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Photophysical properties and estimation of ground and excited state dipole moments of 7-diethylamino and 7-diethylamino-4-methyl coumarin dyes from absorption and emission spectra

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ABSTRACT

In the present work, the effect of solvents on absorption and fluorescence spectra and dipole moments (μ_g, μ_e) of 7-diethylamino coumarin (7DEAC) and 7-diethylamino-4-methyl coumarin (7DEA4MC) have been studied in different solvents of various polarity at room temperature. The solvents have been selected in a way to cover the full range of intermolecular interactions from non-polar hexane to strongly polar formamide. Using the methods of solvatochromism, the difference in the first excited singlet-state (μ_e) and ground state (μ_g) dipole moments was estimated from Lippert-Mataga, Bakhshiev, Kawski-Chamma-Viallet and McRae equations. The Onsager's cavity radius of the probes has been calculated by AM1 and PM3 quantum chemical calculations and also by a direct relation. The change in dipole moment value ($\Delta\mu$) was also calculated by using the variation of Stoke's shift with microscopic solvent polarity parameter (E_T^N). The calculated dipole moments represent new results, as well as some of the solvatochromic results that were not studied earlier in such large number of solvents. It is observed that the values of excited singlet-state dipole moments are higher than the ground state ones in both the molecules, which shows that excited states are more polar than the ground states.

1. Introduction

Coumarins are well known laser dyes [1,2] and are useful probes in different chemical and photochemical studies [3-7]. Most of the coumarins are highly fluorescent and have potential applications as fluorescent indicators [8], sunburn preventives [9], estimation of enzymes *etc.* [10].

In the present work we have estimated the dipole moments (μ_g, μ_e) and change in dipole moment value ($\Delta\mu$) of 7-diethyl amino coumarin (**7DEAC**) and 7-diethylamino-4-methyl coumarin (**7DEA4MC**). Determination of ground and excited state dipole moments is important, because these values give information about the change in electronic distribution upon excitation. Generally the lifetime of excited states is small and dipole moments of short-lived species are of considerable interest because just as for stable molecules, they provide important information on the electronic and geometrical structures of these transients, furthermore dipole moment represents a direct measure of electron distribution in a molecule of known geometry. A prior knowledge of the dipole moments of the electronically excited species is often useful in the design of non-linear optical materials [11] and in the elucidation of the nature of the excited states. Experimental data on excited states are also useful in the parameterization of semi-empirical quantum chemical procedures for such states.

It is known that the electronic spectra of coumarin dyes are influenced by their immediate environment, among the major environmental factors influencing the electronic spectra, solvent effects are of particular importance. The change of solvent affects the ground and excited states differently and a systematic analysis of the solvent effect is useful in understanding the excited state behavior of the molecule. The solvent shifts can be accounted in terms of the overall effect of the interaction forces on the π-electron system of the molecule. It is also known that, as the π-electron system becomes more delocalized, the transition energy becomes smaller resulting in a bathchromic shift (red shift) and its opposite effect gives rise to a hypsochromic shift (blue shift). In order to assign the electronic transitions as $\pi\rightarrow\pi^*$ or $n\rightarrow\pi^*$ the solvatochromic technique is found to be very informative. It is known that $\pi\rightarrow\pi^*$ bands show a red shift in the solvents of increasing polarity while $n\rightarrow\pi^*$ bands show a blue shift [12]. The solvatochromic shifts were also used for the determination of the excited singlet-state dipole moments of some coumarins [13-19].

2. Experimental

Coumarin dyes **7DEAC** and **7DEA4MC** were obtained from Sigma Aldrich Chemicals (USA) and were used as received. The molecular structures of the systems are given in Scheme 1. All the 22 solvents (Formamide, dimethyl sulfoxide, dimethyl formamide, acetonitrile, ethanol, acetone, propanol, butanol, 1-pentanol, dichloromethane, ethyl acetate, ethyl benzoate, ethyl propionate, *n*-butyl acetate, chloroform, toluene, *p*-xylene, benzene, carbon tetrachloride, 1,4-dioxane, cyclohexane and

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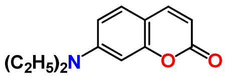
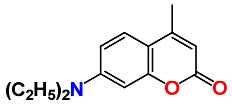
hexane) used were of spectroscopic grade and were found to be transparent and non-fluorescent in the range of excitation and fluorescence emission. The absorption and fluorescence spectra were measured by Shimadzu-UV-Visible spectrophotometer (UV2450) and Shimadzu spectrofluorometer (RF-5301PC), respectively. All the measurements were carried out at room temperature keeping dye concentration low (~10^{-6} M) in order to avoid self absorption.



7-diethylamino coumarin
(**7DEAC**)



7-diethylamino-4-methyl coumarin
(**7DEA4MC**)

Scheme 1

3. Theoretical consideration

In this work we report different solvent parameters e.g. dielectric constant (*ε*), refractive index (*n*) and spectral parameters such as Stoke's shift which is useful for determination of dipole moments. The details of the methods adopted to calculate the dipole moment in ground and excited states of two molecules under consideration based on absorption and fluorescence shifts in various solvents is given below.

3.1. Determination of dipole moment

The dipole moment of a molecule in the excited singlet-state is determined by the effect of electric field (internal and external) on the position of its spectral band. Two methods depending on the internal electric field (solvatochromism) have been employed in the present investigation.

3.1.1. Method I

By employing the simplest quantum-mechanical second order perturbation theory and taking into account Onsager's model, Bilot and Kawski [20,21] have obtained an expression for the spectral shift given by

$$\Delta\nu_{a,f} = -m_{a,f}(1-\alpha f')^{-1}\,[f(1-\alpha f)^{-1} - f'(1-\alpha f')^{-1}] - \frac{\mu_e^2-\mu_g^2}{2hc}(2-\alpha f')f'(1-\alpha f')^{-2} \quad (1)$$

where

$$m_a = \frac{\mu_g(\mu_e-\mu_g)}{hc} \quad (2)$$

for absorption and

$$m_f = \frac{\mu_e(\mu_e-\mu_g)}{hc} \quad (3)$$

for fluorescence α is the mean static isotropic polarizability of the solute. *f* and *f′* are the reaction field factors which depend on the shape and the Onsager's cavity radius *a* of the solute, and on the relative permittivity (*ε*) and refractive index (*n*) of the solvent. ν_a and ν_f are the absorption and fluorescence maxima and *h* and *c* are Planck's constant and velocity of light in vacuum, respectively.

Based on the Equation 1, the following expressions are obtained for (ν_a-ν_f) and (ν_a+ν_f)/2 [21,22];

$$\nu_a - \nu_f = m_1\, f(\varepsilon,n) + \text{constant} \quad (4)$$

$$\frac{1}{2}(\nu_a+\nu_f) = -m_2\,\varphi(\varepsilon,n) + \text{constant} \quad (5)$$

where

$$\varphi(\varepsilon,n) = \frac{1}{2}f(\varepsilon,n) + g(n), \quad (6)$$

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

and

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

The factors *f* and *f′* are simplified when a spherical cavity of radius *a* is assumed, which may be regarded as a sufficient approximation [22]. In this case, solvent polarity parameters *f* (*ε*, *n*) and g(*n*) have the form

$$f(\varepsilon,n) = \frac{((\varepsilon-1)/(2\varepsilon+1)) - ((n^2-1)/(2n^2+1))}{((1-(2\alpha/a^3))((\varepsilon-1)/(2\varepsilon+1))((1-(2\alpha/a^3))(n^2-1)/(2n^2+1))} \quad (9)$$

$$g(n) = \frac{((n^2-1)/(2n^2+1))((1-(\alpha/a^3))((n^2-1)/(2n^2+))}{(1-(2\alpha/a^3))((n^2-1)/(2n^2+1))} \quad (10)$$

If the polarizability of the solute is neglected, i.e. *α* = 0, then Equation 9 leads to Lippert-Mataga relation [23-26]

$$F(\varepsilon,n) = \left[\frac{\varepsilon-1}{2\varepsilon+1} - \frac{n^2-1}{2n^2+1}\right] \quad (11)$$

It is based on the Onsager's reaction field theory, which assumes that the fluorophore is a point dipole residing in the center of a spherical cavity with radius in a homogeneous and isotropic dielectric with relative permittivity ε. The Lippert-Mataga equation breaks down when in addition to the non-specific interactions, specific fluorophore-solvent interactions e.g., hydrogen bonding, electron-pair donor/electron-pair acceptor interactions also contribute significantly to the solute-solvent interaction. Another limitation results from the cavity radius, which is not easy to estimate for non-spherical molecule.

For an isotropic polarizability of the solute, the condition $2\alpha/a^3$=1 is frequently satisfied and justified [22], and functions *f* (*ε*, *n*) and *φ*(*n*) leads to Bakhshiev and Kawski-Chamma-Viallet relations, respectively [27,28]

$$F_1(\varepsilon,n) = \frac{2n^2+1}{n^2+2}\left[\frac{\varepsilon-1}{\varepsilon+2} - \frac{n^2-1}{n^2+2}\right] \quad (12)$$

$$F_2(\varepsilon,n) = \frac{1}{2}F_1 + \frac{3}{2}\frac{(n^4-1)}{(n^2+2)^2} \quad (13)$$

According to McRae theory [29,30] $f(\varepsilon, n)$ can be written as

$$F_3(\varepsilon,n)=\left[\frac{\varepsilon-1}{\varepsilon+2}-\frac{n^2-1}{n^2+2}\right] \quad (14)$$

Using Equations 7 and 8, the values of μ_g and μ_e can be obtained as;

$$\mu_g=\frac{m_2-m_1}{2}\sqrt{\frac{hca^3}{2m_1}} \quad (15)$$

$$\mu_e=\frac{m_1+m_2}{2}\sqrt{\frac{hca^3}{2m_1}} \quad (16)$$

or

$$\mu_e=\left[\frac{m_1+m_2}{m_2-m_1}\right]\mu_g \text{; } m_2>m_1 \quad (17)$$

So the ratio of dipole moments in excited state and ground state is given by

$$\frac{\mu_e}{\mu_g}=\frac{m_1+m_2}{m_2-m_1} \quad (18)$$

The parameters m_1 and m_2 occurring for the differences (ν_a-ν_f) and the sum (ν_a+ν_f)/2 of the wave numbers are linear functions of the solvent polarity parameters $F_1(\varepsilon, n)$ and $F_2(\varepsilon, n)$ and can be determined from the slopes of the straight lines.

3.1.2. Method II (Molecular-microscopic solvent polarity parameter (E_T^N))

The second method is based on the empirical polarity scale proposed by Reichardt [31] and gives results with solvatochromic shift of dipolar molecules that correlates much better with molecular-microscopic solvent polarity parameter E_T^N rather than the traditionally used bulk solvent polarity functions as in the later 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.* [32] and accordingly, the excited state dipole moment is evaluated by equation

$$\nu_a-\nu_f=11307.6\left[\left(\frac{\Delta\mu}{\Delta\mu_B}\right)^2\left(\frac{a_B}{a}\right)^3\right]E_T^N+\text{constant} \quad (19)$$

E_T^N [or equivalently, $E_T(30)$] is the solvent polarity function proposed by Reichardt, based on the absorption wave number, ν_a, of a standard Betaine dye in the solvent. It is expressed as

$$E_T^N=\frac{E_T(\text{solvent})-E_T(\text{TMS})}{E_T(\text{water})-E_T(\text{TMS})} \quad (20)$$

Here $E_T(30)$ value for a solvent is simply defined as molar transition energy of the dissolved betaine dye measured in kcal/mol for the charge transfer absorption band (ν_a) and is expressed as

$$E_T(30)[kcal-mol^{-1}]=2.8591\times10^{-3}\nu_a[cm^{-1}] \quad (21)$$

$\Delta\mu_B$ and a_B are the dipole moment changes on excitation and the Onsager radius respectively, of Betaine dye. $\Delta\mu$ and a are the corresponding quantities of the molecule of interest. Equation 19 clearly illustrates that the Stokes shift (ν_a-ν_f) changes linearly with the solvent polarity function E_T^N. $\Delta\mu$ can be obtained from the slope of Equation 19. Using the reported $\Delta\mu_B$ = 9 D of Betaine dye and its Onsager radius 6.2 Å [33], the change in dipole moment is determined by

$$\Delta\mu=\mu_e-\mu_g=\sqrt{\frac{m\times81}{11307.6\times\left(\frac{6.2}{a}\right)^3}} \quad (22)$$

In the present work, the Onsager's cavity radii of the dye molecules were taken as half the distance between the amino N atom and the carbonyl O atom of the systems, optimized by semiempirical models (AM1 and PM3). This is consistent with the fact that these atoms provide the strongest dipole vector component in all the molecules considered [33]. In addition to this we have also calculated the Onsager's cavity radius by the formula [34]

$$a=\sqrt[3]{\frac{3\text{M}}{4\pi\rho\text{N}}} \quad (23)$$

where M is the molecular weight of the dye; ρ is the density of the dye; N is the Avogadro's number. It is difficult to calculate the density of a compound and the density of the compounds are not listed in literatures so we have approximated [35] the densities of these dyes to be 1 g/cm^{-3}.

4. Results and discussion

Absorption and fluorescence spectra of **7DEAC** and **7DEA4MC** were measured in solvents of different solvent parameters e.g., refractive index and dielectric constant. Estimation of ground state and excited state dipole moments are done experimentally from observed absorption and emission spectra of dye molecules in various polar and non-polar solvents. The photophysical parameters; absorption and emission maxima wave numbers (ν_a, ν_f), Stoke's shift (ν_a-ν_f) and arithmetic mean of Stoke's shift (ν_a+ν_f)/2 values (in cm^{-1}) for both the coumarin dyes in different solvents are tabulated in Table 1. It has been observed that the emission peaks are more pronounced than the absorption peaks for both the molecules with increasing solvent polarity which gives a larger spectral shift in the emission spectra than in the absorption spectra of the molecules. With increase in the polarity of the solvent, the fluorescence emission peak undergoes a bathochromic shift (red shift), confirming a π → π* transition [30]. The less pronounced shift in the absorption spectra observed in all the solvents indicates that the ground-state energy distribution is not affected to a greater extent possibly due to the less polar nature of the dyes in the ground state than in the excited state which further indicates that of μ_e>μ_g. The red shift of the fluorescence wavelengths could be due to the marked difference between the excited-state charge distribution in the solute and the ground-state charge distribution, resulting in a stronger interaction with polar solvents in the excited state.

The values of solvent polarity function $F(\varepsilon, n)$, $F_1(\varepsilon, n)$, $F_2(\varepsilon, n)$, $F_3(\varepsilon, n)$ and E_T^N for solvents used in this work are presented in Table 2. Using linear fit method, the graphs of (ν_a-ν_f) and (ν_a+ν_f)/2 are plotted against solvent polarity functions $F(\varepsilon, n)$, $F_1(\varepsilon, n)$, $F_2(\varepsilon, n)$ and E_T^N, respectively for **7DEAC** (Figures 1-4). The slopes, intercepts and correlation coefficients of these best fit lines are given in Table 3. Figure 5a shows the solvatochromic shifts of the absorption spectra of **7DEAC** in different solvents at room temperature.

Table 1. Spectral data of **7DEAC** and **7DEA4MC** in various solvents.

Solvents	**7DEAC**				**7DEA4MC**			
	ν_a (cm^{-1})	ν_f (cm^{-1})	ν_a-ν_f (cm^{-1})	$(\nu_a+\nu_f)/2$ (cm^{-1})	ν_a (cm^{-1})	ν_f (cm^{-1})	ν_a-ν_f (cm^{-1})	$(\nu_a+\nu_f)/2$ (cm^{-1})
Formamide	25906	21598	4308	23752	26267	21978	4289	24122
DMSO	26315	22321	3994	24318	26680	22727	3953	24703
Dimethyl formamide	26525	22371	4154	24448	27027	22988	4039	25007
Acetonitrile	26737	22301	4436	24519	27107	22946	4161	25026
Ethanol	26490	21978	4512	24234	26780	22271	4509	24525
Acetone	26881	22988	3893	24934	27322	23386	3936	25354
Propanol	26455	22172	4283	24313	26702	22371	4331	24536
Butanol	26455	22123	4332	24289	26716	22471	4245	24593
1-Pentanol	26525	22172	4353	24348	26737	22471	4266	24604
Dichloromethane	26525	22914	3611	24719	26867	23485	3382	25176
Ethyl Acetate	27277	23752	3525	25514	27578	23877	3701	25727
Ethyl Benzoate	26737	23326	3411	25031	27173	23696	3477	25434
Ethyl Propionate	27322	23518	3804	25420	27777	23866	3911	25821
n-Butyl Acetate	27472	23980	3492	25726	27793	23980	3813	25886
Chloroform	26385	22935	3450	24660	26723	23255	3468	24989
Toluene	27442	23866	3576	25654	27855	24213	3642	26034
p-Xylene	27397	23529	3868	25463	27940	24319	3621	26129
Benzene	27247	23724	3523	25485	27777	24154	3623	25965
Carbon tetrachloride	27677	24131	3546	25904	28066	24691	3375	26378
1,4-Dioxane	27397	23685	3712	25541	27700	23752	3948	25726
Cyclohexane	28089	25087	3002	26588	28506	25380	3126	26943
Hexane	28248	25316	2932	26782	28636	25641	2995	27138

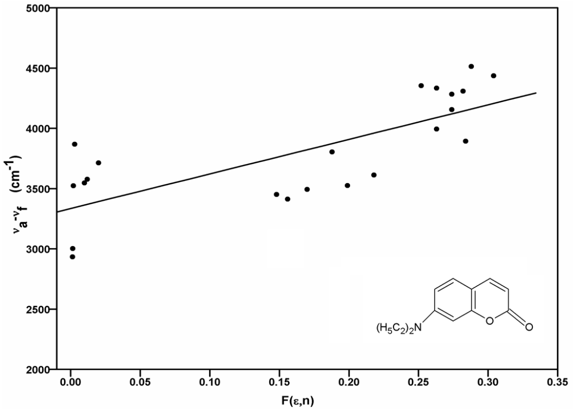


Figure 1. Plot of Stoke's shift ν_a-ν_f (cm^{-1}) versus $F(\varepsilon, n)$ of **7DEAC**.

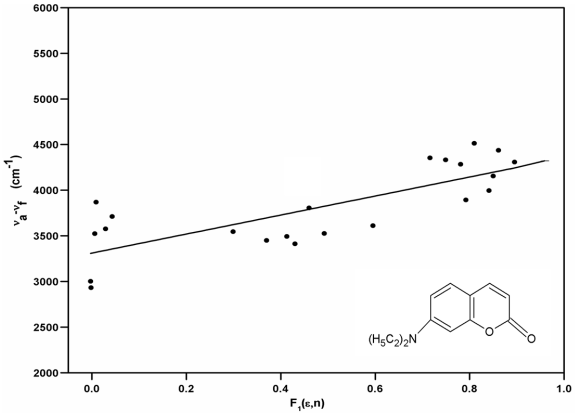


Figure 2. Plot of Stoke's shift ν_a-ν_f (cm^{-1}) versus $F_1(\varepsilon, n)$ of **7DEAC**.

Figure 5b shows a typical example of the solvent effect on the electronic emission spectrum of **7DEAC**. The geometry of these systems was optimized using semi empirical methods AM1, PM3 to obtain the Onsager's cavity radius. The values of Onsager's cavity radius obtained by these methods and by Equation 23 along with the calculated ground (μ_g) and singlet excited-state (μ_e)dipole moments and the ratio (μ_e/μ_g) for both the coumarin dyes estimated by using Equations 15, 16 and 17 are given in Table 4. The difference ($\Delta\mu$) in excited and ground-state dipole moments calculated by using method employed by Lippert-Mataga, Bakhshiev, McRae and molecular-microscopic based on solvent polarity relations are also given in the same table. It can be seen that the $\Delta\mu$ values obtained for both the molecules by Lippert-Mataga method are large as compared to values obtained by all other methods, it is due to the fact that this method does not take into account the polarizability of the solute. A comparison of results obtained in this work with the work reported previously is shown in Table 5.

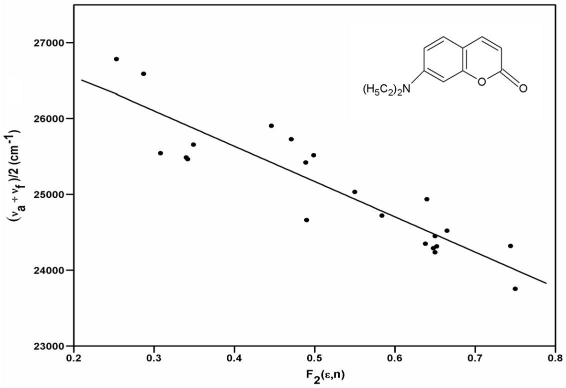


Figure 3. Plot of $(\nu_a+\nu_f)/2$ (cm^{-1}) versus $F_2(\varepsilon, n)$ of **7DEAC**.

The values for the **7DEA4MC** in ground and excited states are in the range of 3.48 D - 6.00 D and 5.13 D - 8.85 D respectively. Earlier, M. Diraisan *et al.* [36] reported the computed value as μ_g = 8.05 D and μ_e = 12.92 D for the said coumarin. The findings of McCarthy and Blanchard [37] shows μ_g = 6.35 D and μ_e = 9.81 D which are in good agreement with our experimental results. This inconsistency of dipole moments with these theoretical work arises because, while computing the parameters the molecule is considered as isolated system (as in gas phase), whereas the experimentally obtained values are in solution phase, where the solvent (matrix) introduces strong perturbation. Further it is evident from Table 4 that in both dye molecules, under investigation, the changes in the dipole moments on electronic excitation is rather small.

Table 2. Refractive index, dielectric constant and various solvent polarity functions of the solvents [a].

Solvents	n^b	ε^b	$F(\varepsilon, n)$	$F_1(\varepsilon, n)$	$F_2(\varepsilon, n)$	$F_3(\varepsilon, n)$	$(E_T^N)^b$
Formamide	1.447	111.0	0.282	0.895	0.750	0.706	0.799
DMSO	1.479	47.24	0.263	0.841	0.744	0.655	0.441
Dimethyl formamide	1.426	37.0	0.274	0.850	0.650	0.664	0.404
Acetonitrile	1.344	36.64	0.304	0.861	0.665	0.710	0.472
Ethanol	1.361	24.30	0.288	0.810	0.650	0.664	0.654
Acetone	1.359	21.01	0.284	0.792	0.640	0.649	0.355
Propanol	1.385	20.6	0.274	0.781	0.652	0.632	0.617
Butanol	1.399	17.40	0.263	0.749	0.648	0.603	0.601
1-Pentanol	1.410	14.80	0.252	0.716	0.638	0.573	0.503
Dichloromethane	1.424	8.93	0.218	0.595	0.584	0.474	0.320
Ethyl Acetate	1.372	6.08	0.199	0.492	0.499	0.398	0.228
Ethyl Benzoate	1.503	5.99	0.156	0.430	0.550	0.328	-
Ethyl Propionate	1.380	5.58	0.188	0.460	0.489	0.372	-
n-Butyl Acetate	1.394	5.00	0.170	0.413	0.471	0.427	-
Chloroform	1.442	4.81	0.148	0.370	0.490	0.292	0.259
Toluene	1.497	2.38	0.012	0.029	0.349	0.020	0.099
p-Xylene	1.496	2.27	0.003	0.009	0.342	0.005	0.077
Benzene	1.501	2.28	0.002	0.006	0.340	0.004	0.117
Carbon tetrachloride	1.459	2.24	0.010	0.299	0.446	0.016	0.055
1,4-Dioxane	1.422	2.22	0.021	0.043	0.308	0.034	0.164
Cyclohexane	1.426	2.02	0.0015	-0.003	0.287	0.0024	0.015
Hexane	1.374	1.88	0.0014	-0.002	0.253	0.0021	0.006

[a] $F(\varepsilon, n)$: Lippert, $F_1(\varepsilon, n)$: Bakhshiev, $F_2(\varepsilon, n)$: Kawski-Chamma-Viallet and $F_3(\varepsilon, n)$: McRae's solvent polarity function.

[b] The values of n, ε and E_T^N (Molecular-microscopic solvent function) are from Ref. [31].

Table 3. Slopes and intercepts of linear fittings.

Molecule	Slope	Intercept	No. of data	Correlation coefficient
Lippert-Mataga correlation				
7DEAC	2867.56	3334.39	22	0.76
7DEA4MC	2559.68	3394.41	22	0.74
Bakhshiev correlation				
7DEAC	1042.18	3311.25	22	0.64
7DEA4MC	898.17	3387.67	22	0.59
Kawski-Chamma-Viallet correlation				
7DEAC	4654.22	27496.18	22	0.81
7DEA4MC	4679.78	27881.08	22	0.79
McRae correlation				
7DEAC	1234.33	3343.44	22	0.77
7DEA4MC	1103.07	3402.01	22	0.76
E_T^N ***correlation***				
7DEAC	1698.68	3289.77	19	0.74
7DEA4MC	1576.36	3309.68	19	0.75

Table 4. Ground and excited-state dipole moments (Debye) and Onsager radius (Å) of **7DEAC** and **7DEA4MC**.

Molecule	Onsager radius, a	μ_g [a]	μ_e [b]	$\Delta\mu$ [c]	$\Delta\mu$ [d]	$\Delta\mu$ [f]	$\Delta\mu$ [g]	(μ_e/μ_g) [h]
7DEAC	3.50(AM1)	3.65	5.75	2.10	3.49	2.29	1.47	1.58
	3.47(PM3)	3.61	5.68	2.09	3.44	2.26	1.46	1.58
	4.41(Eq.19)	5.16	8.14	2.98	5.08	3.23	2.09	1.58
7DEA4MC	3.13(AM1)	3.48	5.13	1.65	2.79	1.83	1.20	1.47
	3.45(PM3)	4.05	5.94	1.89	3.22	2.11	1.40	1.47
	4.50(Eq.19)	6.00	8.85	2.85	4.8	3.15	2.07	1.48

[a] Ground state dipole moments calculated from Equation 15.

[b] Excited state dipole moments calculated from Equation 16.

[c] $\Delta\mu$ calculated from Bakhshiev model.

[d] $\Delta\mu$ calculated from Lippert-Mataga model.

[f] $\Delta\mu$ calculated from McRae model.

[g] $\Delta\mu$ calculated from molecular-microscopic solvent function (E_T^N).

[h] The ratio of excited state and ground state dipole moments calculated from Equation 17.

This suggests that the emission of these dyes originates from a state which although more polar than ground state is probably a locally excited intramolecular-charge transfer (ICT) state. Charge transfer accompanying excitation to lowest excited singlet state usually results in the excited molecule having a greater dipole moment than the ground state [38].The longest absorption and fluorescence maxima shifted to the lower energy end of the spectrum on increasing the solvent polarity for coumarin molecule. It is known that the lowest excited state is *n*→π*, but the substituted coumarin, the energy difference between *n*→π* and π→π* levels becomes smaller with increasing substitution and in some cases even the state order gets inverted [39]. In the present case, there is a bathochromic shift on increasing the solvent polarity which indicates that the transition involved is a π→π* transition and lowest lying state is π→π* (see Table 1). The difference between the values of ground-state dipole moment (μ_g) and excited-state dipole moment μ_e of **7DEAC** and **7DEA4MC** is small, this could be explained as, a CH_3 group at position-4 has small influence on the energy levels of molecules [38]. The effect of amino group in case of **7DEAC** and **7DEA4MC** is considered where unshared pair of electrons on this group resides in molecular orbitals (largely localized to amino group).

Table 5. Comparison of present results with the values reported earlier*.

Solute molecule	m_1 [cm^{-1}]	m_2 [cm^{-1}]	Radius, a, [Å]	μ_g [D]	μ_e [D]	$\Delta\mu = \mu_e$-μ_g [D]	μ_e/μ_g
7DEAC	*Present work (using Method I)*						
	1042.18	4654.22	3.50(AM1)	3.65	5.75	2.10	1.58
			3.47(PM3)	3.61	5.68	2.09	1.58
			4.41(Eq.19)	5.16	8.14	2.98	1.58
	Previous work Ref. [40] Experimental						
	-	-	3.71	3.15	6.35	3.20	2.01
	Previous work Ref. [41] Experimental						
	-	-	4.0	6.34	8.40	2.06	1.32
7DEA4MC	*Present work (using method I)*						
	898.178	4679.78	3.13(AM1)	3.48	5.13	1.65	1.47
			3.45 (PM3)	4.05	5.94	1.89	1.47
			4.50(Eq.19)	6.00	8.85	2.85	1.48
	Previous work Ref. [11] Experimental						
	-	-	3.48	6.35	8.60	2.25	1.35
	Previous work Ref. [37] Theoretical						
	-	-	-	6.35	9.81	3.46	1.54
	Previous work Ref. [41] Experimental						
	-	-	4.0	5.99	8.74	2.75	1.46

* m_1, m_2 are the slopes of ν_a-ν_f vs. $F_1(\varepsilon, n)$ and $(\nu_a+\nu_f)/2$ vs. $F_2(\varepsilon, n)$; 'a' is the Onsager radius; μ_g, μ_e are the dipole moments in ground and excited state, respectively. "-": Values of m_1 and m_2 are not reported in ref. [11], ref. [40], ref. [37] and ref. [41].

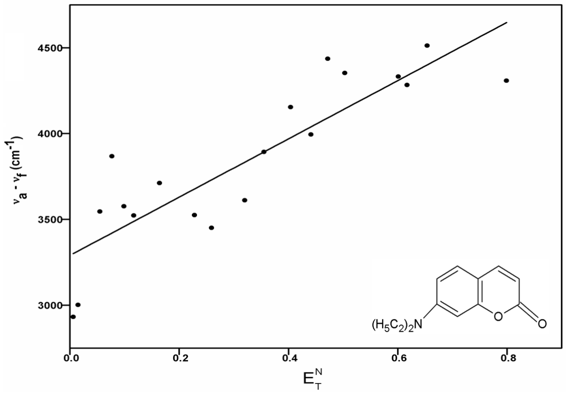
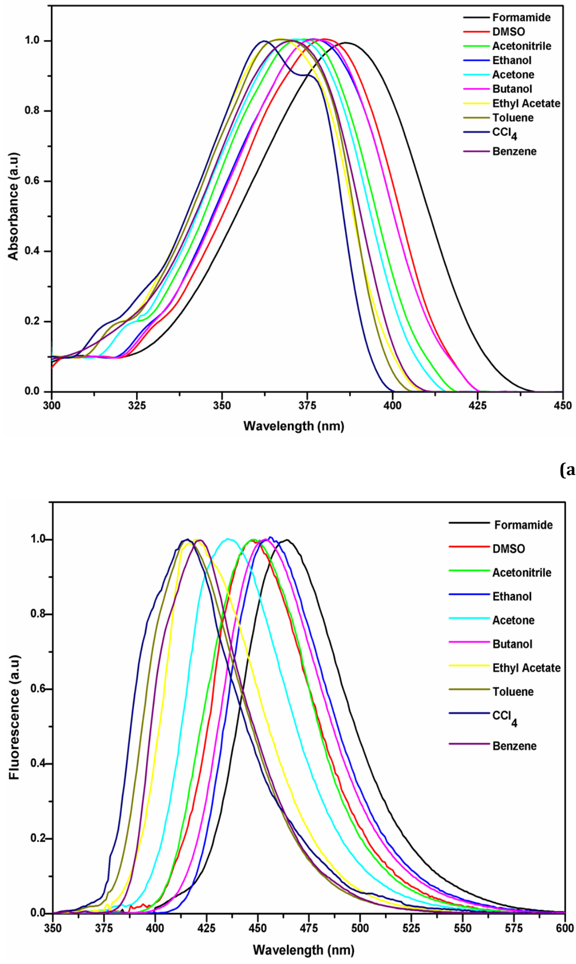


Figure 4. Plot of Stoke's shift ν_a-ν_f (cm^{-1}) versus E_T^N of **7DEAC**.

Thus due to ICT the electronic charge from these functional groups gets substantially delocalized throughout the system. Hence, the energy gap between the highest occupied and lowest unoccupied orbitals of amino substituted molecule is considerably lower than the difference between the highest occupied and lowest unoccupied orbitals of unsubstituted molecules [12,38].

5. Conclusion

The present investigations of the photophysical properties of **7DEAC** and **7DEA4MC**, which are promising active medium for tunable lasers, show that the lowest lying excited state of the molecules is π→π*. The dipole moments of the molecules are higher in the excited state and it is about 1.6 times of the ground state value. Further, dipole moment values for the coumarin dyes differ from each other. This can be attributed to the structural difference between the molecules. The relative positions of π→π* and n→π* depend on the nature of the substituent as well as the solvents. The assumption $2\alpha/a^3$=1 is justified and does not significantly influence the determined value of μ_e, because in most cases α/a^3 is unknown [22]. Equation 17 can be used to estimate the value of the excited-state dipole moment by pre-knowledge of the value of ground-state dipole moment, without the necessity of knowing the Onsager radius of the solute. Further the absorption and fluorescence spectra of the coumarins are studied in 22 different polar and non-polar solvents which were limited to a few solvents in the earlier reported work.



(a)

(b)

Figure 5. Absorption (a) and fluorescence (b) spectra of **7DEAC** in different solvents.

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References

[1]. Fletcher, A. N.; Bliss, D. E. *Appl. Phys.* **1978**, *16*, 289-295.
[2]. Halstead, J. A.; Reeves, R. R. *Opt. Commun.* **1978**, *27*, 273-276.
[3]. Gardecki, J. A.; Maroncelli, M. *J. Phys. Chem.* **1999**, *103*, 1187-1197.
[4]. Levinger, N. E. *Curr. Opin. Colloid Interf. Sci.* **2000**, *5*, 118-124.
[5]. Castner Jr., E. W.; Kennedy, D.; Cave, R. J. *J. Phys. Chem. A* **2000**, *104*, 2869-2885.
[6]. Morandeira, A.; Fulrstenberg, A.; Vauthey, E. *J. Phys. Chem. A* **2004**, *108*, 8190-8200.
[7]. Kumbhakar, M.; Nath, S.; Mukherjee, T.; Pal, H. *J. Chem. Phys.* **2004**, *121*, 6026-6033.
[8]. Schitschek, E. J.; Trias, J. A.; Hammond, P. R.; Henry, R. A.; Atkins, R. L. *Opt. Commun.* **1976**, *16*, 313-316.
[9]. Parkyani, C.; Antonius, M. S.; Aaron, J. J.; Buna, M.; Tine, A.; Cisse L. *Spectrosc. Lett.* **1994**, *27*, 439-449.
[10]. Shermon, W. R.; Robins, E. *Anal. Chem.* **1968**, *40*, 803-805.
[11]. Ravi, M.; Soujanya, T.; Samanta. A.; Radhakrishnan, T. P. *J. Chem. Soc. Faraday Trans.* **1995**, *91*, 2739-2742.
[12]. Mannekutla, J. R.; Mulimani, B. G.; Inamdar, S. R. *Spectochim. Acta A* **2008**, *69*, 419-426.
[13]. Zakerhamidi, M. S.; Ghanadzadeh, A.; Moghadam, M. *Spectrochim. Acta A* **2011**, *78*, 961-966.
[14]. Inamdar, S. R.; Nadaf, Y. F.; Mulimani, B. G. *J. Mol. Struct.* **2003**, *624*, 47-51.
[15]. Kumar, S.; Rao, V. C.; Rastogi, R. C. *Spectrochim. Acta Part A* **2001**, *57*, 41-47.
[16]. Cremers, D. A.; Windsor, M. W. *Chem. Phys. Lett.* **1980**, *71*, 27-32.
[17]. Balu, W.; Reber, R.; Penzkofer, A. *Opt. Commun.* **1982**, *43*, 210-214.
[18]. Sundstrom, V.; Gillbro, T.; Bergstrom, H. *Chem. Phys.* **1982**, *73*, 439-458.
[19]. Sundstrom, V.; Gilbro, T. *Chem. Phys. Lett.* **1984**, *109*, 538-543.
[20]. Bilot, L.; Kawski, A. *Z. Naturforsch.* **1962**, *179*, 621-627
[21]. Kawski, A.; Rabek, J. F. Progress in photochemistry and photophysics, Vol. 5., Boca Raton USA, CRC Press, 1992.
[22]. Kawski, A. *Z. Natureforsch.* **2002**, *57A*, 255-262.
[23]. Lippert, E. *Z. Naturforch, Part A* **1955**, *10*, 541-545.
[24]. Lippert, E. *Elektrochem, Ber. Bunsenges. Phys. Chem.* **1957**, *61*, 962-975.
[25]. Mataga, N.; Kaifu, Y.; Koizumi, M. *Bull. Chem. Soc. Jpn.* **1956**, *29*, 465-470.
[26]. Mataga, N.; Kubota, T. Molecular Interactions and Electronic Spectra, Dekker, New York, 1970.
[27]. Bakshiev, N. G. *Opt. Spektosk. (USSR)* **1964**, *16*, 821-832.
[28]. Chamma, A.; Viallet, P. *C. R. Acad. Sci. Paris, Ser. C* **1970**, *270*, 1901-1904.
[29]. McRae, E. G. *J. Phys. Chem.* **1957**, 61, 562-572.
[30]. Siddlingeshwar, B.; Hanagodimath, S. M.; Kirilova, E. M. *J. Quant. Spectrosc. Radiat. Trans.* **2011**, *112*, 448-456.
[31]. Reichardt, C. Solvents and Solvent Effects in Organic Chemistry, VCH, Weinheim, 1988.
[32]. Ravi, M.; Samanta, A.; Radhakrishnan, T. P. *J. Phys. Chem.* **1994**, *98*, 9133-9136.
[33]. Hasegawa, M.; Suzuki, Y.; Suzuki, F.; Nakaniski, H. *J. Polym. Sci. A* **1969**, *7*, 743-752
[34]. Ghazy, R.; Azim, S. A.; Shaheen, M.; El-Mekawey, F. *Spectrochim. Acta A* **2004**, *60*, 187-191.
[35]. Zachariasse, K. Private communication, 6th International Conference on Solar Energy and Applied Photochemistry, “Solar’01”, 3-8 April 2001, Cairo.
[36]. Diraison, M.; Millie, P.; Mialoq, Gustavsson, T. *Chem. Phys. Letts.* **1998**, *282*, 152-158.
[37]. McCarthy, P. K.; Blanchard, G. J. *J. Phys. Chem.* **1993**, *97*, 12205-12209.
[38]. Sharma, V. K.; Saharo, P. D.; Sharma, N.; Rastogi, R. C.; Mohan, D. *Spectrochim. Acta A* **2003**, *59*, 1161-1170.
[39]. DeMelo, J. S. S.; Becker, R. S.; Mocarita, A. I. *J. Phys. Chem.* **1994**, *98*, 6054-6058.
[40]. Gayathri, B. R.; Mannekutla, J. R.; Inamdar, S. R. *J. Mol. Struct.* **2008**, *889*, 383-393.
[41]. Cisse, L.; Djande, A.; Aaron, J. J. *Spectrochim. Acta A* **2011**, *79*, 428-436.