RESEARCH ARTICLE

Solvatochromic study of coumarin 545 in alcohols for the determination of ground and excited state dipole moments

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Abstract

Solvatochromic behaviour of medium sized dipolar laser dye: coumarin545 (C545) has been studied extensively in alcohols at room temperature. The absorption spectrum of C545 is sensitive to solvent effects which shows bathochromic and hypsochromic shifts with increasing solvent polarity indicating that the transitions involved are $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$. The emission spectra shows hypsochromic shift. The ground and excited state dipole moments were obtained by using solvatochromic correlations. Onsager radius determined from *ab initio* calculation was used in the determination of dipole moments. The ground and excited state dipole moments of the probe computed from *ab initio* calculation was compared with that determined experimentally and the results are interpreted based on its possible resonance structures. It is observed that the excited state dipole moment is larger than its ground state counterpart in all the solvents studied.

Introduction

The investigation of effect of solvents on the absorption and emission spectra of organic (dye) molecules reveal information on the electronic and geometrical structure of the molecules in the excited state. The laser dyes are extensively studied due to their practical applications. A number of techniques e.g. electronic polarization of fluorescence (Kawski et al., 1992), electric dichroism (Liptay et al., 1974), microwave conductivity (Czekalla et al., 1960) and Stark splitting of rotational levels of the 0-0 vibrational bands (Lombardi et al., 1970) are available for the determination of excited state dipole moment (μ_e). The experimental determination of this parameter based on the analysis of solvatochromism of absorption and fluorescence is the simplest and quite popular (McRae et al., 1957). The solvatochromic method is based on a linear correlation between the wave numbers of the absorption and fluorescence maxima with solvent polarity function which involves dielectric constant (ε) and refractive index (n) of the medium. The knowledge of the excited state dipole moments of organic molecules having larger hyper polarizabilities, would be helpful not only in designing efficient non-linear optical materials (Chemla et al., 1987) but also in the design of new molecules for their best performance in particular applications, such as biological and chemical sensors, fluorescent probes and laser dyes (Christie et al., 1999). Coumarin dyes undergo very little nuclear reorganization, yet are solvatochromic owing to the change in electronic distribution resulting in an increase of dipole moments from ground state into excited state (Ravi et al., 1995). The dipole moment of a molecule in the ground state and excited state depend on the electron distribution in these states. Thus a systematic analysis of the solvent effect is useful in understanding the excited state behaviour of the molecule. These properties have been studied as a function of concentration of the dye, viscosity, polarity and polarizability of the solvents, as well as the pH of the solution. The solvent shifts can be accounted in terms of the overall effect of the interaction forces (which are mainly of van der Waals type) on the electron system of the molecule.

The solvatochromic technique is found to be quite useful in order to assign the electronic transitions as $\pi \rightarrow \pi^*$ or $n \rightarrow \pi^*$. It may be noted that, $\pi \rightarrow \pi^*$ bands show a red shift in the solvents of increasing polarity while $n \rightarrow \pi^*$ bands

show a blue shift. Excited state dipole moments of many dyes have been determined using solvatochromic shifts (Cremers et al., 1980; Deepa et al., 2013; Gahlaut et al., 2011; Inamdar et al., 2003; Kumar et al., 2001; Nagachandra et al., 2012; Srividya et al., 1997). Here we present the experimental study of dipole moments of the polar fluorescent dye, C545 (Fig. 1). Alcohols such as methanol to decanol are employed in the present study which have been a subject of a number of studies related to polar solvation (Blanchard et al., 1988 and references therein).

2. Material and methods

The laser grade coumarin dye C545 was of the highest available purity procured from Radiant Dyes Laser GmbH, Germany and was used without further purification. All the solvents used in the study were alcohols of highest available purity (HPLC grade, Fluka). UV–Vis ratio recording spectrophotometer (Hitachi, model U-2800) was used to record absorption spectra. The fluorescence spectra was recorded using, Fluorescence spectrofluorometer (JY Horiba, model Fluoromax-4). All the measurements were carried out at room temperature (298 K) keeping the dye concentration very low in order to reduce the effect of self-absorption and aggregation. The data was analyzed by relevant software. Linear fit was done by using origin8.0 software. Gaussian-03   was used for *ab initio* calculations.

3. Theory

Solvatochromic shifts in solvents of different properties, the bulk dielectric constant (ε), and refractive index (n) of the solvent can be used, for the estimation of ground and excited state dipole moments of the molecule, since they strongly affect the dipole moment. The influence of solvent polarity on the spectral aspects of the solute can be interpreted by means of linear solvation energy relationship (LSER) concept that can be formulated as Kamlet-Abbound-Taft and Katritzky equations (eqns. 1 and 2, respectively) (Fowler et al., 1971).

$$(\nu_a\text{-}\nu_f) = (\nu_a\text{-}\nu_f)_0 + \text{a}\cdot\alpha + b\cdot\beta + s\cdot\pi^* \tag{1}$$

$$(\nu_a\text{-}\nu_f) = (\nu_a\text{-}\nu_f)_0 + \text{a}\cdot\left[\frac{\varepsilon-1}{2\varepsilon+1}\right] + b\cdot\left[\frac{n^2-1}{2n^2+1}\right] + s\cdot E_T(30) \tag{2}$$

where π^* represents the solvent polarity/polarizability (Abboud et al., 1977), α is the scale of the solvent hydrogen bond donor (HBD) acidities (Kamlet et al., 1979), β is the scale of the solvent hydrogen bond acceptor (HBA) basicities (Kamlet et al., 1976). ε, n and $E_T(30)$ respectively are relative permittivity, refractive index and empirical polarity parameter of the solvent. a, b and s in these equations measure the relative susceptibilities of the solute property, such as absorption, fluorescence and other spectroscopic parameters.

The most commonly used expression in fluorescence spectroscopy, first developed by Lippert (Reichardt et al., 2004) and Mataga et al. (Mataga et al., 1956, 1970), is based on the Onsager's reaction field theory that presumes a fluorophore as a point dipole residing at the centre of a spherical cavity with radius (a_0) in a homogeneous and isotropic dielectric with relative permittivity (ε). The so called Lippert–Mataga equation is no longer applicable when, specific fluorophore/solvent interactions such as hydrogen bonding or electron-pair donor/electron-pair acceptor interactions in addition to the non-specific interactions, also contribute significantly to the overall solute–solvent interaction. A further limitation results from the cavity radius, which is difficult to estimate for elongated molecules with an ellipsoidal shape (Reichardt et al., 2004).

Kawski and others (Kawski et al., 1992) obtained a simple quantum mechanical second order perturbation theory of absorption (ν_a) and fluorescence (ν_f) band shifts in different solvents of varying permittivity (ε) and refractive index (n) relative to the band position of a solute molecule based on which the following equations are obtained:

$$\nu_a\text{-}\nu_f = \text{m}_1 f(\varepsilon, n) + \text{const} \tag{3}$$

$$\nu_a + \nu_f = -\text{m}_2\left[f(\varepsilon, n) + 2g(n)\right] + \text{const} \tag{4}$$

where
$$f(\varepsilon,n) = \frac{2n^2+1}{n^2+2}\left[\frac{\varepsilon-1}{\varepsilon+2} - \frac{n^2-1}{n^2+2}\right] \tag{5}$$

is the polarity of the solvent and

$$g(n) = \frac{3}{2}\left[\frac{n^4-1}{(n^2+2)^2}\right] \tag{6}$$

with $\qquad m_1 = \dfrac{2(\mu_e - \mu_g)^2}{hca^3}$ (7)

and $\qquad m_2 = \dfrac{2(\mu_e^2 - \mu_g^2)}{hca^3}$ (8)

h being Planck's constant and c, the velocity of light in vacuum. The parameters m_1 and m_2 can be determined from absorption and fluorescence band shifts [eqns. (3) and (4)], and the values of μ_g and μ_e from eqns. (7) and (8) can be given as

$$\mu_g = \frac{m_2 - m_1}{2} \left[\frac{hca^3}{2m_1}\right]^{1/2}$$ (9)

$$\mu_e = \frac{m_1 + m_2}{2} \left[\frac{hca^3}{2m_1}\right]^{1/2}$$ (10)

or $\qquad \mu_e = \dfrac{m_1 + m_2}{m_2 - m_1} \mu_g \; ; (m_2 > m_1)$ (11)

The parameters m_1 and m_2 can be determined from the slopes occurring for the difference (ν_a-ν_f) and the sum (ν_a+ν_f) of the wave-numbers are linear functions of the solvent polarity parameters $f(\varepsilon, n)$ and $f(\varepsilon, n) + 2g(n)$;

The method based on the empirical polarity scale proposed by Reichardt (Reichardt et al., 2004) gave towering results with solvatochromic shift of dipolar molecules that correlate much better with microscopic solvent polarity E_T^N rather than the traditionally used bulk solvent polarity functions involving dielectric constant (ε) and refractive index (n) as in the latter the error estimation of Onsager cavity radius 'a' has been minimized. The theoretical basis for the correlation as spectral shift with E_T^N has been developed by Ravi et al., and accordingly the excited state dipole moment is evaluated using the equation

$$\nu_a - \nu_f = 11307.6 \left[\left(\frac{\Delta\mu}{\Delta\mu_B}\right)^2 \left(\frac{a_B}{a}\right)^3\right] E_T^N + \text{const}$$ (12)

where $\Delta\mu_B = 9D$ and $a_B = 6.2\text{Å}$ are the dipole moment change on excitation and Onsager radius, respectively, for betaine dye and also are the corresponding quantities for the molecule of interest. E_T^N is defined using water and tetramethylsilane (TMS) as extreme reference solvents with the equation

$$E_T^N = \frac{E_T(solvent) - E_T(TMS)}{E_T(water) - E_T(TMS)} = \frac{E_T(solvent) - 30.7}{32.4}$$ (13)

The change in dipole moment is determined by:

$$\Delta\mu = \mu_e - \mu_g = \sqrt{\frac{m \times 81}{(6.2/a)^3 \, 11307.6}}$$ (14)

where m is the slope of the linear plot of E_T^N vs. Stokes shift.

4. Results and discussions

The observed spectral data values of absorption maxima λ_{max} of C545, in various solvents used are given in Table 1. It is noticed that the absorption maxima of the dye are affected by type of the solvents used in this work and maximum shift ($\Delta\lambda$) for C545 is 4 nm. Hence, this change in spectral position can be used as a probe for different types of interactions between the solute and solvents. The typical absorption and emission spectra of C545 in alcohols are depicted in Fig. 2. The uncertainty in the measured wavelength of absorption and fluorescence maxima is ±0.5 nm. Both absorption and emission spectra of the dye are broad and they shift depending on the solvents used. A shift of about 1 to 4 nm, in the absorption spectra on changing the solvent from methanol to decanol for C545 is observed. Spectral shift observed in the emission spectra is relatively larger compared to the absorption spectra. The large Stokes shift observed is indicative of the charge transfer transition. A lesser variation in the absorption shift

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observed in all the solvents implies that the ground state energy distribution is not affected to a greater extent probably due to the less polar nature of the dye in the ground state rather than the excited state. The higher magnitude of Stokes shift suggests that the excited state geometry could be different from that of the ground state. The pronounced shift in the emission clearly indicates that the dipole moment of the excited state is higher compared to that in the ground state.

The study of solvent effect based on spectral properties of dye solutions were carried out by using the spectral position in the solvents mentioned here and correlating these with the Kamlet-Taft solvent properties namely, π^*, α, β, refractive index (n) and dielectric constant (ε), obtained from literature (Kamlet et al., 1983; Marcus et al., 1993). As the shift in λ_{max} values with solvent type reflects dye-molecule interactions, an attempt was made to study this fact exhaustively. The spectral position of dye in a variety of solvents reveals interesting results. The absorption bands of solute molecules in different solvents with varying polarity have shown bathochromic as well as hypsochromic shifts. These shifts arise depending upon how solute molecule interacts with solvent. The solute molecule finds itself in a cavity inside the solvent, resulting in a net stabilization of their ground state. During electronic transition if the dipole moment of solute increases, the excited state is formed inside the solvent cavity which is surrounded by partly oriented solvent dipoles. The net stabilization of the excited state as compared to the ground state with increasing solvent polarity results in bathochromic shift. Here the excited state is more dipolar than ground state ($\mu_g < \mu_e$). If there is a decrease in dipole moment of solute during the electronic transition, the excited state is formed in a strained solvent cavity of oriented dipoles not correctly disposed for its efficient stabilization. The energy of the ground state lowered more than that of the excited state with increasing solvent polarity results in a hypsochromic shift and in this case ground state is more dipolar than excited state ($\mu_g > \mu_e$). According to the valence-band theory, the extent and direction of sovatochromism depends on whether the zwitterionic mesomeric structure is more important in the ground state or in the excited state (Reichardt et al., 2004). A general observation is, increase in Stokes shift values with increase in solvent polarity indicates that the dipole moment increases upon excitation. In such cases, the relaxed excited state S_1 will be energetically stabilized relative to the ground state S_0. The wave numbers of absorption and fluorescence emission maxima of the solute along with the microscopic polarity scale E_T^N, are summarized in Table 2. Consecutively, to estimate the ground state and excited state dipole moments of the dye molecule, the solvent polarity $f(\varepsilon, n)$ and $f(\varepsilon, n)+2g(n)$ parameters were calculated (Table 3). Fig. 3 shows spectral shifts v_a-v_f and v_a+v_f for the dye which are observed in alcohols, versus the polarity function $f(\varepsilon, n)$ and $f(\varepsilon, n)+2g(n)$, respectively. A linear regression was done and the data were fit to straight lines for both the plots whose slopes were taken as m_1 and m_2. In most cases the correlation coefficients are larger than 0.95 and indicate a good linearity with selected number of Stokes shift data points. In few cases some of the solvents did not participate in the correlation. Generally this deviation from linearity may be due to specific solute–solvent interactions. The deviation from linearity for some solvents might probably be due to hydrogen bonding nature of the molecule and at the same time charge transfer in the excited state cannot be ruled out.

The absorption data of the dye in different solvents was also analyzed in terms of various polarity scales. One such method involves the transformation of λ_{max} of dyes in different solvents into molar transition energies [E_T (dye), kcal/mole] by using the following equation (Reichardt et al., 1994)

$$E_T \text{ (dye)} = 28591/ \lambda_{max} \tag{15}$$

The E_T (dye) values, obtained by using this equation, signify the transition energies that reflect the stabilization of the dye in its ground state in the respective solvent. This may perhaps be due to either hydrogen bond formation or dye-solvent interaction. Hence, E_T (dye) gives a direct empirical measure of dye solvation behaviour (Nagarajan et al., 1987; Kahlow et al., 1988). The use of so-called normalized E_T^N values has been suggested (Eqn. 13). Fig. 4 shows plot of Stokes shift as a function of E_T^N in all the solvents for C545. The linear dependence of Stokes shift on E_T^N reveals the existence of general type of solute-solvent interaction wherein the Stokes shift depends on dielectric constant and refractive index of the solvents.

The Onsager's cavity radius determined by *ab initio* calculations (using volume key word), is found to be 5.55Å for C545. The ground and excited state dipole moments are evaluated using eqns. (9) and (10) (Table 4). The difference in dipole moments calculated from solvent perturbation method and using eqn. (14) are reasonably in good agreement in case of alcohols, obviously indicating the excited state dipole moment to be higher compared to ground state. This also indicates that the excited- state geometry could be different from that of the ground state. The observed ground state dipole moment of C545 is 8.52D in alcohols.

The ground and excited state dipole moments of the solute was also determined from *ab initio* calculations using Density Functional Theory (DFT) and Configuration Interaction Singles (CIS) method (Gaussian 03, 2004), respectively (Table 4). The ground state optimized geometry of the probe obtained using B3LYP functional with 6-

31g basis set is shown in Fig. 5. The arrow in the figure indicates the direction of transition dipole moment in the ground state. It is evident from Table 4 that the ground state dipole moment evaluated from solvatochromic shift method is in fair agreement with that obtained from *ab initio* calculations for C545 probe, and similar accuracy is found for the excited state dipole moment. The dipole moment values of present molecular probe calculated using radii determined by both Edward atomic increment method (Edward, 1970) and Suppan equation (Suppan, 1983) (Table 4), show discrepancy in comparison with that obtained from *ab initio* calculations. Number of reports in literature has shown discrepancy between theoretical and experimental values (Aaron et al., 1995). The excited state dipole moment was computed using CIS method to estimate the minimum of the lowest excited singlet state and optimized using 6-31g. The present report on the study of dipole moments is reasonably appropriate for the exploration of spectroscopic properties.

The observed variations in the dipole moment values can also be understood in terms of its possible resonance structures as shown in Fig. 6(a & b). In case of C545 the nonbonding electrons on carbonyl group, tertiary amino group and ring oxygen contribute towards the mobility of electrons on the aromatic ring. The nitrogen atom of tertiary amino group being sp[3] hybridized has more electron donating tendency. Upon excitation, the carbonyl group becomes highly electrophilic and tertiary amino group becomes strong electron donor. Also there is possibility of electron mobility between ring oxygen and carbonyl group. In the present work, the dipole moment value of C545 being small as compared to other similar molecules, would imply a lesser degree of charge separation as can be seen from the all possibilities of resonance structures.
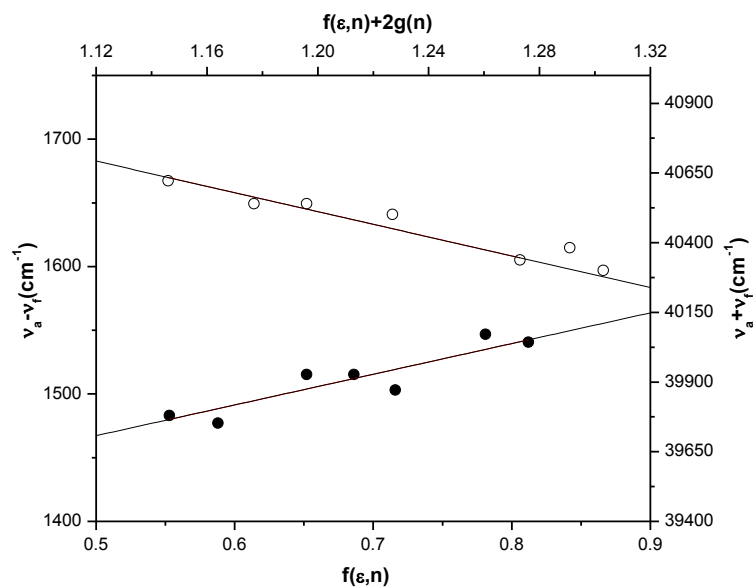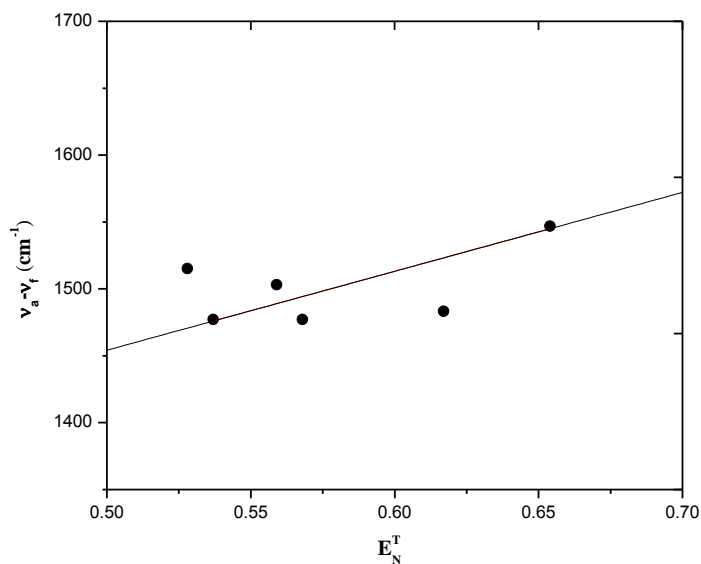
Fig. 1   Molecular structure of Coumarin 545
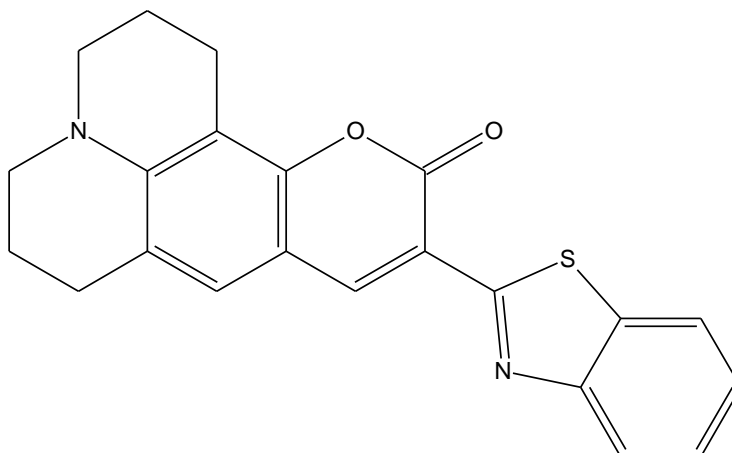
Fig. 2 Typical absorption and fluorescence spectra of C545 in methanol, butanol and decanol
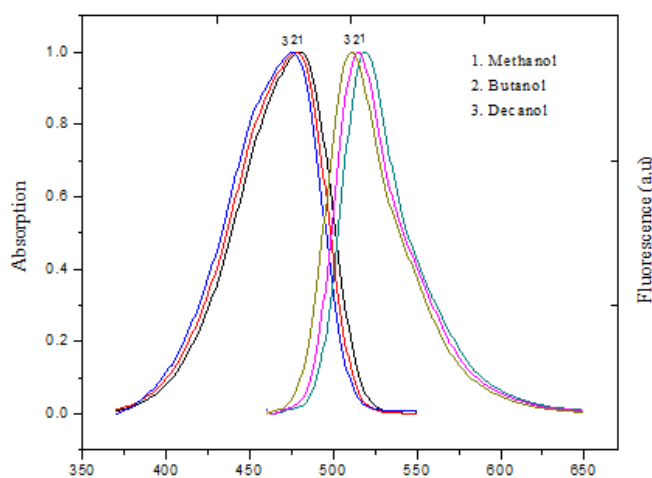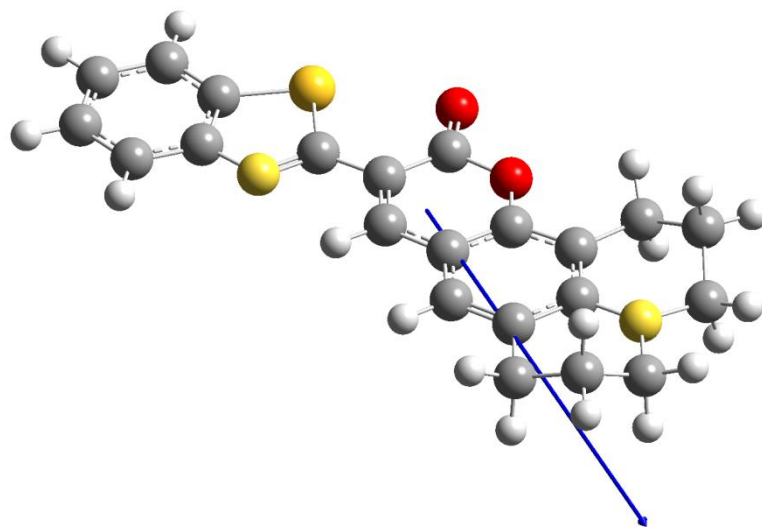
Fig. 3 Plot of $\nu_a\text{-}\nu_f$ **vs.** $f(\varepsilon, n)$ **and** $\nu_a\text{+}\nu_f$ **vs.** $f(\varepsilon, n)\text{+}2g(n)$ **of C545 in alcohols**

Fig. 4 Plot $\nu_a\text{-}\nu_f$ **vs.** E_T^N **of C545 in alcohols**

Fig. 5 Ground state optimized structure of C545

Fig. 6 Possible resonance structures of C545

(a)

(b)
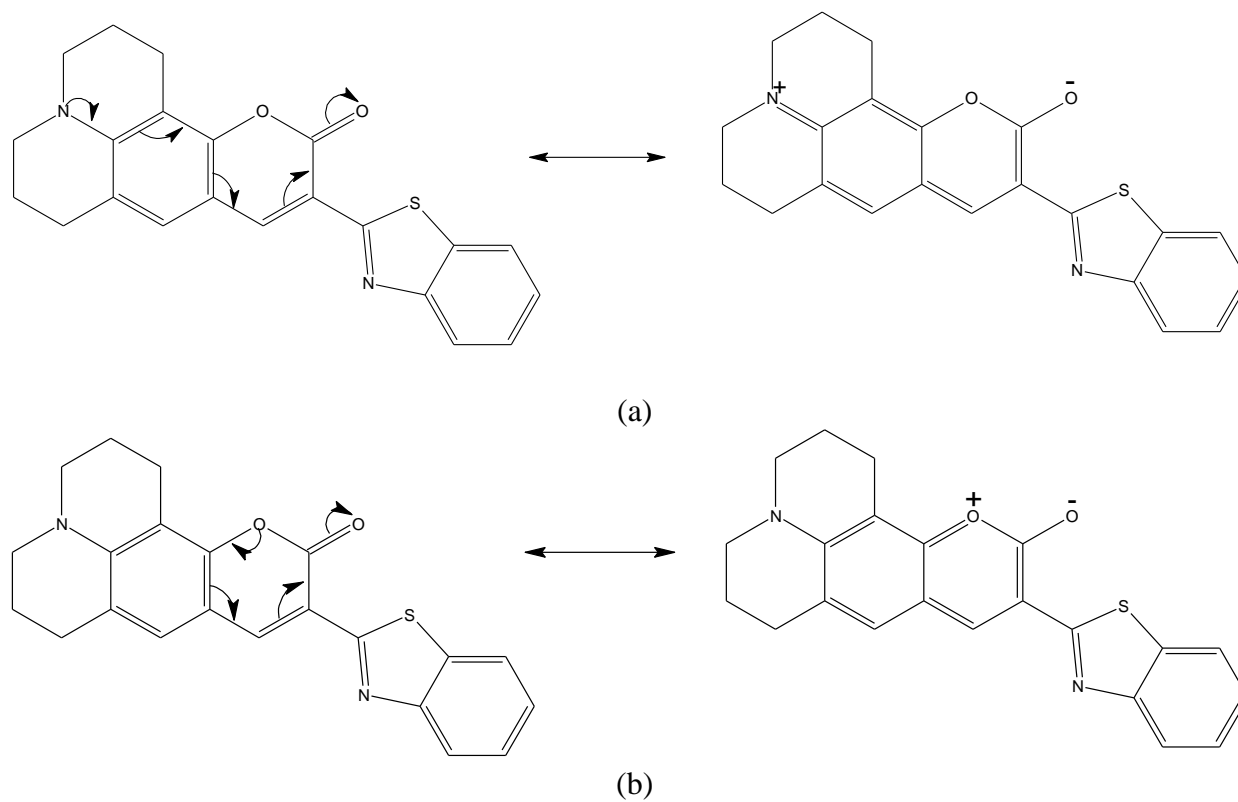
Table 1 Some physical constants of solvents and absorption maxima of C545 in various solvents

Solvents	$n^{\#}$	$\varepsilon^{\#}$	$\pi^{*\#}$	$\alpha^{\#}$	$\beta^{\#}$	λ_{max}(nm)
Methanol	1.329	33.70	0.60	0.98	0.66	479
Ethanol	1.361	24.30	0.54	0.86	0.75	478
Propanol	1.385	20.60	0.52	0.84	0.90	477
Butanol	1.399	17.40	0.47	0.84	0.84	477
Pentanol	1.410	14.80	0.40	0.84	0.86	478
Hexanol	1.418	13.00	0.40	0.80	0.86	476
Heptanol	1.424	11.30	--	--	--	476
Octanol	1.429	9.80	0.40	0.77	0.81	476
Nonanol	1.434	9.00	--	--	--	476
Decanol	1.437	8.00	0.45	0.70	0.82	475

[#] The values of π*, ε, α and β for alcohols are taken from Refs. (Kamlet et al., 1983). The values of n are taken from Fluka Catalogue 2004-05 for alcohols.

Table 2 Some physical constants of solvents and spectral data of C545

Solvents	$E_T(dye)^1$	$E_T(30)^{\#1}$	$E_T^{N\#}$	$\nu_a(cm^{-1})$	$\nu_f(cm^{-1})$
Methanol	59.69	55.4	0.762	20876.83	19267.82
Ethanol	59.81	51.9	0.654	20920.50	19379.84
Propanol	59.94	50.7	0.617	20964.36	19417.48
Butanol	59.94	49.7	0.586	20964.36	19417.48
Pentanol	59.81	49.1	0.568	20920.50	19417.48
Hexanol	60.07	48.8	0.559	21008.40	19493.18
Heptanol	60.07	48.5	0.549	21008.40	19493.18
Octanol	60.07	48.1	0.537	21008.40	19531.25
Nonanol	60.07	47.8	0.528	21008.40	19531.25
Decanol	60.19	47.7	0.525	21052.63	19569.47

[#] $E_T(30)$ values for alcohols are from Ref. (Reichardt et al., 2004). E_T^N values for alcohols are from Ref. (Reichardt et al., 2004). [1] Solvent polarity in the unit of kcal/mol.

Table 3 Calculated values for solvent polarity parameters $f(\varepsilon, n)$, $g(n)$ and $f(\varepsilon, n) + 2g(n)$

Solvents	$f(\varepsilon, n)$	$2g(n)$	$f(\varepsilon, n)+2g(n)$
Methanol	0.857	0.448	1.305
Ethanol	0.812	0.490	1.303
Propanol	0.781	0.524	1.305
Butanol	0.749	0.542	1.291
Pentanol	0.716	0.557	1.273
Hexanol	0.686	0.568	1.254
Heptanol	0.652	0.575	1.227
Octanol	0.614	0.582	1.196
Nonanol	0.588	0.589	1.177
Decanol	0.553	0.593	1.146

Table 4 Cavity radius (a_0), Dipole moments (μ_g and μ_e) in Debye (D), slopes (m_1 and m_2) and correlation factor (r) of C545 molecule

Molecule	a_0(Å)	Solvents	μ_g (D)	μ_e (D)	$\Delta\mu$ (D)	μ_e/μ_g	m_1 (cm^{-1})	m_2(cm^{-1})	r
C 545	5.55[a]	Alcohols	8.52	10.50	1.98(1.74[e])	1.232	240.95	2269.54	0.79:0.97
	4.20[b]	Alcohols	5.61	6.94	1.33(1.15[e])	1.237	240.95	2269.54	0.79:0.97
			8.60[c]	9.16[d]	0.56	1.065			

[a,c] Calculated from B3LYP functional with 6-31g basis set.
[b] Calculated from Edward atomic increment method.
[d] Excited state dipole moment using CI singles (CIS) method.
[e] Calculated using equitation 14.

5. Conclusion

      In this study, we have reported the solvent effect and determined experimentally the ground and excited state dipole moments of the fluorescent dipolar laser dye C545 in alcohols using solvatochromic shift method. Absorption maxima of the dye are dependent on solvent polarity. Both $\pi\rightarrow\pi^*$ and $n\rightarrow\pi^*$ transitions which indicate, a bathochromic and a hypsochromic shift respectively are observed upon increasing the polarity of the solvents for the dye studied. We found that the excited state dipole moment of the probe C545 is greater than its ground state counterpart in all the solvents used. This clearly signifies that, the excited state of C545 is more polar than the ground state. This change in dipole moment on excitation can be explained in terms of nature of the emitting state or intramolecular charge transfer. The present study demonstrates a good correlation between the experimentally determined dipole moments and those from *ab initio* calculations. The increase in planarity on excitation renders the molecule more polar (as compared to ground state) giving rise to a change in the dipole moment on excitation. Further, the presence of general type of solute-solvent interaction in addition to H-bonding interaction in most of the polar solvents can be specified by the linear E_T^N dependence on Stokes shift.

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