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Photophysics and dynamics of coumarin laser dyes and their analytical implications

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Abstract. A comparative study of the fluorescence of selected flexible and rigidized 7-aminocoumarin derivatives (coumarin 6, 138 and its rigidized coumarin 106) has been made in a series of solvents of varied properties. The studies were further augmented by the quantum chemical SCF–CI MO calculations which provide a theoretical basis for interpreting specific interactions and complex formation with the polar solvents in the intramolecular charge transfer singlet state of these dyes. Moreover, rotational relaxation behaviour, as reflected in the fluorescence polarization of these dyes, is correlated with solvent viscosity/free volume. Through measurements of the temperature/viscosity dependence of the fluorescence depolarization ($1/P$) in glycerol, we are able to establish an Arrhenius-like relationship linking ($1/P$) to the free-volume fraction of the medium. Furthermore, depolarization data fitted the Perrin equation with a slope proportional to the sensitivity of the molecular structure towards medium fluidity. The results imply the promising utility of these highly fluorescent dyes as fluorescent probes for local fluidity and polarity of the surrounding medium of interest. We demonstrate possible analytical applications of commercially available coumarin 6 as a promising fluorescent probe for medium properties (e.g. fluidity, polarity and for following micellization in the solutions of some ionic surfactants).

Keywords. Coumarin dyes; fluorescence; quantum chemical calculations; viscosity; probes.

1. Introduction

It appears that fluorescent dyes, in particular those of an electron–donor–acceptor (EDA) type with solvent-dependent intramolecular charge-transfer (ICT) process involving exciplex formation with polar solvents and structure twist by light absorption, have found very broad technqlogical applications. Many of these applications, e.g. in laser dyes, solar energy concentrators in photovoltaic cells, nonlinear optical materials and analytical probes, depend on the photophysical properties of these dyes and have already been used commerically in past years but other potential ones are still under development. It is thus of interest to predict and to control fluorescent dyes properties for a better understanding of the mechanisms involved in these applications and thus extend the field of application. Over the past few years, many investigations have been focussed on the role of the solvent (medium) and the mechanism of solvation in controlling the photoinduced ICT and electron

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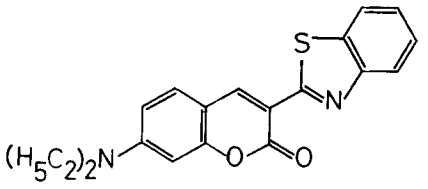
transfer for EDA dye molecules in solutions, in rigid polymeric matrices as well as in the gas-phase employing a supersonic jet expansion technique (Rabek 1982; Demas 1983; Lakowicz 1983; Visser *et al* 1983; O'Connor and Phillips 1984; Williams 1984; Wolfbeis and Bauster 1985; Rettig 1986, 1988; Meech and Phillips 1987; Peng *et al* 1987; Rohatgi-Mukherjee 1987; Jones and Phillips 1988; Posch and Wolfbeis 1988; Cazeau-Dubroca *et al* 1989). Although considerable progress has been made, more information about the photophysics and spectral characteristics of the EDA molecules is needed and it continues to be the subject of a major challenge for chemical research. Coumarin derivatives with a rotatable or rigidized amino group in the 7-position have received great attention from the theoretical and experimental points of view (Schaefer 1973; Reynolds and Drexhage 1975; Jones *et al* 1980; Kubin and Fletcher 1983; Abdel-Mottaleb *et al* 1984; Huppert *et al* 1989; Van Gompel and Schuster 1989). The fundamental information gleaned about the photophysical properties of this group of dyes revealed a number of interesting features. The weak fluorescence intensity and shortening of the fluorescence lifetime (acceleration of fluorescence decay) observed for most flexible amino coumarins, particularly in protic solvents, have been explained in terms of a non-radiative relaxation process of the planar ICT state producing a twisted ICT state (called (TICT)) (Lippert *et al* 1987) via internal rotation of the amino group to an orthogonal geometry. This twisting process occurs in a few picoseconds and critically depends on the kind of interactions exerted by environmental factors. TICT states, accessible in flexible multichromophoric molecules, have been considered as non-radiative tunnels to the ground state (Vogel *et al* 1988). However, based on fluorescence lifetime data, it has been concluded that hydrogen bonding between solvent and a coumarin molecule seems not to be a determining factor for TICT state formation in the case of 7-aminocoumarin derivatives studied (Chu and Yangbo 1987). Using supersonic jet expansion technique, it has been shown that a specific interaction with polar protic or aprotic solvent molecules is a prerequisite for TICT state formation in case of N,N-dimethylaminobenzonitrile (DMABN) (Peng *et al* 1987). It seems that investigations are still required to explain the effect of solute–solvent interactions on the fluorescence quenching of amino coumarins due to excited state complex formation.

As a part of a continuing study on the fluorescence behaviour of a range of coumarin dyes or multichromophoric EDA type (Abdel-Mottaleb *et al* 1989), the present work



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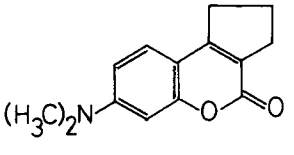

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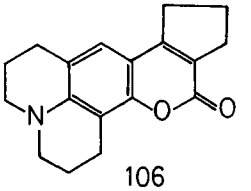

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was taken up to provide a more general information on the flexible coumarins 6 and 138 and its rigidized derivative coumarin 106. For sake of clarity and completeness, the photophysical and dynamical behaviour and the interplay between dye structure and solvent in homogeneous media will be investigated first. These studies are essential prerequisites in order to explain the effect of solute–solvent interactions, particularly specific hydrogen bonding interactions, on the photophysical properties and fluorescence quenching of these 7-substituted amino-coumarins due to excited state complex formation. The results will be discussed on the basis of the electronic structure of these dyes obtained by application of the well-known quantum chemical PPP–SCF–CI MO method. This gives an insight into the singlet excited state properties and hydrogen bonding complexation of these dyes and the dynamics and mechanisms of solute–solvent relaxations. Studies will be extended to and focussed on measurements of fluorescence depolarization in glycerol at different temperatures. These studies are indispensable preliminaries in attempting a more refined analysis of the viscosity/free volume controlling factors affecting the motion of fluorophores incorporated in different systems of industrial and biological interest, e.g. polymers, proteins, micelles, etc. (Guillet 1985; Winnik 1986).

Finally, we report linear correlation between fluorescence depolarization ($1/P$) and medium viscosity ($n(T)$ function) and demonstrate its utility in predicting the average microviscosity of some ionic micelles. As an illustrative example, we explore the analytical application of coumarin 6 as a useful fluorescence probe to determine critical micelle concentration, cmc, in ionic micellar solutions, which have been considered as model systems mimicking biomembranes in biological processes (Turro *et al* 1980; Guillet 1985; Winnik 1986).

2. Experimental

Coumarins 6, 138 and 106 (laser grade) were supplied by Eastman Kodak and were used as received. CTAB and SDS were purchased from Janssen Chimica and used as received. Spectral measurements, fluorescence polarization and quantum yield determinations, and the statistical treatment of data were described before (Abdel-Mottaleb *et al* 1989). A wide range of spectral grade solvents (18 solvents) belonging to different classes were used. Numerical values representing solvent properties are collected from the literature (Reichardt and Goernert 1983). Quantum chemical calculations within the framework of the PPP–SCF–CI–MO method were performed by applying a program supplied by QCPE (Griffiths 1976, 1981; Griffiths *et al* 1988).

3. Results and discussion

3.1 *Solvent effect*

Coumarins 6, 138 and 106 exhibit an intense solvent-dependent visible absorption band: its wavelength is consistent with a transition which has a considerable CT character proportional to the donor–acceptor power within the molecular subunits. The absorption and fluorescence spectra show positive solvatochromic behavior, as shown in table 1 and figure 1. Generally, it is noted that, the absorption spectrum is less sensitive towards the solvent polarity (Reichardt and Goernert 1983) than the

Table 1. Spectroscopic and fluorescence quantum yield data for flexible coumarins 6 and 138 and the rigidized derivative coumarin 106 together with solvent polarity parameter (E_T^N)*.

		λ_a	λ_f	Φ_f	λ_a	λ_f	Φ_f	λ_a	λ_f	Φ_f
Solvent	E_T^N	Coumarin 6			Coumarin 138			Coumarin 106		
1 Water	1·000	490	565	0·03	367	472	0·39	380	490	0·70
2 Methanol	0·765	456	508	0·78	366	454	0·65	384	471	0·90
3 Ethanol	0·654	458	505	0·87	365	448	0·69	386	467	0·90
4 *iso*-Butanol	0·506	453	502	0·87	361	443	0·90	380	462	1·00
5 Acetonitrile	0·472	455	503	0·56	358	433	0·90	378	448	0·74
6 DMSO	0·441	466	515	0·56	363	439	0·80	384	455	0·80
7 DMF	0·404	461	505	0·84	361	433	0·90	380	447	0·81
8 Acetone	0·355	460	500	0·93	356	427	1·00	374	442	1·02
9 Dichloromethane	0·321	455	496	0·94	359	424	0·60	380	440	1·00
10 Chloroform	0·259	455	492	0·93	361	422	0·90	377	440	0·70
11 Ethylacetate	0·228	450	490	0·86	353	418	0·90	368	432	0·62
12 Dioxane	0·164	440	485	1·00	356	424	0·90	376	426	0·97
13 Benzene	0·127	434	487	0·87	355	411	0·80	372	425	0·90
14 *p*-Xylene	0·123	430	480	0·90	348	408	0·90	372	423	0·81
15 Toluene	0·096	433	485	0·86	350	410	0·90	376	425	0·85
16 Cyclohexane	0·077	425	465	0·77	346	395	0·80	369	415	0·88
17 *n*-Hexane	0·075	424	483	0·79	343	394	0·75	368	412	0·80
18 *n*-Heptane	0·052	422	485	1·01	343	395	0·71	360	410	1·00

* The E_T^N values have been reported for over 240 solvents and represent both the general as well as specific solvent properties (Reichardt *et al* 1983).

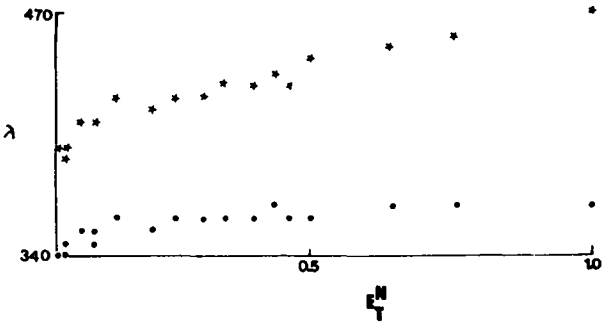


Figure 1. Variation of absorption (•) and fluorescence (•) wavelengths for coumarin 138 with the solvent polarity parameter E_T values. (Noteworthy is that excluding a few solvents results in excellent linear correlations between λ_a or λ_f and E_T values). Similar behaviour was noticed for other coumarins studied (see table 1).

fluorescence spectrum which undergoes a more remarkable red shift as the polarity of the solvent increases (figure 1), and the efficiency of the fluorescence (Φ_f) is slightly affected by solvent change (table 1). Considerable decrease in Φ_f value can be seen in water. This effect is more pronounced in the case of flexible coumarins 6 and 138, reflecting the role played by rotatory freedom and structure twist and could be most probably attributed to local specific interactions including hydrogen bonding complex formation. These results emphasize the obvious ICT nature of the major electronic

transitions under consideration. Same observations and conclusions have been reported from comparative studies of fluorescence decay kinetics for similar dyes (Jones *et al* 1980, 1985; Chu and Yangbo 1987; Van Gompel and Schuster 1989).

Moreover, a steady quenching of the fluorescence intensity concomi.ant with a gradual bathochromic shift of the fluorescence wavelength is observed for all dyes under consideration in dioxane solutions (figure 2) on addition of increasing amounts of water. Upon addition of trace quantities of water (up to about 3% of the total solution volume) the intensity of the initial fluorescence spectrum of the dye in the neat dioxane solution is decreased, and a new red-shifted spectrum appears. No such change in the absorption spectrum of a dye solution was noticed for this low concentration limit (< 1·66 M) of water. The appearance of this new fluorescence component and the isoemissive point (figure 3) are characteristic of excited state hydrogen bonding complex formation of simple stoichiometry with water molecules as previously reported for some dye molecules of EDA type (Lakowicz 1983; Cazeau-Dubroca *et al* 1989) according to the equilibrium:

$$m\,\mathrm{Dye}^{\ddagger} + n\,\mathrm{H_2O} = (m\,\mathrm{Dye}^{\ddagger}{:}n\mathrm{H_2O}).$$

A further increase in the water concentration in the mixed solvents causes an additional gradual bathochromic shift due to the gradual increase in the bulk polarity of the mixed solvent as noticed in figure 2.

Attempted analysis of the spectral data in the low concentration limit of water (up to 1·66 M) by using the equilibrium relation $I_f = K \times [\mathrm{H_2O}]^n$, where I_f is the fluorescence intensity due to complex formation and n is the number of water molecules involved in the complex, is successful. From the slopes and the intercepts of the linear least squares plots of the $\log(I_f)$ vs $\log([\mathrm{H_2O}])$ we obtained the values for n and K, respectively (with a correlation coefficient of 0·99). All dyes form very weak

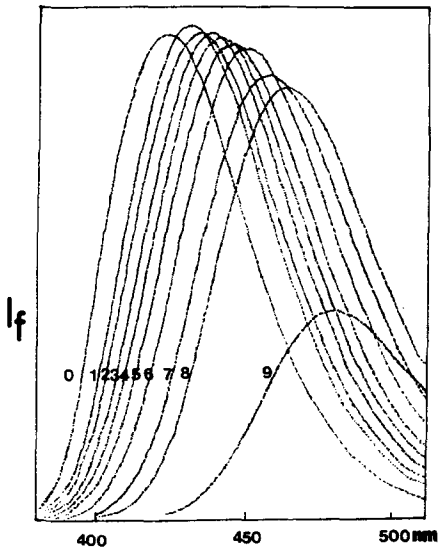


Figure 2. Fluorescence spectra of coumarin 138: (0) pure-dioxane, from (1) to (8) in mixed dioxane-water solvents in which water content is gradually increased, and in (9) pure water. Similar behaviour was observed for coumarins 6 and 106.

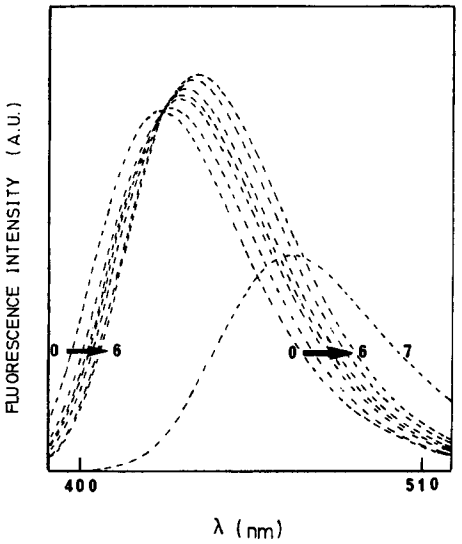


Figure 3. Effect of addition of small quantities of water (up to 1·66 M, spectra 1–6) on the fluorescence spectrum of coumarin 138 in pure dioxane (0). No changes in the corresponding absorption spectrum were noticed indicating excited state complexation with water molecules. Curve 7 represents spectrum in pure water (see §3·1). A similar effect was observed for coumarins 6 and 106.

(dye:H_2O) complexes of simple stoichiometric ratio (1:1). Same results for other EDA dyes have been reported earlier (Visser *et al* 1983; Meech and Phillips 1987; Peng *et al* 1987; Jones and Phillips 1988; Posch and Wolfbeis 1988; Cazeau-Dubroca *et al* 1989).

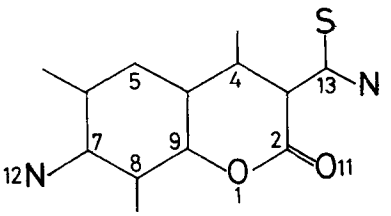
In conclusion, it is shown that upon the formation of a new polar solvation envelope to accommodate the created electron redistribution in the S_1 state of these dyes a reversible photoassociation of simple stoichiometry with water molecules is established. Moreover, in the limit of a large protic solvent concentration, the solvation process can be regarded as continuous (Detoma 1983) and the fluorescent system is under the dynamic control of solvent relaxation process. Similar conclusion has been previously reported (Detoma 1983).

The results above can be rationalized on the basis of quantum chemical data obtained by application of the well-known SCF–CI–MO method (Griffiths 1976, 1981; Griffiths *et al* 1988) which permit us to establish the nature of the lowest excited singlet state and to examine the charge density distributions for the ground (S_0) and excited S_1 states of coumarins 6, 138 and 106. These are presented in table 2. The ground state electron density distributions are similar and characterized by alternate distribution. It can be seen that light absorption results mainly in a more polar charge transfer S_1 (iiii*) state a result which rationalizes the spectral shifts observed (see table 1 and figure 1). Moreover, in the S_1 states of these dyes, electron density alternation is destroyed especially for the lactone ring. This should result in ultrafast solvent-dependent electronic relaxation. It is thus expected that a short range (a small amplitude) geometrical relaxation is achieved in proportion to the strength of solvent interactions. This is reflected in the relatively small Stokes shift observed and the high fluorescence quantum efficiency in aprotic solvents. It seems reasonable to

Table 2. Pi-electron density distributions in the S_0 and $S_{1,ct}$ states of coumarin 6 and coumarin 138 and its rigidized derivative 106.*

	S_0			$S_{1,ct}$		
Atom No.	6	138	106	6	138	106
1	1·858	1·857	1·857	1·873	1·884	1·884
2	0·727	0·729	0·729	0·753	0·874	0·875
3	1·060	1·042	1·046	1·066	1·077	1·085
4	0·909	0·927	0·927	1·175	1·183	1·183
5	0·969	0·974	0·973	1·042	1·086	1·089
6	1·102	1·105	1·112	1·034	0·998	1·004
7	0·973	0·978	0·989	1·004	1·017	1·036
8	1·140	1·143	1·153	1·063	1·029	1·029
9	0·952	0·962	0·961	0·992	0·986	0·988
10	1·095	1·093	1·099	0·991	0·949	0·956
11	1·476	1·502	1·504	1·464	1·558	1·565
12	1·675	1·690	1·651	1·490	1·361	1·304
13	0·828			0·908		
14(N)	1·130			1·331		
15(S)	1·890			1·903		

* The parameters used in the SCF–CI–MO calculations are those of Griffiths *et al* (1988). Perturbations due to the methyl groups were taken into consideration to get best agreement between calculated and observed longest wavelength electronic transition.



conclude that a significant amount of the solvent–solute local hydrogen bonding interactions with the more basic centers in the lactone ring become stronger in the S_1 state of these dyes leading to a more considerable relaxation to the solvated $S_{1,ct}$ state and structure twist can be stabilized in case of flexible coumarins in proportion to the degree of flexibility which is larger for coumarin 6 (due to possible rotation around the bond connecting the benzothiazolyl group). This accounts for the experimentally observed fluorescence quenching in water (see table 1), in particular for coumarin 6 which is characterized by a larger number of basic centers accessible for local hydrogen bonding interactions with water.

3.2 *Fluorescence depolarization*

The obtained fluorescence quantum yield of our dyes is insensitive to solvent viscosity due to a minor contribution of the intramolecular torsional dynamics to the overall nonradiative energy relaxation process. Fluorescence polarization measurements

Table 3. Fluorescence depolarization data for coumarins 6, 138 and 106 as a function of $n(T)$ and of the free volume fraction of glycerol at different temperatures (see text).

T (K)	T/n (K/cP)	$1/f$	$1/P$		
			6	138	106
288·0	0·144	14·59		2·58	2·55
288·7	0·144	14·52	2·13		
294·5	0·245	14·00		2·80	2·64
294·8	0·245	13·98	2·16		
299·0	0·352	13·62	2·19	2·98	2·72
303·3	0·513	13·28		3·07	2·83
303·7	0·514	13·25	2·20		
309·3	0·814	12·83	2·24	3·37	3·23
315·3	1·401	12·41		3·82	3·41
318·7	1·713	12·19	2·29		
324·3	2·270	11·83	2·31	4·72	4·02
329·2	3·359	11·54	2·44	5·50	4·90
337·3	5·190	11·08	2·65	6·76	6·29
346·0	7·854	10·63	2·82	9·01	8·48
351·0	10·320	10·39		10·75	10·31
351·6	10·340	10·36	3·05		

provide an alternative method to prove medium fluidity variation and are very informative about the dynamics of the fluorescent systems. Polarization measurements are also informative about the orientation distribution of fluorophores in different systems of industrial and biological interest (e.g. polymers, proteins etc.) (Turro *et al* 1980; Guillet 1985; Winnik 1986).

The dynamics of molecular rotational relaxation of molecules in solution has been extensively investigated by various spectroscopic techniques (Loutfy and Arnold 1982). Most of the studies have been performed on ionic dyes in a variety of solvents in order to test the validity of the DSE hydrodynamic model against the applicability of the free volume concept. For dyes which undergo a nonradiative intramolecular torsional relaxation the fluorescence quantum yield was found to be high media free-volume dependent.

Our experimentally determined polarization data in glycerol over a range of temperature (294·4 – 346 K) (table 3), fitted the well-known Perrin equation (Perrin 1929):

$$(1/P) = (1/Po) + [(1/Po) - (1/3)](RT/Vn)r,$$

where Po is characteristic value for the same fluorophore in vitrified solution, R is the gas constant, and r is the fluorescence lifetime of the fluorophore of a molecular volume V. The established equations of correlation (with a correlation coefficient of 0·99) are

$$1/P = \begin{cases} 2{\cdot}14 + 0{\cdot}10\ T/n, & \text{for coumarin 6,} \\ 2{\cdot}69 + 0{\cdot}79\ T/n, & \text{for coumarin 138,} \\ 2{\cdot}42 + 0{\cdot}76\ T/n, & \text{for coumarin 106.} \end{cases}$$

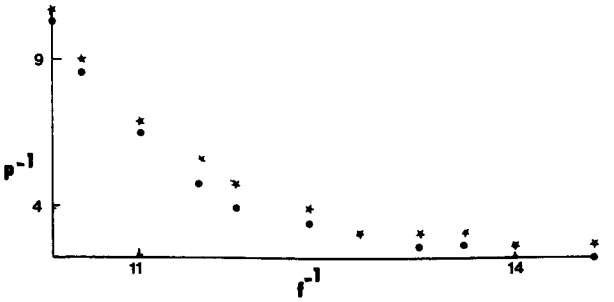


Figure 4. Graphical representation of the noticed variation of degree of fluorescence depolarisation of coumarins 138 (*) and its rigidised derivative 106 (●) with the f^{-1} function for glycerol at different temperatures (see table 3). Depolarization decreases as free volume (f) of medium (glycerol) decreases.

Thus, varying the ratio T/n for glycerol by temperature change (Landolt-Boernstein 1969) and studying the rotational diffusion using fluorescence polarization technique should assist in establishing the dominant solvent relaxation process and provide insight into the role of the molecular structure and its sensitivity to the average medium microviscosity. Comparison of the slopes reflects a higher sensitivity of the more structurally related coumarins 138 and 106 towards average medium viscosity/temperature. The results suggest the promising utility of these commercially available dyes as probes to explore microscopic fluidity pertaining to the interior of industrially and biologically important systems such as polymers, proteins and micelles.

Furthermore, to test the applicability of the free-volume concept in describing the dynamics of these fluorophores we have calculated the change in the free-volume of glycerol with temperature by using the equation $f = f_g + \sigma(T - T_g)$ where $f_g = 0{\cdot}025$, $\sigma = 4{\cdot}4 \times 10^{-4}\,\text{degree}^{-1}$ and $T_g = 189\,\text{K}$ for glycerol (Loutfy and Arnold 1982). We have found that, as the free volume (f) fraction of the medium decreases fluorescence depolarisation ($1/P$) nonlinearly decreases (figure 4).

On correlating ($1/P$) with the calculated $1/f$ values for glycerol at different temperatures (303·3 – 346 K) (table 3), we obtained the following Arrhenius-like regression equations:

$$1/P = \begin{cases} 18\exp(-0{\cdot}17/f), & \text{for coumarin 6,} \\ 1033\exp(-0{\cdot}45/f), & \text{for coumarin 138,} \\ 1166\exp(-0{\cdot}47/f), & \text{for coumarin 106.} \end{cases}$$

These findings confirm the applicability of the free-volume concept in describing the molecular rotational diffusion of these coumarins. Moreover, it reflects the similar depolarisation behaviour of the closely related coumarin 138 and its rigidized derivative coumarin 106.

Since depolarization ($1/P$) is a thermally activated process involving molecular rotational diffusion, it can be expressed in an Arrhenius form as

$$1/P = A\exp(-\Delta E/RT),$$

where A is the preexponential factor and ΔE is the activation energy of depolarization.

Nonlinear least-squares analysis of our data results in the following regression equations

$$1/P = \begin{cases} 64 \exp(-1070/T), & \text{for coumarin 6 (318·7 – 351·6 K),} \\ 6{\cdot}764 \times 104 \exp(-2888/T), & \text{for coumarin 138,} \\ 5{\cdot}091 \times 104 \exp(-3025/T), & \text{for coumarin 106,} \end{cases}$$

(in the temperature range 303·3 – 346 K for coumarins 138 and 106), from which the values for the activation energy of depolarization of coumarins 6, 138 and 106 are calculated, 2·1, 5·78 and 5·84 kcal/mol, respectively, reflecting the greater flexibility for coumarin 6. These values compared to the activation energy of glycerol flow (= 14·25 kcal/mol) (Loutfy and Arnold) imply that the solute molecule is rotating relatively unprohibited within a solvent cage (free-volume) arising from multiple-hydrogen bonding sites in glycerol.

3.3 *Photophysical properties in micellar solutions*

Owing to the importance of micellar aggregates (formed by ionic and nonionic surfactants) as model systems mimicking more complex bioaggregates such as biomembrances, we extend our study to explore the potential of the commercially available and relatively cheaper coumarin 6 laser dye as a probe for micellization processes in case of two ionic surfactants; CTAB and SDS. Of the various physical

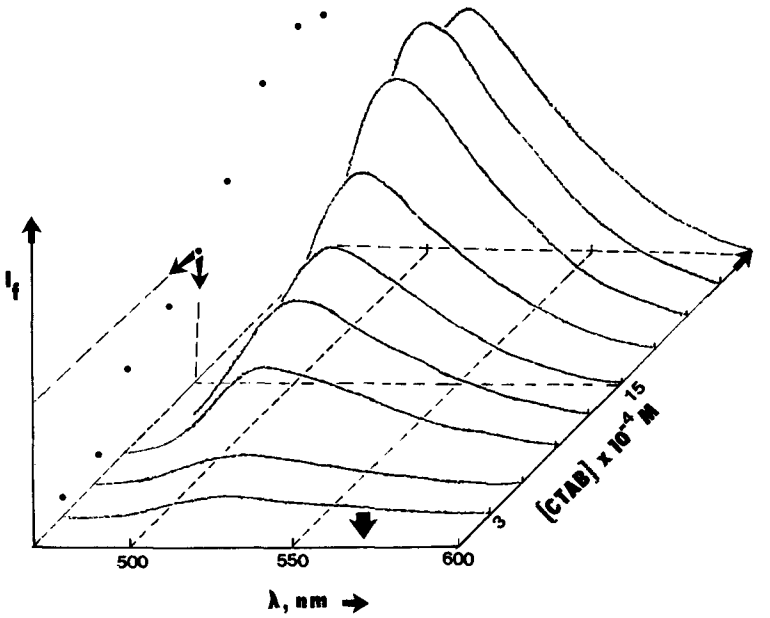


Figure 5. Three-dimensional plot showing the spectra of coumarin 6 in aqueous CTAB solutions of different concentrations. The heavy arrow points to λ_{max} of coumarin 6 in pure water. The points on the left-side represent fluorescence intensity at 510 nm as a function of CTAB concentration. The evaluation of data gives a cmc of 1×10^{-3} M. Similar plot was obtained in case of SDS (see text).

methods employed, fluorescence emission probes have been widely used because of their simplicity, wide applicability and extreme sensitivity at very low probe concentrations (Turro *et al* 1980). Moreover, by comparing the spectral data in micelles with those in homogeneous solvent systems, more can be learned about the structural details of the micellar microenvironment (Turro *et al* 1980).

We have observed that the fluorescence intensity and energy of coumarin 6 aqueous solution exhibit marked change on addition of the surfactant (CTAB or SDS). The fluorescence maximum (= 565 nm) is blue-shifted (1900 cm^{-1}) and the fluorescence intensity of coumarin 6 is enhanced. Moreover, a rapid increase in the fluorescence intensity is observed above the critical micelle concentration of both CTAB (1×10^{-3} M) and SDS (8×10^{-3} M). A three-dimensional representation of these observations in case of CTAB is shown in figure 5. In addition, both observations point to the existence of coumarin 6 probe molecules in a less polar (of $E_T = 0{\cdot}55$ predicted from the linear dependence of λ_f on the E_T value, $\lambda_f = 480 + 45{\cdot}6\,E_T$, excluding water, table 1) aprotic interior of the micellar aggregates of these ionic surfactants. Thus, this behaviour provides a simple and exceptionally high sensitivity method for following micellization.

Finally, it is worth mentioning that information on the average microviscosity or organized assemblies is accessible in a relatively simple way by using the linear dependence of $1/p$ on $n(T)$ function above established. The determined $1/p$ values for coumarin 6 in $2{\cdot}5 \times 10^{-3}$ M CTAB and $2{\cdot}5 \times 10^{-2}$ M SDS solutions (above cmc) at 298 K were 3·1 and 3·7, respectively, and are readily converted to the average microviscosities in the range 18–30 cP which are comparable with these in the literature (Law 1981).

References

Abdel-Mottaleb M S A, Antonious M S, Abo-Ali M M, Ismaiel L F, El-Sayed B A and Sherif A M K 1989 *J. Photochem. Photobiol.* **50** 259

Cazeau-Dubroca C, Lyazidi S A, Cambou P, Peirigua A, Cazeau Ph and Pesquer M 1989 *J. Phys. Chem.* **93** 2347

Chu G and Yangbo F 1987 *J. Chem. Soc., Faraday Trans. I* **83** 2539

Cundall R B and Dale R E (eds) 1983 *Time resolved fluorescence spectroscopy in biochemistry and biology* (New York and London: Plenum Press)

Demas J N 1983 *Excited state lifetime measurements* (New York and London: Academic Press)

Detoma R P 1983 *Time-resolved fluorescence spectroscopy in biochemistry and biology* (eds) R B Cundall and R E Dale (New York and London: Plenum Press) p. 393

Fendler J H and Fendler E J 1975 *Catalysis in micellar and macromolecular systems* (New York: Academic Press)

Griffiths J 1976 *Colour and constitution of organic molecules* (London: Academic Press)

Griffiths J 1981 *Rev. Prog. Coloration* 37

Griffiths J, Lasch J G and Schermaier A G 1988 (QCPE, Indiana University, USA)

Guillet J 1985 *Polymer photophysics and photochemistry* (London: Cambridge University Press)

Huppert D, Ittah V and Kosower E M 1989 *Chem. Phys. Lett.* **159** 267, and references therein

Jones A C and Phillips D 1988 *Laser Chem.* **9** 317

Jones G II, Jackson W R, Choi C and Bergmark W R 1985 *J. Phys. Chem.* **89** 294

Jones G II, Jackson W R and Halpern M A 1980 *Chem. Phys. Lett.* **72** 391

Kessler M A and Wolfbeis O S 1989 *Chemistry and physics of lipids*

Kubin F and Fletcher A N 1983 *Chem. Phys. Lett.* **99** 49

Lakowicz R J 1983 *Principles of fluorescence spectroscopy* (New York and London: Plenum)

Landolt-Boernstein 1969 *Zahlenwerte und funktionen* (Berlin: Springer-Verlag) II Band, 5 Teil

Law K Y 1981 *Photochem. Photobiol.* **33** 799

Lippert E, Rettig W, Bonacic- Koutecky V, Heisel F and Mieche J A 1987 *Adv. Chem. Phys.* **68** 1
Loutfy R O and Arnold B A 1982 *J. Phys. Chem.* **86** 4205
Meech S R and Phillips D 1987 *J. Chem. Soc., Faraday Trans. II* **83** 1941
O'Connor D V and Phillips D 1984 *Time correlated single photon counting* (New York and London: Academic Press)
Peng L W, Dantus M, Zewail A H, Kemnitz K, Hicks J M and Eisenthal K B 1987 *J. Phys. Chem.* **91** 6162
Perrin F 1962 *Ann. Phys. (Paris)* **12** 169
Posch H E and Wolfbeis O S 1988 *Sensors and Actuators* **15** 77
Rabek J F 1982 *Experimental methods in photochemistry and photophysics Part 2* (Chichester, New York: Wiley-Interscience)
Reichardt C and Goernert E H 1983 *Liebigs Ann. Chem.* 721
Rettig W 1986 *Angew Chem., Int. Ed. Engl.* **25** 971
Rettig W 1988 *Appl. Phys.* **B45** 145
Reynolds G A and Drexhage K H 1975 *Opt. Commun.* **13** 222
Rohatgi-Mukherjee K K 1987 *Fundamentals of photochemistry* (New Delhi: Wiley Eastern)
Schaefer F P 1973 *Laser dyes* (Berlin: Springer-Verlag)
Schaffar B P H and Wolfbeis O S 1988 *Analyst* **113** 693
Thomas J K 1980 *Chem. Rev.* **80** 283
Turro N J, Graetzel M and Braun A M 1980 *Angew. Chem., Int. Ed. Engl.* **19** 675
Van Gompel J A and Schuster G B 1989 *J. Phys. Chem.* **93** 1292
Visser R J, Varma C A G O, Konijnenberg J and Bergerf P 1983 *J. Chem. Soc., Faraday Trans. II* **79** 347
Vogel M, Rettig W, Fiedeldei U and Baugaertel H 1988 *Chem. Phys. Lett.* **148** 347
Vogel M, Rettig W, Sens R and Drexhage K H 1988 *Chem. Phys. Lett.* **147** 452, 461
Von Buenau G and Wolf T 1988 *Adv. Photochem.* **14** 273
Williams D J 1984 *Agnew. Chem., Int. Ed. Engl.* **23** 690
Winnik M A (ed.) 1986 *Photophysical and photochemical tools in polymer science, NATO ASI series C 182* (Dordrecht: Reidel)
Wolfbeis O S and Baustert J H 1985 *J. Heterocyclic Chem.* **22** 1215
Zachariasse K A, Van Phu N and Kozankiewicz B 1981 *J. Phys. Chem.* **85** 2676