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Solvent Exchange in Excited-State Relaxation in Mixed Solvents

A. S. R. Koti[1] and N. Periasamy[1,2]

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The fluorescence of styrylthiazoloquinoxaline (STQ) in the solvent mixture methanol and dichloromethane (DCM) and 2-octanol have many common characteristics: biexponential fluorescence decay, wavelength-dependent amplitudes, a negative amplitude for the short-lifetime component at long emission wavelengths, and a time-dependent red shift of the emission spectrum. In octanol, the fluorescence lifetime decreases with increasing temperature, whereas the lifetime increases with temperature in the methanol/DCM mixture. The fluorescence characteristics in 2-octanol ($\eta = 7.29$ cP) are readily explained by the conventional model of excited-state relaxation kinetics by solvent reorientation. This model is not applicable for low-viscosity ($\eta = 0.455$ cP) solvent mixture. A model of excited-state relaxation kinetics involving solvent exchange in the excited state is proposed for the solvent mixture. The model assumes that the solvent compositions around the solute are different in the ground and excited states and the solvent composition is temperature dependent.

KEY WORDS: Fluorescence spectroscopy; lifetimes; methanol; dichloromethane.

INTRODUCTION

Solvent relaxation in the excited state of fluorescent organic molecules in polar liquids has been extensively studied and reviewed [1–4]. The origin of solvent relaxation is due to the difference in the dipole moments of the ground and excited states of the dye molecule. The equilibrium orientation of solvent molecules around the solute is different in the two states. Solvent relaxation in the excited state is manifested in steady-state and time-resolved fluorescence experiments [1,2,4] as (i) a solvent polarity-dependent Stokes shift consistent with the Lippert–Mataga equation [4], (ii) a time-dependent red shift of the fluorescence spectrum, and (iii) multiexponential fluorescence decay, especially in viscous solvents. The red edge effect in fluorescence excitation and emission spectra [5,6] and the dramatic spectral and lifetime changes in single-molecule experiments [7,8] are also due to structures and structural changes in the solvent arrangement around the solute.

The photophysics of fluorescent molecules in solvent mixtures has not been studied as extensively as in pure solvents and the structure and structural changes in the solvent environment around the solute in mixed solvents have not been fully investigated. The solvent environment of the fluorescent molecules in biological complex systems is more akin to a mixed solvent (for example, water and hydrocarbon-like medium near the interface of a bilayer membrane) than a pure solvent. It is therefore important to investigate the photophysical characteristics that are unique to the solvent mixtures. We have identified for the first time the unique feature that the fluorescence lifetime of a dye increases with increasing temperature in a solvent mixture of methanol and dichloromethane (DCM). The results are interpreted

[1] Department of Chemical Sciences, Tata Institute of Fundamental Research, Homi Bhabha Road, Colaba, Mumbai 400 005, India.
[2] To whom correspondence should be addressed. Fax: 091 22 215 2110. e-mail: peri@tifr.res.in

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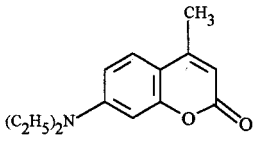
by a model that postulates different solvent composition around the solute in the ground and excited states.

EXPERIMENTAL

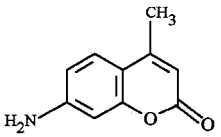
Materials. The laser dyes coumarin 1, coumarin 120, RH421, and Nile red were obtained from Exciton Inc. (USA). The structures of the dyes are shown in Fig. 1. RH 421 was obtained from Molecular Probes Inc. (USA). Styrylthiazoloquinoxaline (STQ) was synthesized and purified as reported in Ref. 9. All the solvents used in this study were analar or spectroscopy grade.

Methods. Steady-state fluorescence emission spectra were obtained on a Spex Fluorolog 1681 T spectrofluorophotometer. Time-resolved fluorescence decay measurements were made using a high-repetition rate picosecond laser (frequency-doubled, mode-locked Ti–sapphire laser or mode-locked Nd–Yag pumped rhodamine 6G laser) coupled to a time-correlated single-photon counting spectrometer described elsewhere [10], currently using a microchannel plate photomultiplier (Hamamatsu 2809) and personal computer for data acquisition and analysis. The dye sample was excited in the absorption band at 600, 380, or 445 nm by vertically polarized laser pulses and the emission at the peak or the total emission (integrated over the spectrum) at a particular wavelength ($\Delta\lambda = 2.5$ nm) was collected with an emission polarizer oriented at the magic angle of 54.7° with respect to the excitation polarization. The full width at half-maximum of the instrument response function was ~160 ps. The typical count rate for each fluorescence decay measurement was 4000–5000 per s (~0.5% of the excitation rate) and the typical peak count was 10,000 at a time resolution of 37.27 ps/channel.

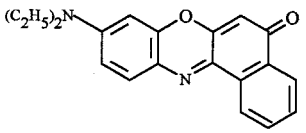
Semiempirical quantum chemical calculations were performed using MOPAC version 6.0 for an AM1 Hamiltonian using a pentium PC. The program was tested to reproduce the reported results (within ±2% error) of heat of formation for the hydrogen bonding/van der Waals complexes of NH_3/H_2O, H_2O/CH_3OH, CH_3OH/H_2O, and $HCOOH/NH_3$ [11].



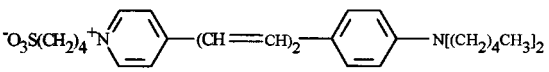
Coumarin 1



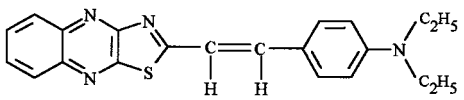
Coumarin 120



Nilered



RH421



STQ

Fig. 1. Structures of the dye molecules.

RESULTS

The fluorescence spectra and decays of a few dyes (coumarin 1, coumarin 120, Nile red, RH 421, and STQ) were studied in methanol and DCM. The structures of the dyes are shown in Fig. 1. Table I gives the spectral maxima and fluorescence lifetimes in the two solvents. The fluorescence decay is single exponential for all the dyes in the two solvents. The fluorescence lifetimes of coumarin 1, Nile red, RH 421, and STQ are shorter in

Table I. Emission Maxima and Lifetimes for Different Dyes

Dye	Solvent	λ_{em} (max)	τ_1 (ns)	χ^2
Coumarin 1	Methanol	455	2.02	1.02
	DCM	422.5	3.34	0.97
Coumarin 120	Methanol	429	3.95	1.00
	DCM	399.5	3.05	1.06
Nile red	Methanol	635	2.82	1.07
	DCM	601	4.55	1.00
STQ	Methanol	632.5	0.05	1.32
	DCM	593	1.62	1.04
RH-421	Methanol	700	0.63	1.13
	DCM	687	2.22	1.16

methanol than in DCM. On the other hand, the fluorescence lifetime of coumarin 120 showed the opposite trend, with a longer lifetime in methanol. It is to be noted that the lifetime of STQ is very short (0.05 ns) in methanol and very long (1.62 ns) in DCM, indicating drastic differences in the photophysics of the dye in the two solvents. Hence, this dye was chosen for the fluorescence photophysical study in the mixed solvent methanol and DCM.

Multiexponential fluorescence decay for a dipolar fluorophore ($\Delta\mu \neq 0$) is commonly observed in pure polar solvents, especially viscous liquids. The fluorescence photophysics of one of the dyes (STQ) was studied in viscous octanol. The fluorescence decay at different wavelengths in the emission spectrum was also double exponential and the lifetimes were reasonably constant over the entire spectrum: $\tau_{short} = 0.41 \pm 0.15$ and $\tau_{long} = 1.94 \pm 0.08$ ns. The variation in the amplitudes (α_s and α_1) with wavelength for the two lifetimes is shown in Fig. 2A. The amplitude for the short lifetime, α_s, was positive for $\lambda < 630$ nm and negative for $\lambda > 630$ nm. The wavelength-dependent amplitudes and steady-state emission spectrum are used to construct the spectra of the two species (see Discussion for equations) associated with the short and long lifetimes shown in Fig. 2B.

The fluorescence decay of STQ in the mixed solvent methanol and DCM (1:5.7, mol/mol, or 1:9, v/v) was investigated at different emission wavelengths. The fluorescence decays at all emission wavelengths could be fitted to two exponentials for a short-lifetime component of $\tau_{short} = 0.15 \pm 0.06$ ns and a long-lifetime component of $\tau_{long} = 0.99 \pm 0.05$ ns. The variation of amplitudes (α_s and α_1) for the short and long lifetimes are shown in Fig. 3A. As in the case of octanol, the amplitude for the short lifetime was negative for $\lambda > 630$ nm. Figure 3B also shows the spectra associated with the short and long lifetimes which were calculated using the amplitudes and steady-state spectrum.

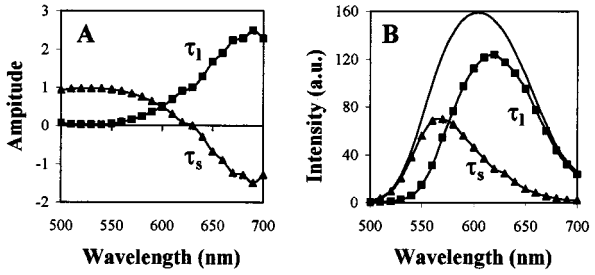


Fig. 2. (A) Wavelength dependence of the amplitudes of τ_s and τ_1 for the two-exponential fit of the fluorescence decays of STQ in 2-octanol. (B) The Spectra of the two species associated with the lifetimes τ_s and τ_1. The solid line is the steady-state fluorescence spectrum.

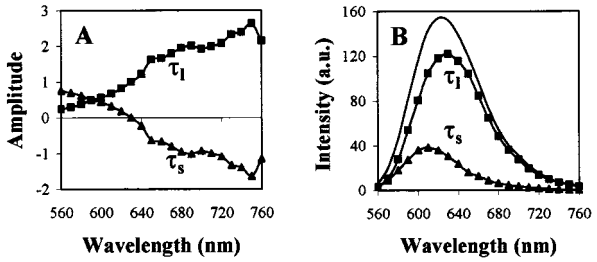


Fig. 3. (A) Wavelength dependence of the amplitudes of τ_s and τ_1 for the two-exponential fit of the fluorescence decays of STQ in the solvent mixture of methanol and DCM (1: 5.7, mol/mol, or 1:9, v/v). (B) The Spectra of the two species associated with the lifetimes τ_s and τ_1. The solid line is the steady-state fluorescence spectrum.

The temperature dependence of the fluorescence decay of STQ was investigated in methanol, DCM, octanol, and the mixed solvent methanol and DCM (1:5.7, mol/mol). The fluorescence lifetime decreased with increasing temperature in methanol, DCM, and octanol, which is the normal trend for fluorescent molecules. The lifetime decreased from 2.101 ns at 5°C to 1.124 ns at 45°C for STQ in DCM. Contrary to the general observation of a decreasing lifetime with temperature, the fluorescence decay of STQ in the methanol/DCM mixture showed the opposite trend. That is, the fluorescence lifetime increased with temperature. Figure 4 shows the fluorescence decay of STQ at 5 and 45°C. The fluorescence decay parameters for STQ in the solvent mixture at different temperatures are given in Table II. It is observed that the long lifetime increased with temperature.

The unusual observation of an increasing lifetime with increasing temperature was noted only in the solvent

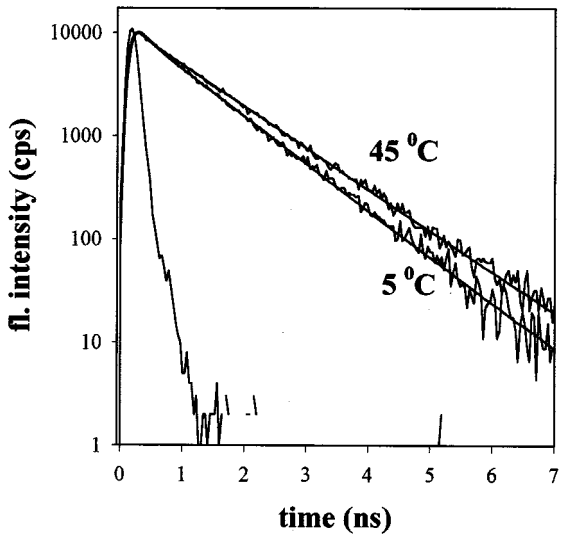


Fig. 4. Fluorescence decays of STQ in the methanol–DCM mixture (1:5.7, mol/mol, or 1:9, v/v) at 5 and 45°C.

Table II. Temperature Dependence of Total Fluorescence Decay Parameters of STQ in Methanol/DCM

T(°C)	λ_{ex} (max) (nm)	λ_{em} (max) (nm)	τ_{short} (ns)	λ_{long} (ns)	α_s	α_l	χ^2
5	502.5	622	0.149	0.948	0.333	0.667	1.23
15	502	619	0.133	0.979	0.360	0.640	1.02
25	498.5	617	0.100	1.001	0.354	0.646	1.09
35	495	614	0.088	1.049	0.391	0.609	1.01
45	494	610.5	0.090	1.074	0.378	0.622	1.00

Table III. Heats of Formation (kcal/mol) for a 1:1 Complex of Dye and Solvent

Dye	Geometry	CH_2Cl_2	$CHCl_3$	CCl_4
TEA	N . . . H	−2.797	−2.223	
	RH . . . Cl	−0.149	−0.161	−0.115
STQ	N . . . H	−0.170	−0.014	
	RH . . . Cl	−0.492	−0.294	−0.027
Coumarin 1	N . . . H	−0.287	−0.450	
	RH . . . Cl	−0.539	−0.094	−0.068
Coumarin 120	N . . . H	−0.727	−0.779	
	RH . . . Cl	−1.078	−0.009	−0.087

mixture. The substantial differences in the lifetimes in methanol and DCM indicate that the interactions of the dye with the two solvents are qualitatively different. The fluorescence lifetime of the STQ dye in the following solvents, which are in the range of viscosity 0.4–1.0 cP, dielectric constant 3–40, and refractive index 1.33–1.46, showed considerable variations: methanol (0.050 ns), carbon tetrachlroride (0.15 ns), toluene (0.274 ns), DMSO (0.420 ns), chloroform (1.309 ns), and DCM (1.621 ns). The fluorescence lifetimes in chloroform and DCM are substantially longer than in other solvents. Interestingly, among the chloro solvents the lifetime in carbon tetrachloride was not long. Chloroform and DCM have both Cl and H atoms which appear to be important in increasing the fluorescence lifetime of STQ, presumably by specific interaction with the dye molecule. Examination of the structure of the dyes suggested that DCM and chloroform could be forming a complex with the dye by interaction with the $-N(C_2H_5)_2$ group of the dye molecule by an interaction similar to that of triethylamine and chloroform in forming a 1:1 complex [12–14]. Semiempirical quantum chemical calculations were therefore carried out to determine the stable geometry for the dye–solvent complex and heat of formation.

Triethylamine (TEA) was used as the model compound for the calculations because it is reported to form a 1:1 complex with chloroform [12–14]. The optimized geometry for the 1:1 complex of TEA and DCM or TEA and chloroform revealed two stable structures for the complex. In one structure, the H atom of DCM was directed toward the nonbonding orbital of the N atom of TEA. In the second structure, the Cl atom of DCM was closer to the secondary H atoms of TEA. The heat of formation for the first structure (N . . . H interaction) was more negative, suggesting that it is a more stable complex than the second one (H . . . Cl interaction) in TEA. The heats of formation for the 1:1 complexes of TEA with DCM, chloroform, and carbon tetrachloride are given in Table III. The values given are the averages of 8–10 trials with different initial values which led to successful minimization of the energy of the complex. The heats of formation for the 1:1 dye–solvent complexes were calculated for the same geometries indicated by the TEA–solvent complex and the results are given in Table III.

DISCUSSIONS

Photophysics in Pure Solvents. The standard model of the excited-state kinetics of an ideal fluorescent molecule in a noninteracting solvent assumes emission from rapidly (subpicosecond time scale) thermalized energy levels of the excited state and single-exponential fluorescence decay. The fluorescence lifetime is independent of the emission wavelength. Interaction of the solvent with the dye molecule is indicated primarily by the spectral shift (relative to the inert solvent, typically *n*-hexane or gas phase) and secondarily by the time-dependent emission spectra indicating excited-state kinetics. The excited-state kinetics may or may not be a single-exponential decay, depending on the details of the solute and solvent parameters and the nature of the excited-state product species. Universal, nonspecific solvation of a solute is due to the dipolar interaction between the dipole moment of the solute and that of the solvent. In this case, the spectral shift between the absorption and the emission maxima is related to the difference in the dipole moments of the ground and excited states and the polarity parameter of the solvent, which is a function of the dielectric constant and refractive index (Lippert–Mataga equation) [15]. The excited-state kinetics is dominated by the viscosity-dependent solvent reorientation, leading to a solvent-relaxed excited-state population. The characteristics of strong solvation effects are nonexponential fluorescence decay and time-dependent fluorescence spectra. These characteristics are easily observed in viscous solvents (such as octanol) because of slower solvent reorientation. In low-viscosity solvents (methanol and DCM)

the solvent reorientation is very rapid (<5 ps) and the observable fluorescence decay in TCSPC experiments may be from the solvent-relaxed species only.

The fluorescence lifetime of a solvent-relaxed species is determined by the radiative (k_r) and nonradiative (k_{nr}) rates. The radiative rate varies as the square of the refractive index (Strickler–Berg equation [16]), and the nonradiative rate is collision dependent and higher in low-viscosity solvents [16]. The standard model described above suggests that the fluorescence lifetime of the dye in organic solvents of similar viscosity is expected to vary only marginally. Comparison of the fluorescence lifetimes of STQ in methanol (η = 0.59 cP, τ_f = 0.05 ns), carbon tetrachloride (η = 0.97 cP, τ_f = 0.15 ns), chloroform (η = 0.58 cP, τ = 1.309 ns), DCM (η = 0.45 cP, τ_f = 1.62 ns), and toluene (η = 0.59 cP, τ_f = 0.274 ns) indicates a wide quantitative variation. The unusually long lifetimes in chloroform and DCM and the unusually short lifetime in methanol do not seem to follow the trend of either viscosity or the dielectric constant or refractive index of the solvents: methanol (ϵ = 32.6, n = 1.328), carbontertachloride (ϵ = 2.24, n = 1.460), chloroform (ϵ = 4.81, n = 1.446), DCM (ϵ = 8.93, n = 1.424), and toluene (ϵ = 2.38, n = 1.497). One concludes that there is a specific interaction between the dye and the solvent and the standard model of photophysics does not apply for this dye.

The structure of STQ consists of three important components: an *N*,*N*-diethyl group, a styryl group, and a thiazoloquinoxaline group. The fluorescence of a few dye molecules which had a side chain of an *N*,*N*-diethyl group (coumarin 1, RH 421, and Nile red) was investigated in methanol and DCM. The fluorescence lifetimes of coumarin 1, RH 421, and Nile red were found to be longer in DCM than in methanol. However, the difference in the two values was not as great as that observed in STQ. On the other hand, coumarin 120, in which the *N*,*N*-diethyl group is replaced by an amino group, showed, an opposite trend. That is, the fluorescence lifetime of the dye is shorter in DCM than in methanol. These results indicate that the *N*,*N*-diethyl group is likely to be the perturbation site for the DCM/methanol interaction.

STQ dye showed maximum variation of the fluorescence lifetime in methanol and DCM. The nature of the solvent arrangement around the dye appears to be qualitatively different for methanol and DCM so that the radiative and/or nonradiative rate of the dye–solvent complex are perturbed in opposite ways. For this reason, STQ dye was chosen to study the effect of solvent composition on the excited-state dynamics in the methanol–DCM mixture. It will be useful now to discuss the solvent relaxation process for STQ dye in a pure solvent for comparison with the solvent relaxation process in a solvent mixture, discussed subsequently.

Solvent Relaxation in the Excited State in Pure Liquids. According to the standard model, solvent molecules around the ground-state dye molecule retain the same orientational arrangement during the electronic transition upon excitation. If the dipole moment of the excited state is different, then solvent molecules reorient to a new equilibrium orientational distribution. The mechanism and time course of solvent reorientation and the spectroscopic shifts have been studied and discussed extensively [1,4]. Figure 5 shows a model of solvent relaxation in the excited state. s and s′ represent the arrangements (orientations) of solvent molecules around the dye molecule in the ground state and "relaxed" excited state, respectively. M_s is the solvated ground state, M_s^* is the excited state immediately after excitation, $M_{s'}^*$ is the excited state after solvent relaxation, and $M_{s'}$, is the ground state immediately after emission of the photon. It is assumed that the population of the ground-state dye molecule with the solvent arrangement s′ is negligible. $1/\tau_1$ and $1/\tau_2$ are the rate constants (sum of radiative and nonradiative rates) for the two excited states, and k is the rate constant of solvent relaxation. By virtue of the energy relation between the two excited states, the emission spectrum of $M_{s'}^*$, will be red-shifted with respect to that of M_s^*. A two-state model as shown in Fig.5 predicts that the fluorescence decay at any emission wavelength is proportional to the sum of the population decays of M_s^* and $M_{s'}^*$ [17].

$$I_\lambda(t) = a_\lambda [M_s^*]_t + b_\lambda [M_{s'}^*]_t \quad (1)$$

where a_λ and b_λ are the intensity contributions of the two species at λ, and,

$$[M_s^*]_t = C_0 \exp\{-t(k + (1/\tau_1))\} \quad (2)$$

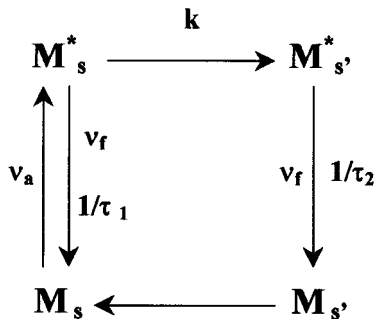


Fig. 5. Solvent relaxation model for the excited state of the dye molecule in a pure solvent. s and s′ represent two arrangements of solvent molecules, and k is the rate constant of solvent rearrangement in the excited state.

$$[M_s^*]_t = C_0[k/(k + (1/\tau_1) - (1/\tau_2))]\,[\exp(-t/\tau_2) - \exp\{-t(k + (1/\tau_1))\}] \quad (3)$$

C_0 is the concentration of M_s^* at $t = 0$. Replacing $(k + 1/\tau_1) = 1/\tau_{s(hort)}$ and $\tau_2 = \tau_{l(ong)}$, one gets

$$I_\lambda(t) = x_\lambda \exp(-t/\tau_s) + y_\lambda\,[\exp(-t/\tau_1) - \exp(-t/\tau_s)] \quad (4)$$

or

$$I_\lambda(t) = \alpha_\lambda \exp(-t/\tau_s) + \beta_\lambda \exp(-t/\tau_1) \quad (5)$$

where $x_\lambda = \alpha_\lambda + \beta_\lambda$, and $y_\lambda = \beta_\lambda$. It is recognized that α_λ can be negative at long emission wavelengths when $y_\lambda > x_\lambda$. Experimentally, negative values for α_λ have been observed for emission wavelengths higher than 630 nm for STQ in 2-octanol (Fig. 2). According to Eq. (4) the contribution to the steady-state intensity at λ will be at the ratio of $x_\lambda\tau_s$:$y_\lambda(\tau_l - \tau_s)$ for the two species M_s^* (associated with τ_s) and $M_s^{*'}$, (associated with τ_l), respectively. The individual spectrum of the two species M_s^* and $M_s^{*'}$, and the steady-state spectrum are shown in Fig. 2B. The spectrum of $M_s^{*'}$ is red-shifted to that of M_s^* as expected.

The important parameters of the solvent relaxation model (Fig. 5) are k, τ_1, and τ_2. These are related to the experimentally measured values of lifetimes: $\tau_2 = \tau_{l(ong)}$, whereas $(\tau_l^{-1} + k) = 1/\tau_{s(hort)}$. τ_1 and τ_2 are the molecular properties (radiative and nonradiative) of the excited dye molecule with two solvent arrangements and it is reasonable to assume that $\tau_1 \sim \tau_2$. One may therefore calculate the value of k for the solvent rearrangement in the excited state. Using the experimental values for τ_s (0.406 ns) and τ_l (1.944 ns) at 25°C, k is calculated to be 1.95×10^9 s^{-1}. The solvent reorientation is viscosity dependent and hence faster at higher temperatures. It was observed that τ_s and τ_l decreased and k increased with increasing temperature (results not shown).

Solvent Exchange in the Excited State in the Solvent Mixture. The experimental results for the fluorescence photophysics of STQ in the solvent mixture methanol and DCM (1:5.7 mol/mol) have all the characteristics of the solvent relaxation model discussed above. The fluorescence decays were wavelength dependent but the lifetimes remained constant: $\tau_s = 0.15 \pm 0.05$ ns and $\tau_l = 1.00 \pm 0.05$ ns. The amplitudes of the two lifetimes were positive for $560 < \lambda_{em} < 630$ nm but the amplitude for the short-lifetime component became negative for $\lambda_{em} > 630$ nm (Fig. 4). At the longest emission wavelength of 760 nm the amplitudes were at the ratio of −0.534:1. An amplitude ratio of −1:1 would have meant that the emission at this wavelength is due entirely to the product species of excited-state kinetics.

The available evidence indicates that the excited-state kinetics for STQ in the methanol/DCM mixture is a two-state model similar in all respects to the solvent relaxation model of STQ in octanol discussed before. The emission spectra for the two species were computed using the steady-state fluorescence spectrum and the fractional intensity for the two species, $x_\lambda\tau_s$:$y_\lambda(\tau_l - \tau_s)$, from Eq. (4). The spectrum for the species associated with a long lifetime is red-shifted (Fig. 3) as in the case of STQ in octanol.

The fluorescence results of STQ in the solvent mixture were qualitatively and quantitatively similar to the model of two-state solvent relaxation by reorientation of solvent molecules. However, solvent reorientation is expected to be very fast in low-viscosity solvents such as methanol, DCM, and the mixture. The viscosities were 0.59, 0.45, and 0.455 cP for methanol, DCM, and the mixture, respectively. The rotational correlation time of a molecule depends on the molecular volume and viscosity ($\tau_{rot} = \eta V/k_B T$, where k_B is the Boltzmann constant, T the temperature, η the viscosity, and V the molecular volume) [18]. The reorientational relaxation rate (equated to the rotational correlation time) of either methanol or DCM is calculated to be less than 5 ps, which is too fast to be observed in our measurements of fluorescence decays. Therefore, the excited-state kinetics that is unambiguously evident (Fig. 3) for STQ in the methanol/DCM mixture cannot be attributed to reorientational solvent relaxation of methanol or DCM.

We propose a new model of solvent relaxation in the excited state by a solvent exchange mechanism in solvent mixtures. Figure 6 shows a two-state model of solvent exchange which is similar in all aspects to the reorientational solvent relaxation model (Fig. 5). M_{mn} is

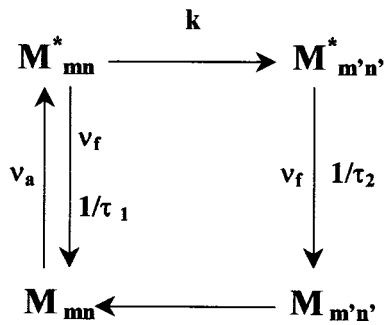


Fig. 6. Solvent exchange model for the excited state of the dye molecule in a solvent mixture. *mn* and *m′n′* represent the compositions of the two solvent molecules around the dye molecule in the ground state and "relaxed" excited state. *k* is the rate constant of solvent exchange in the excited state.

the solvated dye molecule in the ground state; *m* and *n* are the average numbers of solvent molecules of the two types which solvate the dye molecule. Upon excitation, M^*_{mn} is formed that retains the same composition (*mn*) as the ground state. Reorientational relaxation, if any, of the solvent molecules could occur (<5 ps) without changing the composition *mn*. The solvent-relaxed excited state with a different composition $m'n'$ is denoted by $M^*_{m'n'}$ in Fig. 6. *k* is the rate constant for solvent exchange between the dye–solvent complex and the bulk solvent. The anomalous temperature dependence of the lifetime in the solvent mixture and the hypsochromic spectral shift with temperature provide convincing evidence that the solvent composition around the dye is a sensitive property.

It was observed that the value of the short lifetime decreases and that of the long lifetime increases with increasing temperature (Table II). The increase in the long lifetime is self-evident from the raw fluorescence decays at 5 and 45°C (Fig. 4). An increase in fluorescence lifetime with increasing temperature is an unusual phenomenon. This can be explained within the standard photophysical model only by a decrease in radiative or nonradiative rate with temperature. It was observed that in pure DCM, the fluorescence lifetime of STQ decreased with increasing temperature, 2.101 ns at 5°C and 1.124 ns at 45°C, which is attributable to an increase in nonradiative rate with temperature. Hence, it is not likely that the radiative and nonradiative rates decrease with temperature in the DCM/methanol mixture.

To explain the increase in lifetime with temperature, we propose that the structure of the dye–solvent complex changes with temperature. That is, the solvent composition around the solute changes with temperature. The change in solvent composition is clearly indicated by the hypsochromic shift of the excitation and emission peak with temperature (Table II). The fluorescence emission peak occurs at 593 nm in DCM and at 632.5 nm in methanol (Table I). The hypsochromic spectral shift with temperature indicates that the solvent composition is methanol-rich at low temperatures, even though the bulk solvent is DCM-rich (1:5.7 mol/mol). An increasing temperature increases the DCM fraction in the solvation sphere, bringing the composition closer to the bulk composition. Since the fluorescence lifetime is longer in DCM, the lifetime is expected to increase with temperature, which is observed experimentally.

The composition *mn* or $m'n'$ associated with M^*_{mn} or $M^*_{m'n'}$ need not be the same as that of the composition in the bulk of the solvent mixture. *mn* and $m'n'$ are determined solely by the relative solvation energies of the two solvents. A solvent that is strongly interacting with the dye molecule is expected to associate with the dye molecule even if the bulk composition is statistically unfavorable. In other words, the dye molecule would act as a nucleating agent to create a solvent environment and composition that is different from the bulk composition. In the case of STQ it was observed that the fluorescence lifetime was 50 ps in methanol and 1.62 ns in DCM. The average lifetimes for STQ in solvent mixtures of methanol/DCM (mol/mol) were 0.16 ns (1:0.16), 0.213 (1:0.42), 0.474 (1:1.48), and 0.68 (1:5.7). These results indicate that methanol has a stronger association with STQ even when its mole fraction in the bulk is considerably less.

Dye–Solvent Complex Structure. The results presented in this paper show that specific solvent effects are observed in the chlorosolvents, DCM and chloroform, but not in carbon tetrachloride. The effect of DCM (and chloroform) on the dye molecule increased the fluorescence lifetime of some dyes (Table I), most prominently in STQ, presumably by formation of a dye–solvent complex. The possible structure of such a complex was examined. The dyes (Fig. 1 and Table I) which showed increased lifetimes in DCM have a common structural component, namely, an *N*,*N*-diethyl group. It is reported that triethylamine (TEA) forms a stable complex with chloroform [12–14]. Quantum chemical calculations on TEA and DCM (or chloroform) confirmed that a stable 1:1 complex is formed and the heat of formation of the TEA–solvent complex was −2.2 to −2.8 kcal/mol or DCM and chloroform. In contrast, the heat of formation for the complex with carbon tetrachloride was less. The favorable geometry for the 1:1 complex are those in which either the hydrogen atom (having a positive electron density of +0.129) of DCM was directed toward the N atom (having a negative electron density of −0.276) of TEA of the Cl atom of DCM (having a negative electron density of −0.077) toward the H atom (having a positive electron density of +0.047) of TEA. The stabilization energy was higher for the H . . . N complex than the Cl . . . H complex (Table III). The stabilization energy for CCl_4, which cannot form an N . . . H complex, was considerably low. One may therefore expect stable complex formation with *N*,*N*-diethyl groups in other molecules such as STQ.

Calculations for the dye–solvent complexes indicated reasonable stabilization energies for the complexes of similar geometries (as in TEA) involving the *N*,*N*-diethyl group of the dye and DCM or chloroform. The unusually long fluorescence lifetime for STQ in chloroform or DCM may be explained as follows. Stable complex structures between the *N*,*N*-diethyl group and DCM or chloroform would decrease the mobility (side chain rotation) of the *N*,*N*-diethyl group. A decrease in intramo-

lecular mobility would decrease the rate of internal conversion or intersystem crossing in the excited state. Thus, a decrease in the nonradiative rate increases the fluorescence lifetime in these two solvents.

CONCLUSIONS

The results presented in this paper indicate that some dyes, particularly STQ, containing *N*,*N*-diethyl amino groups, form solvent complexes in DCM and methanol that affect the radiative and nonradiative rates more significantly than normally predicted by viscosity and solvent polarity. The fluorescence dynamics of STQ in the methanol–DCM mixture had all the characteristic features attributable to excited-state kinetics and an anomalous feature of increasing fluorescence lifetime with temperature. The results are interpreted using a new model of solvent dynamics involving a change in solvent composition around the dye in the excited state.

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