Solute/solvent interactions and their empirical determination by means of solvatochromic dyes

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Abstract: The solvatochromism, thermochromism, piezochromism, halochromism, and potential chiro-solvatochromism of solutions of various pyridinium N-phenoxide betaine dyes have been used by us and others to study UV/Vis-spectroscopically the dye/solvent interactions in organic solvents of different polarity, different temperature, different external pressure, different electrolyte concentration, and different chirality.

INTRODUCTION

Solvents can have a strong influence on reaction rates, on the position of chemical equilibria, as well as on the position and intensity of spectral absorption bands located in various spectroscopic regions (UV/Vis, IR, NMR, etc.). Today, this is well-known to all chemists since the pioneering work of Berthelot and Saint-Gilles (Paris 1862) as well as Menschutkin (St. Petersburg 1890) on solvent effects on reaction rates, and of Claisen (Aachen 1896), Hantzsch (Würzburg 1896), Knorr (Jena 1896), and Wislicenus (Würzburg 1896) on the solvent dependence of chemical equilibria (e.g. tautomeric equilibria) (ref. 1). For example, the S_N1 solvolysis of 2-chloro-2-methylpropane is ca. 10^{11} times faster in water than in the less polar solvent benzene. The enol content of ethyl acetoacetate is 62 mol-% in cyclohexane, but only 6.5 mol-% in water (ref. 1).

Chemists have usually attempted to understand solvent effects in terms of the 'polarity of the solvent'. But what does solvent polarity really mean ? The simplicity of idealized electrostatic models for the description of solvation of ions or dipolar molecules, considering solvents as a non-structured continuum, has led to the use of the relative permittivity (ε_r), the permanent dipole moment (μ), and the refractive index (n) – or functions thereof – as macroscopic, physical solvent polarity parameters. But solute/solvent interactions take place on a molecular-microscopic level, with individual solvent molecules surrounding the ions or molecules of the solute. Therefore, the simple electrostatic approach often failed because intermolecular forces between solute and solvent include in addition to the nonspecific coulombic, directional, inductive, and dispersion interactions also specific interactions such as hydrogen bonding, electron-pair donor (EPD)/electron-pair

acceptor (EPA), and solvophobic interactions. Hence, from a more pragmatic point of view, it seems to be more favorable to define 'solvent polarity' as the **overall solvation capability** (solvation power) for (i) reactants and products (⟶ chemical equilibria), (ii) reactants and activated complexes (⟶ reaction rates), and (iii) molecules in the electronic ground and excited state (⟶ light absorption), which in turn depends on the action of **all** possible, nonspecific **and** specific, intermolecular interactions between solute and solvent molecules - excluding such interactions leading to definite chemical alterations of the solute molecules by the solvent as consequence of a normal chemical reaction between them (refs. 1, 2).

Obviously, solvent polarity such defined cannot be measured by means of macroscopic, physical parameters such as permittivity or dipole moment. Other indices of solute/solvent interactions on a molecular-microscopic scale are sought. For this reason, empirical parameters of solvent polarity have been introduced, using a well-selected, strongly solvent-dependent, particular chemical reaction (the rate or equilibrium of which are studied) or spectral absorption as suitable models for all other solvent-dependent processes. If one carefully selects an appropriate, sufficiently solvent-dependent reference process (or similarity model; cf. ref. 3), an empirical measure of solvent polarity can be derived from it, which is believed to provide a more comprehensive measure of the overall solvation capability of the solvents than do their individual physical data.

K. H. Meyer (Munich 1914) introduced the so-called **desmotropic constant L** as empirical measure of the enolization capability of solvents, using the solvent-dependent tautomerization of ethyl acetoacetate as reference reaction (ref. 4), whereas Winstein and Grunwald (Los Angeles 1948) developed the **Y-values** as measures of the solvent ionizing power, with the S_N1 solvolysis reaction of 2-chloro-2-methylpropane as standard reaction (ref. 5). Meanwhile, a considerable number of empirical solvent parameters have been introduced, based on various solvent-dependent reactions and absorptions (refs. 1 - 3, 6 - 9), sometimes combined to multiparameter correlation equations with different empirical parameters for the various solute/solvent interactions (refs. 1, 10, 11).
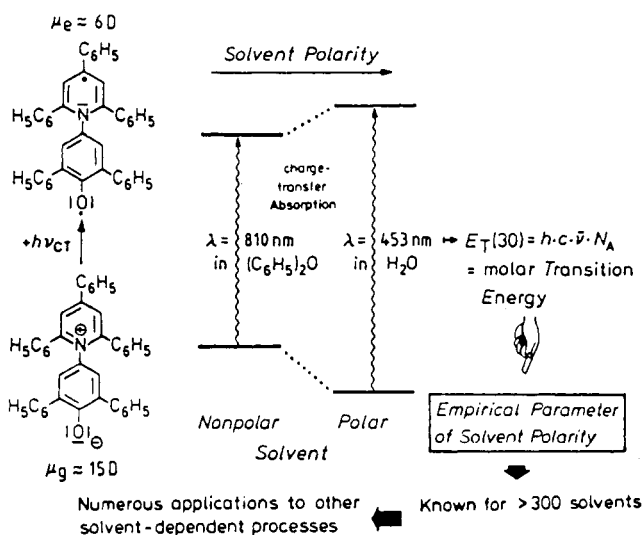

Fig. 1. Qualitative representation of the solvent effect on the CT absorption of betaine dye 3 ($\mu_g > \mu_e$) and the definition of $E_T(30)$ values as molar transition energies.

SOLVATOCHROMIC BETAINE DYES

The first suggestion that solvatochromic dyes such as the zwitter-
ionic 4-hydroxystyryl-pyridinium dye **1** can serve as empirical
indicators of solvent polarity was made by Brooker et al.
(Rochester 1951; ref. 12), but Kosower (New York 1958) was the
first to set up a real UV/Vis spectroscopic solvent scale, called
Z-scale, based on the intermolecular charge-transfer (CT) absorp-
tion of the 4-methoxycarbonyl-1-ethylpyridinium iodide **2** as
solvent-sensitive reference process (ref. 13). By virtue of its
exceptionally large negative solvatochromism, the 2,6-diphenyl-4-
(2,4,6-triphenyl-1-pyridinio)-phenolate **3** (and its more lipo-
philic, even in hydrocarbons soluble penta-tert-butyl-substituted
derivative **4**) has been proposed by us as a new spectroscopic indi-
cator of solvent polarity (Marburg 1963; refs. 14 - 16), called
the $E_T(30)$-**scale** (ref. 17 and Fig. 1).
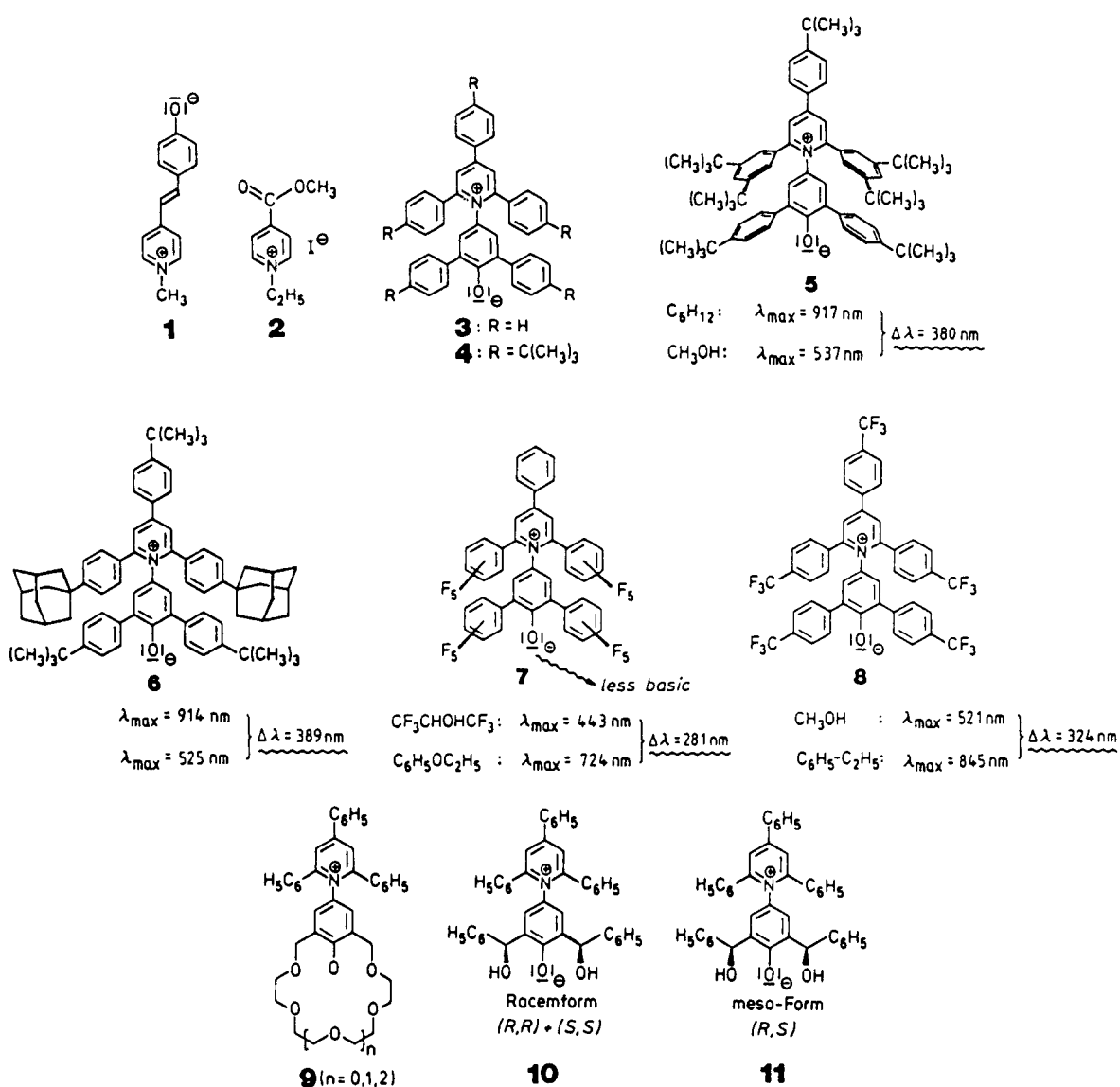
Scheme 1. Negatively Solvatochromic Dyes 1 - 11
(1: Brooker; 2: Kosower; 3 - 11: Reichardt)

The following peculiar properties of 3 are obviously responsible for the solvent-mediated stabilization of its highly dipolar electronic ground state, relative to its less dipolar excited state, the latter resulting from an intramolecular charge transfer by light absorption within the visible spectral region (cf. Fig. 1): (i) it exhibits a large permanent dipole moment, suitable for the registration of dipole/dipole and dipole/induced dipole interactions; (ii) it possesses a large polarizable π-electron system suitable for the registration of dispersion interactions; and (iii) with the phenoxide oxygen atom it exhibits a highly basic electron-pair donor centre, suitable for interactions with weak Brönsted acids (H-bonding) and Lewis acids (EPD/EPA-bonding). The positive charge of the pyridinium moiety is delocalized and sterically shielded. Therefore, the CT absorption of 3 depends strongly on the electrophilic solvation power of the solvents, i. e. on their HBD ability and Lewis acidity (= EPA behaviour), rather than on their nucleophilic solvation capability (= EPD behaviour).

$E_T(30)$-values are simply defined as molar transition energies (in kcal/mol) of betaine dye 3, dissolved in the solvent under study (cf. Figs. 1 and 2). A high $E_T(30)$-value corresponds to high solvent polarity. $E_T(30)$-values range from 30.7 for tetramethylsilane (the least polar solvent) up to 63.1 kcal/mol for water the most polar solvent); they are known for more than 300 organic solvents and numerous binary solvent mixtures (ref. 1). Only for two groups of solvents are $E_T(30)$-values not directly available: acidic solvents and perfluorohydrocarbons. In acidic solvents, dye 3 is protonated and the solvatochromic CT absorption band disappears, and in perfluorohydrocarbons the betaine dyes 3 and 4 are not soluble. In order to increase the betaine solubility in nonpolar solvents, the lipophilic hepta-tert-butyl-substituted dye 5 and the bis-(1-adamantyl)-tris-tert-butyl-substituted dye 6 as well as the 'fluorophilic' eicosafluoro-substituted dye 7 and the penta-trifluoromethyl-substituted dye 8 have been recently synthesized (ref. 18). Unfortunately, all four betaine dyes 5-8 are not soluble in perfluorohydrocarbons such as perfluorooctane and perfluorodecalin. However, the introduction of electron-withdrawing groups reduces the basicity of the phenoxide oxygen and permits the direct determination of E_T-values of 7 in slightly acidic solvents such as hexafluoro-2-propanol. By means of a particular
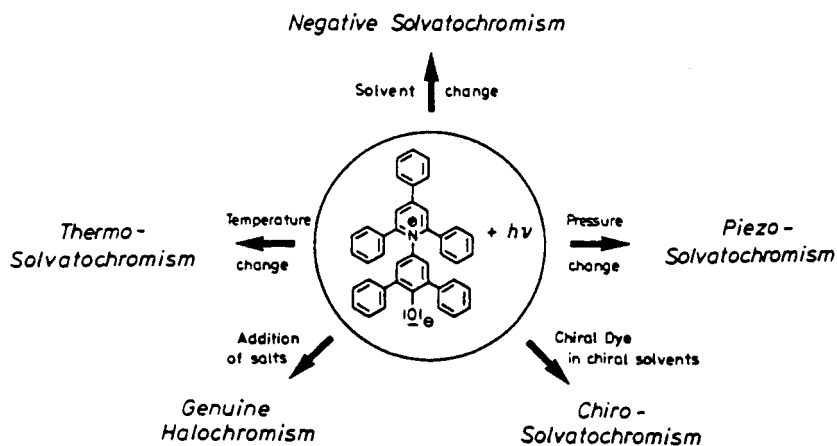

Fig. 2. Different responses ('chromisms') of betaine dye 3 to various environmental changes (i.e. solvent, temperature, external pressure, addition of salts, chiral solvents).

dilution technique, $E_T(30)$-values of **3** for 55 substituted phenols have been directly obtained (ref. 19). On the other hand, the solubility of betaine dye **3** in water is also very low ($< 2 \cdot 10^{-6}$ mol/l). Therefore, by introduction of hydrophilic substituents (e.g. $CO_2^- Na^+$, SO_2CH_3) into **3**, its solubility in water has been slightly increased (ref. 20). Quite recently, a reasonable estimate for the $E_T(30)$-value of betaine dye **3** as isolated molecule in the gas phase (= 27.1 kcal/mol) has been made (refs. 14b, 21).

The empirical solvent polarity parameter $E_T(30)$ has found manifold applications some of which are compiled in Scheme 2. The application of the $E_T(30)$-values to chemical reactivity (ref. 22) and analytical chemistry (ref. 23) has been reviewed.

In addition to its negative solvatochromism, pyridinium N-phenoxide betaine dyes such as **3** exhibit also the phenomena of thermosolvatochromism, piezo-solvatochromism, genuine halochromism, and possibly chiro-solvatochromism, as schematically shown in Fig. 2. (ref. 16). That is, the position of the long-wavelength CT absorption band of dissolved **3** depends on the solution temperature (ref. 24), on external pressure (ref. 25), on the addition of salts (ref. 20b, 26), and, in the case of chiral betaine dyes such as **10** and **11** possibly on the configuration of enantiomerically pure solvents in which they are dissolved (ref. 27).
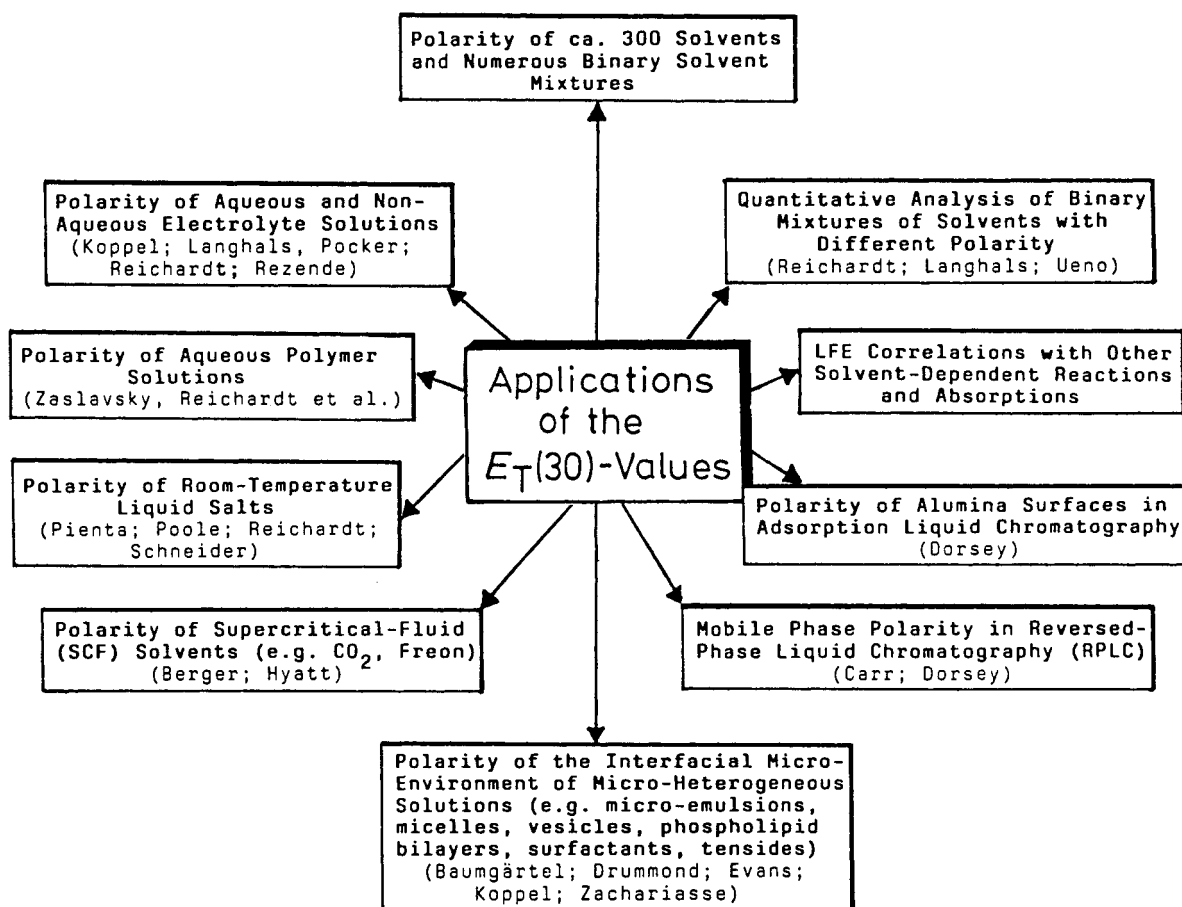
Scheme 2. Applications of $E_T(30)$-values

Are aqueous or nonaqueous electrolyte solutions more polar than the pure solvents ? The addition of salts to solutions of betaine dye **3** causes hypsochromic shifts of its solvatochromic CT absorption band, corresponding to an increase of the $E_T(30)$-value. For example, the addition of LiI, NaI, KI, RbI, CsI, CaI$_2$, SrI$_2$, and BaI$_2$ to solutions of **3** in acetonitrile leads to a differential hypsochromic band shift with this electrolyte (ionophore) order, i.e. with increasing charge density (= ion charge/Pauling cation radius) of the cation (ref. 26a). The hypsochromic shifts are concentration-dependent, they increase with increasing salt concentration, Surprisingly, there exists a linear correlation between the $E_T(30)$-values of the electrolyte solutions studied and the charge density of the cations of the salts added, as shown in Fig. 3. Obviously, loose ion-pair formation between the phenoxide oxygen atom and the metal cation increases the ionization energy of the electron-donor moiety of **3**, whereas the electron-acceptor part of **3** (the pyridinium moiety) remains unchanged (no association with the anion of the salts added). As result, the intramolecular CT absorption band is hypsochromically shifted, corresponding to an increase in the $E_T(30)$-value and, hence, to an increase of the polarity of the solvent by the addition of salts.
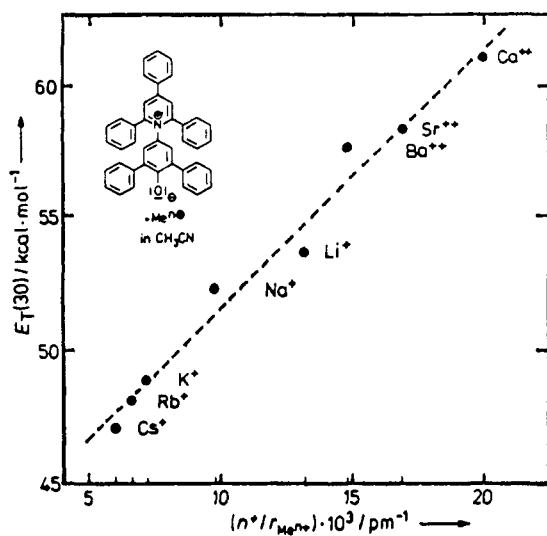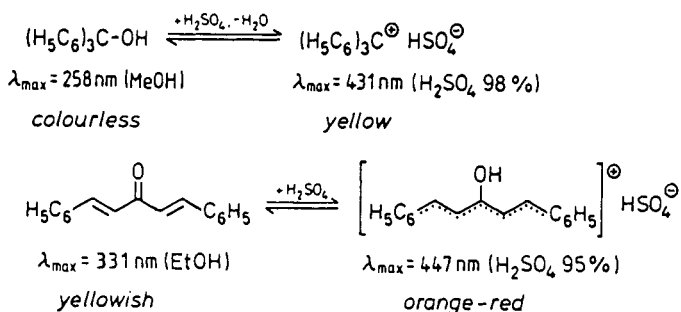

Fig. 3. Linear correlation between $E_T(30)$ of betaine dye **3**, measured in acetonitrile, after addition of an excess of salt, and the effective charge of the respective metal cation M^{n+} of the salt added (slope = 0.992; r = 0.989) (ref. 26a).

The salt-dependent solution spectra of **3** constitute a new type of genuine halochromism, in contrast to the trivial halochromism first found by Baeyer and Villiger (Munich 1902). Examples of this trivial halochromism are acid/base reactions in solution in which a colourless reactant forms a coloured product during a chemical reaction, as shown in Scheme 3. The genuine halochromism of **3**, however, is produced without any chemical alteration of the halochromic dye ! We have recently proposed to speak of negative (positive) genuine halochromism then only when the UV/Vis absorption band of a dissolved compound is hypsochromically (bathochromically) shifted on addition of an electrolyte, and when this band shift is not accompanied by a chemical alteration of the chromophore (refs. 20b, 26a).

„Trivial" Halochromism

A. Baeyer, V. Villiger, Ber. Dtsch. Chem. Ges. **35** (1902) 1189; *e.g.*

$(H_5C_6)_3C-OH$ $\xrightleftharpoons{+H_2SO_4, -H_2O}$ $(H_5C_6)_3C^{\oplus} \ HSO_4^{\ominus}$

$\lambda_{max} = 258\,nm\ (MeOH)$ $\qquad \lambda_{max} = 431\,nm\ (H_2SO_4\ 98\,\%)$

colourless $\qquad\qquad$ *yellow*

$H_5C_6\diagdown\diagup\diagdown\!\!\overset{\overset{\displaystyle O}{\|}}{\diagup}\!\!\diagdown\diagup C_6H_5$ $\xrightleftharpoons{+H_2SO_4}$ $\left[H_5C_6\diagdown\diagup\diagdown\overset{\overset{\displaystyle OH}{|}}{\diagup}\diagdown\diagup C_6H_5 \right]^{\oplus} HSO_4^{\ominus}$

$\lambda_{max} = 331\,nm\ (EtOH)$ $\qquad\qquad \lambda_{max} = 447\,nm\ (H_2SO_4\ 95\%)$

yellowish $\qquad\qquad\qquad$ *orange-red*

Scheme 3. Examples for the 'trivial' halochromism of Baeyer.

A particular cation-selective genuine halochromism has been recently observed in solutions of the new crown-ether substituted betaine dyes **9**. As shown in Fig. 4, addition of sodium iodide to a solution of **9** (n = 0) in acetonitrile leads to a family of curves which meet at an isosbestic point. For [**9** (n = 0) + Na^+I^-] in acetonitrile, the complex formation constant K_c amounts to ca. 8008 $(mol/l)^{-1}$. As shown in Fig. 5, addition of 0.01 M potassium iodide to a 0.001 M solution of **9** (n = 1) in acetonitrile gives rise to a colour change from violet to dark-red. Again, an enforced ion-pair formation between alkali metal cation and the phenoxide part, supported by the crown-ether ring, is responsible for this rather large halochromic shift of the intramolecular CT band of **9**. This negative halochromism depends on the radius of the cation of the added salt as well as on the size of the crown-ether ring. Therefore, the new betaine dyes **9** represent a new class of cation-selective chromo-ionophores, possibly useful as cation indicators (ref. 26b).
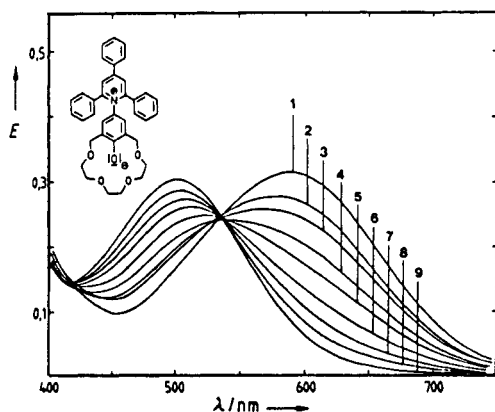
Fig. 4. UV/Vis spectra of dye **9** (n = 0), measured in acetonitrile before (curve 1) and after addition of increasing amounts of NaI (curves 2 - 9); Isosbestic point at ca. 534 nm (ref. 26b).
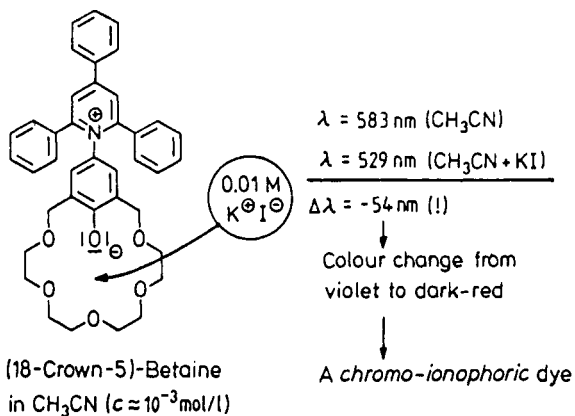
$\lambda = 583\,nm\ (CH_3CN)$

$\lambda = 529\,nm\ (CH_3CN + KI)$

$\Delta\lambda = -54\,nm\ (!)$

Colour change from violet to dark-red

A *chromo-ionophoric* dye

(18-Crown-5)-Betaine in CH_3CN ($c \approx 10^{-3} mol/l$)

Fig. 5. The halochromic betaine dye **9** (n = 1) as cation (potassium) selective indicator (chromo-ionophore) (ref. 26b).

Finally, the racemic betaine dye **10** and its achiral counter-
part **11** (meso-Form) should be able to form diastereomorphic sol-
vates in pairs of homochiral solvents [e.g. (R)- and (S)-butane-
1,2-diol], giving rise to a phenomenon called chiro-solvatochromism
(ref. 27, 28). The first preliminary results with such chiral
betaine dyes are promising (ref. 27).

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