

SOLVENT EFFECT ON THE ELECTRONIC TRANSITIONS IN HYDROXY AND METHOXY COUMARINS



Physics

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Rajeev

Physics Section, Department of Applied Sciences & Humanities, Faculty of Engineering & Technology, Jamia Millia Islamia(a Central University), New Delhi-110025, India

Mudassir M Husain

Department of Applied Sciences & Humanities NGF College of Engineering & Technology, 71K.M Stone, N.H.-2, Palwal, (Hr.)

Anjani K Tiwari

Department of Radiopharmaceutical Sciences; INMAS; Delhi 110054, India

S Kaushik

Director-Principal, NGF College of Engineering & Technology, 71K.M Stone, N.H.-2, Palwal, (Hr.)

ABSTRACT

The solvation characteristics of the ground and excited states of three coumarins namely 7-Methoxy-4-(trifluoromethyl); 7-Hydroxy-4-(trifluoromethyl) and 6,7-Dihydroxy-4-(trifluoromethyl) were investigated in a variety of solvents. The spectral shifts are correlated by Kamlet-Taft parameters (π^* and δ) and dielectric continuum model. Multiple linear regression analysis shows that both non-specific dipolar interaction and specific hydrogen bonding interaction play an important role in the position of the absorption and fluorescence maxima in the solvents.

INTRODUCTION

The energetic of electronic transitions in condensed phases can be substantially influenced by solvents. Solute-solvent interaction has an important role in the physical process [1-2]. Although these interactions individually are about an order of magnitude weaker than covalent bond strength; they are often crucial in determining the rate and the overall energy process [3-6]. As specific solute-solvent interactions play a significant role in the molecular recognition process and as they are important in biological systems, it becomes important to study the phenomena associated with the solvation of a solute and its dynamics.

The electronic state solvation i.e the response of the solvent to the electronic structure of a solute, can be classified into three categories: polar solvation, as a result of the interaction between the solvent dipoles and the solute charge distribution; non-polar solvation produced by repulsive and dispersion forces; and "specific" interaction, which most often results from hydrogen bonding. The first two types of interactions can be described as "general" solute-solvent interaction

and the third is described as "specific" solvent-solute interaction. The general solute-solvent interactions result from interactions of the dipole moments of the fluorophore with the reactive field induced in the surrounding solvent; specific effects result from the short range interactions between the fluorophore with one or more solvent molecules in its first solvation shell, an example being hydrogen bond as discussed above. One problem in understanding the role of the general and specific solvent effects arises from the inherent difficulty in separating these two types of interactions in the interpretation of experimental measurement of absorption and emission energies.

There are various theories for treating the solute-solvent interactions. Some of these consider the solvent as a continuum dielectric; others treat the solvent as having both bulk interactions and those arising from particular molecular properties. In the present work we have chosen the empirical solvatochromic scale of Kamlet and Taft [7-10] to separate the bulk and specific effects of solvents on a solvatochromic equation. The values of the solvent solvatochromic parameters used in these equations are empirically determined by fitting a general equation to a large amount of data from a variety of

spectroscopic and other experiments. In the present work we have taken three coumarins: 7-Hydroxy-4-(trifluoromethyl) [7H4TFMC]; 6,7-Dihydroxy-4-(trifluoromethyl) [67DH4TFMC]; 7-Methoxy-4-(trifluoromethyl) [7M4TFMC]. The electronic transition energy, ν , observed for a particular solute is expected to follow [7-11], the linear solvation energy relationship (LSER)

$$\nu = \nu_0 + a\alpha + s\pi^* \quad (1)$$

where ν_0 is the transition energy in the absence of the solvent effect (gas phase), α is a measure of the hydrogen bond donating ability of the solvent which denotes the ability of a solvent to donate a proton for solvent to solute hydrogen bonding and π^* measures the polarity/ polarizability of the solvent. In this equation a and s are susceptibility constants and their magnitude (and sign) give the relative influence of the corresponding solute-solvent interactions on the electronic transition energy.

The linear solvation energy relationship (LSER) is widely used in the understanding of solvation effects in solutions [12-14]. This method considers the above mentioned two kinds of attractive solute-solvent interactions separately: non-specific and specific interactions. This method provides explicit measures for polarity interaction (π^*) and the hydrogen bond donating ability (α) of the solvent.

In another approach Horng et al [15] found that a more theoretical analysis of solvatochromism based on the dielectric continuum model [16-18] provided a reasonably good fit to both the aprotic and protic solvents. According to them, the solvent polarity can be described in terms of a reaction field), $F(\epsilon_0, n)$;

$$F(\epsilon_0, n) = \frac{\epsilon_0 - 1}{\epsilon_0 + 2} - \frac{n^2 - 1}{n^2 + 2} \quad (2)$$

Where ϵ_0 is the static dielectric constant and n is the refractive index of the solvent. This reaction field factor arises from dielectric continuum theories of solvatochromic shifts. We assume that a spherical cavity/ point dipole solute and that the solvent interacts with the electronic transition $1 \rightarrow 2$ mainly by virtue of the change of the solute's dipole moment. Then, the electronic transition energy is expected to

vary with solvent dielectric properties

$$v = v_0 + A_u F(\epsilon_0, n) + B_u \left(\frac{n^2 - 1}{n^2 + 2} \right) \quad (3)$$

where A_u, B_u are solute dependant factors which depend on ground and excited state dipole moments (μ_i) and the radius (a) of the (assumed spherical) solute cavity

$$A_u = \frac{2\mu_1(\mu_1 - \mu_2)}{hca^3}, B_u = \frac{\mu_1^2 - \mu_2^2}{hca^3} \quad (4)$$

The A_u term in eq (3) accounts for contribution due to polarizability of solvent nuclear co-ordinates while B_u term involves the electronic polarizability of the solvents [12]

In the present work we have tried to compare the validity of these two theoretical approaches to the electronic transitions of three coumarins derivatives as mentioned above in different solvents. We fit the two models [eq (1) and (3)] to spectroscopic data taken in a number of solvents and compare their effectiveness in describing the observed solvatochromism.

EXPERIMENTAL DETAILS

Chemical used

Coumarins taken at the highest purity from Sigma Aldrich Chemical Co. were used. All chemicals were used without further purification. The optimized molecular structures of these solutes are given in fig. (1). All the solvents (listed in Table (1)) used were of spectroscopic grade and are found to be transparent and non fluorescent in the range of excitation and fluorescence emission.

Spectroscopic measurements

The absorption and fluorescence spectra were recorded using a Shimadzu UV-Vis spectrophotometer (UV 2450) and a Shimadzu RF-5301 spectrofluorometer respectively. The Fluorescence emitted was observed perpendicular to the direction of exciting beam. All the measurements were carried out at room temperature keeping dye concentration very low to avoid selfabsorption.

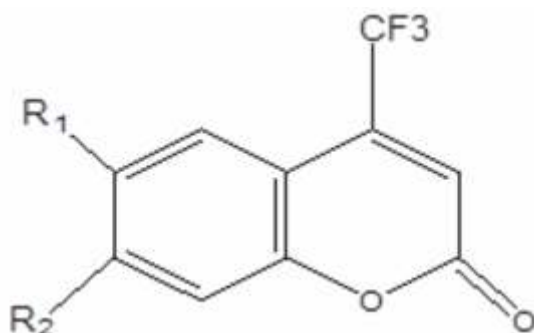


Figure 1: Molecular structure of coumarins

Where $R_1=H, R_2=OH$ for 7H4TFMC; $R_1=OH, R_2=OH$ for 67DH4TFMC and $R_1=H, R_2=OCH_3$ for 7M4TFMC

RESULTS

The solvents used are listed in Table 1, along with relevant solvent parameters. The absorption and emission energies for each of the coumarins are given for each solvent in Table 2

Table 1
Solvent parameters of various solvents

Sr. No.	Solvent	π^*	α	ϵ_0	n	$F(\epsilon_0, n)$
1.	n-Hexane	-0.11	0	1.88	1.370	0.00
2.	Cyclohexane	0	0	2.02	1.426	0.00
3.	CCl4	0.21	0	2.30	1.460	0.03
4.	Ehtylacetate	0.45	0	6.02	1.372	0.40
5.	p-Xylene	0.45	0	2.27	1.496	0.01
6.	Butyl Acetate	0.46	0	5.01	1.383	0.34
7.	Ethyl Proionate	0.47	0	5.58	1.380	0.37
8.	Toulene	0.49	0	2.43	1.497	0.03
9.	1,4-Dioxan	0.49	0	2.27	1.422	0.04
10.	Benzene	0.55	0	2.40	1.501	0.02
11.	Ethyl Benzoate	0.68	0	5.59	1.503	0.33
12.	DMF	0.88	0	36.71	1.428	0.67
13.	DMSO	1.00	0	46.45	1.478	0.66
14.	Acetone	0.62	0.08	20.56	1.356	0.65
15.	Acetonitrile	0.66	0.19	36.94	1.342	0.71
16.	CH2Cl2	0.82	0.13	8.93	1.424	0.47
17.	Chloroform	0.69	0.44	4.89	1.446	0.30
18.	Formamide	0.97	0.71	111.0	1.447	0.71
19.	Methanol	0.60	0.93	32.60	1.331	0.71
20.	Ethanol	0.40	0.83	24.30	1.361	0.67
21.	Propanol	0.40	0.78	20.60	1.385	0.63
22.	Butanol	0.40	0.79	17.80	1.399	0.61
23.	Pentanol	0.40	0.33	14.80	1.410	0.57
24.	Hexanol	0.40	0.33	13.3	1.417	0.55
25.	Heptanol	0.40	-	12.10	1.423	0.45
26.	Octanol	0.40	-	10.34	1.428	0.41
27.	Decanol	0.40	-	8.10	1.437	0.35

ϵ_0 and n values are predominantly from the listing in ref [11,12] is $F(\epsilon_0, n)$ is as defined in Eq.(2). α and π^* values are from ref.[7-11] and [15]

Table 2 Absorption and emission energies, v , of 7M4TFMC, 7H4TFMC and 67DH4TFMC in various solvents

Sr. No.	Solvent	7M4TFMC		7H4TFMC		67DH4TFMC	
		v_{abs}	v_{em}	v_{abs}	v_{em}	v_{abs}	v_{em}
1.	n-Hexane	30.59	25.00	30.74	24.75	28.82	22.35
2.	Cyclohexane	30.42	24.84	30.67	24.69	28.61	21.54
3.	CCl4	30.17	24.78	30.84	24.33	--	--
4.	Ehtylacetate	30.33	24.18	30.22	24.09	28.12	21.17
5.	p-Xylene	30.04	24.10	30.22	23.98	28.31	21.38
6.	Butyl Acetate	30.32	24.33	30.12	24.24	28.00	21.40
7.	Ethyl Proionate	30.34	24.40	30.15	24.81	27.90	21.26
8.	Toulene	29.96	24.32	30.30	24.44	28.31	22.19
9.	1,4-Dioxan	30.35	24.27	30.33	24.09	28.09	21.50
10.	Benzene	30.04	24.16	30.31	24.24	28.36	22.00

11.	Ethyl Benzoate	29.85	24.09	29.79	24.21	27.70	21.34
12.	DMF	30.03	23.82	29.64	23.41	26.85	19.53
13.	DMSO	29.94	23.84	29.50	23.03	26.93	19.46
14.	Acetone	30.28	24.13	30.06	24.03	27.90	20.93
15.	Acetonitrile	30.30	24.05	30.27	24.15	28.20	20.95
16.	CH ₂ Cl ₂	29.99	24.29	30.45	24.39	27.86	21.86
17.	Chloroform	29.91	24.48	29.82	24.15	28.38	21.34
18.	Formamide	29.72	23.77	29.47	22.67	26.76	19.60
19.	Methanol	30.15	23.75	29.72	23.06	27.23	20.06
20.	Ethanol	30.05	24.13	29.61	23.67	26.93	20.68
21.	Propanol	30.04	24.03	29.47	23.72	26.87	20.58
22.	Butanol	29.99	24.13	29.36	23.77	26.67	20.17
23.	Pentanol	29.93	24.18	29.37	23.82	26.81	20.68
24.	Hexanol	29.93	24.16	29.38	23.72	26.75	20.62
25.	Heptanol	29.91	24.03	29.25	23.59	26.75	20.67
26.	Octanol	30.04	24.27	29.37	24.00	26.84	21.22
27.	Decanol	29.96	24.21	29.37	23.98	26.99	20.85

Energies, ν , are in units of 10^3 cm^{-1}

Model I: Comparison of experimental result with LSER equation

Figures 2(a,b) ;3(a,b) and 4(a,b) show a plot of the experimental absorption and emission energies of all the three coumarins respectively as a function of π^* . The data for the solvents follow a nearly linear dependence on π^* . The alcohols all have same value of π^* (0.40) [10-11] and somewhat away from the line of other solvents. Separation of this kind of transition energies in protic/dipolar and alcohols has been described previously for Coumarin 153[12]. The data for all the solvents are well fit by solvatochromic Eq. (1) for all the three coumarins. It is seen from the figures 3(a,b) and 4(a,b) that data is well fit by the Eq(1) for absorption energies of 7-Hydroxy-4-(trifluoromethyl) coumarin; 6, 7-Dihydroxy-4-(trifluoromethyl) coumarin but there is a little deviation for the emission energies of the two coumarins. The results of the multiple regression are presented in table 3, and the calculated transitions using these fit equations are also plotted in Figures 2(a,b) ; 3(a,b) and 4(a,b). In all the cases correlation coefficients are high. Thus Eq(1) is describing well the transition energies in the solvents for all the three coumarins.

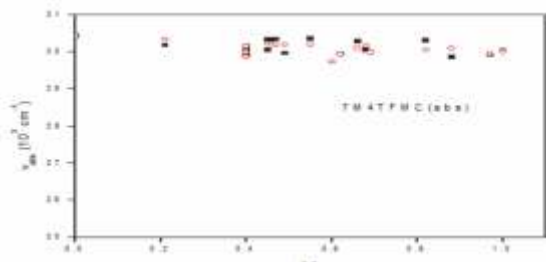


Figure 2(a). Absorption energies of 7M4TFMC as a function of π^* . Open symbols indicate calculated values based on multiple reg. fit of data to eq (1). Filled symbols represent experimental values. The regression results are presented in Table 3.

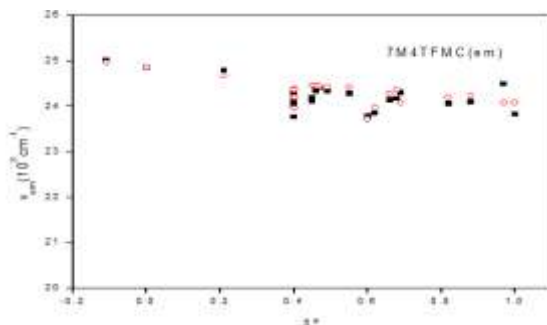


Figure 2(b). Emission energies of 7M4TFMC as a function of π^* . Open symbols indicate calculated values based on multiple reg. fit of data to Eq(1). Filled symbols represent experimental values. The regression results are presented in Table 3

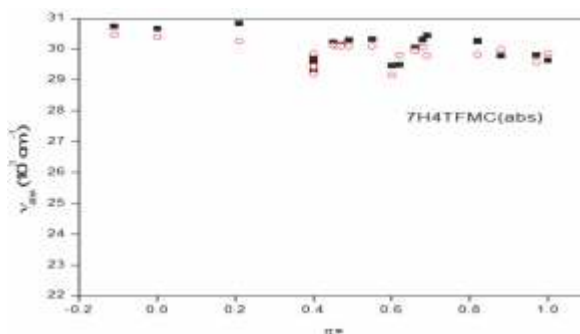


Figure 3(a). Absorption energies of 7H4TFMC as a function of π^* . The regression results are presented in Table 3. Symbols as for fig. 2(a, b)

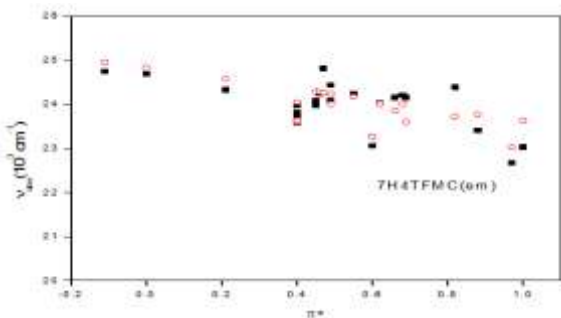


Figure 3(b). Emission energies of 7H4TFMC as a function of π^* . The regression results are presented in Table 3 Symbols as for fig. 2(a, b)

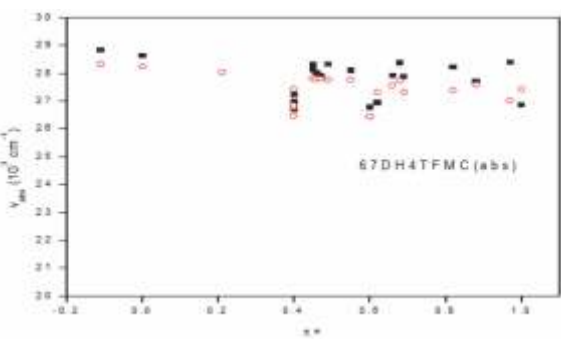


Figure 4(a). Absorption energies of 67DH4TFMC as a function of π^* . The regression results are presented in Table 3 Symbols as for fig. 2(a, b)

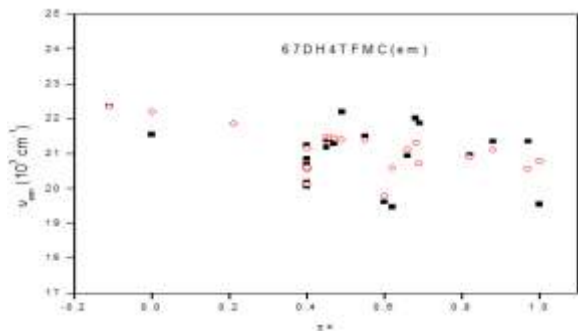


Figure 4 (b). Emission energies of 67DH4TFMC as a fn of π^* . The regression results are presented in Table 3 Symbols as for fig.2(a,b)

Table 3

Regression fits to solvatochromic parameters (Eq. (1))

Sr. No.	Molecule	(103 cm-1)	(103 cm-1)	(103 cm-1)	R
1.	7M4TFMC abs	30.43	-0.5	-0.3	0.57
2.	7M4TFMC em	24.86	-0.9	-0.4	0.76
3.	7H4TFMC abs	30.40	-0.6	-0.9	0.34
4.	7H4TFMC em	24.83	-1.2	-0.9	0.59
5.	67DH4TFMC abs	28.21	-0.9	-1.3	0.30
6.	67DH4TFMC em	22.18	-1.6	-1.2	0.53

Model-II Comparison of experimental results with Dielectric Continuum Model

In figures 5(a,b); 6(a,b) and 7(a,b) the absorption and emission energies for all the three coumarins are plotted as a function of $F(\epsilon_r, n)$ The same symbols as in figs. 2(a,b) to 4(a,b) are used. The Eq. (3) was fit to data from all of the solvents and the results of these fits are presented in Table 4. For 6, 7-Dihydroxy-4-(trifluoromethyl) coumarin the correlation coefficients are high. Whereas for 7-Methoxy-4-(trifluoromethyl) coumarin, the dielectric continuum model as represented by Eq. (3) does not fit nearly as well. The calculated transition energies are also plotted in the figs. 5(a,b) to 7(a,b) for all the three coumarins. It is seen from the figures that the calculated transition energies are less than the corresponding experimental energies for both absorption and emission spectra.

Table 4

Regression fits to reaction field parameters (Eq. (3))

Sr. No.	Molecule	(103 cm-1)	(103 cm-1)	(103 cm-1)	R
1.	7M4TFMC abs	30.22	-0.3	-7	0.36
2.	7M4TFMC em	24.61	-0.8	-5	0.72
3.	7H4TFMC abs	30.54	-1.3	-7	0.68
4.	7H4TFMC em	24.61	-1.3	-8	0.69
5.	67DH4TFMC abs	28.58	-2.0	-9	0.73
6.	67DH4TFMC em	22.24	-2.4	-7	0.80

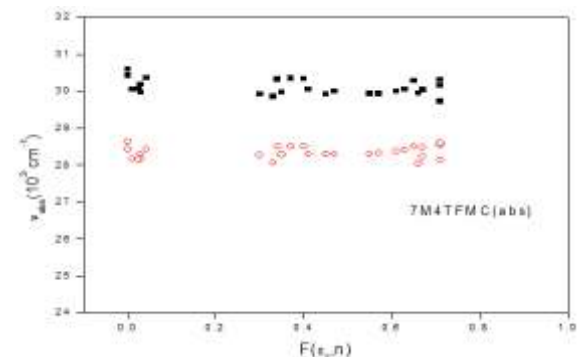


Figure 5(a). Absorption energies of 7M4TFMC as a function of $F(\epsilon_r, n)$ Symbols as for fig.2. The calculated values are based on a multi regression fit of all the data to Eq. (3) . The regression

results are presented in table 4.

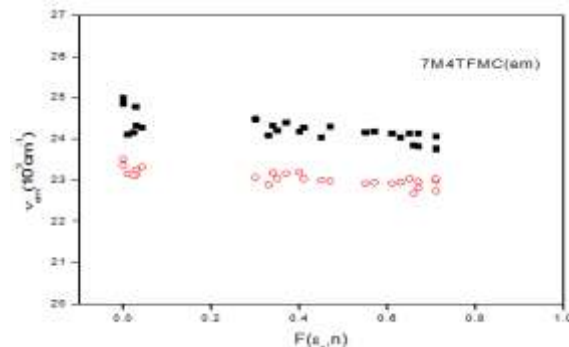


Figure 5(b). Emission energies of 7M4TFMC as a function of $F(\epsilon_r, n)$ Symbols as for fig.2.The calculated values are based on a multi regression fit of all the data to Eq. (3) . The regression results are presented in table 4.

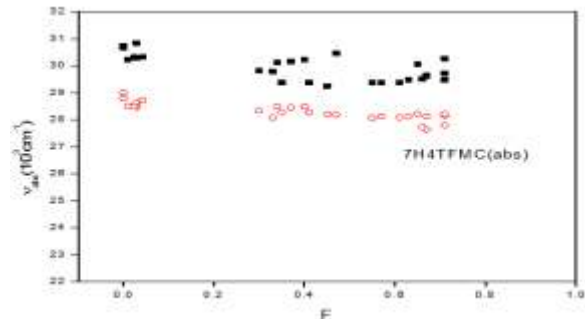


Figure 6(a). Absorption energies of 7H4TFMC as a function of $F(\epsilon_r, n)$ Symbols as for fig.2.The calculated values are based on a multi regression fit of all the data to Eq. (3) . The regression results are presented in table 4.

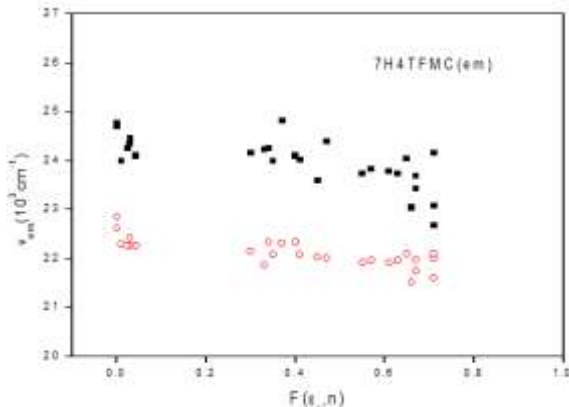


Figure 6(b). Emission energies of 7H4TFMC as a function of $F(\epsilon_r, n)$ Symbols as for fig.2.The calculated values are based on a multi regression fit of all the data to Eq. (3) . The regression results are presented in table 4.

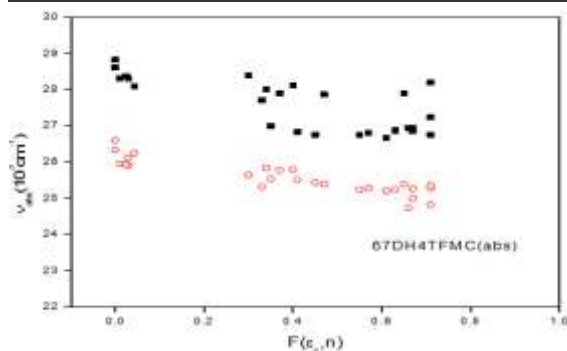


Figure 7(a). Absorption energies of 67DH4TFMC as a function of $F(\epsilon_s, n)$. Symbols as for fig.2. The calculated values are based on a multi regression fit of all the data to Eq. (3). The regression results are presented in table 4.

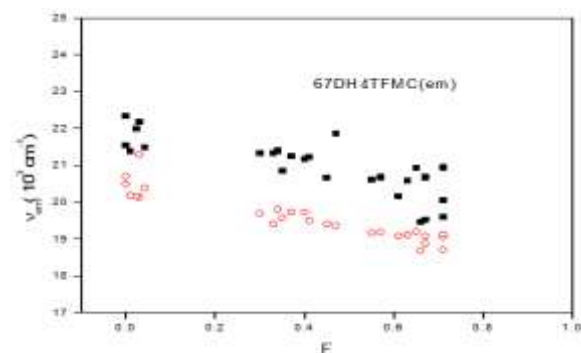


Figure 7(b). Emission energies of 67DH4TFMC as a function of $F(\epsilon_s, n)$. Symbols as for fig.2. The calculated values are based on a multi regression fit of all the data to Eq. (3). The regression results are presented in table 4.

Discussion

The solvatochromic parameter model (Eq. (1)) gives a good fit to both the absorption and emission data. Moreover the calculated transitions energies are nearly equal to the experimental values for both absorption and emission spectra. The values of ρ and σ for 7-Methoxy-4-(trifluoromethyl) coumarin are less than those of the other two hydroxy coumarins. This suggests that the solute-solvent interaction is less in 7-Methoxy-4-(trifluoromethyl) coumarin than the other two hydroxy coumarins. This may be due to the fact that 7-Hydroxy-4-(trifluoromethyl) coumarin and 6,7-Dihydroxy-4-(trifluoromethyl)coumarin have hydroxy substituent which is more prone to specific solvent-solute interaction. Similar results can be seen from Table 4. It is also observed that all the three molecules have some groups capable of participating in specific interaction with solvent [19-21]. Due to hydrogen bond donor ability of solvent there is a tendency to interact with the oxygen from carbonyl group, as well as hydrogen bond donation ability of the hydroxyl group, these are likely sites for intermolecular hydrogen bonding in protic compounds. The solvent induced spectral shifts are attributed to solvent polarizability/polarity effects and hydrogen bonding donating and accepting.

CONCLUSIONS

The solvatochromic parameter method provides a good model for characterizing the electronic transitions energies in all the three coumarins. The theoretically based reaction field approach is also effective in describing these energies in the absence of strong hydrogen-bonding interaction between solvent and solute.

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