Photophysics and dynamics of rigidized coumarin laser dyes

PHOTOPHYSICS AND DYNAMICS OF RIGIDIZED COUMARIN LASER DYES

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Summary

This paper describes some photophysical properties, the results of CNDO molecular orbital (MO) calculations and excited state complex formation for two solvatochromic coumarin laser dyes of the rigidized multichromophoric electron donor–acceptor type (coumarins 314 and 337). Light absorption results in the population of an almost fully fluorescent polar charge transfer singlet state characterized by non-alternate electron density distributions and a remarkable sensitivity to solvent properties. Useful non-linear, linear and multiparameter relationships between the quantum yield of fluorescence, the emission and absorption maxima and the Stokes shift and some solvent parameters are established. Hydrogen-bonding solvents such as ethanol cause quenching and a bathochromic shift of fluorescence due to ground state complexation. Excited state equilibrium studies reveal the formation of weak (with equilibrium constant of 2 - 19 l mol^{-1}) hydrogen-bonding complexes with a stoichiometry of 2:1 (dye:ethanol). The fluorescence polarization behaviour in glycerol at various temperatures shows that the molecular rotational diffusion is controlled by the free volume of the medium. The results point to a possible use of these highly fluorescent dyes as bifunctional fluorescent probes for determining the rigidity and polarity of the surrounding medium of interest.

1. Introduction

Fluorescent dyes have found widespread application as laser dyes, solar energy concentrators and fluorescent probes [1 - 20]. Therefore it is of

interest to predict and control the properties of fluorescent dyes. In recent years many investigations have focused on the role of the solvent in controlling the intramolecular charge transfer (ICT) process for electron donor–acceptor (EDA) dye molecules in solution [4, 6, 7, 15, 21 - 31], as well as in the gas phase using supersonic jet expansion techniques [32]. Certain dye families of the EDA type are good fluorescers (*e.g.* the oxazines, rhodamines and coumarins) [4, 33] and they have been used as laser dyes and solar energy concentrators.

Of the vast number of coumarins of the EDA type studied, coumarin derivatives with an amino group in the 7-position have received most attention from a theoretical and experimental point of view [4, 21, 22, 23]. The fundamental photophysical and photochemical properties of this group of dyes suggest that coumarin dyes can be divided into two families on the basis of the flexibility of the substituted amine group. For dyes having a rotatable amine group or alkylated amine group, fluorescence quantum yield and lifetime are sharply reduced in a polar protic solvent, but recover in viscous or glassy media. This effect has been found to be more pronounced for a polar dye with electron-withdrawing substituents in the lactone ring. The results have been explained in terms of a non-radiative relaxation process of the planar ICT state producing a biradical state [33] (called twisted ICT (TICT) [28]). This biradical state has an energy minimum at the orthogonal geometry produced via internal twisting which occurs in a few picoseconds and critically depends on the types of interaction exerted by environmental factors [34]. Knowledge of the factors which control TICT formation [30] can help in the provision of new and more efficient laser dyes. Structural rigidization of the amino group by substituent linkage results in another family of coumarin dyes which show a much higher fluorescence efficiency even in polar protic solvents [22, 23].

Investigations are still required to explain the effect of solute–solvent interactions, particularly specific hydrogen-bonding interactions, on the photophysical properties and fluorescence quenching of amino coumarins due to excited state complex formation. This information is highly desirable for the characterization of dye–solvent laser systems and could be useful in providing fluorescent probes with unique features for possible analytical applications.

This work reports on some photophysical properties of the rigidized amino coumarins 314 and 337 of the EDA type which have the same donor group but different electron acceptor moieties. The results are discussed on the basis of the electronic structure of the dyes obtained by application of the all-valence electrons quantum chemical CNDO method. The photophysical behaviour and the interplay between dye structure and solvent in homogeneous media are explored. Studies are extended to various solvents, mixed ethanol–ethyl acetate solvents at constant temperature and glycerol at various temperatures. This provides an insight into the excited state properties and hydrogen-bonding complexation of the dyes.
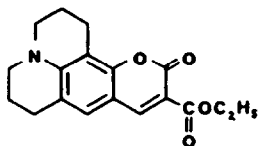
coumarin 314
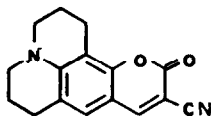
coumarin 337

2. Experimental details

The coumarin dyes 314 and 337 were of laser grade (Eastman Kodak Company) and were used as received. Solvents were purified by standard techniques and were non-fluorescent under the experimental conditions used.

The absorption spectra were measured on a Perkin–Elmer spectrophotometer. A Shimadzu RF 510 spectrofluorometer equipped with a rhodamine B quantum counter, a temperature regulated cell holder and a polarizer attachment was used to record the fluorescence, excitation and polarization spectra. The fluorescence quantum yields were determined relative to a quinine fluorescence standard (ϕ_f = 0.55 in 0.1 N H_2SO_4) using the comparative method described in ref. 35. The concentration of the final dye solutions was of the order of 5×10^{-6} M. The absorbance of the measured solutions at the excitation wavelength was less than 0.10.

Molecular orbital computations within the framework of the all-valence-electron CNDO method were performed using a program supplied by QCPE [36]. The values used for the bond lengths and angles were obtained from the literature.

The least-squares regression analysis and the procedure for fitting the data to the non-linear, linear and multiparameter equations were performed using the Simfit program [36] with error minimization by the sequential simplex statistical procedure. An AT&T PC-XT 6300 personal computer was used for data analysis.

3. Results and discussion

3.1. Photophysical properties and excited state interactions

The absorption and fluorescence spectra of the coumarin dyes 314 and 337 exhibit positive solvatochromic behaviour as shown in Tables 1 - 3. It should be noted that the absorption spectrum is less sensitive to the solvent polarity [37 - 39] than is the fluorescence spectrum which undergoes a more significant red shift as the polarity of the solvent increases. Both dyes exhibit a Stokes shift ($\Delta E = \bar{\nu}_a - \bar{\nu}_f$) which correlates well with solvent properties. Furthermore, the fluorescence spectra of the dyes in ethanol glass show a small blue shift (of about 30 nm) in the emission maximum relative to that obtained at room temperature. However, the fluorescence quantum yield ϕ_f values do not change because of the absence of the rotational or twisting routes for the non-radiative energy dissipation for the rigid structures of

TABLE 1

Spectral data and fluorescence quantum yield for coumarins 314 and 337 in various solvents at 295 K

	Solvent	E_T^N	λ_a (nm)[a]		$\Delta\bar{\nu}_{1/2}$ (cm^{-1})		λ_f (nm)		ϕ_f	
			314	337	314	337	314	337	314	337
1	H$_2$O	1.000	445(4.68)[a]	452(3.36)[a]	2872	2968	493	500	0.670	0.438
2	MeOH	0.765	432(4.99)	437(4.01)	2739	2688	482	492	0.670	0.784
3	EtOH	0.654	432(4.70)	437(3.90)	2653	2736	481	490	0.650	0.829
4	isoBuOH	0.506	430(4.68)	434(3.80)	2679	2762	477	485	1.000	0.879
5	CH$_3$CN	0.472	423(4.68)	435(3.80)	3452	2556	480	485	1.000	0.574
6	DMSO	0.441	436(4.41)	442(4.01)	2665	2720	486	495	1.000	0.930
7	DMF	0.404	426(4.32)	437(3.69)	2868	2736	483	490	1.000	1.104
8	Acetone	0.355	424(4.41)	434(3.80)	2858	2788	473	485	1.000	0.935
9	CH$_2$Cl$_2$	0.321	430(4.68)	442(4.27)	2931	2460	470	478	1.000	1.100
10	CHCl$_3$	0.259	430(4.50)	440(3.69)	2540	2483	464	475	1.000	0.961
11	Ethyl acetate	0.228	420(4.32)	428(3.47)	2956	2909	465	475	1.000	0.960
12	Bromobenzene	0.210	430(5.13)	440(4.34)	3452	2823	465	474	0.890	0.574
13	Dioxane	0.164	419(3.96)	424(3.58)	2600	2783	460	465	1.000	0.940
14	Benzene	0.127	424(4.95)	433(3.80)	3211	2528	456	465	1.000	0.791
15	Toluene	0.096	423(4.77)	430(3.69)	3023	2616	453	463	1.000	0.814
16	Cyclohexane	0.077	414(5.49)	422(4.40)	3357	2584	445	450	1.000	0.816
17	n-Hexane	0.075	412(4.50)	421(4.12)	3078	2409	438	450	0.900	0.863
18	n-Heptane	0.052	412(4.88)	418(3.25)	3369	2445	440	455	1.000	1.034

[a]log ϵ_{max}.

TABLE 2

Relationships between the spectral and photophysical properties (Y) of coumarins 314 and 337 and solvent properties (X) according to the general equation $Y = A + BX$

Y	X	A		B		r^2	n_{obs}[a]	Excluded solvents
		314	337	314	337			
λ_a	E_T^N	417.8	423	20.0	22.3	0.997	12	1, 6, 10, 12, 17, 18
λ_f	E_T^N	453	458	43.8	47.7	0.998	12	1, 6, 7, 16 - 18
log E[b]	E_T^N	3.153	3.150	1.1	0.97	0.967	9	1 - 5, 7, 11, 13, 17
ϕ_f	E_T^N	—	1.05	—	−0.38	0.986	9	1, 6, 8, 10, 13, 15 - 18

[a]n_{obs} = number of solvents included.
[b]E = stokes shift ($\bar{\nu}_a - \bar{\nu}_f$).

coumarins 314 and 337. These findings indicate emission from a planar polar excited state. The dipole moment of the emitting state is different from the singlet excited state (planar). However, a small increase in the S$_1$ (Franck–Condon strained state (FC)) dipole moment can explain the small solvatochromic effect observed in the absorption spectra. The S$_1$(FC) state under-

TABLE 3

Multilinear relationships according to the multiparameter equation $Y = Y_0 + A\alpha + B\beta + C\pi*$

Y			A		B		C		r^2	n_{obs}	Excluded solvents
	314	337	314	337	314	337	314	337			
λ_a	406	420	12.0	10	—	−6	28.0	22.0	0.98	12	1, 5, 7, 16 - 18
λ_f	425	449	25.9	17	—	12	58.6	29.0	0.99	12	1, 5, 7, 16 - 18
$\Delta\bar{\nu}_s$	1570	1553	−218	497	860	—	572	949	0.97	9	1 - 5, 7, 11, 13 17
ϕ_f	—	0.82	—	−0.17	—	0.21	—	—	0.97	9	1, 6, 8, 10, 13, 15 - 18

goes an ultrafast solvent-dependent relaxation process to generate a low lying, highly polar, efficiently emitting $S_{1,CT}$ state.

Following the method described previously [40], we calculated the relative dipole moments (μ_g/μ_e) in the ground and excited states of the dyes from the solvatochromic measurements. The summary of the results (Table 4) supports the above conclusions.

The photophysical data given in Table 1 indicate that absorption of a photon switches the molecule to a singlet excited state characterized by a higher dipole moment and an extensive solvent-dependent fluorescence deactivation process. A summary of the established relationships between some photophysical properties and solvent properties is presented in Tables 2 and 3. A consequence of these correlations is that the interplay between solute–solvent interactions is mainly controlled by the solvent properties (polarity and hydrogen-bonding abilities). These established relationships

TABLE 4

Calculation of the relative dipole moments (μ_g/μ_e) in the S_0 and S_1 states for coumarins 314 and 337 from the slope ratios of the linear dependence of the spectroscopic shifts (Y) on the bulk dielectric and refractive indices (X) of the solvent according to the general equation $Y = A + BX$

Y	$A \times 10^{-4}$		B		X	$R = B(1)/B(2)$[a]		μ_g/μ_e[b]	
	314	337	314	337		314	337	314	337
(1) $(\bar{\nu}_a - \bar{\nu}_f)$	0.1553	0.1577	939	1051	$F_2(D, n)$[c]	0.304	0.387	0.53	0.44
(2) $(\bar{\nu}_a + \bar{\nu}_f)/2$	2.4129	2.3516	−3087	−2714	$F_7(D, n)$[c]				

[a]$B(1) = C(\mu_e - \mu_g)^2$, $B(2) = C(\mu_g^2 - \mu_e^2)$ and C = constant.
[b]$\mu_g/\mu_e = (1 + R)/(1 - R)$.
[c]Defined in refs. 39 and 40.

suggest an analytical application of these dyes as sensitive fluorescent probes [9, 25, 26, 41]. Moreover, some information emerges from the data of Tables 2 and 3 which merits discussion.

(a) In all cases water is omitted because of the strong deviation from the established relationships due to specific hydrogen-bonding donor–acceptor interactions.

(b) The influence of the solvent hydrogen-bonding donor property (the α parameter [38]) on the absorption, emission and Stokes shift of these dyes is pronounced (see Tables 2 and 3). The solvent properties have a small effect on the ϕ_f value of coumarin 337 via the control of the energy gap between the excited state and the ground state probably due to local specific interactions including hydrogen-bonding complex formation. This effect is pronounced in the case of the fully fluorescent coumarin dye 314; in ethanol its fluorescence is significantly quenched ($\phi_f = 0.65$).

These results can be rationalized on the basis of quantum chemical data obtained by application of the CNDO method; this method permits us to establish the nature of the lowest excited singlet state and to examine the charge density distributions and bond orders for the ground S_0 and excited S_1 states of coumarins 314 and 337. These are presented in Fig. 1. The ground state electron density distributions and bond orders of both dyes are similar and are characterized by alternate distribution. It can be seen that light absorption results mainly in a charge transfer $S_1(\pi\pi^*)$ state which is slightly more polar in coumarin 314, a result which rationalizes the relative dipole moment data obtained by application of the spectral shift method (see Table 4). Moreover, in the S_1 states of these dyes, electron density alternation is destroyed and the bond orders become more uniform especially for the lactone ring. It is thus expected that a short-range (a small amplitude) geometrical relaxation due to solvent interactions is achieved. This is reflected in the relatively small Stokes shift observed and the high fluorescence quantum efficiency in aprotic solvents. It seems reasonable to conclude that local hydrogen-bonding interactions with the more basic centres in the lactone ring become stronger in the S_1 state of the dyes. This is reflected in the fluorescence quenching and the larger Stokes shift in protic solvents.

Several workers have considered that the size of the Stokes shift is an indication of the extent of the charge transfer during an electronic transition and an important criterion of the local solute–solvent interactions such as hydrogen-bonding complex formation in the excited state [4, 15, 42]. A steady quenching of the fluorescence intensity concomitant with a gradual bathochromic shift of the fluorescence wavelength is observed for both dyes in ethyl acetate solutions (Fig. 2) on addition of increasing amounts of ethanol. This prompted us to carry out a more detailed study to determine the role played by the specific hydrogen-bonding interactions in the S_0 and S_1 states of these dyes. The absorption spectra of the dyes in the ethyl acetate–ethanol mixtures exhibit a sharp isosbestic point, indicating an established ground state equilibrium between solute and ethanol (Fig. 3).

Fig. 1. π-charge density and π-bond orders in the S_0 and S_1 states of coumarins 337 (a) and 314 (b).
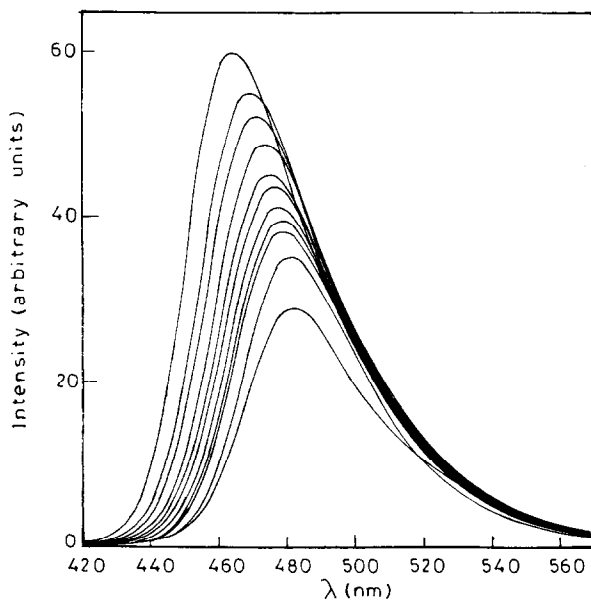
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Fig. 2. Quenching of fluorescence intensity (concomitant with bathochromic shift) on addition of small amounts of ethanol (top to bottom) to an ethyl acetate solution of coumarin 314. A similar behaviour was observed for coumarin 337.
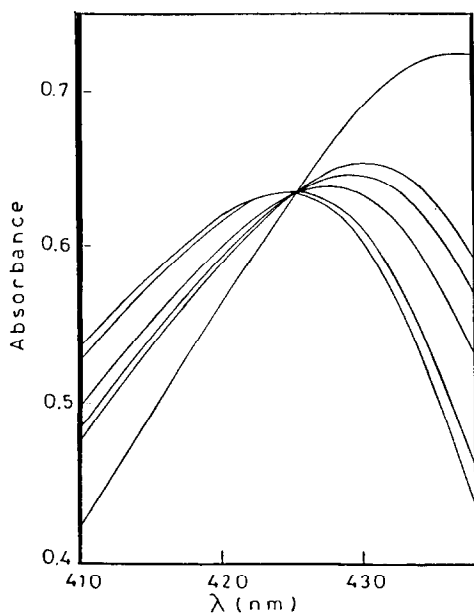

Fig. 3. Absorption spectral changes of an ethyl acetate solution of coumarin 314 on addition of ethanol. The isosbestic point indicates the existence of ground state hydrogen-bond complex formation. Similar results were obtained for coumarin 337 in ethyl acetate–ethanol mixtures.

This reaction should result in a static fluorescence quenching or sensitization [43] depending on the nature of the electronic transition. In the case of population of an $S_1(\pi\pi^*, (CT))$ state, specific hydrogen-bonding interactions lead to fluorescence quenching [23].

Moreover, the examination of the fluorescence spectra in a variety of ethyl acetate–ethanol solvents can provide evidence for local hydrogen-bonding interactions with the fluorophores. The addition of low concentrations of ethanol, which are too small to alter the bulk properties of the solvent, result in substantial spectral shifts (Fig. 4). On addition of trace quantities of ethanol, the intensity of the initial spectrum of the dye in neat ethyl acetate solution decreases, and a new red-shifted spectrum appears. The appearance of this new fluorescence component and the sharp isoemissive point are characteristic of excited state hydrogen-bonding complex formation according to the equilibrium

$$m \text{ Dye}^* + n \text{ } C_2H_5OH \rightleftharpoons (m \text{ Dye}^*:n \text{ } HOC_2H_5)$$
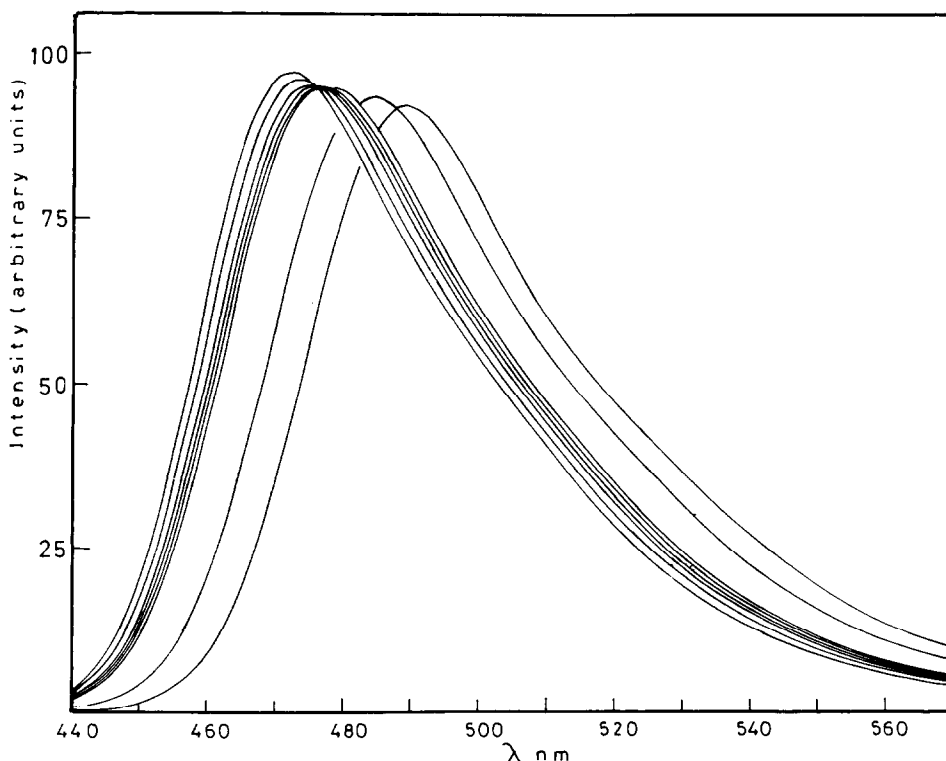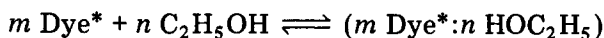

Fig. 4. Fluorescence emission spectra of coumarin 337. Spectra are shown in ethyl acetate to which small amounts of ethanol were added (in the case of the first six spectra the quantity of ethanol ranges from 0% to 5% from left to right; these spectra exhibit a clear isoemissive point). Further addition of ethanol results in a deviation from the isoemissive point due to the change in the bulk polarity of the solvent (see text). A similar spectral behaviour was observed for coumarin 314.

A further increase in the ethanol concentration in the mixed solvents causes an additional gradual bathochromic shift due to the gradual increase in the bulk polarity of the mixed solvent (Fig. 4).

By analysing the spectral data, more quantitative data on the presumed excited state equilibrium can be obtained. We calculate the equilibrium constant K for complex formation and the stoichiometry of the excited state complex using a simplified equilibrium relation

$$I_f = K[\text{EtOH}]^n$$

where I_f is the fluorescence intensity due to complex formation and n is the number of ethanol molecules involved in the complex. From the slopes and the intercepts of the linear least-squares plots of $\log I_f$ vs. $\log [\text{EtOH}]$ we obtained the values for n and K respectively. Both dyes form weak 2:1 (dye: EtOH) complexes ($K = 2 - 15 \, \text{l mol}^{-1}$ and $n = 0.5$).

3.2. Fluorescence depolarization

The dynamics of molecular rotational relaxation of molecules in solution have been extensively investigated by various spectroscopic techniques [44 - 47]. Most of the studies have been performed on ionic dyes in a variety of solvents in order to test the validity of the Debye–Stokes–Einstein (DSE) hydrodynamic model against the applicability of the free-volume concept. For dyes which undergo a non-radiative intramolecular torsional relaxation, the fluorescence quantum yield has been found to be highly dependent on the free volume of the medium.

Because the fluorescence quantum yields of our dyes are insensitive to solvent viscosity due to the absence of intramolecular torsional dynamics, experimental support for the application of the free-volume concept as the controlling factor for molecular rotational relaxation in high viscosity media can be obtained by studying the fluorescence polarization behaviour of the coumarin dyes 314 and 337 in glycerol as a function of temperature.

It has been known for many years that the polarization of fluorescence increases with the viscosity of the medium containing the fluorophore. A quantitative theory connecting the phenomenon with the molecular rotational diffusion of the emitting species was formulated by Perrin in 1929 and has been applied successfully by many workers [9, 42]. The rate of molecular motion can be estimated by determining the degree of polarization P. When the molecular motion is fast enough compared with the fluorescence lifetime, the emission polarization P or emission anisotropy r, defined in eqns. (1) and (2), fall to zero

$$P = (I_{\parallel} - I_{\perp})/(I_{\parallel} + I_{\perp}) \tag{1}$$

$$r = (I_{\parallel} - I_{\perp})/(I_{\parallel} + 2I_{\perp}) \tag{2}$$

where $I_{\parallel}$ and $I_{\perp}$ denote the measured intensities of the emitted light (at right angles to the incident beam) polarized parallel and perpendicular to the plane of polarization of the exciting radiation. These quantities are significant

measures of the extent to which the emitted light is polarized after excitation of the sample with plane polarized light. Polarization measurements are also informative about the orientational distribution of fluorophores in different systems (*e.g.* polymers and proteins) [9, 17, 18, 25, 26, 41, 42].

According to the Perrin equation

$$1/P - \tfrac{1}{3} = (1/P_0 - \tfrac{1}{3})\{1 + (RT/V\eta)\tau\} \tag{3}$$

It is thus expected that a plot of $1/P$ *vs.* T/η should give a straight line with a slope of $(1/P_0)(R\tau/V)$ and an intercept of $(1/P_0)$, where P_0 is the characteristic value for the same fluorophore in vitrified solution, R is the gas constant and τ is the fluorescence lifetime of the fluorophore of molecular volume V. Our experimental data are collected in Table 5 and fit the Perrin equation. The established equations of correlation (with a correlation coefficient of 0.99) are

$$1/P = 2.22 + 0.25 T/\eta \qquad \text{for coumarin 314}$$

$$1/P = 2.16 + 0.53 T/\eta \qquad \text{for coumarin 337}$$

Thus varying the ratio T/η for glycerol by changing the temperature and studying the rotational diffusion using the fluorescence polarization technique should assist in the establishment of the dominant solvent relaxation process and the sensitivity of the highly fluorescent coumarins 314 and 337 to the viscosity of the medium. (Viscosity values were interpolated or extrapolated from the linear least-squares equation $\ln(1/\eta) = 4.838 - 7312/T$ based on viscosity values taken from ref. 48.) The result shows a higher degree of sensitivity of coumarin 337 to viscosity, suggesting its promising use as a probe to explore the microscopic fluidity pertaining to the interior

TABLE 5

Fluorescence depolarization of coumarins 314 and 337 in glycerol as a function of T/η and $1/f$ of glycerol (see text)

T (K)	T/η^{a} (K cP^{-1})	$1/f^{\text{a}}$	$1/P$	
			$C314$	$C337$
288.7	0.1444	14.52	2.084	2.262
294.8	0.2457	13.98	2.322	2.262
299.0	0.3518	13.62	2.411	2.317
303.7	0.5147	13.25	2.414	2.339
309.3	0.8139	12.83	2.631	2.473
318.7	1.713	12.19	2.841	2.474
324.3	2.268	11.83	3.507	2.828
329.2	3.359	11.54	3.767	3.168
337.3	5.189	11.08	5.162	3.452
346.0	7.864	10.63	6.295	4.052
351.6	10.34	10.36	7.656	4.833

[a]See text and ref. 48.

of industrially and biologically important systems such as polymers, proteins and micelles [9, 17, 18, 41, 42, 49].

The change in the free volume of glycerol with temperature can be calculated using the equation

$$f = f_g + \alpha(T - T_g) \tag{4}$$

where $f_g = 0.025$, $\alpha = 4.4 \times 10^{-4}$ K^{-1} and $T_g = 189$ K for glycerol [47].

Attempted correlations between $\ln(1/P)$ and the calculated $1/f$ values for glycerol at various temperatures (Table 5) result in the following linear regression equations

$\ln(1/P) = 5.0 - 0.33/f$ for coumarin 314

$\ln(1/P) = 7.5 - 0.53/f$ for coumarin 337

in the temperature range 318.7 - 351.6 K. These findings point to the applicability of the free-volume concept in describing the molecular rotational diffusion of these coumarins.

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

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

where A is the pre-exponential factor and ΔE is the activation energy of depolarization. The plots of $\ln(1/P)$ vs. $1/T$ are linear (in the temperature range 318.7 - 351.6 K); from the slopes of these plots the values of the activation energy of depolarization for coumarins 314 and 337 are calculated; least-squares analysis of the data listed in Table 5 gives the values 4.2 and 7.0 kcal mol^{-1} respectively. These values compared with the activation energy of glycerol viscosity (14.25 kcal mol^{-1} [47]) imply that the solute is relatively unhindered in its rotation.

Acknowledgment

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