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Solvents effect on the absorption and fluorescence spectra of 7-diethylamino-3-thenoylcoumarin: Evaluation and correlation between solvatochromism and solvent polarity parameters

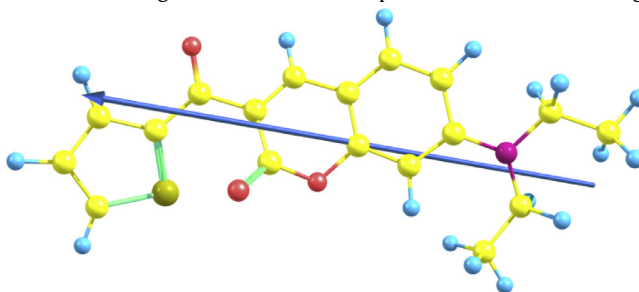
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HIGHLIGHTS

- DETC is a well known laser dye in the blue-green region.
- Solvatochromic correlations are used to estimate excited state dipole moment (μ_e).
- It is observed that $\mu_e > \mu_g$.
- Specific solute–solvent interaction is operating in the system.
- No synergistic effect is observed in the preferential study.

GRAPHICAL ABSTRACT

Effect of solvents of varying polarities on absorption and fluorescence spectra and dipole moment of laser dye: 7-diethylamino-3-thenoylcoumarin (DETC) has been investigated. A small band shift is obtained in the absorption spectra compared to emission spectra. The spectral shifts were correlated with Catalan's parameters using linear solvation energy relationship. It reveals that non-specific interaction measured by solvent polarity has more influence on absorption and solvent dipolarity contribution is significant in case of fluorescence. A bathochromic shift observed in absorption and emission spectra with increasing solvent polarity, which implied that the transition involved is $\pi \rightarrow \pi^*$. The solvatochromic correlations were used to estimate the excited state dipole moment using experimentally determined ground state dipole moment. The observed single-state excited state dipole moment is found to be greater than the ground state.



Optimised Molecular structure of DETC

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ABSTRACT

Effect of solvents of varying polarities on absorption and fluorescence spectra and dipole moment of laser dye: 7-diethylamino-3-thenoylcoumarin (DETC) has been investigated. A small band shift is obtained in the absorption spectra compared to emission spectra. The spectral shifts were correlated with Catalan's parameters using linear solvation energy relationship. It reveals that non-specific interaction measured by solvent polarity has more influence on absorption and solvent dipolarity contribution is significant in case of fluorescence. A bathochromic shift observed in absorption and emission spectra with increasing solvent polarity, which implied that the transition involved is $\pi \rightarrow \pi^*$. The solvatochromic correlations were used to estimate the excited state dipole moment using experimentally determined ground state dipole moment. The observed single-state excited state dipole moment is found to be greater than the ground state.

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Introduction

Coumarin and its derivatives show remarkable biological, chemical and physical properties and are useful probes in photochemical studies [1–4]. Because of their fluorescence properties, coumarins are extensively used in life sciences [5,6]. Physicists are generally interested in coumarin dyes as active medium in dye lasers. The knowledge of absorption and fluorescence characteristics of the compounds with different substituents under varying conditions of solvents [7,8], temperature [9,10], pH [11–13], etc. is crucial in understanding the working of tunable dye lasers and operating them at maximum efficiency. When electronic spectra are measured in solvents of different polarities and hydrogen bond donor/acceptor ability, it is found that the position, intensity and shape of the bands are usually affected by solvents. This phenomenon is referred as solvatochromism. The changes are due to solute–solvent intermolecular forces. These forces may be non-specific electrostatic interaction and/or specific interactions such as hydrogen bonding or electron donor/acceptor interaction [14–19]. In order to analyze the interactions between solute and solvent molecules, the most successful approach has been the solvatochromic comparison method proposed by Catalan [20,21]. In this method, empirical parameters are used to quantify specific interactions and to separate them from non-specific interactions [22–24].

Another methodology for the study of solute–solvent interactions is the use of binary mixture of solvents. The behavior of a solute in a solvent is different from the behavior in mixed binary systems. In these kinds of systems, the solute may induce a change in the composition of the solvents in the cybotatic region compared to that in the bulk, leading to preferential solvation. Studies involving mixed solvents have become very important in the fields such as kinetics, spectroscopy, thermodynamics, analytical chemistry and industrial process [25–28].

Further, the solvatochromic analysis, using Stokes' shift data is useful in calculating the ground and excited state dipole moments. The dipole moments of an electrochemically excited state of a molecule is an important property that providing information of the electronic and geometrical structure of the molecule in the short lived state [29–33]. A prior knowledge of the dipole moments of the excited states is often useful in the design of non-linear optical materials. The 7-amino coumarins compose the special class of compounds among the coumarin dyes, due to their superior laser activity. Most of the 7-aminocoumarin dyes show very large Stokes shifts, as a result of large change in dipole moments upon excitation and these Stokes shifts are very sensitive to the polarities of the solvents and the microenvironments [29,34]. Owing to these interesting properties, a number of 7-aminocoumarin dyes have found applications in studying many physicochemical processes in condensed phase.

As a part of our spectroscopic studies on fluorophores, in this paper we have studied the effect of solvents, preferential solvation to understand the solute–solvent interactions and evaluated the ground (μ_g) and excited state (μ_e) dipole moment of 7-diethylamino-3-thenoylcoumarin (DETC) which is used as a laser dye in the blue-green region.

Experimental

The laser dye 7-diethylamino-3-thenoylcoumarin (DETC) was procured from Exciton, USA and used without further purification. All the solvents used were of HPLC grade, transparent and non-fluorescent in the range of excitation and fluorescence emission (SD Fine Chemicals Ltd., India). The absorption spectra were recorded using Hitachi F2000 absorption spectrophotometer and

fluorescence spectra were recorded using Horiba Scientific Fluoromax – 4S Spectrofluorometer. All the measurements were carried out at room temperature keeping dye concentration very low at about 2×10^{-5} M to avoid the self absorption.

Theoretical considerations

Analysis of solvatochromism

Multiple linear regression method proposed by Catalan [20,21] was used to correlate UV–visible absorption and emission energies. In this method, the generalized treatment of solvent effect based on four mutually independent, empirical solvent scales namely: SA, SB, SP and SdP which characterize the solvent acidity (SA), basicity (SB), polarizability (SP) and dipolarity (SdP) respectively (Eq. (1)).

$$y = y_0 + a_{SA}SA + b_{SB}SB + c_{SP}SP + d_{SdP}SdP \quad (1)$$

where y_0 stands for the physicochemical property of interest in gas phase; a_{SA} , b_{SB} , c_{SP} and d_{SdP} are adjustable coefficients that reflect the sensitivity of the physicochemical property in a given solvent to SA, SB, SP and SdP respectively. The SA, SB, SP and SdP values for solvents are given in Table 1.

Preferential solvation study in binary mixture

If the binary mixture is considered an ideal one, \bar{v}_{\max} of the solute should follow a linear additive model according to the following equation [35]

$$\bar{v}_{12}^{ideal} = \bar{v}_1X_1 + \bar{v}_2X_2 \quad (2)$$

In this equation X_1 and X_2 are the mole fractions of solvents 1 and 2, and \bar{v}_1 , \bar{v}_2 and \bar{v}_{12} are the values of \bar{v}_{\max} of the solute in solvent 1 and 2 and in the binary mixture, respectively. The \bar{v}_{12}^{ideal} values in the mixture can be calculated by using above equation over the entire range of solvent composition.

However, if solvation shell is made up of independent sites that are always occupied in the non-ideal binary mixture, then \bar{v}_{12} can be expressed by an equation [36]

$$\bar{v}_{12} = \bar{v}_1X_1^L + \bar{v}_2X_2^L \quad (3)$$

where X_1^L and X_2^L are the local mole fractions of solvent 1 and 2 in the cybotatic region respectively and are calculated using equation

$$X_2^L = \frac{\bar{v}_{12} - \bar{v}_1}{\bar{v}_2 - \bar{v}_1} = 1 - X_1^L \quad (4)$$

The index of preferential solvation (δ_{S2}) may be taken as a measure of preferential solvation with respect to the co-solvent and can be defined as the difference between X_2^L and X_1^L [37].

$$\delta_{S2} = X_2^L - X_1^L \quad (5)$$

According to Frenkel et al. [36] the preferential solvation of the solute in binary mixture can be obtained quantitatively by the preferential solvation constant K_{12} (exchange constant).

$$K_{12} = \frac{(X_1^L/X_2^L)}{(X_1/X_2)} \quad (6)$$

If $K_{12} < 1$, it indicates a preference for solvent 1 over the solvent 2 and $K_{12} > 1$ signifies the opposite trend.

Determination of ground-state dipole moment

The ground state dipole moment (μ_g) was determined theoretically by quantum chemical calculations. The computations were carried out using Gaussian 03 program [38] on a Pentium – 4 PC.

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