

# Effect of binary solvent mixtures (DMSO/water) on the dipole moment and lifetime of coumarin dyes

B.R. Gayathri, J.R. Mannektla, S.R. Inamdar \*

*Laser Spectroscopy Programme, Department of Physics, Karnatak University, Dharwad, Karnataka 580 003, India*

Received 13 September 2007; received in revised form 22 January 2008; accepted 18 February 2008

Available online 26 February 2008

## Abstract

Absorption and fluorescence spectra of four coumarin laser dyes, Coumarin 440 (C440), Coumarin 450 (C450), Coumarin 466 (C466) and Coumarin 151 (C151), have been recorded in binary mixtures of DMSO and water at room temperature (298 K) to study the solvent effect and to evaluate the ground and excited state dipole moments using solvatochromic shift method. The anomalous feature in the complex systems of these mixtures due to the structural heterogeneities is discussed. The effect of solvent polarity parameters of binary mixture on the ground and excited state dipole moments was examined. Experimental results indicate that the dipole moments in the excited state, for all the molecules investigated, are higher than the corresponding values in the ground state. The ground and excited state dipole moments of these probes have also been computed from *ab initio* calculations and compared with those obtained experimentally. Fluorescence lifetimes of all the probes measured using time domain fluorescence spectrometer employing time correlated single photon counting technique, show a nonlinear variation with the composition of binary mixture.

© 2008 Elsevier B.V. All rights reserved.

**Keywords:** Binary solvent; Stokes shift; Solvatochromic shift; Dipole moment; Lifetime

## 1. Introduction

In recent years, due to fast progress in photochemistry, studies of electric dipole moments in the excited states have gained greater importance. The excitation of a molecule by a photon causes redistribution of the electron density and correspondingly a change in the dipole moment. A non-equilibrium state is created as the solvent environment cannot follow the sudden change in the dipole moment. During the relaxation of the solvent towards a new equilibrium state, the interaction energy between the solvent and solute changes and hence the fluorescence band of the probe molecule shifts [1]. This results in an increase or decrease of the excited state dipole moment as compared to that in the ground state. Similarly, when a solute molecule in a polar solvent is excited optically, its dipole moment in the excited state changes due to modified charge

distribution. A change in solvent is generally accompanied by a change in polarity, dielectric constant or a change in the polarizability of the surrounding medium. These parameters can easily be altered by mixing two solvents in different proportions. Hence, the study of binary solvent system and its role in biochemical processes has spurred the measurement of some excess properties. The mixtures of several solvents have been extensively used as media for carrying out physico-chemical investigations of organic molecules [2–4]. The dielectric behavior is one of the key ways of characterizing polar liquid environments as reaction media. It is found that the dielectric properties of the polar mixtures depart significantly from what one might expect on the basis of ideal mixing [5]. In hydrogen bonding systems such as alcohol–water mixtures, intermolecular correlations are strong, and consequently the dielectric properties [6,7] of the mixtures are usually not simply related to those of the individual components [8]. The use of solvent mixtures also facilitates a systematic variation of polarities [9] and thus, a binary mixture with different

\* Corresponding author. Tel.: +91 836 2215289; fax: +91 836 2771275.  
E-mail address: [him\\_lax3@yahoo.com](mailto:him_lax3@yahoo.com) (S.R. Inamdar).

proportions of the component solvents affects the excited state differently. Upon mixing, new solvent–solvent and solute–solvent interactions often create solvent properties that were not present in the pure solvents. Many mixtures of water with organic solvents show properties that deviate from ideality. For the system consisting of water and dimethyl sulphoxide (DMSO), extreme deviations from additivity are observed for a wide range of properties, such as dielectric constant, density, viscosity and adiabatic and isothermal compressibility [10]. Analysis of these mixtures are hindered by the fact that it represents one more complicated binary systems, namely an associating component plus a second component, capable of forming hydrogen bonds with the first. DMSO and its aqueous solutions are among the most widely used solvents in organic chemistry, chemical technology and cell biology [11,12]. DMSO ((CH<sub>3</sub>)<sub>2</sub>SO) is a polyfunctional molecule with a polar S=O group and two hydrophobic groups. Hence, its structure enables it to solubilize a variety of compounds [4]. A systematic analysis of binary solvent effect is, therefore, informative and proves useful in studying the excited state behavior of the molecule.

Coumarins are a family of molecules that have been studied extensively because of their application as laser dyes and their substantial state-dependent variation in static dipole moment. Indeed, the latter gives rise to characteristically large Stokes shift, sometimes of the order of 100 nm [13]. The knowledge of absorption and fluorescence characteristics of these compounds with different substituents under varying conditions of solvents, temperature and pH is crucial in understanding the working of tunable dye-lasers and operating them at maximum efficiency. The coumarin molecules as such in aqueous solution are non-fluorescent, but they do become highly fluorescent on substitution [14]. The emission characteristics of a fluorophore depend upon the position and nature of the substituent as well as the nature of the surrounding medium [15,16]. The magnitude of the spectral changes due to substituent/solvent is linked to the structural aspects of the molecule and serves as a tool for its detailed investigations. The wide spread occurrence of coumarins and their variety of applications such as fluorescent indicators and whiteners in detergent products, sunburn preventives, as laser dyes, for the estimation of enzymes, for studying biological systems and also in other interesting areas have given importance to the study of their fluorescence characteristics ([14] and references therein). These molecules form an important class of laser dyes in the blue-green spectral region.

Most of the methods available for the determination of dipole moment of the singlet-excited state are based on the spectral shift caused externally by electrochromism [17] or internally by solvatochromism [18]. In both these techniques Lippert–Mataga equation [19,20] is used, which is based on the spectral shift of absorption and fluorescence maximum and solvent polarity parameters dielectric constant ( $\epsilon$ ) and refractive index ( $n$ ). A thermo-chromic method [21], similar in principle, where the variation of

dielectric constant and refractive index is brought about by temperature changes, is also employed. The solvatochromic method to determine the excited state dipole moments is preferred due to simplicity of the experimental procedure and ease of data analysis.

In this paper, the ground and excited state dipole moments of a set of 7-amino coumarin dyes viz., C440, C450, C466 and C151 in polar solvent mixtures of dimethyl sulphoxide (DMSO) and water following solvatochromic shift technique is presented for the first time. The experimental results are compared with the theoretical ground and excited state dipole moments obtained from *ab initio* calculations [22] using DFT and CIS method, respectively. Further, fluorescence lifetime of these probes at each solvent mixture to check the excited state behavior of all the probes under study were also measured. The paper is divided into five sections. The theory relevant to the present study is given in Section 2, the experimental techniques are described in Section 3 followed by results and discussions in Section 4. Conclusions from the present work are given in Section 5.

## 2. Theory

The bulk dielectric constant ( $\epsilon$ ) and refractive index ( $n$ ) of a solvent strongly affect [23–25] the dipole moment of the solute molecules. An interaction with environment affects various electronic states in a different way. The interaction between the solute and solvent molecules depends upon dielectric constant, refractive index of the solvent and the dipole moment of the solute molecules.

By employing quantum-mechanical second-order perturbation theory [26], following equations have been obtained for the absorption ( $v_a$ ) and emission ( $v_f$ ) band shifts (in wave numbers) in different solvents of varying permittivity ( $\epsilon$ ) and refractive index ( $n$ ):

$$v_a - v_f = m_1 f(\epsilon, n) + \text{const.} \quad (1)$$

$$v_a + v_f = -m_2 \phi(\epsilon, n) + \text{const.} \quad (2)$$

with

$$f(\epsilon, n) = \frac{2n^2 + 1}{n^2 + 1} \left[ \frac{\epsilon - 1}{\epsilon + 2} - \frac{n^2 - 1}{n^2 + 2} \right] \quad (3)$$

being the solvent polarity function and

$$\phi(\epsilon, n) = f(\epsilon, n) + 2g(n), \quad (4)$$

where

$$g(n) = \frac{3}{2} \left[ \frac{n^4 - 1}{(n^2 + 2)^2} \right], \quad (5)$$

with

$$m_1 = \frac{2(\mu_e - \mu_g)^2}{hca_0^3} \quad (6)$$

and

Download English Version:

<https://daneshyari.com/en/article/1411721>

Download Persian Version:

<https://daneshyari.com/article/1411721>

[Daneshyari.com](https://daneshyari.com)