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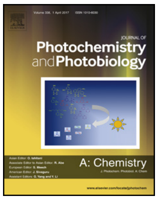

Refractive index dependence of solvatochromism

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ABSTRACT

Refractive index (n) function $\phi(n^2)$ ($\phi(n^2) = (n^2-1)/(n^2+2)$) stands for average electronic polarizability density of the matter. Sets of nonpolar and highly polar ($\varepsilon \geq 25$) liquids were used in parallel for recording the $\phi(n^2)$ dependence of absorption and fluorescence spectra of several push-pull chromophores. Fluorescence maxima of Nile Red (NR) and laser dye 4-dicyanomethylene-2-methyl-6-(p-dimethylaminostyryl)-4H-pyran (DCM) shift much less in polar solvents (coefficient corresponding to the sensitivity to $\phi(n^2)$, $p \sim -4000\,\mathrm{cm}^{-1}$). Fluorescence in nonpolar solvents, as well as absorption in both solvent sets has almost constant and much larger p of $\sim -8000\,\mathrm{cm}^{-1}$. Similarly, zwitter-ionic Betaine 30 has also different p values in nonpolar and highly polar media for absorption (Renge, J. Phys. Chem. A 114 (2010) 6250). The $\phi(n^2)$ dependent induction shift is a function of solute dipole moments squared ($\mu_g^2 - \mu_e^2$). This shift is suppressed in polar environment, if the dipole of the initial state is large (μ_e for fluorescence, μ_g for absorption), in qualitative agreement with Li theory of non-equilibrium solvation (Huang et al., J. Theor. Comput. Chem. 5 (2006) 355). As compared to absorption, conspicuous fluorescence bandwidth narrowing by a factor of ~2 takes place in highly polar liquids for NR and DCM. The unusual narrowing indicates a dramatic molecular structure change in the excited state affecting the Franck-Condon factors for vibronic coupling. The reaction field created by the large dipole of solute in polar liquid exceeding 10^9 V/m can modulate the bond alternation in a conjugated polymethine system. Dipole moments μ_g, μ_e and the polarizability difference $\Delta\alpha$ were estimated for NR as 14 ± 3 D, 18 ± 3 D, and $38 \pm 10\,\text{Å}^3$, respectively. Finally, a set of guidelines for solvatochromic data assessment is proposed.

1. Introduction

The effect of refractive index (n) on (bio)chemical reaction rates and equilibria is usually much weaker than the influence of polarity. Compared to the full scale of static dielectric constant ε, the high frequency contribution n^2 to ε spans over a limited range of 1.8–2.4 in common liquids. However, in the processes involving electronically excited states the solvent polarizability dependent dispersion and polarization (induction) forces can be prominent. Solvatochromic shift of UV–vis spectra originates from the difference in ground state (g) and excited state (e) properties, mainly the polarizability (α) and dipole moment (μ) of the solute. The dispersive part of shift arises from $\Delta\alpha$ ($\Delta\alpha = \alpha_e - \alpha_g$), and the induction (polarization of solvent by solute dipole) from a difference $\mu_g^2 - \mu_e^2$. The absorption and luminescence energies are linearly related to solvent polarizability density characterized by function $\phi(n^2)$ ($\phi(n^2) = (n^2-1)/(n^2+2)$). If the solubility permits, band shifts are easy to follow in nonpolar liquids from n-pentane ($n = 1.36$) to n-hexadecane ($n = 1.43$) [1–4]. In spite of narrow fitting range, the regression line extrapolates remarkably precisely to transition energy for free, nonsolvated molecules [3]. This very fact means that the Lorentz-Lorenz function $\phi(n^2)$ is a correct expression for polarizability density of environment that interacts with the polarizability and dipole moment of solute.

The "pure" refractive index dependence can be studied either in non(di)polar solvents where $n^2 \sim \varepsilon$, or, alternatively, in highly polar liquids ($\varepsilon > 25$) where the dipole-dipole interaction saturates. Aprotic, highly polar solvents were utilized to estimate $\Delta\alpha$ for cyanines and oxonols, since ionic dyes are soluble only in solvents with high ε [4]. It is usually assumed that both dispersion and induction shifts remain the same in absorption and fluorescence, and, moreover, independent on polarity ε. Still, nontrivial exceptions can occur. Evidence is accumulating that the Franck-Condon profile in the vibronic absorption spectra can vary between the gas and liquid phase [5], and also in different solvents [6,7]. As a rule, spectra gradually lose vibronic structure with increasing polarity (and temperature) due to broadening. Sometimes the spectral contour can have smaller full-widths at half-maximum (fwhm) in polar solution [5]. Substantial narrowing has been

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documented in fluorescence of several dyes [8,9], pointing to electronic structure change of the chromophore system, self-inflicted by the high reaction field strength of solute dipole in (di) polar environment.

Spectral transformations extending beyond trivial broadening would mean that the solute-solvent interaction is no longer described with dipole moments and polarizabilities as molecular constants [10]. Thus, comparative measurements of absorption and emission shifts as a function of $\phi(n^2)$ in apolar and polar solvents would be of considerable interest. This work will focus on solvatochromism in highly polar, aprotic solvents with $\varepsilon > 25$ [3,4]. Additional sets of solvents will be applied for reference. Monofunctional solvents, obeying the point dipole model of Onsager are used for the polarity dependence to estimate μ_g and μ_e. Solvent polarizability and polarity effects are formally separated by bilinear regression analysis applied to combined sets of alkanes and well-behaving polar liquids. A procedure was adopted for determination of effective polarity ε' [11], basing on Ref. [12], instead of using the difference $\phi(\varepsilon) - \phi(n^2)$ of doubtful validity [12–14]. Besides dispersive and electrostatic interactions, extra solvatochromic shifts in protic and aromatic environments were revealed for Nile Red absorption [15].

2. Experimental

Nile Red (NR, Phenoxazone 9) and 4-dicyanomethylene-2-methyl-6-(*p*-dimethylaminostyryl)-4H-pyran (DCM) (Fig. 1) were purchased as laser dyes from Lambda Physik (Göttingen). Solvents of high purity were provided by Aldrich. Liquids were dehydrated by Drierite® and 3 Å molecular sieves if necessary. Absorption spectra are recorded on a Jasco V-570 UV/VIS/NIR Spectrophotometer at 295 K in 1 and 10 mm path length silica cells. The instrument was calibrated with 536.5 nm line of 0.25 M $HoCl_3$ in 0.1 M aqueous HCl [16], and found reproducible within 0.1 nm, with the systematic error not exceeding 0.5 nm. Fluorescence spectra were run on Horiba scientific Fluoromax-4 Spectrofluorometer in 10 mm cells for diluted solutions with absorbance not exceeding 0.1 at excitation band maximum. Spectra were recorded in wavelength scale and not corrected for the refractive index of air (0.14 nm or $-5.6\,\text{cm}^{-1}$ at 500 nm).

3. General considerations

3.1. Continuous dielectric approaches to solvatochromism

Starting from early fifties our understanding of solvent effects on optical spectra has been evolving rather slowly [17–43]. Extensive use of quantum theory by several authors [19–21,30,33,36], as well as elaborations on theory of dielectrics by others [23,29] has lent the complicated equations an appearance of completeness. However, the usable expressions boil down to the simplest approximations in terms of Onsager theory [23,25–29,39]. About a dozen leading authors often disagree with each other in important points, and the papers, reviews [29,30,32,34,36,39,42,43], and several books [22,27,41] form an entangled detective story. A number of contradictions is still pending. As a rule, we have handled the theoretical formulas as (semi)empirical ones [3–5,11,44–48].

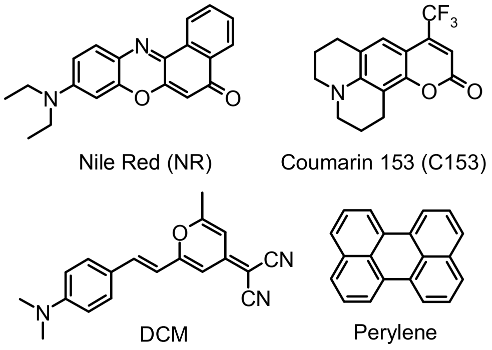

Fig. 1. Chemical structure of chromophores.

The interaction between solute and solvent molecules treated as polarizable dipoles involves four obvious energy contributions: dispersion, polarization of solute by solvent dipole, induction (polarization of solvent by solute dipole), and the interaction between the dipoles [18,22,25]. We hasten to mention that the influence of polarization of (nonpolar) solute by the "cavity field" of polar solvent [12,31,32] is perhaps smaller than the higher order reaction field effects [40,45], and will be neglected in this communication. As for three remaining "interactions", the induction and dipole components are referred to as electrostatic, besides a joint dispersion/repulsion interaction that was commented upon on several occasions [3,5].

The dispersion and induction spectral shift components depend on solvent polarizability density, defined by the Lorentz-Lorenz function $\phi(n^2)$ of refractive index n ($\phi(n^2) = (n^2 - 1)/(n^2 + 2)$), on one hand, and on polarizability change upon excitation $\Delta\alpha$ and the difference of squared dipole moments $(\mu_g{}^2 - \mu_e{}^2)$ of the solute, on the other hand. The formula for dispersive solvent shift introduced first by Bakhshiev [25,26] has been calibrated using $\Delta\alpha$ values from electrochromism [4]. The poorly defined cubed interaction radius $a_0{}^3$ (in Å^3) turned out to be very close to molecular weight M_W in Dalton units [4]:

$$\Delta\nu_{disp}[\text{cm}^{-1}] = -5.5 \times 10^4(\alpha_e - \alpha_g)M_W{}^{-1}\phi(n^2) \qquad (1)$$

The difference $\Delta\alpha$ has been assigned conventionally a "+" sign, if $\alpha_e > \alpha_g$. The solute dipole moment change in the excited state causes induction shift [26,44]:

$$\Delta\nu_{ind}[\text{cm}^{-1}] = 6.3 \times 10^3(\mu_g{}^2 - \mu_e{}^2)M_W{}^{-1}\phi(n^2) \qquad (2)$$

where dipole moments are in Debye units ($1\,\text{D} = 3.336 \times 10^{-30}\,\text{Cm}$). The Eq. (2) is not empirically calibrated and the coefficient amounts to $(3.336 \times 10^{-30})^2(10^{-30} \times 4\pi\varepsilon_0 hc)^{-1}(2n^2+1)(n^2+2)^{-1}$ for average $n^2 \sim 2$, in the expression by Bakhshiev [26]. The $\phi(n^2)$ dependence of fluorescence must remain the same, since swopping indices "g" and "e" yields the same coefficients as in Eqs. (1) and (2) for absorption, when taken with opposite sign.

The Lorentz-Lorenz function $\phi(n^2)$ as a measure of space-average solvent polarizability density forms a basis of concept of polarizable continuum [49,50]. We have emphasized that $\phi(n^2)$ is well applicable to aliphatic liquids consisting of elements H, C, N, and O that possess relatively uniform polarizability density [3,5,46,47], and lack extensive branching [1]. Perfectly linear plots of peak maxima against $\phi(n^2)$ in normal alkanes C_n when used as a reference set can expose "anomalies" for several apolar media, due local polarizability density variations. For example, the shift is often enhanced in CCl_4 and CS_2, because of high polarizability of Cl and S atoms, for their relatively small van der Waals volumes, and conversely, suppressed in perfluorinated alkanes [2] (see discussion in Refs. [3,46,47]). Dioxane and benzene deviate, because of their (pseudo)polarity owing to the quadrupole moment [48,51] that is not contributing to static dielectric constant ε. The widely used polarizable continuum model of solvation in computer chemistry [49,50] is ignorant about quadrupolar solvation and hydrogen bonding.

Finally, the dipole-dipole solvation energy is calculated as linear Stark effect on solute dipole moment in its own reaction field. The respective dielectric functions are written in the form $(\varepsilon - 1)/$