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Photophysical Properties of Coumarin-500 (C500): Unusual Behavior in Nonpolar Solvents

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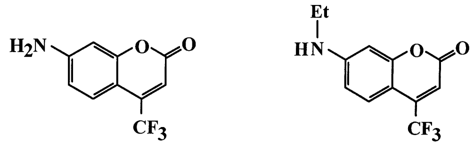
Photophysical properties of 7-NHEt-4-CF_3-1,2-benzopyrone dye (coumarin-500, C500), have been investigated in different solvents and solvent mixtures using optical absorption and fluorescence measurements. In nonpolar solvents, namely, hexane, cyclohexane, methylcyclohexane, 2-methylpentane, 3-methylpentane, and Decalin, the dye displays unusual properties in comparison to those in other solvents. Thus, in the former solvents, the Stokes' shifts $\Delta\bar{\nu}$ and the fluorescence lifetimes (τ_f) for C500 are found to be unusually low. Though in these solvents the fluorescence quantum yields Φ_f are seen to be only marginally higher, the radiative decay rate constants k_f are found to be unusually higher than those in the other solvents. From comparing the results of C500 with those reported earlier for its lower analogue, C151 (coumarin-151, 7-NH_2-4-CF_3-1,2-benzopyrone; Nad, S.; Pal, H. *J. Phys. Chem. A.* **2001**, *105*, 1097), it is inferred that just like C151, in nonpolar solvents the dye C500 also exists in nonpolar structures, whereas in all other solvents the dye exists in a polar intramolecular charge transfer (ICT) structure. Unlike C151, the C500, however, does not show any activation-controlled nonradiative deexcitation channel for the S_1 state in nonpolar solvents, which arises due to the flip-flop motion of the 7-amino group. Due to the heavier mass, the flip-flop motion of the 7-NHEt group in C500 is supposed to be much slower than that of the 7-NH_2 group in C151. Thus, such a motion cannot introduce any deexcitation channel, which can compete with the intrinsic fluorescence k_f and the internal conversion k_{IC} rates in the excited C500 dye. Thus, unlike C151, there is no activation-controlled nonradiative deexcitation channel for C500 in nonpolar solvents though both the dyes appear to exist in similar structural forms in these solvents, which are different than those existing in other solvents of lower to higher polarities.

1. Introduction

The derivatives of 1,2-benzopyrone, commonly known as the coumarin dyes, are the well-known laser dyes for the blue-green region.[1−7] The coumarin dyes having 7-amino or 7-substituted amino groups (commonly known as 7-aminocoumarins) compose the special class of compounds among the coumarin dyes, due to both their superior laser activity and their applicabilities to other applications in investigating many physicochemical processes. The 7-aminocoumarin dyes are usually very strongly fluorescent, with their fluorescence quantum yields Φ_f often close to unity.[1−10] Though in some of these coumarin dyes the internal conversion (IC) process contributes to some extent to the deexcitation of the fluorescence (S_1) state, the contribution of the intersystem crossing (ISC) process in these compounds is usually very low or negligible.[8−10] For most of the 7-aminocoumarin dyes, there is a large change in the dipole moments upon exciting these molecules from the ground to their excited singlet states.[1−10] All the 7-aminocoumarin dyes show very large Stokes' shifts between their absorption and the fluorescence maxima.[8−17] These Stokes' shifts are again very sensitive to the polarities of the solvents and the microenvironments.[8−17] Due to these interesting properties, a number of 7-aminocoumarin dyes have found their applications in studying many physicochemical processes in condensed phase, namely, the solvatochromic behaviors, polarities of different environments, measurement of the solvent relaxation times τ_s using dynamic Stokes' shift method, and many others.[12−17]

CHART 1



(C151; I) (C500; II)

Though there are many reports on the photophysical properties of the 7-aminocoumarin dyes,[8−10] a number of unusual behaviors of some of these dyes display under different conditions are not yet properly explored, understood, or explained. Few years back Rechthaler and Kohler[18] have reported that the photophysical properties of the 7-aminocoumarin dyes with unsubstituted 7-amino group (7-NH_2) are unusually different in nonpolar solvents compare to those in other solvents. Thus coumarin-151 (C151, 7-NH_2-4-CF_3-1,2-benzopyrone; structure **I**, Chart 1) is reported to show unusually low fluorescence quantum yields Φ_f and lifetimes τ_f in nonpolar solvents in comparison to those in other solvents of moderate to higher polarities. Though Rechthaler and Kohler[18] have proposed a higher ISC process for C151 in nonpolar solvents to explain their observation, this explanation appeared to be unlikely as the ISC process in coumarin dyes are normally very negligible.[8−10] Thus, in one of our recent work we have thoroughly investigated the photophysical properties of C151 in different solvents and at different temperatures to understand the reason for the unusual behavior of the dye in nonpolar solvents.[19] It has been shown from picosecond laser flash photolysis and pulse radiolysis experiments that for C151 there

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is in fact no contribution from the ISC process in the deexcitation of the S_1 state of the dye. From a detailed solvent polarity and temperature-dependent studies it has been inferred that in nonpolar solvents a new activation-controlled nonradiative deexcitation channel is introduced for the S_1 state of C151, arising due to the flip-flop motion of the 7-NH_2 group. It has been understood that in nonpolar solvents the dye exists in a nonpolar structure whereas in all other solvents the dye exists in a polar intramolecular charge transfer (ICT) structure. In nonpolar solvents, due to the introduction of the new nonradiative deexcitation channel, the deactivation of the S_1 state of C151 becomes much faster and consequently the Φ_f and τ_f values reduce drastically in comparison to those in other solvents. Further, as C151 exists in nonpolar structures in nonpolar solvents compared to the ICT structure in other solvents, the Stokes' shifts between the absorption and fluorescence maxima in the former solvents are much lower compared to those in the latter solvents. In the present work, we have extended our work to investigate the photophysical properties of a higher analogue, namely the coumarin-C500 (C500, 7-NHEt-4-CF_3-1,2-benzopyrone; structure **II**, Chart 1) in different solvents and solvent mixtures to understand if the unusual behavior in coumarin dyes is specifically related to the 7-NH_2 group only. The chemical structures of C151 and C500 dyes are shown in Chart 1.

2. Materials and Methods

Laser grade C500 was obtained from both Lambda Physik and Exciton and used without further purification. Experiments were carried out with both these samples and similar results were obtained. All the solvents used were of spectroscopic grade, obtained from Spectrochem India, and used as received. The dielectric constants ϵ and refractive indices n of the pure solvents were taken from the literature.[20] For mixed solvents (MS), the dielectric constant ϵ_{MS} and refractive index n_{MS} values were estimated from the volume fractions f of the cosolvents using eqs 1 and 2, respectively,[21−24]

$$\epsilon_{MS} = f_A\epsilon_A + f_B\epsilon_B \tag{1}$$

$$n_{MS}^2 = f_A n_A^2 + f_B n_B^2 \tag{2}$$

where the subscripts "A" and "B" represent the respective cosolvents. The polarities of the solvents were estimated using the ϵ and n values of the solvents following the polarity function Δf defined by Lippert and Mataga.[24−27]

$$\Delta f = \frac{\epsilon - 1}{2\epsilon + 1} - \frac{n^2 - 1}{2n^2 + 1} \tag{3}$$

The solvent polarity parameter Δf thus estimated using the ϵ_{MS} and n_{MS} values of the mixed solvents as obtained using eqs 1 and 2 is reported to correlate nicely with a variety of physicochemical properties of many probe molecules in different solvents and solvent mixtures.[19,21−23,28−30]

Absorption spectra were recorded using Shimadzu model UV-160A spectrophotometer. Steady-state fluorescence measurements were carried out using a Hitachi model F-4010 spectrofluorimeter. All the fluorescence spectra were recorded after correction for the wavelength-dependent instrument responses. For all the measurements, the optical density of the solutions were kept quite low (O.D. ∼ 0.2) at the excitation wavelength. The corresponding dye concentrations in the solutions were about 1×10^{-5} mol dm^{-3}. The Φ_f values were measured using the comparative method.[31,32] Corrections were also made for the differences in the refractive indices of the solvents.[31,32] The Φ_f of C151 in HX was used as the reference ($\Phi_f^R = 0.19$)[18] for all the quantum yield measurements in other solvents.

A nanosecond time-resolved (TR) fluorescence spectrometer (model 199, Edinburgh Instrument, U.K.) was used for all the fluorescence lifetime measurements. The instrument works on the principle of time-correlated-single-photon-counting (TCSPC).[33,34] Details of the TR fluorescence spectrometer have been described elsewhere.[35,36] The observed fluorescence decays were analyzed (using reconvolution procedure) either as a single-exponential or a biexponential function, which was, in general, defined as

$$I(t) = \sum_i B_i \exp(-t/\tau_i) \tag{4}$$

where B_i and τ_i are the preexponential factor and the fluorescence lifetime respectively for the ith component. The single-exponential and biexponential nature of the fluorescence decays were judged by comparing the reduced chi-square χ^2 values and the distribution of the weighted residuals among the data channels. For the accepted fits the χ^2 values were close to unity and the weighted residuals were randomly distributed among the data channels.[33,34] The minimum fluorescence lifetime measurable with our TCSPC system is about 0.2 ns.

3. Results

3.1. Absorption and Fluorescence Spectral Characteristics of C500 in Different Solvents. Absorption and fluorescence spectra of C500 were recorded in different solvents and solvent mixtures. It is seen that both the absorption and fluorescence spectra are strongly dependent on the polarities of the solvents used. Table 1 lists the wavelengths in nm for the absorption and the fluorescence maxima (λ_{abs}^{max} and λ_{fl}^{max}, respectively) for C500 in different solvents. Table 1 also lists the solvent polarity function Δf as estimated using eq 3.[24−27]

Figure 1 plots the absorption and fluorescence maxima in cm^{-1} ($\bar{\nu}_{abs}$ and $\bar{\nu}_{fl}$, respectively) for C500 against Δf. It is seen that for almost all the solvents of lower to higher polarities the plots are linear within experimental error. Marginal deviations for alcoholic solvents (closed circles in Figure 1) are attributed to intermolecular hydrogen bonding interaction between the dye and the solvent molecules.[8−10,19] For nonpolar solvents, namely, hexane, cyclohexane, methylcyclohexane, 2-methylpentane, 3-methylpentane, and Decalin, it is, however, seen from Figure 1 that both $\bar{\nu}_{abs}$ and $\bar{\nu}_{fl}$ values are unusually blue shifted compare to those observed for rest of the solvents. Present observations clearly indicate that C500 behaves differently in nonpolar solvents than in the other solvents. To be noted that exactly similar observations have also been made in our earlier work on the photophysical properties of an another homologous dye, C151.[19]

Since no specific solute−solvent interaction is expected in nonpolar solvents, the unusually higher $\bar{\nu}_{abs}$ and $\bar{\nu}_{fl}$ values for C500 in these solvents appears to be an interesting observation. To substantiate these results further, we also correlated the Stokes' shifts ($\Delta\bar{\nu} = \bar{\nu}_{abs} - \bar{\nu}_{fl}$) in different solvents with Δf. It is generally assumed that the longer wavelength absorption and the fluorescence bands of a molecule arise due to the transitions between the same two ground and excited electronic states.[24−27,31,32] Thus, the $\Delta\bar{\nu}$ for a molecule is expected to systematically vary with the solvent polarities.[24−27,31,32] Lippert and Mataga derived the following simple linear relationship (eq

TABLE 1: Photophysical Characteristics of C-500 in Different Solvents and Solvent Mixtures

solvents[a]	Δf	λ_{abs}^{max}/nm	λ_{em}^{max}/nm	$\Delta\bar{\nu}$/cm^{-1}	Φ_f	τ_f/ns	$k_f/10^7 s^{-1}$	$k_{nr}/10^7\ s^{-1}$
HX	0	360	417	3739	0.76	3.3	23.03	7.27
2MP	0	360	415	3681	0.77	3.38	22.78	6.80
3MP	0	361	415	3604	0.75	3.39	22.12	7.37
CHX	0	364	417	3567	0.74	3.56	20.79	7.30
MCHX	0	364	417	3567	0.77	3.55	21.69	6.48
DL	0.002	365	420	3588	0.72	3.67	19.62	7.63
$M_{70}D_{30}$	0.008	372	457	5000	0.68	4.4	15.45	7.27
$M_{95}E_5$	0.025	376	467	5182	0.68	4.57	14.88	7.00
$M_{90}E_{10}$	0.046	375	463	5186	0.68	4.64	14.65	6.89
$M_{80}E_{20}$	0.081	373	463	5211	0.69	4.53	15.23	6.84
$M_{60}E_{40}$	0.128	377	469	5130	0.62	4.65	13.33	8.17
$M_{40}E_{60}$	0.160	380	472	5129	0.62	4.91	12.63	7.74
EA	0.201	382	478	5229	0.61	4.83	12.63	8.07
HxOH	0.243	392	490	5107	0.54	5.23	10.33	8.79
BuOH	0.263	391	493	5304	0.53	5.24	10.11	8.97
^{i}PrOH	0.277	392	490	5143	0.54	5.14	10.51	8.95
ACT	0.284	388	485	5221	0.53	5.08	10.43	9.25
EtOH	0.290	394	500	5405	0.47	5.04	9.33	10.51
ACN	0.305	385	485	5355	0.56	5.23	10.71	8.41
MeOH	0.309	392	500	5550	0.46	4.84	9.50	11.16

[a] Abbreviations for the solvents are HX (hexane), 2MP (2-methylpentane), 3MP (3-methylpentane), CHX (cyclohexane), MCHX (methylcyclohexane), DL (Decalin), EA (ethyl acetate), HxOH (hexanol), BuOH (butanol), ^{i}PrOH (2-propanol), ACT (acetone), EtOH (ethanol), ACN (acetonitrile), MeOH (methanol), $M_{70}D_{30}$ (70% 3MP and 30% 1,4-dioxane v/v), $M_{95}E_5$ (95% 3MP and 5% EA v/v), $M_{90}E_{10}$ (90% 3MP and 10% EA v/v), $M_{80}E_{20}$ (80% 3MP and 20% EA v/v), $M_{60}E_{40}$ (60% 3MP and 40% EA v/v), and $M_{40}E_{60}$ (40% 3MP and 60% EA v/v).

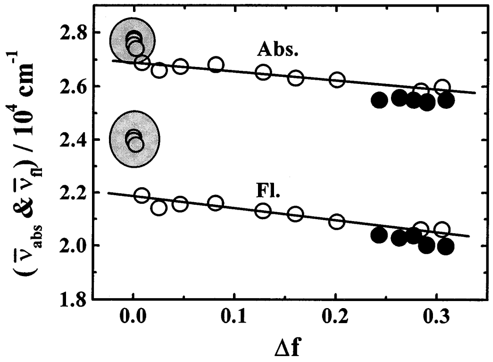


Figure 1. Plot for the absorption (Abs) and fluorescence (Fl) maxima of C500 ($\bar{\nu}_{abs}$ and $\bar{\nu}_{fl}$, respectively) against the solvent polarity function, Δf. As indicated by large shaded circles, the $\bar{\nu}_{abs}$ and $\bar{\nu}_{fl}$ in nonpolar solvents show unusual blue shifts in comparison to those in other solvents. The closed circles represent the data points for the alcoholic solvents.

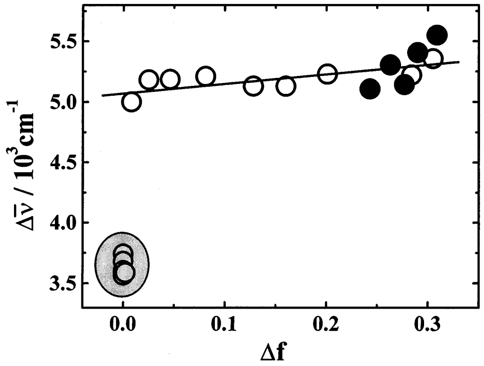
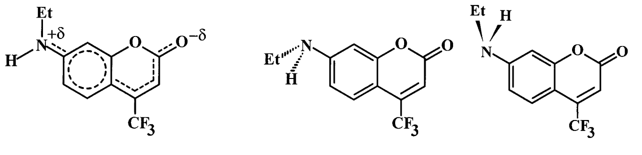


Figure 2. Plot of Stokes' shifts $\Delta\bar{\nu}$ for C500 against the solvent polarity function Δf. As indicated by large shaded circle, the $\Delta\bar{\nu}$ values in nonpolar solvents are unusually lower in comparison to those in rest of the solvents. The closed circles represent the data points for the alcoholic solvents.

CHART 2



(I) (II) (III)

Planar ICT structure (Polar in nature)

Nonplanar structures (Nonpolar in nature)

5) to correlate $\Delta\bar{\nu}$ with Δf.[26,27]

$$\Delta\bar{\nu} = \Delta\bar{\nu}_0 + \frac{2\Delta\mu^2}{hcr^3}\Delta f \tag{5}$$

where $\Delta\mu = \mu_e - \mu_g$ is the difference between the excited and ground-state dipole moments, μ_e and μ_g, respectively; h is the Plank's constant; c is the velocity of light; and r is the Onsager radius for the interaction sphere of the dipole in a solvent. Table 1 lists the $\Delta\bar{\nu}$ values for C500 in different solvents and solvents mixtures. Figure 2 shows the $\Delta\bar{\nu}$ vs Δf plot obtained for C500 in different solvents. It is seen from this figure that, though for almost all the solvents and solvent mixtures the $\Delta\bar{\nu}$ vs Δf plot is linear within experimental error, the $\Delta\bar{\nu}$ values for the nonpolar solvents are largely deviated toward lower energies. It is indicated from this observation that C500 behaves differently in nonpolar solvents than in other solvents.

From the slope of the linear $\Delta\bar{\nu}$ vs Δf plot obtained for different solvents excluding the nonpolar solvents, a μ_e value of 8.65 D was estimated for C500 using eq 5, considering the μ_g and r values to be 6.05 D[37−39] and 3.62 Å,[40,41] respectively. A μ_e value of 8.65 D indicates that the S_1 state of the dye is quite polar in nature. We attribute this state to be of intramolecular charge transfer (ICT) character, where a large extent of charge is transferred from the 7-NHEt group to the 1,2-benzopyrone moiety (cf. structure **I**, Chart 2).[8−10,19] In this ICT structure, the 7-NHEt group is supposed to be in plane with the 1,2-benzopyrone moiety. Considering the μ_g value of 6.05 D,[37−39] the S_0 state of the dye is also expected to have substantial ICT character. Due to these ICT characters of both the S_0 and S_1 states, the absorption and fluorescence maxima of C500 undergo substantial red shifts on increasing the solvent polarity in the lower to the higher polarity region, for which the $\Delta\bar{\nu}$ vs Δf plot shows the linear Lippert and Mataga correlation (cf. eq 5).[8−10,19]

In nonpolar solvents, as Figure 2 indicates, the Stokes' shifts are unusually less compared to those in other solvents. It is thus indicated that in these solvents both S_1 and S_0 states do not have the ICT characteristics as in the other solvents. Comparing the present results of C500 with those of C151 reported earlier,[19] the unusual behavior in nonpolar solvents is rationalized with the assumption that the dye exists in the nonpolar structures in these solvents in contrary to the polar ICT structure in all other solvents. It is supposed that in the nonpolar structures the 7-NHEt group of the dye remains in the pyramidal configuration and consequently out of the plane of the 1,2-benzopyrone moiety (cf. structures **II** and **III**, Chart 2). Thus, with this configuration of the 7-NHEt group, both S_0 and S_1 states of the dye will be of quite nonpolar in nature, and consequently, the $\bar{\nu}_{abs}$ and $\bar{\nu}_{fl}$ values are expected to be much higher in energy compared to those in the other solvents.[19] For the same reason the Stokes' shifts for C500 are also expected to be much less in nonpolar solvents in comparison to those in other solvents.[19]

It is interesting at this point to consider if the unusual spectral shifts for C500 in nonpolar solvents were simply due to aggregation of the dye molecules in these solvents rather than the configurational changes of the 7-NHEt group as discussed above. To verify for this possibility, the absorption spectra of C500 were recorded in nonpolar solvents with varying dye concentrations. It is seen that irrespective of the dye concentrations used, the shape of the absorption spectra remains unchanged. Further, the normalized absorption spectra for all the dye concentrations used ($\sim 4.8 \times 10^{-6} - 6.6 \times 10^{-5}$ mol dm^{-3}) were seen to be nicely overlapping to each other. It was also found that the O.D. vs [C500] plots follow nice linear correlation. It is thus indicated from these results that there is no aggregation for C500 in nonpolar solvents.

3.2. Fluorescence Quantum Yields of C500 in Different Solvents. Fluorescence quantum yields Φ_f of C500 were estimated at ambient temperature (26 ± 1 °C) in different solvents and solvent mixtures. The Φ_f values thus estimated are listed in Table 1. It is seen from Table 1 that for all the solvents the Φ_f values are reasonably high and decrease slowly with an increase in Δf. The most interesting point to be noted from Table 1 is that unlike C151, there is no unusual reduction in the Φ_f values for C500 in nonpolar solvents. This appears to be an unexpected observation based on the fact that the spectral shifts for C500 in different solvents corresponded very nicely with those observed for C151 dye and thus indicated similar type of configurational changes for both the dye molecules in nonpolar and other solvents. Though at this point it is difficult to justify the observed higher Φ_f values for C500 in nonpolar solvents in comparison to those of C151, we feel that the reason lies on the relative contributions of the radiative and different nonradiative processes of the excited states of the two dye molecules. We will discuss this point further in section 3.3 where the rates of different radiative and nonradiative processes for the excited dye molecules will be presented.

3.3. Fluorescence Decays of C500 in Different Solvents and Solvent Mixtures. Fluorescence decays of C500 in different solvent and solvent mixtures were measured at ambient temperature. All these measurements were carried out at the fluorescence maxima of the dye in the respective solvents. It is seen that, in all the solvents and solvent mixtures studied, the fluorescence decays of C500 always fit well with a single-exponential function. The fluorescence lifetimes τ_f for C500 obtained in different solvents are listed in Table 1.

In relation to the fluorescence decay characteristics, it is very interesting to compare the behavior of C500 in different solvents with that of C151 observed in our earlier work.[19] For C151, it was seen that the fluorescence decays in nonpolar solvents always fit well with a biexponential function, though in rest of the solvents the decays were single-exponential. The differences in the nature of the fluorescence decays of C151 in nonpolar and other solvents were rationalized based on the possible pyramidal (cf. structures such as **II** and **III** in Chart 2) and coplanar (cf. structure such as **I** in Chart 2) configurations of the 7-NH_2 group with respect to the 1,2-benzopyrone moiety.[19] In C151, since the 7-NH_2 group is a lighter substituent, the two possible nonpolar structures of the dye in nonpolar solvents (cf. structures equivalent to **II** and **III** in Chart 2) can interconvert to each other due to the flip-flop motion of the amino group via a large number of intermediate configurations. Thus the fluorescence decay of C151 in nonpolar solvents appeared to follow a non-single-exponential behavior, which could reasonably be fitted with a biexponential function. For C500 dye, since the 7-NHEt group is much heavier compared to the 7-NH_2 group in C151, the interconversion of the two nonpolar structures **II** and **III** (Chart 2) appears to be very slow. Thus, unlike C151, the fluorescence decays of C500 in nonpolar solvents effectively follow a single-exponential function. In all other solvents, since both C151 and C500 exist in a single ICT configuration (cf. structure **I**, Chart 2), the fluorescence decays obviously show the single-exponential behavior.

The τ_f values of C500 in different solvents are plotted in Figure 3 against Δf. It is seen from this figure that for almost all the solvents but excluding the nonpolar solvents, the τ_f values vary almost linearly with Δf. For the nonpolar solvents, however, the τ_f values of C500 are seen to be substantially lower in comparison to the linear correlation observed for rest of the solvents. It is thus indicated from these results that the nature of the fluorescent state of C500 in nonpolar solvents must have been different than that in the other solvents.

That the nature of the fluorescent state of C500 in nonpolar and other solvents are different can also be understood if we consider the radiative k_f and nonraditive k_{nr} decay rate constants of the dye excited states with solvent polarities. Such an analysis also helps us to understand the observed higher Φ_f values for C500 in nonpolar solvents (cf. section 3.2). From the definitions of Φ_f and τ_f, one can write the following expressions correlating the k_f and k_{nr} values of the excited dye molecules.

$$\Phi_f = \frac{k_f}{k_f + k_{nr}} \tag{6}$$

$$\tau_f = \frac{1}{k_f + k_{nr}} \tag{7}$$

$$k_{nr} = k_{IC} + k_{AM} \tag{8}$$

In eq 8, k_{IC} is the rate constant for the intrinsic IC process and k_{AM} is the effective nonradiative decay rate introduced by the flip-flop motion of the 7-NHEt group of the dye, arising due to its nonpolar structures in the nonpolar solvents.[19] In writing eq 8, the nonradiative decay due to the ISC process (k_{ISC}) has been considered to be negligible, as for most of the coumarin dyes the ISC process does not simply contribute in the deexcitation of the S_1 state of the molecules.[8−10] In fact, for the dye C151, using picosecond laser flash photolysis and pulse radiolysis studies, it has been clearly shown that there is no contribution from the ISC process in the deexcitation of the S_1 state of the dye.[19] Since C500 is structurally very similar to C151, the contribution of ISC process for the present molecule is also

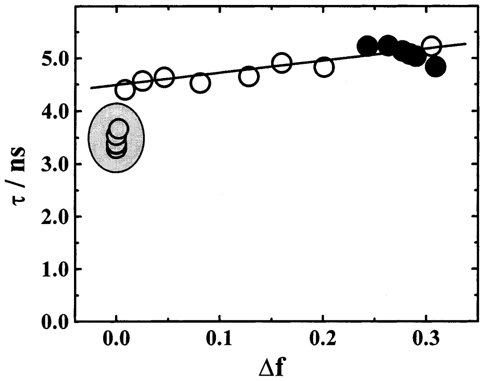


Figure 3. Variations in the fluorescence lifetimes τ_f of C500 with the solvent polarity function Δf. As indicated by large shaded circle, the τ_f values are substantially lower in nonpolar solvents in comparison to those in the other solvents. The closed circles represent the data points for the alcoholic solvents.

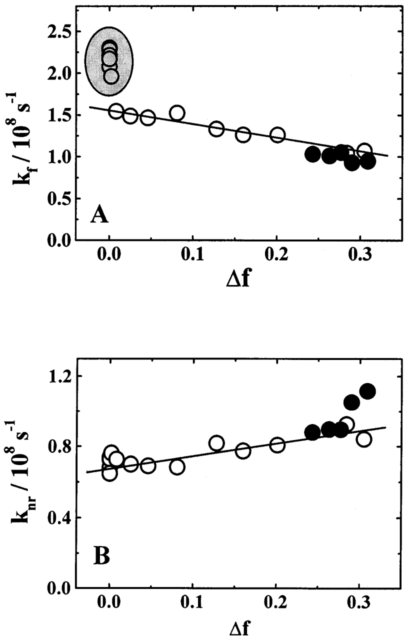


Figure 4. Plots of (A) radiative k_f and (B) nonradiative k_{nr} decay rate constants for C500 against the solvent polarity function Δf. As indicated by large shaded circle, the k_f values in nonpolar solvents are unusually higher in comparison to those in other solvents. The closed circles represent the data points for the alcoholic solvents.

expected to be negligible. Using eqs 6 and 7 the k_f and k_{nr} values for C500 were estimated in different solvents and solvent mixtures using the experimentally measured Φ_f and τ_f values. The k_f and k_{nr} values thus obtained are listed in Table 1. Figure 4A,B shows the plots of k_f and k_{nr} values against Δf. It is seen from Figure 4A that the k_f vs Δf plot is more or less linear for almost all the solvents excluding the nonpolar solvents. For the nonpolar solvents, however, the k_f values are unusually higher compared to those in rest of the solvents. These results thus clearly indicate that the fluorescent state of C500 in nonpolar solvents must have been of different characteristics than in the other solvents. Thus the k_f vs Δf correlation supports the results and inferences drawn from the polarity dependent Stokes' shift studies for C500 (cf. section 3.1).

It is seen from Figure 4B that the k_{nr} values only marginally increase with the solvent polarities and follow more or less a linear correlation with Δf. Somewhat higher k_{nr} values for some of the alcoholic solvents (closed circles in Figure 4B) are not unlikely as the intermolecular hydrogen bonding between C500 and the solvent molecules is expected to cause an enhancement in the nonradiative decay process.[42-45] Upon comparing the k_f and k_{nr} values of C500 in nonpolar solvents, it is seen that the former is about 3 times higher than the latter. Further the k_f values in nonpolar solvents are as such higher than those in the other solvents. Thus following eq 6 it is not surprising that the Φ_f values for C500 in nonpolar solvents are somewhat higher than the values observed in the other solvents (cf. Table 1).

The most interesting point to be noted from Figure 4B is that, unlike for C151,[19] for C500 there is no unusual enhancement in the k_{nr} values in nonpolar solvents. As was inferred from the solvent polarity and temperature-dependent studies for C151 that in nonpolar solvents an activation-controlled fast nonradiative process (k_{AM} in eq 8) operates for the dye excited state due to the flip-flop motion of the 7-NH_2 group.[19] From the present results it is clearly indicated that for C500 there is no such fast nonradiative process is involved for the S_1 state of the dye in nonpolar solvents. These results apparently indicate that as the 7-NHEt group in C500 is much heavier than the 7-NH_2 group in C151, the flip-flop motion of the former substituent is much slower than the latter and thus the nonradiative rate k_{AM} (cf. eq 8) introduced due to such motions cannot compete with the other deexcitation channels, such as k_f and k_{IC}. Because k_{AM} is negligible, the Φ_f values for C500 in nonpolar solvents appears to be unusually higher in comparison to those of C151 dye. It is, however, clearly indicated from the detailed analysis of the photophysical properties of C151 and C500 dyes that the absence of the fast nonradiative deexcitation process for C500 in nonpolar solvents is not a general disagreement between the properties of the C500 and C151 dyes, rather these are the outcome of the relative importance of the different deexcitation processes for the fluorescent states of the excited dye molecules. To be noted that for C500 in nonpolar solvents though the k_{AM} appears to be negligible, the k_{nr} values are having quite reasonable magnitudes in comparison to the k_f values. We infer that the observed k_{nr} for C500 in nonpolar solvents arises mostly due to the IC process (i.e., $k_{nr} \approx k_{IC}$; cf. eq 8).

3.4. Temperature Effect on Φ_f and τ_f Values of C500 in Different Solvents.

Temperature effect on the SS fluorescence properties of C500 was investigated in some selective nonpolar and other solvents. It has been observed that in none of the solvents studied, there is any appreciable temperature effect on the SS fluorescence intensities. These results thus indicate that the Φ_f values of C500 in different solvents are independent of temperature. It is interesting at this point to compare these results with those of C151 observed in our earlier work.[19] For C151, in all the solvents excluding the nonpolar solvents, the Φ_f was found to be temperature independent, a result very similar to the results observed for C500 in the present work. In nonpolar solvents, however, it was observed that the Φ_f values of C151 are strongly temperature dependent. From a critical analysis of the temperature dependent Φ_f and τ_f values of C151 in nonpolar solvents, it was inferred that a new activation-controlled fast nonradiative deexcitation channel operates for the excited dye molecules in nonpolar solvents, which arises due to the flip-flop motion of the 7-NH_2 group of the dye.[19] The fact that the Φ_f values of C500 is independent of temperature even in the nonpolar solvents clearly indicates that unlike C151 there is no such activation-controlled deexcitation channel for C500. The temperature independent Φ_f values for C500 in nonpolar solvents thus should be rationalized based on the assumption that the flip-flop motion of the 7-NHEt group in C500 is much slower than that of the 7-NH_2 group in C151,[19] and cannot introduce any new deexcitation channel for the S_1 state of the former molecule.

Temperature effects were also investigated on the fluorescence decays of C500 in some selective solvents. As expected from the temperature independent Φ_f values, the τ_f values of C500 are also found to be temperature independent in all the solvents studied. To be mentioned here that for C151, the τ_f values in nonpolar solvents were seen to be strongly temperature dependent, though the values were temperature independent in rest of the solvents.[19] The strongly temperature dependent τ_f values of C151 in nonpolar solvents clearly supported the participation of a new activation-controlled nonradiative deexcitation channel for the dye excited state.[19] That both Φ_f and τ_f values of C500 are temperature independent in nonpolar solvents clearly indicate that the flip-flop motion of the 7-NHEt group in C500 is much slower than that of the 7-NH_2 group in C151. Thus, unlike C151, there is no activation-controlled nonradiative deexcitation channel for the S_1 state of C500 in nonpolar solvents, though both the dyes are indicated to be existing in the relatively nonpolar structures in nonpolar solvents contrary to the polar ICT structures in rest of the solvents (cf. Chart 2). To be mentioned here that ours is the only report to show that the dye C500 also behaves differently in nonpolar solvents than in the other solvents. Unlike C151, there is no such report in the literature indicating the unusual photophysical behavior of C500 in nonpolar solvents. In the present work we could explain, based on the similar configurational changes for C151 and C500 dyes in nonpolar and other solvents (cf. Chart 2), that some of the photophysical properties of the two dyes show quite good similarities where as some of the properties show apparently very dissimilar behavior. Since the coumarin dyes are the well-known probes in investigating many physicochemical processes in condensed phase, present results will help in interpreting the data in many of these studies, whereby the fluorescence properties of the coumarin dyes are used as the detection tool.

4. Conclusions

The photophysical properties of coumarin-500 (C500) are seen to be quite unusual in nonpolar solvents. Thus in these solvents the Stokes' shifts $\Delta\bar{\nu}$ and fluorescence lifetimes τ_f of C500 are seen to be unusually lower in comparison to those in other solvents. Though the Φ_f values of C500 in nonpolar solvents are seen to be only marginally higher than those in the other solvents, the radiative decay rate constants k_f in nonpolar solvents are found to be abnormally higher. The abnormally lower τ_f values, unusually higher k_f values, and substantially lower $\Delta\bar{\nu}$ values for C500 in nonpolar solvents in comparison to those in the other solvents indicate that in the former solvents the excited dye molecules exist in a relatively nonpolar structure. Excluding the nonpolar solvents, in all other solvents of lower to higher polarities, the dye appears to exist in the polar ICT structure, where there is a large extent of charge transfer from the 7-NHEt group to the 1,2-benzopyrone moiety. The majority of the behavior of C500 in nonpolar solvents is quite similar to those observed earlier for a lower coumarin analogue, C151, supporting their existence in different structural forms in nonpolar and other solvents. Unlike C151, however, the C500 dye does not show any activation-controlled nonradiative deexcitation process in nonpolar solvents. It is inferred that with lighter 7-NH_2 group, the excited dye C151 can undergo fast nonradiative deexcitation in nonpolar solvents due to the fast flip-flop motion of the 7-NH_2 group. In C500, though a similar flip-flop motion is also possible for the 7-NHEt group, this motion is supposed to be very slow, as the 7-NHEt group is much heavier than the NH_2 group in C151. This slower flip-flop motion of the 7-NHEt group in C500 cannot thus introduce any deexcitation channel k_{AM} to compete with the fluorescence decay rate k_f and the intrinsic IC rate k_{IC} for the S_1 state of the dye. Thus the dye C500 shows the overall deexcitation behavior in the S_1 state apparently different than that observed for C151 in nonpolar solvents.

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