

Fluorescence properties of some coumarin dyes and their analytical implication

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Abstract. Fluorescence characteristics of two substituted coumarin dyes have been investigated. The effect of solvent polarity and viscosity on the fluorescence properties of these dyes was examined. It was found that the fluorescence quantum yield (ϕ_f) is a steep function of the viscosity. The dependence of ϕ_f on viscosity is successfully explained on the basis of the free volume theory of viscosity. Moreover, fluorescence depolarization measurements in media of different viscosities assist in the establishment of an analytical method for microviscosity determination in the interior of some micellar assemblies.

Keywords. Fluorescence; coumarin; depolarization.

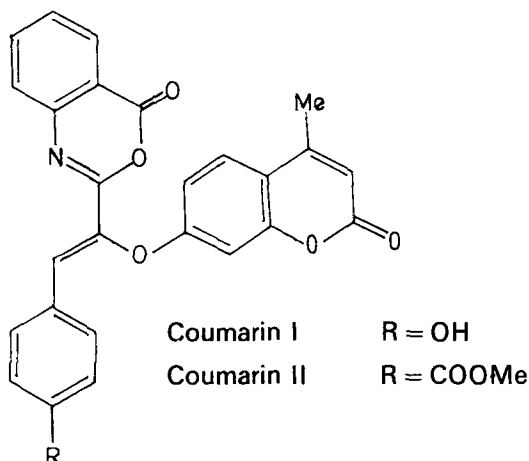
1. Introduction

The spectroscopic properties of coumarins have received considerable attention due to their ability to lase in the blue-green region (Drexhage *et al* 1973). Coumarin dyes display fluorescence which is remarkably sensitive to medium polarity and viscosity (Jones *et al* 1980; Law 1980, 1981; Jones and Jackson 1984; Abdel-Mottaleb *et al* 1989).

As a part of an investigation of photophysical and photochemical properties of coumarin dyes (Jones *et al* 1980; Jones and Jackson 1984; Abdel-Mottaleb *et al* 1989), we have included studies of dye behaviour in media of differing polarities and viscosities.

We report our investigation on two coumarin dyes, I and II, in a series of solvents of differing polarities at room temperature and in glycerol at different temperatures. It was found that these dyes are very sensitive to medium viscosity rather than solvent polarity. The preliminary studies of such compounds as a function of solvent viscosity suggested that the extremely fast deactivation rate of the singlet excited state of these compounds was attributed to torsional relaxation (Luotfy and Law 1980). The temperature variation studies also enable the activation energy for the reorientation rate ΔE_{Kor} , to be obtained and compared with that of solvent viscosity (Luotfy and Law 1981). The sensitivity of the fluorescence of these dyes to glycerol viscosity at different temperatures should help in obtaining information about the microviscosity prevailing in the micellar assemblies.

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2. Experimental details

Optically pure solvents were used. Absorption spectra were recorded on Perkin-Elmer Lambda 3B spectrophotometer. Fluorescence spectra were taken on a Shimadzu RF 510 spectrofluorometer. Fluorescence quantum yields were determined by comparison with a quinine fluorescence standard ($\phi_f = 0.55$ in 1 N H_2SO_4). The measurements were done at relatively low concentrations (about 10^{-6} mol/l) to avoid aggregation and dimer formation. Glycerol viscosity was varied by temperature in the range of 20–75°C. Free volume calculations were determined using the methods described in Luotfy and Arnold (1982). Least-squares regression analyses were performed for all data.

3. Results and discussion

The absorption and fluorescence spectral data of coumarin dyes I and II, in a variety of solvents, are given in tables 1 and 2. The absorption and fluorescence maxima (figure 1) of these compounds are insensitive to solvent polarity (tables 1 and 2). The most striking photophysical properties of these compounds are the dependence of fluorescence quantum yield ϕ_f on solvent viscosity (tables 3 and 4). The quantum yield (ϕ_f) increases as the viscosity of glycerol increases by decreasing temperature. The results of a comparative study of ϕ_f of these compounds in alcoholic solvents of different viscosities (tables 1 and 2), indicate that ϕ_f is larger in more viscous media. So, the high ϕ_f value observed in glycerol is thus entirely due to enhanced viscosity. The triplet T, T^* state is known to be able to deactivate by isomerizing the C=C bond (Hammond 1964). The rigidity dependence (Salteil *et al* 1968), viscosity (Sharafy and Muszkat 1971) and temperature effect (Geglou *et al* 1968) on the fluorescence quantum yield of stilbene derivatives obviously support this view. Recently, the rate constant of twisting the C=C bond of *trans* stilbene in hexane has been measured. The rate is $\sim 10^{10} \text{ s}^{-1}$ which is qualitatively in agreement with the estimation ($\sim 10^{11} \text{ s}^{-1}$). This

Table 1. Spectral and photophysical data of coumarin I.

Solvent	λ_a (nm)	λ_f (nm)	$\phi_f \times 10^{-3}$	$\epsilon \times 10^{-4}$	$\Delta\nu_{1/2}$ (cm^{-1})	$K_r \times 10^{-9}$ (s^{-1})	$K_n \times 10^{-11}$ (s^{-1})
Water	315	383	13	0.091	5636	0.691	0.52
MeOH	316	387	10	1.175	5806	10.940	10.07
EtOH	317	388	10	1.050	5773	9.680	8.83
<i>n</i> -PrOH	316	403	29	1.235	6838	4.130	2.66
<i>n</i> -BuOH	317	385	15	1.175	5571	7.650	4.91
<i>Iso</i> -BuOH	317	390	17	1.095	5905	6.200	3.45
<i>Iso</i> -PrOH	314	387	20	1.087	6007	5.430	1.34
CH ₃ CN	312	385	13	1.042	6077	7.650	5.44
DMSO	315	385	93	1.200	5772	1.290	0.12
DMF	317	392	21	1.125	6036	5.150	2.31
Acetone	321	415	5	1.450	7056	26.510	48.20
CH ₂ Cl ₂	312	383	9	1.177	5942	11.920	11.90
CHCl ₃	312	390	7	1.300	6410	16.310	20.30
Ethyl- acetate	310	390	7	1.087	6617	1.39	1.66
Dioxane	310	365	26	1.337	4861	4.99	1.18

Table 2. Spectral and photophysical data of coumarin II.

Solvent	λ_a (nm)	λ_f (nm)	$\phi_f \times 10^{-3}$	$\epsilon \times 10^{-4}$	$\Delta\nu_{1/2}$ (cm^{-1})	$K_r \times 10^{-9}$ (s^{-1})	$K_n \times 10^{-11}$ (s^{-1})
Water	310	390	20	0.750	6617	3.620	1.71
MeOH	310	391	34	0.792	6683	2.300	0.64
EtOH	312	390	38	0.720	6410	1.880	0.47
<i>n</i> -PrOH	313	395	65	0.850	6632	1.300	0.18
<i>n</i> -BuOH	313	392	45	0.850	6439	1.850	0.38
<i>Iso</i> -BuOH	313	390	60	0.775	6308	1.280	0.19
<i>Iso</i> -PrOH	313	385	64	0.820	5945	1.280	0.18
CH ₃ CN	312	390	29	0.905	6410	3.090	1.02
DMSO	315	385	157	0.775	5772	0.490	0.02
DMF	316	390	40	0.800	6005	1.950	0.45
Acetone	320	395	18	1.050	5934	5.550	2.67
CH ₂ Cl ₂	308	385	33	0.922	6484	2.790	0.81
CHCl ₃	312	387	23	1.080	6212	4.500	1.83
Ethyl- acetate	308	388	25	0.850	6694	3.380	1.31
Dioxane	312	386	64	0.825	6145	1.29	0.18

rate is viscosity dependent (Luotfy and Arnold 1982; Rice and Kenny-Wallace 1980) and exceeds that of radiative decay ($\sim 3 \times 10^8 \text{ s}^{-1}$). This is not attributable to intersystem crossing from S^1 to T^1 since the rate of intersystem crossing of triplet T , T^* states is normally $\sim 10^6$ – 10^7 s^{-1} . These results lead us to conclude that the major deactivation process of the S_1 state of these compounds in solution at room temperature is due to internal geometrical relaxation.

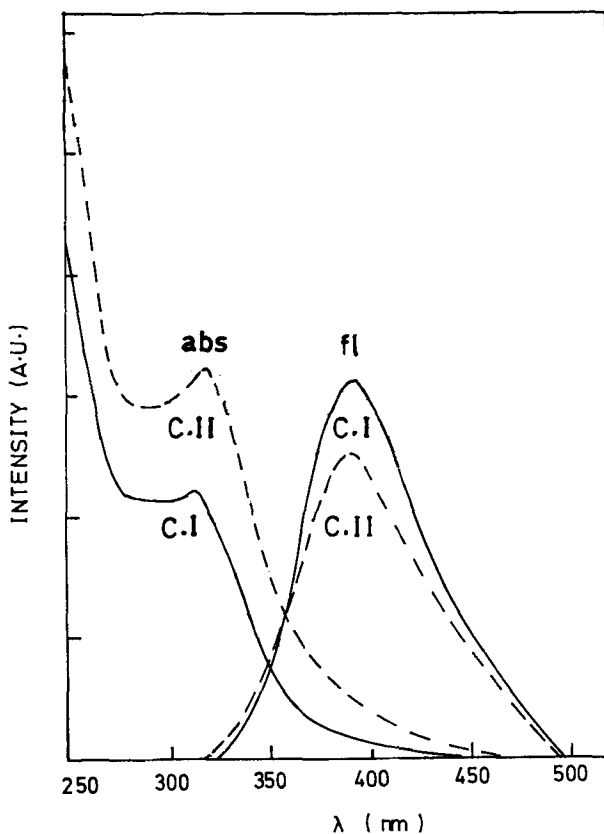


Figure 1. Absorption and fluorescence spectra of coumarins I and II (C.I and C.II).

Table 3. Effect of viscosity on fluorescence quantum yield of coumarin I.

T (K)	η (cP)	ϕ	f^a	τ_{or}^b (ps)	$K_{or}^c \times 10^{-11}$ (s^{-1})
293	1392.7	0.02560	0.02610	4.7	2.13
298	926.0	0.02235	0.63850	3.2	3.16
304	577.5	0.01847	0.06595	2.1	4.64
312	316.5	0.01586	0.06875	1.5	6.31
318	205.7	0.01402	0.07085	1.2	8.09
322	155.7	0.01191	0.07225	0.9	11.24
328	103.8	0.01169	0.07435	0.8	11.66
333	75.0	0.01061	0.07610	0.7	14.17
340	48.2	0.00959	0.07855	0.6	17.37

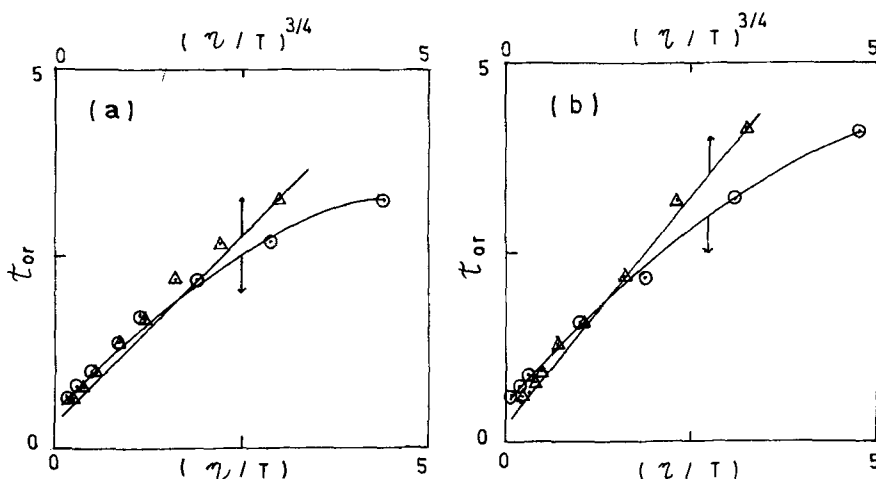
^a Free volume calculated from Luotfy and Arnold (1982)

^b Orientation relaxation time calculated from Luotfy and Arnold (1982)

^c $K_{or} = 1/\tau_{or}$.

Table 4. Effect of viscosity on fluorescence quantum yield of coumarin II.

T (K)	η (cP)	ϕ	f^a	τ_{or}^b (ps)	$K_{or}^c \times 10^{-11}$ (s ⁻¹)
294.0	1282.0	0.0575	0.0625	32.7	0.306
299.0	854.8	0.0523	0.0642	26.9	0.372
304.0	577.5	0.0476	0.0660	22.2	0.450
309.0	395.1	0.0421	0.0677	17.3	0.578
314.0	273.7	0.0383	0.0695	14.1	0.709
321.5	161.2	0.0335	0.0721	10.4	0.962
327.5	107.3	0.0296	0.0742	8.4	1.191
333.0	74.9	0.0265	0.0761	6.7	1.493
338.0	54.6	0.0244	0.0779	5.6	1.786

^a Free volume calculated from Luotfy and Arnold (1982)^b Orientation relaxation time calculated from Luotfy and Arnold (1982)^c $K_{or} = 1/\tau_{or}$.**Figure 2.** Orientation relaxation times of coumarin I (a) and of coumarin II (b) as a function of viscosity.

In order to examine the availability of free volume as a controlling factor in the torsional relaxation, figure 2 shows the deviation of orientation relaxation time τ_{or} from linear viscosity dependence (Luotfy and Arnold 1982). Nevertheless, plots of τ_{or} against $(\eta/T)^{3/4}$, give reasonably good straight lines (figure 2), indicating agreement with the Forster and Hoffman (1971) scheme. Also, the observed linearity of $\ln \phi_f$ with respect to $1/f$ (figure 3) (where f is the free volume fraction for glycerol), supports (Luotfy and Arnold 1982; Abdel-Mottaleb *et al* 1989) the validity of the free-volume concepts as the controlling factor of torsional motion of the excited state of these compounds.

The activation energies for glycerol, ΔE_n , and that of the rate constant orientation relaxation (Luotfy and Arnold 1982), $\Delta E_{K_{or}}$ are listed in table 5 and figures 4 and 5. These data show that $\Delta E_{K_{or}}$ is less than ΔE_n . Previous observation on other large

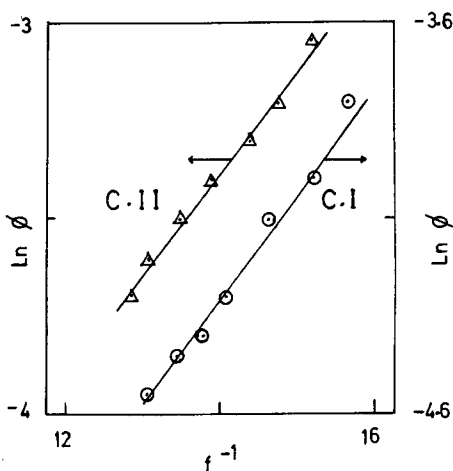


Figure 3. Dependence of the fluorescence quantum yields of coumarin I (C.I) and coumarin II (C.II) on the free-volume fraction of glycerol.

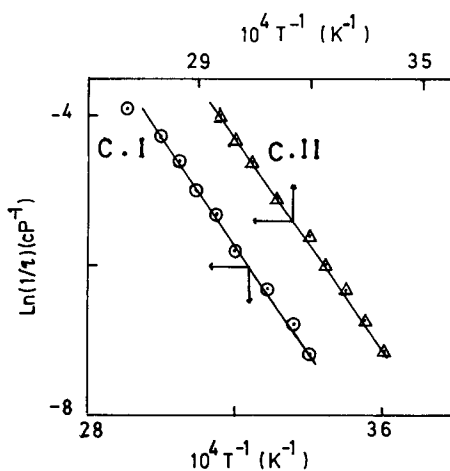


Figure 4. Plot of $\ln(1/\eta)$ vs $1/T$ for coumarins I and II (C.I and C.II).

Table 5. Activation energy for internal relaxation (ΔE_{kor}) and solvent viscosity $\Delta E(\eta)$.

ΔE_{kor}^* (coumarin I)	7.786
ΔE_{kor}^* (coumarin II)	7.305
ΔE_{η}^* (glycerol)	14.087

*In kcal mol

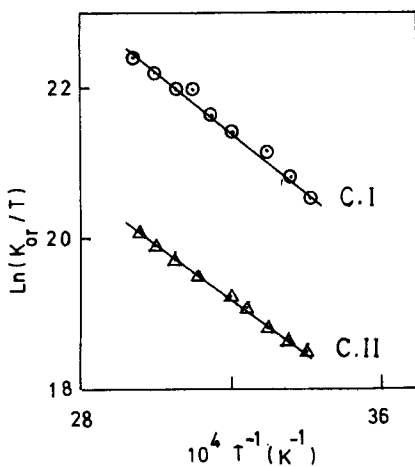


Figure 5. Plot of $\ln(K_{or}/T)$ vs $1/T$ for coumarins I and II (C.I and C.II).

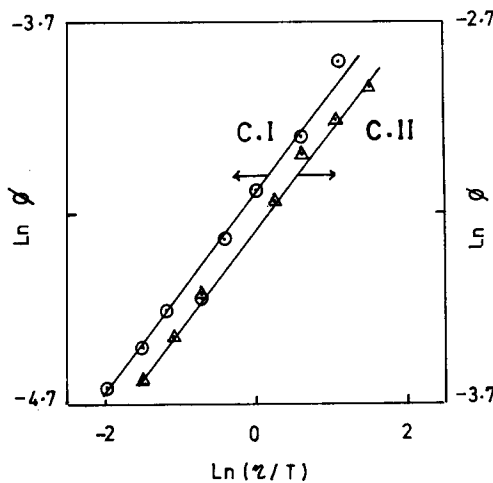


Figure 6. Dependence of the fluorescence quantum yield of coumarins I and II (C.I and C.II) on η/T .

molecular dye systems (Rice and Kenny-Wallace 1980; Luotfy and Arnold 1982) where ΔE_n is larger than ΔE_{kor} suggested that the solute is unhindered in its rotation.

The viscosity of the medium η is related to the fluorescence yield according to Luotfy and Arnold (1982),

$$\phi_f = B(\eta/T)^x$$

Plots of $\ln \phi_f$ vs η/T should be straight lines (figure 6). The above relationships indicate that the fluorescence yields of dyes which exhibit rotation-dependent, non-radiative decay increase with decreasing free volume and increase with the viscosity of the solvent.

Studying the fluorescence polarization behaviour of the two compounds should assist in the establishment of the sensitivity of these compounds to solvent viscosity. According to the Perrin (1929) equation, the plots of $1/p$ vs T/η give straight lines, the data are listed in tables 6 and 7. The established relationships are:

$$1/p = 2.133 + 0.092 T/\eta \quad (\text{for coumarin I})$$

$$1/p = 0.772 + 0.0126 T/\eta \quad (\text{for coumarin II})$$

with a correlation coefficient of 0.99. Hence, the determined $1/p$ in micellar solutions can be converted to viscosities (Forester and Hoffmann 1971; Shinitzky *et al* 1971). The results listed in table 8 show that coumarin I can be used to report on the microviscosity in the interior of the micellar assemblies.

Table 6. Polarization data for coumarin I.

T (K)	T/η (KcP ⁻¹)	$1/f$	$1/p$
307	0.670	12.853	2.190
311.5	0.950	12.535	2.270
319	1.660	12.037	2.273
323	2.220	11.793	2.310
331	3.220	11.793	2.451
335	6.079	11.096	2.600
339	6.606	10.884	2.765

Table 7. Polarization data for coumarin II.

T (K)	T/η (KcP ⁻¹)	$1/f$	$1/p$
299	0.349	13.463	2.155
308	0.723	12.781	2.175
323	2.220	11.787	2.222
338	6.189	10.936	2.330
343	8.540	10.679	2.440
348	11.680	10.434	2.480

Table 8. Microviscosity of CTAB and SDS in coumarins I and II.

Comp/Micelle	$1/p$	η (cp)
Coumarin I CTAB	3.500	20.04
SDS	3.595	18.74
Coumarin II CTAB	3.819	1.23
SDS	3.671	1.30

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