_T(30)$ and $E_T(30)°$ are the empirical solvent polarity parameters of the binary solvent mixture and of its pure, less polar component, respectively; c_p is the molar concentration of the pure, more polar component of the binary solvent mixture, and E_D as well as c^* are adjustable parameters specific for the binary mixture under study.[8] Equation 5 has been found valid for about 60 different binary solvent mixtures.[8]

$$E_T(30) = E_D \ln(c_p/c^* + 1) + E_T(30)^\circ \quad (5)$$

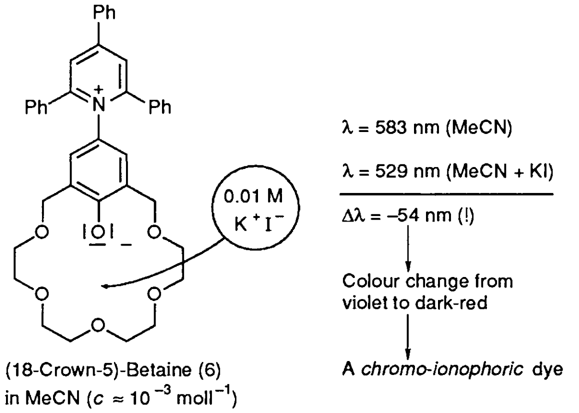
$$E_T(30) = A \ln(c/c^* + 1) + E_T(30)^\circ \quad (6)$$

It is now of particular interest to note that the polarity of electrolyte solutions can be treated in the same way as the polarity of binary solvent mixtures, the salt added being equivalent to the more polar solvent component.[8,25c] The polarity of an alcoholic electrolyte solution as a function of the salt concentration can be analogously described by equation 6, in which $E_T(30)$ and $E_T(30)°$ are the polarity parameters of the salt solution and of the pure solvent, respectively; c is the molar salt concentration; A and c^* are again adjustable parameters specific for the electrolyte solution under study.[25c] Equation 6 has been applied successfully to twenty combinations of salts and alcohols.[25c] That is, added inorganic salts behave as more polar 'co-solvents', at least in alcoholic electrolyte solutions. The validity of equation 6 for other, non-alcoholic salt solutions has still to be proven.

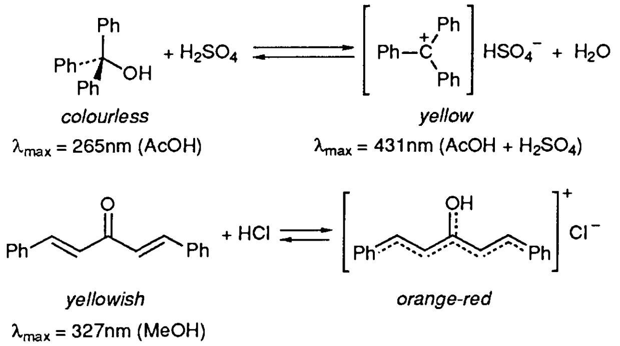


(5) $n = 0$
(6) $n = 1$
(7) $n = 2$

The halochromism-producing intermolecular betaine–cation interaction should be strengthened utilizing crown-ether substituted betaine dyes such as (5)—(7), which have been synthesized very recently.[27] This is indeed the case. For example, addition of potassium iodide to an acetonitrile solution of the [18]crown-5-betaine (6) causes a distinct colour change from violet to dark-red, which corresponds to a hypsochromic CT band shift of − 54 nm (Scheme 2).[27] The crown-ether substituted betaines (5)—(7) constitute a very sensitive, new class of so-called chromoionophoric dyes. Chromoionophores are dye molecules which contain chromophoric and ionophoric subunits. By the way, the chromoionophoric dyes (5)—(7) exhibit also a pronounced negative solvatochromism: a solvent-change from chloroform (λ_{max} = 668 nm) to water (λ_{max} = 433 nm) shifts the long-wavelength CT band of (6) hypsochromically by 235 nm![27]



Scheme 2



Scheme 3

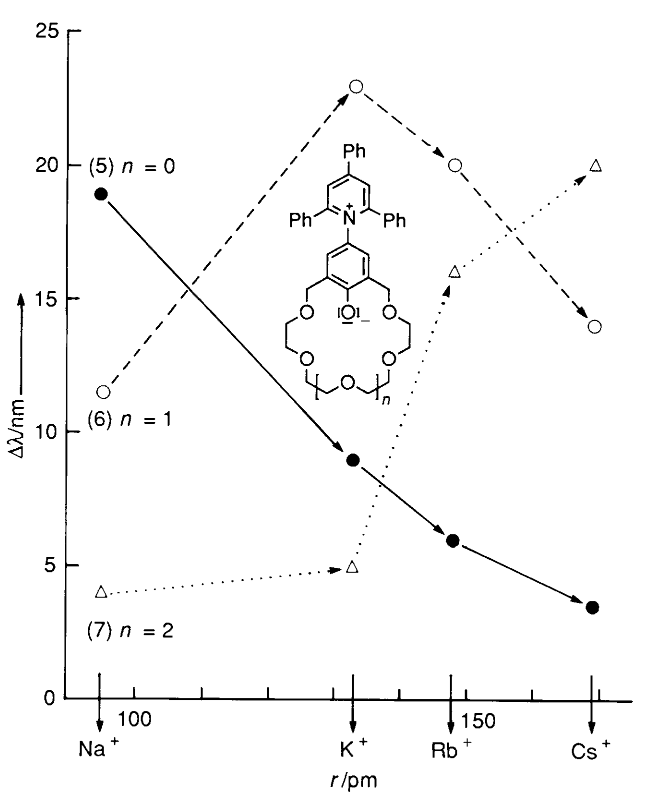


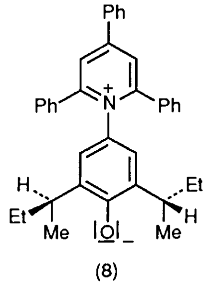
Figure 4 Cation-selective halochromism of (5)—(7) in methanol at 25 °C as function of the Pauling cation radius *r* of the alkali metal iodides NaI, KI, RbI, and CsI (betaine concentration *ca.* 10^{-3} M; salt concentration 10^{-2} M). $\Delta\lambda = \lambda_{max}$ (without salt) $- \lambda_{max}$ (with salt).[27]

Depending on the size of the crown-ether ring, the betaine dyes (5)—(7) show a definite cation-selective UV/Vis behaviour, as illustrated in Figure 4. From the dependence of the λ_{max}-shifts of (5)—(7), measured in methanol, on the size of the alkali metal ion of the iodide salt added, it follows that [15]crown-4-betaine (5) complexes preferably with Na^+, [18]crown-5-betaine (6) with K^+, and [21]crown-6-betaine (7) with Cs^+.[27] Treatment of Na^+-selective (5) in methanol with a mixture of Na, K, Rb, and Cs iodide, results in a hypsochromic band shift as if NaI alone were added. Addition of lithium and alkaline earth metal salts to solutions of (5)—(7) in methanol or acetonitrile leads to the disappearance of their long-wavelength, halochromic CT absorption band due to stronger betaine–cation complexation – similar to the effect of protonation.

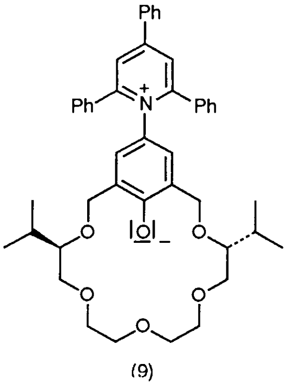
The halochromism of the betaine dyes (1), (3), (5)—(7), as mentioned before, constitutes a new type of 'genuine' halochromism.[6,27] The term 'halochromism' was first introduced by Baeyer and Villiger in 1902,[26] and was simply defined as the colour change of a dissolved compound on addition of acid or base, during which a chemical reaction transforms a colourless compound into a coloured one. Typical examples of this 'trivial' halochromism are the acid–base reactions given in Scheme 3.[26] In contrast to this trivial halochromism, the genuine halochromism of pyridinium *N*-phenoxide betaine dyes refers to a colour change on addition of an electrolyte to the dye solution, *not* accompanied by chemical change of the dissolved, halochromic compound. We have suggested the designation 'negative (positive) true halochromism' for a hypsochromic (bathochromic) shift of the UV/Vis absorption band of a dissolved substance on increasing electrolyte concentration (or increasing ionic strength), provided this shift is not caused by chemical alterations of the chromophore.[6,27]

6 Attempts at the Detection of Chiro-Solvatochromism

The extreme spectral sensitivity of pyridinium *N*-phenoxide betaine dyes to small changes in the surrounding solvation shell should make it possible to detect a phenomenon called by us chiro-solvatochromism, using chiral derivatives of these dyes, dissolved in pairs of enantiomeric, homochiral solvents.[28,29] That is, the formation of diastereomorphic solvates between chiral solvatochromic solutes [*e.g.* an (*S*)-configured chiral betaine dye] and pairs of enantiomorphic solvent molecules [*e.g.* (*R*)- and (*S*)-configurated alcohols such as octan-2-ol] ought to result in a shift of the solvatochromic UV/Vis absorption band of the chiral solute, as compared to its position in the corresponding racemic solvent. A recent review describes first attempts to differentiate UV/Vis-spectroscopically between enantiomorphic guest molecules by means of chiral crown-ether substituted dyes as optical sensors.[28]



(8)



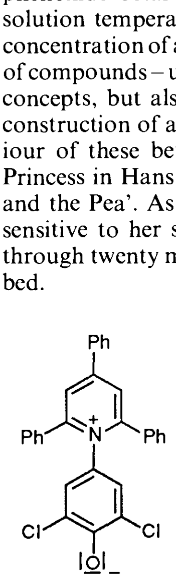
(9)

In order to be get such chiro-solvatochromic dyes, we have recently synthesized the chiral betaine dyes (8) and (9).[29] The negatively solvatochromic (*S*,*S*)-configurated s-butyl substituted dye (8) was prepared from homochiral (*S*)-(−)-2-methylbutan-1-ol (optically active amylalcohol from fermentation),[29a] and the (*R*,*R*)-[18]-crown-5-betaine dye (9) was obtained in a 10-step procedure from natural (*S*)-(+)-valine.[29b]

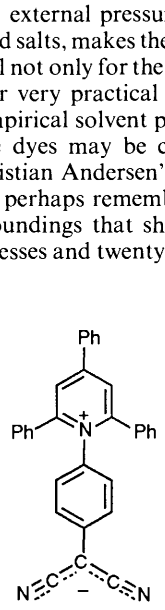
Disappointingly, solutions of these chiral betaine dyes in pairs of enantiomeric homochiral solvents such as butan-2-ol, octan-2-ol, neomenthol, 2-amino-butan-1-ol, and 1-phenylethylamine do not exhibit any chiro-solvatochromism, at least at room temperature. The small band shifts observed are within the limits of experimental error.[29] Further attempts to get chiro-solvatochromic betaine dyes are in progress.[20b,29b]

7 Concluding Remarks

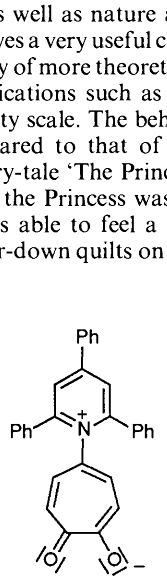
The outstanding sensitivity of the long-wavelength, intramolecular charge-transfer UV/Vis absorption of the pyridinium-*N*-phenoxide betaine dyes to small changes in solvent polarity, solution temperature, external pressure, as well as nature and concentration of added salts, makes these dyes a very useful class of compounds – useful not only for the study of more theoretical concepts, but also for very practical applications such as the construction of an empirical solvent polarity scale. The behaviour of these betaine dyes may be compared to that of the Princess in Hans Christian Andersen's fairy-tale 'The Princess and the Pea'. As one perhaps remembers, the Princess was so sensitive to her surroundings that she was able to feel a pea through twenty mattresses and twenty eider-down quilts on her bed.



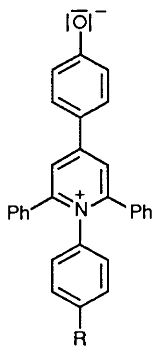
(10)



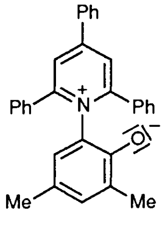
(11)



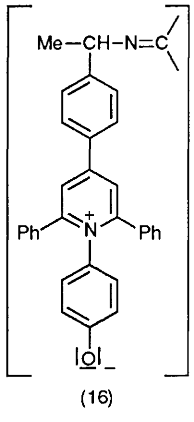
(12)



(13) R = Me
(14) R = OMe



(15)



(16)

Over the past few years attempts have been made to obtain further pyridinium *N*-phenoxide betaine dyes with special and improved properties. Other zwitterionic dyes such as (10)—(16) have been synthesized recently and investigated spectroscopically.[14,20,30] The chloro-substituted betaine dye (10) is less basic than (1) ($pK_A = 4.78$ for the corresponding acid) and is suitable as a solvent polarity probe in more acidic solvents.[14] The negatively solvatochromic dyes (11)[30a] and (12)[30b] seem to have an even larger solvatochromic range than (1), whereas the likewise negatively solvatochromic dyes (14)[30c] and (15)[20] exhibit a weaker solvatochromism than (1). Betaine dyes such as (15) have been tested for applications in non-linear optics such as second-harmonic generation (*i.e.* frequency doubling of laser radiation).[20b] Finally, the polymeric betaine dye (16) has been prepared, by polymerization of the corresponding isocyano-substituted monomer with $NiCl_2$, and is a promising candidate for the construction of polymeric photoconductors.[30d]

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