

Solvatochromism of Intramolecular Charge-Transfer Dyes

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Solvatochromism can be defined as the phenomenon whereby a compound changes color, either by a change in the absorption or emission spectra of the molecule, when dissolved in different solvents. Solvatochromic effects are best monitored by means of UV/VIS spectroscopy. A hypsochromic shift of the UV/VIS absorption band, with increasing solvent polarity is usually called "negative solvatochromism". The corresponding bathochromic shift, with increasing solvent polarity is termed "positive solvatochromism".

1. Indophenol Dye

Indophenol dyes are blue in color and are typical donor-acceptor chromogens. The indophenol dye can be prepared by condensing α -naphthol with *p*-nitroso-dimethylaniline, or by the oxidation of a mixture of α -naphthol and *p*-aminodimethylaniline. For the basic structure of indophenol, the π -electron density changes accompanying the 1st transition are shown in Fig 1. Intramolecular charge-transfer(CT) chromophores can be defined as chromophores in which movement of π -electron density from the donor to acceptor accompanies the 1st excitation. The electronic absorption spectra of indophenol were observed in various solvents. The absorption maximum wavelength of the CT band shifted from 533 nm (in Hexane) to 593 nm (in Ethanol). In this present work, reasonably linear plots were obtained on plotting λ_{\max} versus the solvent parameter E_T (Fig. 2). As the solvent polarity increased, a bathochromic shift was observed (i.e, positive solvatochromism).

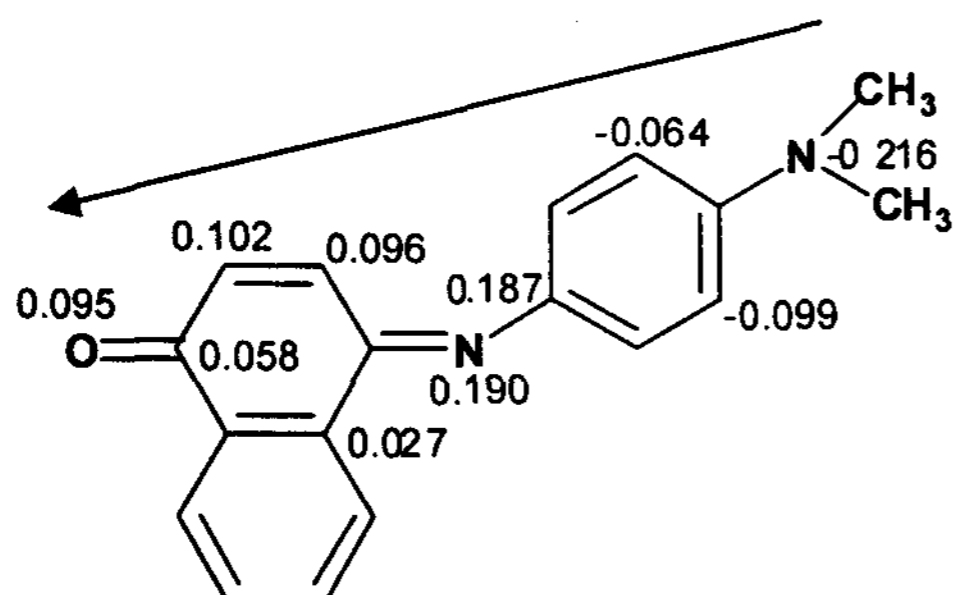


Fig. 1. π -electron density changes for 1st excitation.

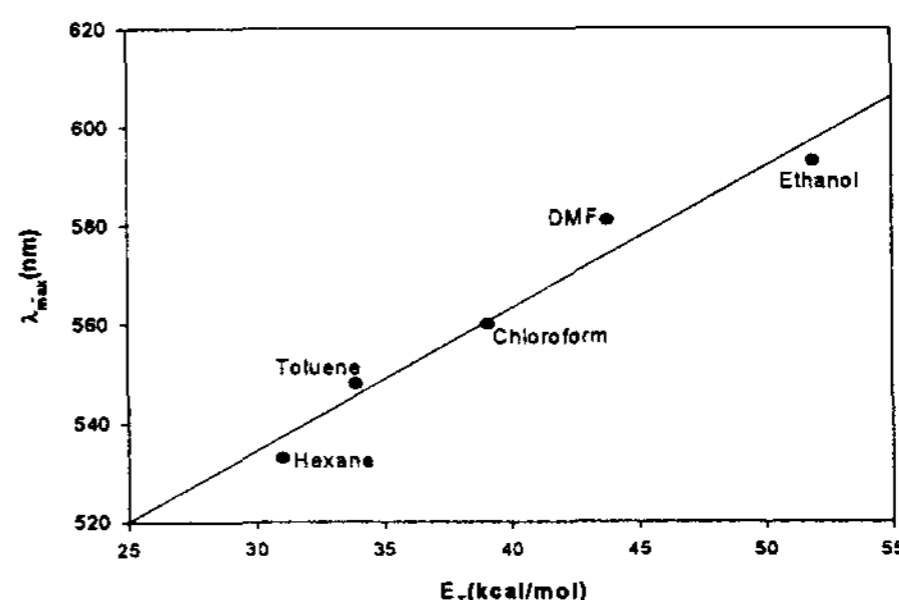
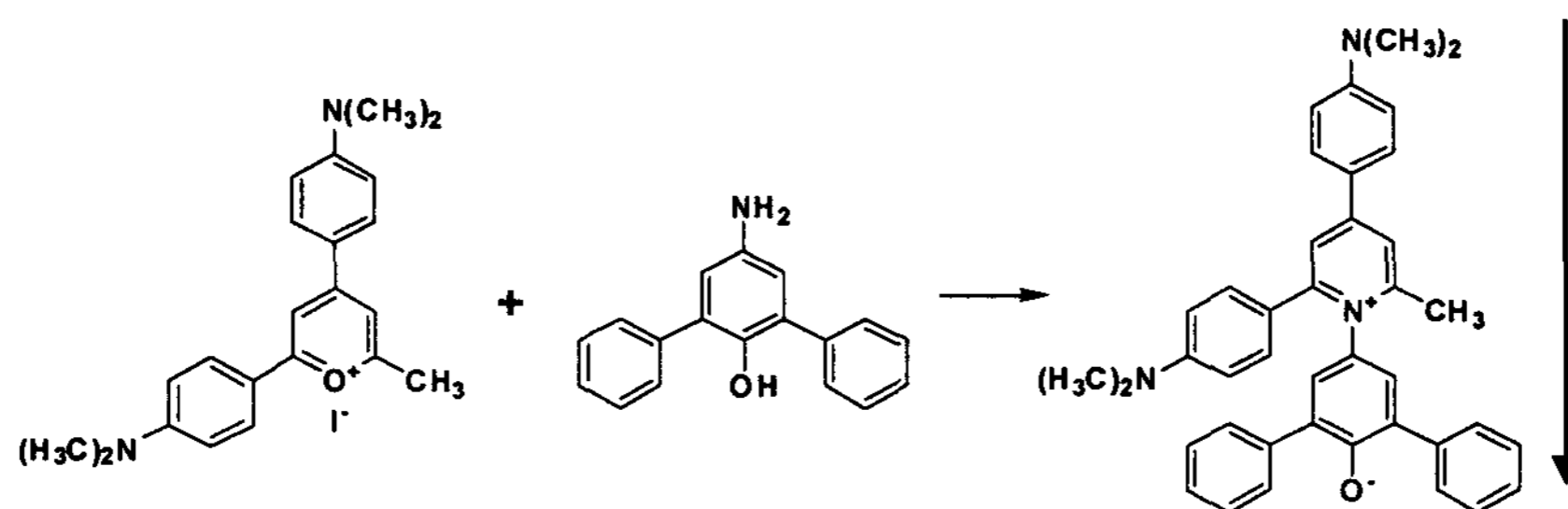


Fig. 2. Plots of λ_{\max} vs. E_T value in various solvents.

2. New Pyridinium N-Phenolate Betain Dye

Solutions of the pyridinium N-phenolate betain dyes are solvatochromic and frequently used to determine the polarity of the medium experimentally. Herein, we designed and synthesized a new pyridinium N-phenolate betain dye. The key step in the synthesis of pyridinium N-phenolate betain dye is the condensation reaction between 2-methyl-4,6-bis-(4-N,N-dimethylaminophenyl) pyrylium and 4-amino-2,6-diphenylphenol.



Betaine dye reflects environmental influences by shifts of its absorption as well as emission band. A large dipole moment of 17.24 debye was calculated in the ground state, which is much larger than the 5.69 debye value of 1st excited state. Betaine dye exhibits extreme negative solvatochromism on going from ethyl acetate to methanol as solvents, the absorption band of dye is hypsochromically shifted by $\Delta\lambda=291$ nm, comparable to that of the standard Reichardt's dye ($\Delta\lambda=227$ nm).

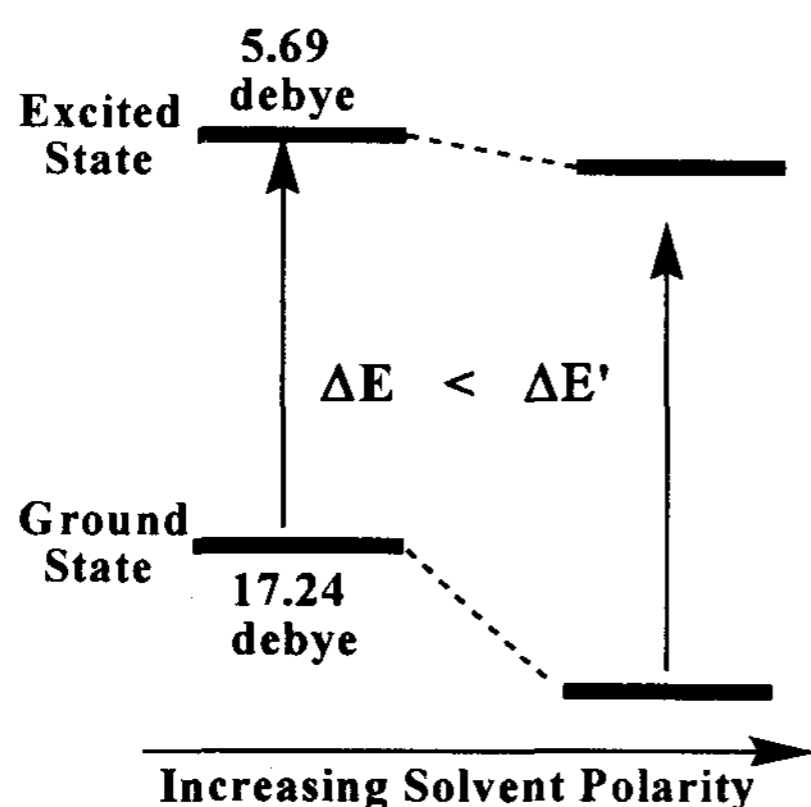


Fig. 3. Effect of solvent polarity on the transition energy of betaine dye.

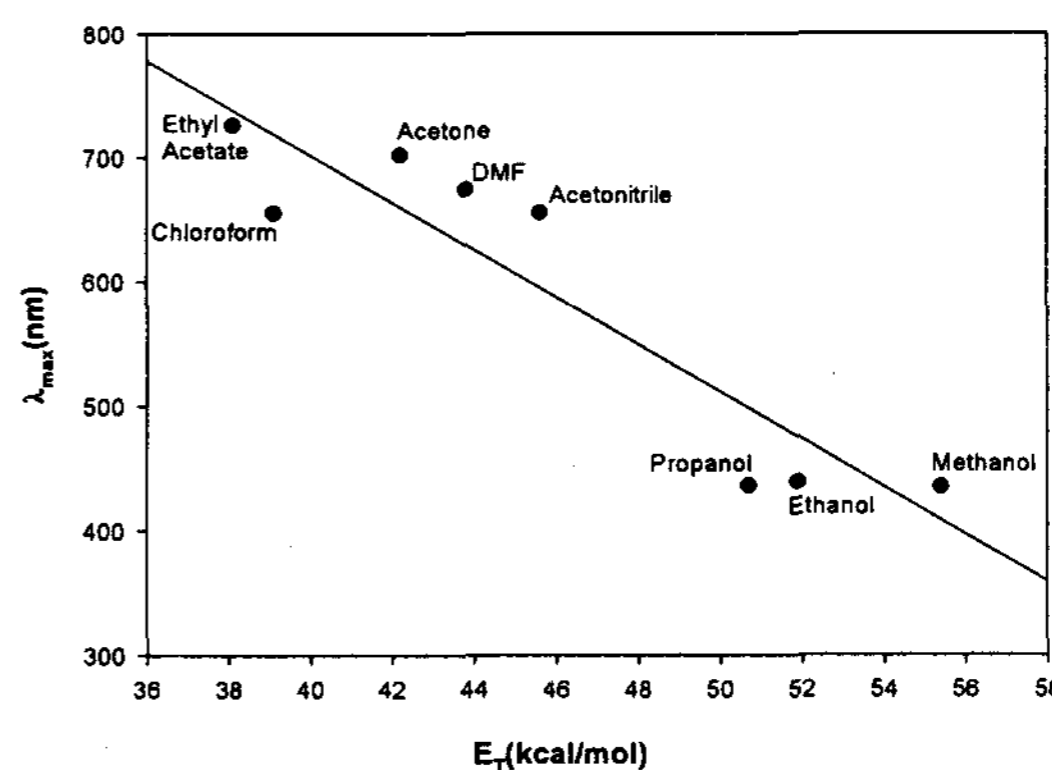


Fig. 4. Plots of λ_{\max} vs. ET value in various solvents.

References

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