Solvent effect on the spectral properties of dipolar laser dyes: Evaluation of ground and excited state dipole moments

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ABSTRACT

The effect of solvents on absorption and fluorescence spectra and dipole moments of two medium sized dipolar laser dyes 2-(2,7-dichloro-6-hydroxy-3-oxo-3*H*-xanthen-9-yl) benzoic acid (Fluorescein 27) (F27) and *N*-[6-diethylamino]-9-(2,4-disulfophenyl)-3*H*-xanthen-3-ylidene]-*N*-ethylhydroxid (Sulfarhodamine B) (SRB) have been studied comprehensively in polar protic and polar aprotic solvents at room temperature (298 K). The bathochromic shift observed in absorption and fluorescence spectra of F27 and SRB with increasing solvent polarity signifies that the transition involved are π→π*. Solvatochromic correlations were used to obtain the ground and excited state dipole moments. The observed excited state dipole moments are found to be larger than their ground state counterparts in all the solvents studied. The ground and excited state dipole moments of these probes have also been computed from *ab initio* calculations and compared with those determined experimentally. Further, the experimentally obtained changes in dipole moment (Δμ) were compared with those using normalized polarity terms E_T^N from Reichardt equation.

1. Introduction

It is a renowned fact that the chemical processes are influenced by the properties of solvents in which they are carried out. These include the dipole moment, refractive index, polarity, polarizibility, dielectric constant and the nature of solute solvent interactions [1]. Solvent polarity is the most significant property which can alter the position of the absorption or emission band of molecules by solvating a solute molecule or any other molecular species introduced into the solvent milieu. Numerous articles on the studies of simple organic molecules with regard to their interactions in different solvents are reported in literature [2-9]. On the other hand, the fluorescent dye molecules are complex organic molecules which might carry charge centers and are thus prone to absorption changes in different media [10,11]. They help in understanding several physical-organic reactions of these macromolecules that might become important in different fields of pure and applied chemistry such as extraction of dyes from solution, photodynamic therapy, synthetic chemistry and chelation processes [12-14].

Determination of the ground and exited-state dipole moments of the molecules is imperative, since these values of dipole moments provide information about the change in the electronic charge distribution upon excitation. There are various techniques of determining excited state dipole moment μe with electro optical methods like electrochromism of absorption and fluorescent bands [15], Stark splitting of rotational levels of the 0-0 vibrational bands and the effect of an external electric field on the fluorescence anisotropy

[16,17], nevertheless the solvent-shift method based on the analysis of solvatochromism of absorption and fluorescence maxima is the simplest and the most widely used. In order to study the changes in electronic charge distribution in excited states of solute molecules, the solvent-induced shift of electronic bands of molecules has been used extensively [18].

Knowledge of excited state properties provides the information that is useful not only in the design of new molecules but also for the optimum performance in a particular application. In this perspective, the spectroscopic properties of fluorescein dyes are renowned with the dyes having applications ranging from dye lasers [19] to tracers in flow visualization and mixing studies [20-22]. Fluorescein dyes are very attractive due to their high fluorescence quantum yield (ϕ > 0.9), water-solubility, low cost, non-toxicity and low-staining potential. They are commonly used in laser industry [23,24] as well as for fluorescein angiography in medical treatment [25]. SRB has been used to measure drug-induced cytotoxicity and cell proliferation for large-scale drug-screening applications [26]. Though, fluorescein dyes undergo very little nuclear reorganization, they are solvatochromic owing to the change in electronic distribution resulting in increased dipole moment in the excited state as compared to that of ground state [27]. The excited state dipole moment (μe) of fluorescent dyes also establishes the tunability range of the emission energy as function of the medium.

The strong emission of dyes results from the polar character of low-lying excited states. It has been identified that the electronic spectra of these molecules are affected by their milieu. The solvent effects are of particular importance, among

the principal environmental factors. The dipole moments of a molecule in the ground and excited states depend on the electron distribution in these states. A change in solvent is always associated by a change in polarizability, dielectric constant and polarity of the immediate medium. Hence, the change of solvent affects the ground and the excited states differently and a systematic analysis of the solvent effect is thus valuable in understanding the excited state behaviour of the molecule. These properties have been studied as a function of concentration of the dye, polarity, viscosity and polarizability of the solvents, as well as pH of the solution. The solvent dependent spectral shift can arise from specific (ex: hydrogen bonding) and/or non-specific (dielectric enhancement) solvent-solute interactions. The solvent shifts can be accounted in terms of the broad-spectrum effect of the interaction forces (which are mostly of van der Waals type) on the π-electron system of the molecule. It is a well-known fact that, as the π-electron system becomes less localized, the transition energy becomes smaller resulting in a bathochromic shift (red shift) and its opposite effect gives rise to a hypsochromic shift (blue shift). In order to assign the electronic transitions as $\pi \to \pi^*$ or $n \to \pi^*$ the solvatochromic technique is found quite useful. Note that, $\pi \to \pi^*$ bands show a red shift in the solvents of increasing polarity while $n \to \pi^*$ bands show a blue shift. The solvatochromic shifts have also been used for the determination of the excited state dipole moments of some dyes [28-33].

To examine the influence of the nature of solvents on the dipole moments in the excited state and the ground state, a number of solvents have been selected for the present study. Firstly, the non hydrogen-bond donating solvents (non-HBD solvents) such as acetone, acetonitrile, DMF and DMSO. Secondly, the hydrogen-bond donating solvents (HBD solvents) such as formamide, glycerol and alcohols are used, which have been a subject of a number of studies related to polar solvation [34 and references therein]. The importance of choice of proper solvents in the estimation of dipole moments of molecules has been the subject of a recent study [7].

As part of our spectroscopic research programme on laser dyes, we present the experimental dipole moment studies of two dipolar fluorescent dyes, namely, Fluorescein 27 (F27) and Sulfarhodamine B (SRB) (Figure 1) in the ground and excited states. Solvents covering wide range from non-HBD to HBD solvents have been preferred. Thus, we have chosen various (*i*) aprotic (ε = 21.01 to 47.24, from acetone to DMSO) and (*ii*) protic solvents (ε = 7.93 to 33.6, from decanol to methanol, glycerol ε = 42.5 and formamide ε = 111). To the best of our knowledge, this is the first experimental study on the evaluation of dipole moments of these dyes.

2. Theory

For quantitative assessment of the solvent-solute interactions, multi-parameter solvent polarity scale and spectroscopic shifts can be used. Effect 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 (Equation 1 and 2, respectively) [35,36].

$$(v_a - v_f) = (v_a - v_f)_0 + a.\alpha + b.\beta + s.\pi^* \tag{1}$$

$$(v_a - v_f) = (v_a - v_f)_0 + a.\left[\frac{\varepsilon - 1}{2\varepsilon + 1}\right] + b.\left[\frac{n^2 - 1}{2n^2 + 1}\right] + s.E_T(30) \tag{2}$$

where π^* is a measure of the solvent polarity/polarizability [37], α is the scale of the solvent hydrogen solvent bond donor (HBD) acidities [38], β is the scale of the solvent hydrogen solvent bond acceptor (HBA) basicities [39]. ε, n and E_T(30) are

relative permittivity, refractive index and empirical polarity parameter of the solvent, respectively. Equation 2 estimates independent contributions of solvent dipolarity, polarizability and other specific interactions like hydrogen bonding, extra π-π interaction, etc. All the parameters should be re-normalized and re-scaled for Equation 2, to have comparable *a*, *b* and *s* values. $(v_a - v_f)_0$ is the regression value of the solute property in the reference solvent. The regression coefficients *a*, *b* and *s* in these equations measure the relative susceptibilities of the solute property, such as absorption, fluorescence and other spectroscopic parameters.
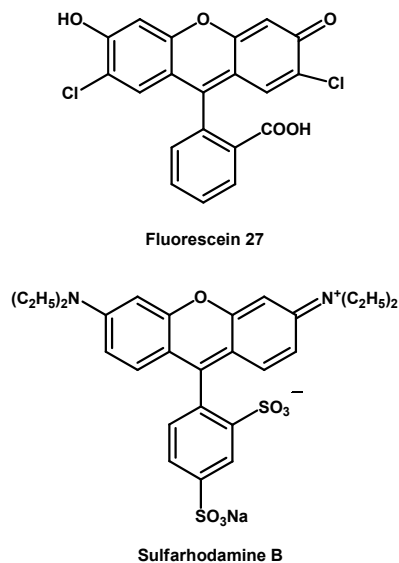

Fluorescein 27

Sulfarhodamine B

Figure 1. Molecular structures of (a) Fluorescein 27 (F27) and (b) Sulfarhodamine B (SRB).

Based on the Onsager's reaction field theory, that presumes a fluorophore as a point dipole residing in the centre of a spherical cavity with radius (*a*) in a homogeneous and isotropic dielectric with relative permittivity (ε), the commonly used expression in fluorescence spectroscopy was first developed by Lippert [40,41] and Mataga [42,43]. The Lippert-Mataga equation is no longer applicable when, in addition to the non-specific interactions, specific fluorophore/solvent interactions such as hydrogen bonding or electron-pair donor/electron-pair acceptor interactions also contribute significantly to the overall solute-solvent interaction. An additional constraint results from the cavity radius, which is not easy to approximate for elongated molecules with an ellipsoidal shape [1].

Kawski and others [44-46] obtained a simple quantum mechanical second order perturbation theory of absorption (v_a) and fluorescence (v_f) band shifts in different solvents of varying permitivity (ε) and refractive index (*n*) relative to the band position of a solute molecule based on which the following equations are obtained:

$$v_a - v_f = m_1 f(\varepsilon, n) + const. \tag{3}$$

$$v_a + v_f = -m_2 [f(\varepsilon, n) + 2g(n)] + const. \tag{4}$$

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 [44] and

Table 1. Some physical constants of solvents and absorption maxima of F27 and SRB in various solvents*.

Solvents	n	ε	π^*	α	β	λ_{max}(nm)	
						F27	SRB
Acetone	1.359	21.01	0.71	0.08	0.43	527.0	548.5
Acetonitrile	1.344	36.64	0.75	0.19	0.40	525.5	551.0
DMF	1.430	38.25	0.88	0.00	0.69	533.0	553.5
DMSO	1.479	47.24	1.00	0.00	0.76	533.0	560.0
Formamide	1.447	111.00	0.97	0.71	0.48	515.5	566.0
Glycerol	1.489	42.50	0.62	1.21	0.51	510.0	565.0
Methanol	1.329	33.70	0.60	0.98	0.66	511.0	556.0
Ethanol	1.361	24.30	0.54	0.86	0.75	518.0	554.0
Propanol	1.385	20.60	0.52	0.84	0.90	520.0	553.0
Butanol	1.399	17.40	0.47	0.84	0.84	521.5	553.0
Pentanol	1.410	14.80	0.40	0.84	0.86	522.0	554.0
Hexanol	1.418	13.00	0.40	0.80	0.86	521.5	554.5
Heptanol	1.424	11.30	-	-	-	523.0	554.5
Octanol	1.429	9.80	0.40	0.77	0.81	521.0	554.5
Nonanol	1.434	9.00	-	-	-	521.0	554.5
Decanol	1.437	8.00	0.45	0.70	0.82	521.5	554.5

* The values of π^*, ε, α and β for general solvents and alcohols are from taken from Ref. [48,49]. The values of n are taken from Fluka Catalogue 2004-05 for general solvents and alcohols.

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

with

$$m_1 = \frac{2(\mu_e - \mu_g)^2}{hca^3} \tag{7}$$

and

$$m_2 = \frac{2(\mu_e^2 - \mu_g^2)}{hca^3} \tag{8}$$

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 (equation 3 and 4), and the values of μ_g and μ_e from equation 7 and 8 can be given as [33].

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

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

or

$$\mu_e = \frac{m_1 + m_2}{m_2 - m_1}\mu_g \; ; (m_2 > m_1) \tag{11}$$

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

The method based on the empirical polarity scale proposed by Reichardt [1] 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.* [27] and accordingly the excited state dipole moment is evaluated using the equation

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

where $\Delta\mu_B = 9D$ and $a_B = 6.2$ 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 an equation 1.

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

The change in dipole moment is determined by:

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

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

3. Experimental

3.1. Chemicals used

The laser dyes F27 and SRB were of the highest available purity procured from Lambda Physik GmbH, Germany and were used without further purification. All the solvents used in the study were procured from Fluka (HPLC grade) and were chosen as they are transparent and non-fluorescent in the range of excitation and fluorescence emission.

3.2. Spectroscopic measurements

Absorption spectra were recorded using UV-visible double beam ratio recording spectrophotometer (Hitachi, Model U-2800). Fluorescence spectrofluorometer (Hitachi, Model F-7000) was used to record the fluorescence spectra. All the measurements were carried out at room temperature (298K) keeping the dye concentration very low (10^{-5} - 10^{-6} M) in order to avoid or minimize self-absorption and aggregation. The excitation wavelength used for F27 and SRB are 490 nm and 550 nm, respectively.

4. Results and discussion

The values of absorption maxima λ_{max} of F27 and SRB in the solvents used are given in Table 1. From this table, one can observe that the absorption maxima of the dyes are affected by the type of solvent and maximum shifts ($\Delta\lambda$) for F27 and SRB are 23 and 18 nm, respectively for the solvents used in this work. Hence, this change in spectral position can be used as a probe for different types of interactions between the solute and solvents. 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 [48,49]. The solvent parameters essential for this work are shown in Table 1. The spectral position of dye in a variety of solvents has revealed interesting results. Since all the solvents used in this study were polar in nature, one would expect that the solute would bind more strongly to a more polar solvent and consequently cause the spectra to shift to lower wavelengths. However, this is not observed from our results as λ_{max} is lowest in the case of glycerol for F27 and acetone for SRB. This may be due to the reason that all other solvents used in this work are more polar than these two solvents in which λ_{max} is lowest and can engage more strongly in a solvent-solvent type of interaction or their ability to interact with the dye molecules reduces. These solvents, glycerol (for F27) and acetone (for SRB) are less polar and interact with dye molecules in terms of dipole-dipole interactions, leading to a net stabilization of the ground state of the solute molecule and thus a hypsochromic shift in the spectrum of these solvents is observed. Alternatively, λ_{max} value is shifted to lower energies in highly polar solvents such as formamide because of strong solvent-solvent interaction or specific interaction between the solvent and hydrogen present in the functional groups of the dye molecule.

Figure 2a and 2b illustrate the plot of λ_{max} versus the dielectric constant (ε) values in different non-HBD and HBD solvents for SRB dye. From this figure, it can be seen that with increase in ε values, the spectrum is shifted to longer wavelengths. In case of F27, λ_{max} of dye solution in DMSO (aprotic or non-HBD) and glycerol (protic or HBD) were found to be at lower wavelengths as compared to other solvents although their dielectric constants are higher among respective non-HBD and HBD solvents. This might be due to the formation of strong hydrogen bond between dye and solvent molecule. The variation of λ_{max} versus π* in different non-HBD and HBD solvents for SRB shown in Figure 3a and 3b, wherein an increase in λ_{max} values with π* specifies that dye interaction changes with increasing capability of a given solvent to form hydrogen bonds in solution.

The effect of solvents on the absorption and emission spectra of SRB in aprotic (acetone to DMSO) and of F27 in protic (formamide and alcohols) solvents are shown in Figure 4a and 4b, respectively. The uncertainties in the measured wavelength of absorption and fluorescence maxima are ±0.5 nm and ±1 nm, respectively. The observed absorption and emission spectra of these two dyes are broad and they shift depending on the solvent used. The charge transfer band shows a shift of about 4-23 nm in the absorption spectra on changing the solvent from decanol to formamide for F27 and that in case of SRB is 3-13 nm. A relatively larger spectral shift observed in the emission spectra as compared to the absorption spectra. A lesser variation in the absorption shift 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 these dyes in the ground state rather than the excited 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 large Stokes' shift observed is also an indicative of the charge transfer transition. The higher magnitude of Stokes' shift indicates that the excited state geometry could be different from that of the ground state. A general observation is, increase in Stokes' shift values with increase in solvent polarity indicating 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 and hence, a significant red shift of the fluorescence will be observed.
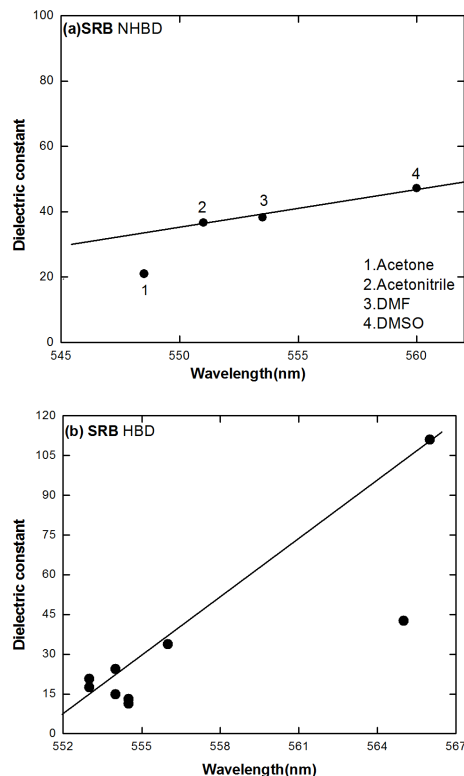

Figure 2. (a) Absorption shift of SRB dye solution as a function of dielectric constant in non-hydrogen-bond donating solvents, (b) Absorption shift of SRB dye solution as a function of dielectric constant in hydrogen-bond donating solvents.
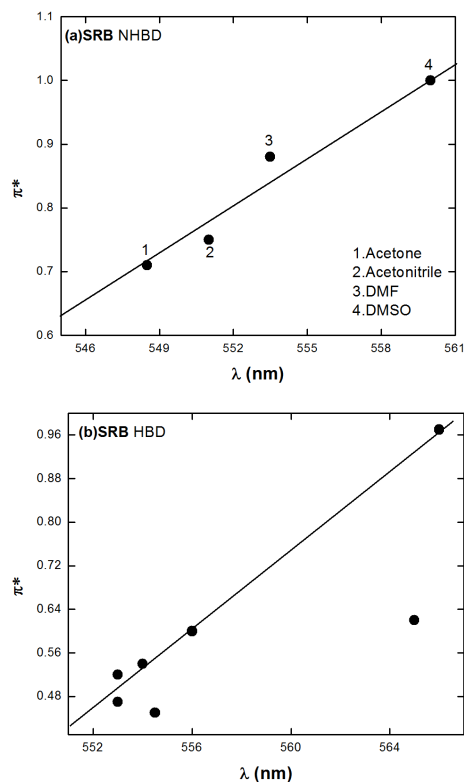

Figure 3. (a) Absorption shift of SRB dye solution as a function of solvent Polarizibility (π*) in non-HBD solvents, (b) Absorption shift of SRB dye solution as a function of solvent Polarizibility (π*) in HBD solvents.

Table 2. Some physical constants of solvents and spectral data of F27 and SRB*.

Solvents	$E_T(dye)$		$E_T(30)$	E_T^N	ν_a (cm⁻¹)		ν_f (cm⁻¹)	
	F27	SRB			F27	SRB	F27	SRB
Acetone	54.25	52.13	42.2	0.355	18975	18232	18215	17476
Acetonitrile	54.41	51.89	45.6	0.460	19029	18149	18376	17361
DMF	53.64	51.65	43.2	0.386	18762	18067	17986	17259
DMSO	53.64	51.06	45.1	0.444	18762	17857	17973	17082
Formamide	55.46	50.51	55.8	0.775	19399	17668	18362	16920
Glycerol	56.06	50.60	57.0	0.812	19608	17699	18349	16667
Methanol	55.95	51.42	55.4	0.762	19569	17986	18622	17247
Ethanol	55.19	51.61	51.9	0.654	19305	18051	18636	17283
Propanol	54.98	51.70	50.7	0.617	19231	18083	18382	17337
Butanol	54.82	51.70	49.7	0.586	19175	18083	18587	17403
Pentanol	54.77	51.61	49.1	0.568	19157	18051	18553	17319
Hexanol	54.82	51.56	48.8	0.559	19175	18034	18450	17325
Heptanol	54.67	51.56	48.5	0.549	19120	18034	18546	17331
Octanol	54.88	51.56	48.1	0.537	19194	18034	18532	17337
Nonanol	54.88	51.56	47.8	0.528	19194	18034	18546	17379
Decanol	54.82	51.56	47.7	0.525	19175	18034	18601	17397

* $E_T(30)$ values for both general and alcohols solvents are from Ref. [1,48,49]. E_T^N values for both general and alcohols solvents are from Ref. [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	$f(\varepsilon, n)$	$2g(n)$	$f(\varepsilon, n)+2g(n)$
Acetonitrile	0.861	0.469	1.330
DMF	0.839	0.583	1.423
DMSO	0.841	0.648	1.489
Formamide	0.895	0.606	1.501
Glycerol	0.830	0.661	1.491
Methanol	0.857	0.448	1.305
Ethanol	0.812	0.491	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	0.612	0.582	1.196
Nonanol	0.588	0.589	1.177
Decanol	0.553	0.593	1.146
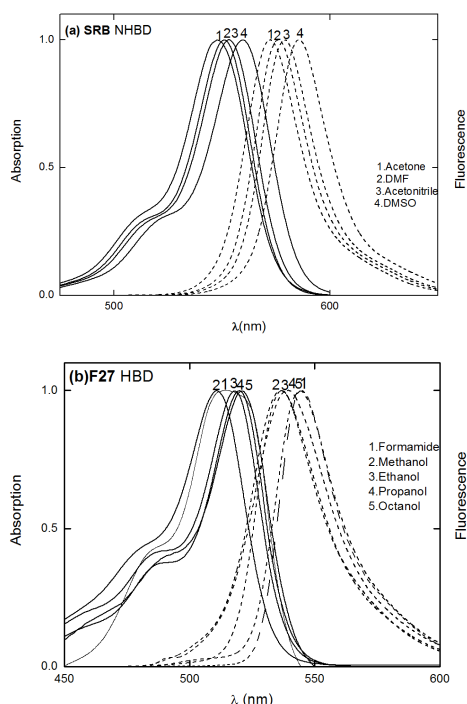
Figure 4. Absorption and fluorescence spectra of (a) SRB in non-HBD and (b) F27 in HBD solvents.

The absorption data of dyes in different solvents was also analyzed in terms of various polarity scales. One among such methods 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 [50],

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

The E_T (dye) values, obtained using equation 15, 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. One can notice from Table 2 that, E_T (dye) value is the highest as compared to other solvents in the case of glycerol for F27 and acetone for SRB. The reason for this being the same as described earlier.

The wave numbers of absorption and fluorescence emission maxima of the solutes along with the microscopic polarity scale E_T^N, are summarized in Table 2. Consequently, to estimate the ground state and excited state dipole moments of the dye molecules, the solvent polarity $f(\varepsilon, n)$ and $f(\varepsilon, n)+2g(n)$ parameters were calculated (Table 3). Figure 5 show the respective spectral shifts ν_a-ν_f and ν_a+ν_f for both the dyes which are observed in non-HBD and HBD solvents 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. For polar solutes, like F27 and SRB, the interaction with non-polar solvents depend on the dipole-induced-dipole forces, while with aprotic (polar but non-HBD) solvents, the solute-solvent interaction depends on the stronger dipole-dipole forces. In HBD solvents (polar protic), in addition to dipole-dipole interaction, specific interaction such as H-bonding may be effective as the intermolecular charge transfer (ICT) character is favourable for H-bonding with hydroxyl groups present in
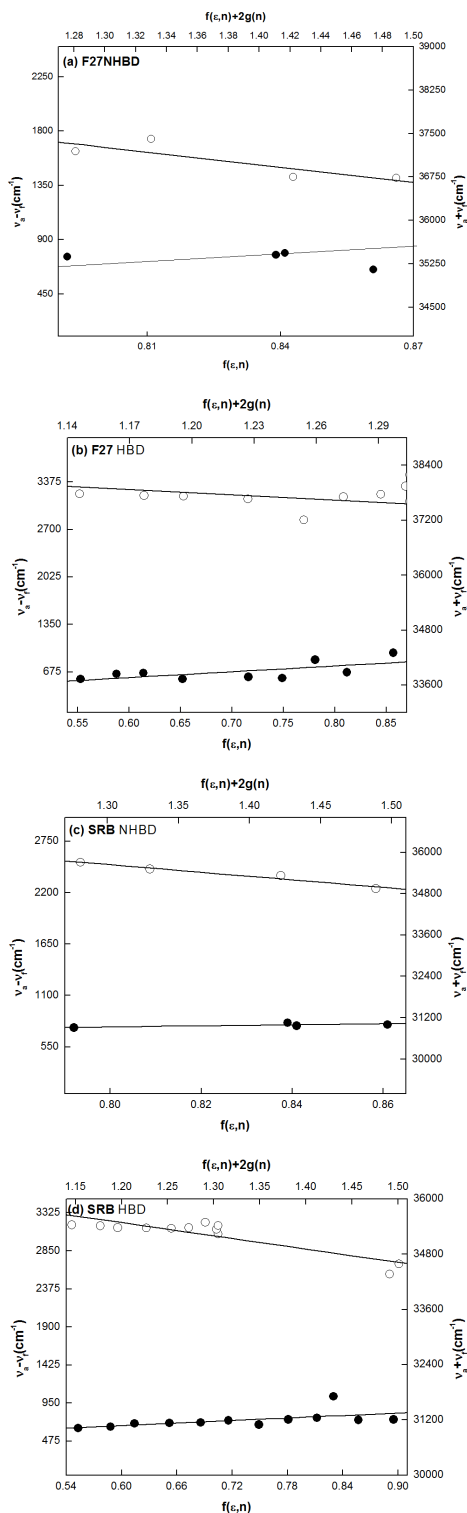
Figure 5. Plot of v_a-v_f vs. $f(\varepsilon, n)$ and v_a+v_f vs. $f(\varepsilon, n)$+2g(n) of F27 in (a) non-HBD (b) HBD solvents and SRB in (c) non-HBD and (d) HBD solvents studied.

protic solvents. Hydrogen bonding interaction usually puts a severe restriction on the validity of the eqns. (3) and (4). It is consequently useful as pointed out by others also [51,52] to use $E_T(30)$ function which is the empirical measure of the solvent polarity [53] for understanding the polarization dependence of spectral characteristics.

The solvent polarity parameter E_T (30), which also considers other interactions besides those of specific nature, was related with the absorption values. E_T (30) values were acquired from literature for different solvents used in this study and are shown in Table 2. Figure 6 depicts the correlation between the absorption value (in wavenumber) and E_T(30) for F27 dye. Linear correlation of absorption energy over a range of E_T (30) represents the presence of specific interactions between the solute and solvents. Unfortunately, E_T (30) values have the dimension of kcal/mol, a unit which should be discarded in the framework of SI units [1]. For that reason, the use of the so-called normalized E_T^N values have been suggested, as defined in equation 13. Figure 7a and 7b show the plots of Stokes' shift as a function of E_T^N in all the solvents for F27 and SRB, respectively. The linear E_T^N dependence of Stokes' shift reveal the existence of general type of solute-solvent interaction in which the Stokes' shift depends on dielectric constant and refractive index of the solvents.
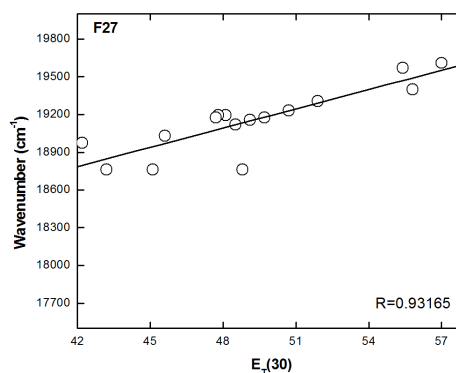

Figure 6. Plot of absorption value of F27 (in wavenumber) vs. E_T(30) in all solvents studied.

The Onsager's cavity radius is calculated using both Edward's increment method [54] and from Suppan equation [55]. These two methods collectively yield almost the same cavity radius of 4.15 Å and 4.93 Å for F27 and SRB, respectively. Using equation 9 and 10 the ground and excited state dipole moments are evaluated and summarized in Table 4 along with the slopes m_1 and m_2. The difference in dipole moment calculated from solvent perturbation method and the one calculated using equation 14 are reasonably in good agreement in case of protic solvents, obviously indicating the excited state dipole moment to be higher compared to ground state.

The observed ground state dipole moment of F27 and SRB are 2.65 D and 6.85 D in aprotic solvents 2.20 D and 5.61 D in protic solvents, respectively. The disparity in the values of dipole moments of F27 and SRB can also be explained on the basis of their possible resonance structures as shown in Figure 8a and 8b. In case of F27 dye, non-bonding electrons on the oxygen of pyran ring, hydroxyl group, carbonyl group and carboxylic acid group along with chlorine contribute towards the mobility of electrons on the aromatic ring. Alcohols form strong hydrogen bonding, thus oxygen atom of –OH can better contribute to the resonance structure. On excitation, the oxygen atom of the carbonyl group and that of pyran ring also contribute towards the mobility of electrons on the aromatic ring group by delocalizing their non-bonding electrons.

Whereas SRB (anion), is a model hydrophilic probe. The π electron mobility is more in SRB because of more electron tendency of nitrogen atom. The nitrogen atom of diethylamine group in SRB has lone pair of electrons. These non-bonding electrons on the nitrogen atom of tertiary amino group -$N(C_2H_5)_2$ contribute towards the mobility of electrons on the aromatic ring.

Table 4. Dipole moments, slopes (m_1 and m_2) and correlation factor (r) of F27 and SRB molecules.

Molecules	Radius (Å)	Solvents	μ_g (D)	μ_e (D)	$\Delta\mu$ (D)	μ_e/μ_g	m_1 (cm^{-1})	m_2 (cm^{-1})	r
F27	4.15	Aprotic	2.65	5.34	2.69 (1.010[c])	2.015	1023.39	3034.03	0.756:0.864
		Protic	2.20	4.62	2.42 (2.596[c])	2.100	824.60	2324.92	0.906:0.915
			6.19[a]	8.26[b]	2.07	1.334			
SRB	4.93	Aprotic	6.85	9.37	2.52 (1.101[c])	1.370	536.31	3441.53	0.804:0.978
		Protic	5.61	8.11	2.50 (2.115[c])	1.446	521.86	2891.93	0.853:0.881
			12.12[a]	14.64[b]	2.52	1.208			

[a] Calculated from B3LYP functional with 6-31G* basis.
[b] Excited state dipole moment using CI singles (CIS) method.
[c] Calculated using equation 14.
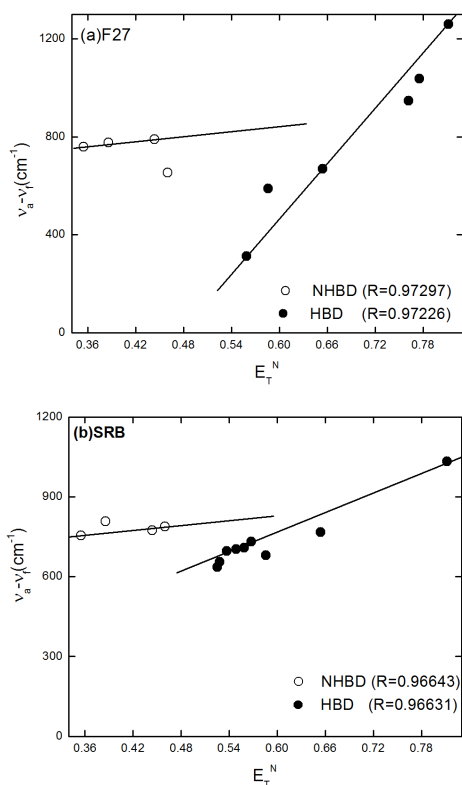
Figure 7. Plot ν_a-ν_f vs E_T^N of (a) F27 and (b) SRB in all solvents studied.

Since the nitrogen atom of tertiary amino group is sp^3 hybridized, its electron donating tendency is more. Upon excitation the tertiary amino group becomes strong electron donor. This is precisely the reason why SRB possess higher dipole moment than F27.

The ground and excited state dipole moments of the solutes were also determined from *ab initio* calculations using DFT [56] and CIS method, respectively (Table 4). The ground state optimized geometries of these probes acquired using B3LYP functional with 6-31G* basis are shown in Figure 9a and 9b. 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 moments evaluated from solvatochromic shift method are smaller than those obtained from *ab initio* calculations for F27 and SRB probes. Numerous reports in literature have shown disagreement between theoretical and experimental values [57]. The excited state dipole moments were computed using CIS method to estimate the minimum of the lowest excited singlet state and optimized using 6-31G*.

Acemioglu *et al.* [2] reported such study on fluorescein molecule and found that it possesses higher dipole moment in the excited state than in the ground state in n-alcohols.
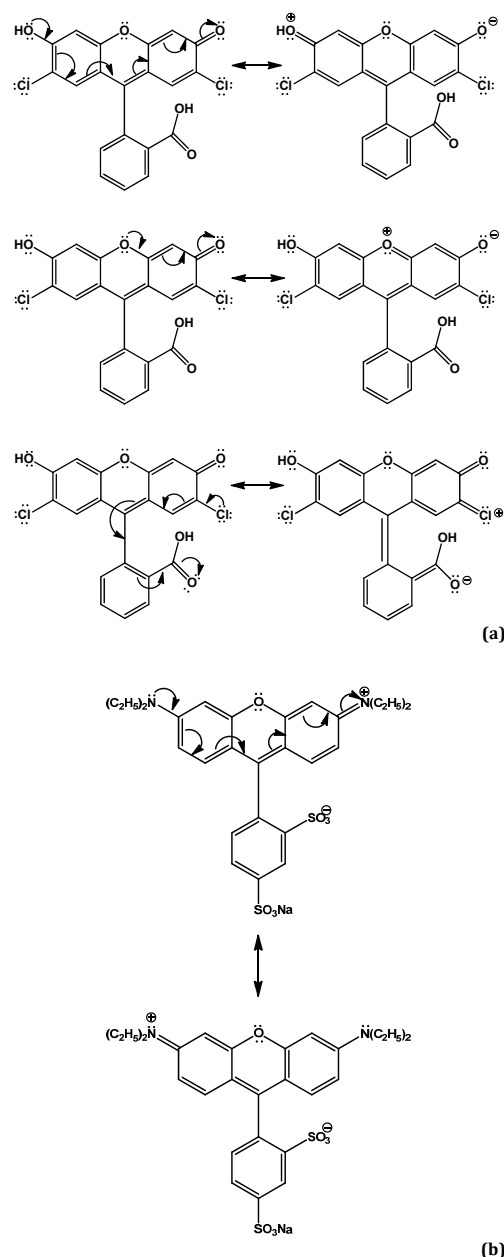
Figure 8. Possible resonance structures of (a) F27 and (b) SRB.

However, it possessed lower dipole moment in the exited state than in the ground state in acetonitrile (AN) and acetonitrile-benzene (AN-BN) solvent mixtures. The authors opined that the excited state of fluorescein is more stable with solvents than the ground state in n-alcohols while the ground state is more stable than the exited state in AN and AN-BN

solvent mixtures. The molecule F 27 studied here is a derivative of fluorescein with two additional Cl⁻ groups. Our results, interestingly do not lead to any values of excited state dipole moment being smaller than those of ground state in protic solvents. Also, in the present study the ground and excited state dipole moment values have been determined from *ab initio* calculations and it is found that the values of dipole moments are higher in excited state than in ground state, which further supports our experimental observations. The observation of lower dipole moments in the excited state for fluorescein molecule in AN and AN-BN solvent mixtures appears to be a rare one as most molecules exhibit higher dipole moment in the excited state owing to change in electronic distribution [27].
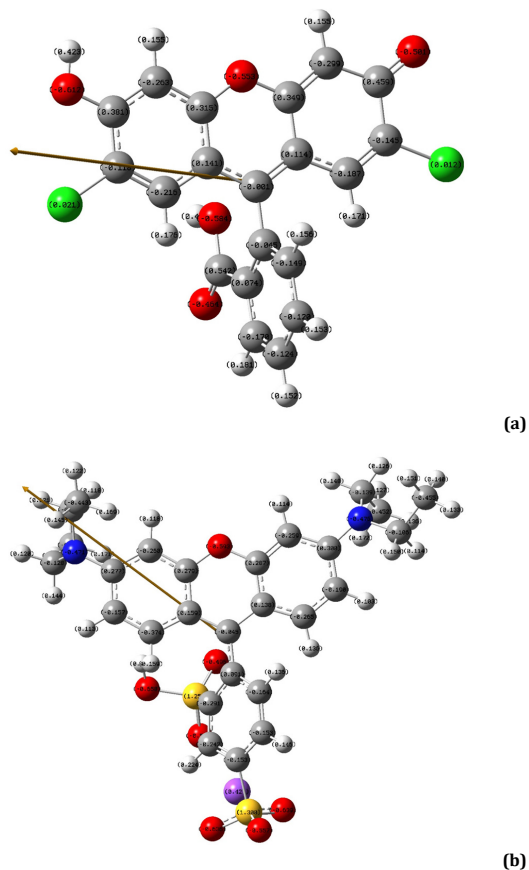
(a)

(b)

Figure 9. Ground state optimized structures of (a) F27 and (b) SRB molecules obtained using B3LYP functional with 6-31G* basis is shown along with the distribution of charges. The arrow indicates the direction of dipole moment.

5. Conclusions

In this paper, we have described the solvent effect by examining dipole moments of two fluorescent dipolar laser dyes namely F27 and SRB in various solvents. Absorption maxima of these dyes are reliant on solvent polarity. Solvation of probe molecules takes place by means of dipole-dipole interactions in aprotic solvents, whereas in protic solvents the phenomenon is more hydrogen bonding in nature. A bathochromic shift is observed upon increasing the polarity of the solvent for both the dyes indicating $\pi \rightarrow \pi^*$ transition which is further confirmed by calculating dipole moments using solvatochromic technique and the one using equation 14. We found that the probes F27 and SRB possess higher dipole moments in the excited state than in the ground state in the solvents used. This clearly signifies that, the excited state of F27 and SRB is more polar than the ground state. Further, the

linear E_T^N dependence on Stokes' shift specifies the presence of general type of solute-solvent interaction in addition to H-bonding interaction in most of the polar solvents.

References

[1]. Reichradt, C. Solvents and Solvent Effects in Organic Chemistry, 3rd edition, Wiley-VCH, Verlag, GmbH and Co., 2004.
[2]. Acemioglu, B.; Arik, M.; Efeoglu, H.; Onganer, Y. *J. Mol. Struct.* (Theochem) **2001**, *548*, 165-171.
[3]. Cremers, D. A.; Windsor, M. W. *Chem. Phys. Lett.* **1980**, *71*, 27-32.
[4]. Adeoye, M. D.; Adeogun, A. I.; Adewui, S.; Odozi, N. W.; Obi-Egbeedi, N. O. *Sci. Res. Essays* **2009**, *4*, 107-111.
[5]. Inamdar, S. R.; Nadaf, Y. F.; Mulimani, B. G. *J. Mol. Struct. (Theochem)* **2003**, *624*, 47-51.
[6]. Mannekutla, J. R.; Inamdar, S. R.; Mulimani, B. G. *Spectochim. Acta A* **2008**, *69*, 419-426.
[7]. Rautela, R.; Joshi, N. K.; Joshi, H. C.; Tewari, N.; Pant, S. *J. Mol. Liq.* **2010**, *154*, 47-51.
[8]. Tewari, N.; Joshi, N. K.; Rautela, R.; Gahlaut, R.; Joshi, H. C.; Pant, S. *J. Mol. Liq.* **2011**, *160*, 150-153.
[9]. Gahlaut, R.; Tewari, N.; Bridhkoti, J. P.; Joshi, N. K.; Joshi, H. C.; Pant, S. *J. Mol. Liq.* **2011**, *163*, 141-146.
[10]. Bevilaqua, T.; Goncalves, T. F.; Venturini, C. G.; Machado, V. G. *Spectochim. Acta A* **2006**, *65*, 535-545.
[11]. Oliveira, C. S.; Bronco, K. P.; Baptista, M. S.; Indig, G. L. *Spectochim. Acta A* **2002**, *58*, 2971-2982.
[12]. Ishikawa, M.; Ye, J. Y.; Maruyama, Y.; Nakatsuka, H. *J. Phys. Chem. A* **1999**, *103*, 4319-4331.
[13]. El-Kemary, M. A.; Khedr, R. A.; Etaiw, S. H. *Spectochim. Acta A* **2002**, *58*, 3011-3014.
[14]. Jedrzejewska, B.; Kabatc, J.; Paczkowski, J. *Dyes Pigm.* **2007**, *74(2)*, 262-268.
[15]. Czekalla, J. *Z. Electrochem.* **1960**, *64*, 1221-1228.
[16]. Liptay, W. Dipole moments and Polarizibilities of Molecules in Excited States, in E. C. Lim, Ed. , Excited States, Vol. 1, pp. 129-229, Academic Press, New York, 1974.
[17]. Baumann, W. Determination of Dipole Moments in Ground and Excited States, in Rossiter, B. W.; Hamilton, J. F. , Eds. , Methods of Chemistry, Vol. 3B, pp. 45-131, John Wiley and Sons, New York, 1989.
[18]. McRae, E. G. *J. Phys. Chem.* **1957**, *61*, 562-572.
[19]. Lindqvist, L. *Arkiv Kemi.* **1960**, *16*, 79-138.
[20]. Koochesfahani, M. M.; Dimotakis, P. E. *J. Fluid Mech.* **1986**, *170*, 83-112.
[21]. Dahm, W. J. A.; Southerland, K. B.; Buch, K. A. *Phys. Fluids A* **1991**, *3*, 1115-1127.
[22]. Karasso, P. S.; Mungal, M. G. *Exp Fluids* **1997**, *23*, 382-387.
[23]. Schafer, F. P. Dye Lasers, Springer-Verlag, Berlin, 1973.
[24]. Demas, J. M.; Grossby, G. A. *J. Phys. Chem.* **1971**, *75(8)*, 911-1024.
[25]. Yu, H. G.; Kim, M. J.; Oh, F. S. *Ocul. Immunol. Inflamm.* **2009**, *17(1)*, 41-46.
[26]. Voigt, W. *Methods Mol. Med.* **2005**, *110*, 39-48.
[27]. Ravi, M.; Soujanya, T.; Samanta, A.; Radhakrishnan, T. P. *J. Chem. Soc. Faraday Trans.* **1995**, *91*, 2739-2742.
[28]. Sundstrom, V.; Gillbro, T.; Bergstrom, H. *Chem. Phys.* **1982**, *73*, 439-458.
[29]. Balu, W.; Reber, R.; Penzkofer, A. *Opt. Commun.* **1982**, *43*, 210-214.
[30]. Sundstrom V.; Gillbro, T. *Chem. Phys. Lett.* **1984**, *109*, 538-543.
[31]. Srividya, N.; Ramamurthy, P.; Ramakrishnan, V. T. *Spectrochim. Acta A* **1997**, *53*, 1743-1753.
[32]. Kumar, S.; Rao, V. C.; Rastogi, R. C. *Spectrochim. Acta A* **2001**, *57*, 41-47.
[33]. Kawski, A. *Z. Naturforsch. A* **2002**, *57a*, 255-262.
[34]. Blanchard, G. J. *J. Phys. Chem.* **1988**, *92*, 6303-6307.
[35]. Kamlet, M. J.; Abboud, J. M.; Taft, R. W. *Prog. Phys. Org. Chem.* **1981**, *13*, 485-630.
[36]. Fowler, F. W.; Katritzky, A. R.; Rutherford, R. J. D. *J. Chem. Soc. B* **1971**, 460-469.
[37]. Abboud, J. M.; Kamlet, M. J.; Taft, R. W. *J. Am. Chem. Soc.* **1977**, *99*, 8325-8327.

[38]. Kamlet, M. J.; Jones, M. E.; Taft, R. W. *J. Chem. Soc. Perkin Trans.* **1979**, *2*, 349-356.
[39]. Kamlet, M. J.; Taft, R. W. *J. Am. Chem. Soc.* **1976**, *98*, 377-383.
[40]. Lippert, E. *Z. Naturforsch. A* **1955**, *10*, 541-545.
[41]. Lippert, E. *Z. Elektrochem. Ber. Bunsenges. Phys. Chem.* **1957**, *61*, 962-975.
[42]. Mataga, N.; Kaifu, Y.; Koizumi, M. *Bull. Chem. Soc. Jpn.* **1956**, *29*, 465-470.
[43]. Mataga, N.; Kubota, T. Molecular Interactions and Electronic Spectra, Dekker, New York, 1970.
[44]. Kawski, A. Progress in photochemistry and photophysics, Ed. Rabek, J. F., CRC Press Boca Raton, Boston, Vol. V. pp. 1-47, 1992 and references therein.
[45]. Bilot, L.; Kawski, A. *Z. Naturforsch.* **1962**, *17a*, 621-627.
[46]. Kawski, A. *Acta Phys. Polon.* **1966**, *29*, 507-518.
[47]. Kawski, A. *Acta. Phys. Polon.* **1964**, *25(2)*, 285-290.
[48]. Kamlet, J. M.; Abboud, J. M.; Abraham, M. H.; Taft, R. W. *J. Org. Chem.* **1983**, 48, 2877-2887.
[49]. Marcus, Y. *Chem. Soc. Rev.* **1993**, *22*, 409-416.
[50]. Reichrardt, C. *Chem. Rev.* **1994**, *94*, 2319-2358.
[51]. Nagarajan, V.; Brearley, A. N.; Tai, J. K.; Barbara, P. F. *J. Chem. Phys.* **1987**, *86*, 3183-3196.
[52]. Kahlow, M. A.; Tai, J. K.; Barbara, P. F. *J. Chem. Phys.* **1988**, *88*, 2372-2378.
[53]. Reichrardt, C. (ed). Molecular interactions. Wiley, New York, 1982.
[54]. Edward, J. T. *J. Chem. Edu.* **1970**, *47*, 261-270.
[55]. Suppan, P. *Chem. Phys. Lett.* **1983**, *94*, 272-275.
[56]. Gaussian 03, Revision C.02, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; and Pople, J. A.; Gaussian, Inc., Wallingford CT, 2004.
[57]. Aaron, J. J.; Maafi, M.; Parkanyi, C.; Boniface, C. *Spectrochim. Acta A* **1995**, *51*, 603-6171