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Determination of ground and excited state dipole moments of some naphthols using solvatochromic shift method

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ABSTRACT

Solvatochromic behavior of 1-naphthol (N1) and 2-naphthol (N2) has been studied in different solvents at room temperature (298 K). The ground and first excited singlet state dipole moments are estimated using solvatochromic shift method. Bakhshiev and Kawski and Bilot correlations based on bulk solvent polarity parameters are applied. The results are further verified by using the microscopic solvent polarity parameter E_T^N. For both molecules investigated, the excited state dipole moments are larger than the corresponding values in the ground state. Moreover, for N1, the values obtained in aprotic solvents are much less than those obtained when protic solvents are included, which underlines the presence of specific interaction in case of protic solvents.

1. Introduction

Applications of fluorescence to various fields such as biology, medicine, material science, analytical chemistry etc., have developed tremendously in the last 3 decades. This is because of the inherent high sensitivity, selectivity and versatility of the luminescence. For example, the fluorescent probe method is now widely used for studying cells, proteins, and tissues [1,2]. The local dielectric properties of cells, proteins and tissues are of great importance for diagnostics as well as for the investigation of their functionality. The best known method for the estimation of the local dielectric constant in complex macromolecules is based on using standard equations describing the dependence of the position of the electronic spectra of fluorescence probes on the dielectric constant, refractive index of the medium, and on the dipole moments of the probe in its ground and excited states. If the dipole moments in the relevant electronic states are known, the local dielectric constant may be determined by these equations from the spectral position of the electronic spectra [3–9].

It is known that the spectral behavior of an organic molecule is strongly related to its structure in both ground and excited states. The knowledge of the solvent effect on absorption and fluorescence spectra is of particular importance. A change in solvent is accompanied by a change in polarity, dielectric constant or polarizability of the surrounding medium. Thus, the change of solvent affects the ground state and excited states differently. A systematic analysis of the solvent effect is, therefore, informative and proves quite fruitful in studying the excited state behavior of the molecule.

Just as for stable molecules, dipole moments of short-lived species are of considerable interest because they provide important information about excited states. This is also useful in the parameterization of semi empirical quantum chemical methods employed for these systems. The excited state dipole moments of a molecule control the tunability range of their emission energy as a function of solvent polarity and can be useful in optimizing the efficiency or performance of a laser dye [10].

Among the techniques available for the determination of the excited-state dipole moments, the most popular is that based on Lippert–Mataga equation [11,12]. In this technique, absorption and fluorescence shifts follow bulk solvent polarity, described by dielectric constant (ε) and refractive index (η). Other electro-optic methods such as electronic polarization of fluorescence [13], electric-dichroism [14], microwave conductivity [15] and stark splitting [16] are generally considered to be very accurate. However, their use is limited because they are equipment intensive and hence these studies have been confined to relatively simpler molecules. In fact, the experimental determination of this parameter based on the analysis of the solvatochromism is often used. Many workers have reported ground state and excited-state dipole moments using different methods [17–28].

The solvent effect on the spectral properties of 1-naphthol (N1) and 2-naphthol (N2) has been extensively studied in the past due to the unusual large red shift in fluorescence emission on changing the polarity (from nonpolar to polar solvents) [29–37].

The basic fluorophore unit in naphthols is the naphthalene ring. Naphthalene possesses nearly degenerate singlet excited states, ^1L_a

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and ^1L_b, which are polarized either along the long axis ("through-bond", or ^1L_b) or along the short axis ("through-atom",or ^1L_a). Substitution of hydroxyl group (−OH) at the 1 and 2 positions of naphthalene ring reduces the symmetry, which means that the two states are heavily mixed. This is more pronounced for N1, in which both ^1L_a and ^1L_b bands overlap in absorption as well as emission spectra. However, for N2 they are well separated in the absorption spectrum and only ^1L_b emission is observed in the emission spectrum. The larger polarity of the ^1L_a state is believed to explain the higher reactivity of N1 [38]. Dissimilar frequency shifts in the fluorescence have been interpreted from the difference of emitting state ^1L_a for N1 and ^1L_b for N2 [39].

In the past, studies had been undertaken to find the dipole moments both theoretically as well as experimentally. However, the estimation of dipole moment gets complicated because of the specific solute solvent interaction as well as presence of cis and trans forms of the present probes. The goal of the present work is to estimate the experimental dipole moments of N1 and N2 using the solvatochromic correlations and also to bring out the role of solvents in their estimation. The study has been performed in various non polar, polar aprotic and polar protic solvents to monitor general as well as specific solvent effects.

To estimate the dipole moments, solvents were categorized in two groups i.e. G1 and G2. G1 is the group of aprotic polar and nonpolar solvents for excluding intermolecular hydrogen bonding effect (if it exists) whereas G2 is the group of solvents which contains nonpolar to polar (aprotic and protic both) solvents. Such categorization of solvents has received recent attention [40,41] and illustrates the role of the solvents in the determination of dipole moment from solvatochromic shift methods [42–45].

2. Method

The following two formulae were used to determine the excited singlet state dipole moments by the solvatochromic method.

(i) Bakhshiev's formula [42]

$$\bar{\nu}_a - \bar{\nu}_f = S_1 F_1(\varepsilon,\eta) + Constant \tag{1}$$

Here $\bar{\nu}_a$ and $\bar{\nu}_f$ are the wavenumbers of the absorption and emission maxima respectively. F_1 the bulk solvent polarity function and S_1 are defined as follows:

$$F_1(\varepsilon,\eta) = \frac{2\eta^2+1}{\eta^2+2}\left[\frac{\varepsilon-1}{\varepsilon+2} - \frac{\eta^2-1}{\eta^2+2}\right] \tag{2}$$

and

$$S_1 = \frac{2\left(\mu_e-\mu_g\right)^2}{hca_0{}^3} \tag{3}$$

here, h denotes the Planck's constant, c is the velocity of light in vacuum, μ_g is the dipole moment in the ground state, μ_e is the dipole moment in the excited singlet state, a_0 is the Onsager cavity radius, ε is the solvent dielectric constant and η is the solvent refractive index.

(ii) Bilot–Kawski formula [43,44]

$$\frac{\bar{\nu}_a + \bar{\nu}_f}{2} = -S_2 F_2(\varepsilon,\eta) + Constant \tag{4}$$

here the meaning of the symbols is the same as in Eqs. (1) and (2), except for F_2 and S_2 which are defined as follows:

$$F_2(\varepsilon,\eta) = \frac{2\eta^2+1}{2(\eta^2+2)}\left[\frac{\varepsilon-1}{\varepsilon+2} - \frac{\eta^2-1}{\eta^2+2}\right] + \frac{3}{2}\left[\frac{\eta^4-1}{(n^2+2)^2}\right] \tag{5}$$

and

$$S_2 = \frac{2\left(\mu_e{}^2-\mu_g{}^2\right)}{hca_0{}^3} \tag{6}$$

The parameters S_1 and S_2 can be obtained from the absorption and fluorescence band shifts [Eqs. (1) and (4)]. Basically S_1 and S_2 are the slopes which can be calculated using Eqs. (1) and (4) respectively. Assuming the ground and excited states to be parallel, the following expressions are obtained on the basis of Eqs. (3) and (6) [43,45]:

$$\mu_g = \frac{S_2-S_1}{2}\left[\frac{hca_0{}^3}{2S_1}\right]^{1/2} \tag{7}$$

$$\mu_e = \frac{S_1+S_2}{2}\left[\frac{hca_0{}^3}{2S_1}\right]^{1/2} \tag{8}$$

and

$$\mu_e = \frac{S_1+S_2}{S_2-S_1}\mu_g;\ (S_2 > S_1) \tag{9}$$

The value of the solute cavity radius (a_0) was calculated from the molecular volume according to Suppan's equation [46]

$$a_0 = \left(\frac{3M}{4\pi\delta N}\right)^{1/3} \tag{10}$$

where δ is the solid state density of the solute molecule, M the molecular weight of the solute and N is the Avogadro number.

3. Experimental

N1 and N2 (obtained from Aldrich) of 99% purity were tested for their fluorescence purity and used as such. All the solvents used were either of spectroscopic grade or were checked for their fluorescence purity. Steady state absorption spectra, at room temperature (298 K) were recorded by dual beam JASCO V-550 spectrophotometer. The emission spectra were recorded by using JASCO FP-777 spectrofluorimeter and data were analyzed by the related software. The spectra were corrected for the detector response. Density of the probe was estimated by ACD/ChemSketch software. Data were fitted to a straight line using Origin 6.0 software.

4. Results and discussion

The molecular structures of N1 and N2 are shown in Fig. 1. In order to estimate the dipole moments of N1 and N2 in the both ground and excited states, steady state absorption and fluorescence spectra were recorded in various solvents of different polarities. Steady state data are summarized in Table 1. Absorption maximum of N1 is at 322 nm in hexane and at 323 nm in methanol while the absorption maximum of N2 is observed at 328 nm in hexane and at 331 nm in methanol. With increase in the solvent polarity, minute red shift in absorption maximum for both N1 and N2 is observed (Figs. 2 and 3). Fluorescence spectra of both probes exhibit bathochromic shift