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SOLVENT EFFECT ON ABSOLUTE FLUORESCENCE QUANTUM YIELD OF RHODAMINE 6G DETERMINED USING TRANSIENT THERMAL LENS TECHNIQUE

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Dual beam thermal lens technique is successfully employed for the determination of absolute fluorescence quantum yield of rhodamine 6G laser dye in different solvents. A 532 nm radiation from a Q-switched Nd:YAG laser was used for the excitation purpose. The fluorescence quantum yield values are found to be strongly influenced by environmental effects. It has been observed that fluorescence yield is greater for rhodamine 6G in ethylene glycol system than in water or in methanol. Our results also indicate that parameters like concentration of the dye solution, aggregate formation and excited state absorption affect the absolute values of fluorescence yield significantly.

1. Introduction

Fluorescence quantum yield (Q_{f}) is one of the key photophysical quantities that are amenable to direct experimental determination. The quantum yield of fluorescence is a measure of the rate of nonradiative transitions that compete with the emission of light. The knowledge of fluorescence quantum efficiency of organic dyes and its concentration dependence are essential for selecting efficient laser media. Conventional measurements require the use of accurate luminescence standard samples and comparison of the given sample with a standard for which the fluorescence yield is known.[1] The reliability of such relative determinations is then limited by both the accuracy of the standard yield value and by the confidence that can be placed on the comparison technique. Even after making various corrections for system geometry, re-absorption, polarization, etc., the accuracy of the quantum yield values obtained from photometric measurements is rather poor. In order to evaluate absolute quantum efficiency, we have to consider both the radiative and nonradiative processes taking place in the medium. As the contribution from nonradiative processes is not directly measurable using the traditional optical detection methods, thermo-optic

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techniques such as photoacoustic and thermal lens methods have been adopted recently for this purpose.[2,3] Measurements based on photothermal effects are capable of giving fluorescence yields of highly fluorescent solutions with high accuracy and reproducibility.

The thermal lens effect[4–6] is one of the thermo-optical methods usually employed for measurements at very low absorption limit. This effect can be observed using moderate laser intensities in media with absorption coefficient as low as $10^{-7}\,\mathrm{cm}^{-1}$.[7] Thermal lensing or thermal blooming occurs when energy absorbed from a Gaussian beam produces a local heating within the absorbing medium around the beam axis. In such experiments, the sample is exposed to a laser beam which has Gaussian beam profile and it causes excitation of the molecules along the beam path. Thermal relaxation of the excited molecules dissipates heat into the surroundings thereby creating a temperature distribution which in turn produces a refractive index gradient normal to the beam axis within the medium. This acts as a diverging lens and is called thermal lens (TL). Using thermal lensing method, we have determined the fluorescence quantum efficiency of the common laser dye rhodamine 6G (Rh6G) in three different solvents viz. methanol, water and ethylene glycol. An advantage of thermal lens is the ease with which it can measure Q_f over a wide range of concentration. This technique is known to be a sensitive tool able to cope with extremely weak absorptives. At the same time, reabsorption–reemission problems are to be much reduced, since photons need only escape from the submillimeter dimensions of a focused laser beam. The TL method offers significant advantages over conventional methods because absolute values of quantum yield can be measured and no standard sample is necessary.[8–10]

1.1. *Theory*

The method is based on the principle of energy conservation. If P_0 is the power of the incident excitation beam and P_t is the power of the transmitted beam, the absorbed power is the sum of the luminescence emission power P_f and the thermal power degraded to heat P_th, provided that any photochemical reaction is absent. Hence,

$$P_0 = P_\mathrm{th} + P_\mathrm{f} + P_\mathrm{t} \tag{1}$$

so that the transmission ratio is given by

$$T = \frac{P_\mathrm{t}}{P_0}\,. \tag{2}$$

Absorbance is given by

$$A = 1 - T\,. \tag{3}$$

Thus, the absorbed power is given by

$$AP_0 = P_\mathrm{th} + P_\mathrm{f}\,. \tag{4}$$

Then,

$$P_{\mathrm{f}} = AP_0 - P_{\mathrm{th}}\,. \tag{5}$$

In order to circumvent uncertainties originating from the measurement of the absorbance of the fluorescent sample and its comparision with that of the reference absorber, a second method has been proposed, using fluorescence quenched samples as references. The signal for a fluorescent sample is compared with that obtained with the same compound, the fluorescence of which has been completely quenched. If a quenched luminescent sample is used as the reference absorber, the problems can be solved because the quenched sample has the same light absorption coefficient as the luminescent sample. In the case of a totally fluorescence quenched sample, we can consider entire excitation energy to be converted into nonradiative relaxation process and hence, the fluorescence quantum yield Q_{f} is given by Ref. 10,

$$Q_{\mathrm{f}} = \frac{P_{\mathrm{f}}}{AP_0}\,\frac{\lambda_{\mathrm{f}}}{\lambda} = \left(1 - \frac{P_{\mathrm{th}}}{P_\alpha}\right)\frac{\lambda_{\mathrm{f}}}{\lambda} \tag{6}$$

where

$$P_\alpha = AP_0 \tag{7}$$

and the ratio of the fluoresence peak wavelength λ_{f} to excitation wavelength λ takes account of the Stokes shift. P_{th} is directly proportional to the TL signal η and P_α is proportional to TL signal η_α corresponding to the concentration at which the fluorescence intensity is quenched completely. By knowing λ_{f}, η and η_α, one can directly calculate the quantum efficiency Q_{f} from the equation

$$Q_{\mathrm{f}} = \frac{\lambda_{\mathrm{f}}}{\lambda}\left(1 - \frac{\eta}{\eta_\alpha}\right)\,. \tag{8}$$

The thermal lens signal η has been measured using the standard technique available in the literature.[7] The TL signal is taken as variation of light intensity at the center of the probe beam (He–Ne laser beam) arising due to the thermal lensing effect in the medium.

2. Experimental

The experimental setup used in this work is similar to that described earlier.[1,12] The thermal lens spectrophotometer consists of a frequency doubled Q-switched Nd:YAG laser (pulse width 9 ns, maximum energy 110 mJ) as the heating source and an intensity stabilized He–Ne laser as the probe beam. The sample solution taken in a quartz cuvette having pathlength 5 mm is placed in the pump beam bath. The pump and probe beams are focused onto the sample cell and made to pass collinearly through it using suitable convex lenses and by the use of a dichroic mirror. The excitation beam is blocked by a filter after the sample cuvette. The TL signal is detected by sampling the intensity of the center portion of the probe beam through a small aperture. In the present work, the intensity of the center portion of

the transmitted probe beam is detected by using an optical fiber. The polished tip of long graded index optical fiber (200 μm core, NA 0.22) placed at 90 cm away from the center of the sample cuvette serves both as an aperture and as a light guide for the probe beam to a monochromator–PMT assembly. The monochromator–PMT assembly tuned to the probe beam wavelength (632.8 nm) provdes further filtering of the signal. The TL signal is recorded using a digital averaging oscilloscope (100 MHz, Tektronix TDS 220) which provides a complete time domain representation of the signal. The oscilloscope is triggered by a synchronous trigger pulse from the Nd:YAG laser operated at 5 Hz.

For fluorescence studies, the front surface emission is collected and focused by a lens onto the aperture formed by the tip of another optical fiber attached to the entrance slit of a 1 m Spex monochromator (Model 1704, grating with 1200 grooves per mm blazed at 500 nm, maximum resolution 0.015 nm) which is coupled to a PMT (Throne EMI) having S20 cathode. The PMT output is fed to a boxcar averager/gated integrator (Standford Research Systems, SRS 250) for further processing. The averaged output from the boxcar averager is fed to a chart recorder. The emission is wavelength scanned in the desired region. The emission shows the characteristic fluorescence spectrum.

3. Results and Discussion

3.1. *Solvent effects on fluorescence spectra*

A knowledge of possible environmental effects on spectra and quantum yields of fluorescence is necessary for the utilization of fluoresence technique at its maximum potential. A list of the environmental factors that affect fluorescence phenomena include interactions with solvent and other dissolved compounds, temperature, pH and the concentration of the fluoresence species. The effects that these four parameters have upon fluoresence vary from one fluorescent species to another. Both the absorption and emission spectra as well as the quantum yields of fluorescent molecules are influenced by these parameters. Solvent effects on the absorption and emission spectra of various dyes have been investigated by several authors.[13–16] Before discussing the results for fluorescence efficiency values of Rh6G there are a number of other aspects of the measurements that should be considered.

Fluorescence studies were carried out for Rh6G laser dye in different solvents. Figure 1 shows the recorded fluorescence spectra of Rh6G in water, methanol and ethylene glycol. For these measurements, the emission from the front surface geometry was utilized. Concentration-dependent changes in the fluorescence spectra was observed. The fluorescence spectrum for the highest concentration differs strongly from that recorded at lowest concentrations. The difference between these are significant in the case of red shift of fluoresence and enhancement of the half width of the fluorescence spectrum with increasing concentration. Figure 2 represents the peak fluorescence wavelength (pfw) of Rh6G as a function of concentration in alcoholic, aqueous and ethylene glycol solutions. The spectral shifts observed can be

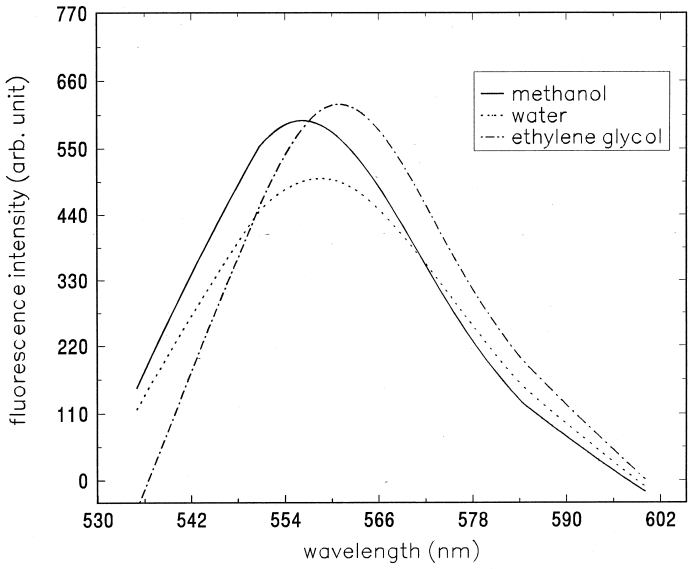

Fig. 1. Typical fluorescence spectra obtained for Rh6G in different solvents.

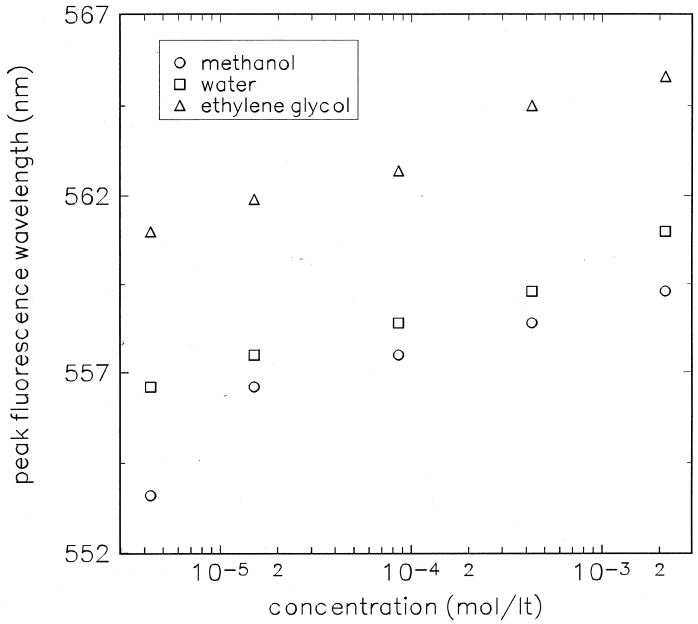

Fig. 2. The variation of peak fluorescence wavelength with concentration for Rh6G for different solvents.

used as a guide to the interaction of the dye with the solvent media. It can be seen that the pfw increases with concentration. In other words, the fluoresence spectrum of the dye is shifted to smaller energies when the dye concentration is increased. To determine the emission of the aggregates produced, Arbeloa *et al.*[17] carried out these experiments with varying optical pathlengths of the sample and they found that the fluorescence spectrum of concentrated solutions recorded using very short optical path has the same shape as that observed in dilute solutions. Therefore, the aggregates do not emit at room temperature and the spectral shift is a consequence of the reabsorption and reemission phenomena.[18–21]

The solvent parameters, dielectric constant and refractive index can be correlated with the Stokes shift (the shift between the ground and excited state transitions of R6G). A variety of equations have been proposed[22,23] to describe the effects of the physical properties of the solvent upon the emission spectra of fluorophores. In all these treatment, the solvent is regarded as a continuum in which the fluorophore is contained. The interactions between the solvent and fluorophore molecules affect the energy difference between the ground and the excited states. This energy difference is a property of the refractive index (n) and dielectric constant (ϵ) of the solvent. Within the zeroth-order approximation, the solute–solvent interaction is considered to be primarily of dipole–dipole nature including dispersion interactions. The relation proposed by Chamma and Viallet[24] is

$$\frac{\overline{\nu_a} + \overline{\nu_f}}{2} = -\frac{2\Delta\mu^2}{a^3 hc} F \tag{9}$$

where $\overline{\nu_a}$ and $\overline{\nu_f}$ are the 0–0 absorption and emission frequencies, respectively, and $\Delta\mu^2 = (\mu_e - \mu_g)^2$ where μ_e and μ_g are the permanent dipole moments in the excited and ground states, respectively, h is the Planck's constant, c is the speed of light in a vacuum and a is the Onsager cavity radius, assuming the solvent to be a medium of continuous dielectric constant and refractive index. F is given by the equation

$$F = \frac{2n^2+1}{2(n^2+2)}\left[\frac{D-1}{D+2} - \frac{n^2-1}{n^2+2}\right] + \frac{3}{2}\,\frac{n^4-1}{2(n^2+2)^2} \tag{10}$$

where n and ϵ are the refractive index and dielectric constant of the solvent medium, respectively.

The sensitivity of a fluorophore to solvent polarity is expected to be proportional to $\Delta\mu$.[25] This term is expected to be constant for a given fluorophore. The slope of the plot of the left-hand side of the Eq. (9) versus F (Fig. 3) yields the value of $\Delta\mu = 0.88$ Debye. The Stokes shift in the ground and excited state spectra can be explained using the Franck–Condon Principle. Several workers[26] have correlated the solvent polarity parameter involving the dielectric constant with the Stokes spectral shift as in Eq. (9).

The emission spectra clearly contain a good deal of information concerning the fluorophore–solvent interaction which occurs between absorption and emission. No single physical property of the solvent such as orientation polarizability, viscosity,

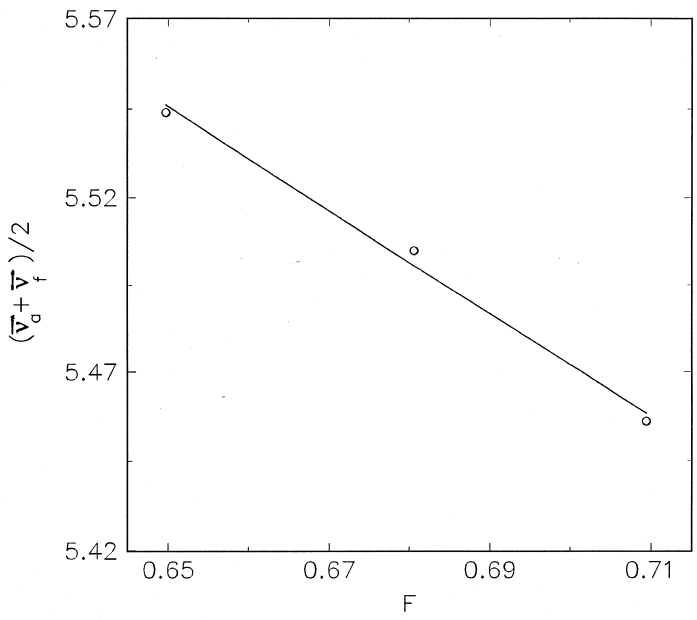

Fig. 3. The plot of $(\overline{\nu_a} + \overline{\nu_f})/2$ versus F.

polarity, dielectric constant or refractive index can fully explain this peculiar emission properties. The important physical constants of the three solvents used in the present study are given in Table 1. From the magnitudes of F, one may judge that spectral shifts will be larger in ethylene glycol. Our experimental observations also indicate that pfw shift is found to be greater in Rh6G:ethylene glycol system and lower in Rh6G:methanol system. Thus, our observed results are very consistent with the value of F. It has been reported that the fluorescence quantum yield increases and the emission maximum shifts to shorter wavelengths as the solvent polarity decreases.[23]

Table 1. Important physical constants of the solvents used.

Parameter	Methanol	Water	Ethylene glycol
Refractive index	1.326	1.332	1.429
Dielectric constant	32.63	78.54	37
Dipole moment	1.7 Debye	1.85 Debye	2.28 Debye
F	0.64	0.68	0.71

The half-width ($\Delta\lambda_{1/2}$) of the fluorescence band increases distinctly with increase in concentration. For example, taking the case of Rh6G:methanol system, the half-width of the fluorescence spectrum for the highest concentration

(8.5×10^{-3} mol/l) studied is 52 nm, which is much greater than that for the lowest concentration ($\Delta\lambda_{1/2} = 31$ nm at 8.7×10^{-7} mol/l) studied where almost only monomers exist. These regularities were also observed for coumarin dyes by Jones *et al.*[20] indicating the presence of fluorescent aggregates in the most condensed solutions. Bojarski *et al.*[27] treated these concentration changes as evidence for the presence of fluorescent dimers of Rh6G in concentrated solutions. The formation of fluoresent dimers of Rh6G with a very low quantum yield has been found in water and in methanol.[28–32] Scully *et al.*[33] made a hypothesis on the existence of fluorescent dimers of Rh6G in concentrated ethylene glycol solutions. The changes in the $\Delta\lambda_{1/2}$ for the concentrated solutions confirm the hypothesis on the presence of higher aggregates in the solution.

3.2. *Thermal lensing measurements*

Thermal lensing measurements were made in Rh6G solutions in different solvents for the determination of quantum yield (Q_{f}) values. The absorption spectra of Rh6G in methanol, water and ethylene glycol showed that absorption at 632 nm is very small and hence, any perturbation due to the probe beam can be neglected. The TL signal measurements were carried out in the dye solution in the concentration range of 3.47×10^{-3} to 8.7×10^{-6} mol/l. Dependence of TL signal on laser power for Rh6G:methanol, Rh6G:water and Rh6G:ethylene glycol systems was studied and the results showed that thermal lens signal intensity varies linearly for the range of laser power used for fluorescence quantum yield measurements.

Figure 4 shows the variation of Q_{f} obtained in TL measurements using Eq. (8) for Rh6G in methanol, water and ethylene glycol as a function of concentration. The Q_{f} obtained using TL method showed values of 0.98, 0.95 and 0.97 at a concentration of 8.5×10^{-7} mol/l with methanol, water and ethylene glycol as solvents, which are in good agreement with the values reported using other calorimeter methods.[34–36] It must be noted that the quantum yield of the dye solution decreases at higher concentrations irrespective of the solvent used. The major mechanisms that may quench the fluorescence emission at these concentrations are triplet state absorption and aggregate formation. The role of triplet state absorption can be neglected here since pulse width of the pump laser t_p is $\sim$9 ns such that $t_p \ll 1/k_{st}$ where k_{st} is the $S_1 \rightarrow T_1$ intersystem crossing rate which is 4.2×10^5 s^{-1} in Rh6G.[35] The rapid decrease in Q_{f} at higher concentrations can be attributed mainly to the formation of dimers and higher aggregates which have zero or very small fluorescence quantum yield. The competition between increasing dimer absorption and decreasing monomer absorption at 532 nm with increasing concentration plays a comparable (or even greater) role than direct self-quenching of fluorescence for the decrease in quantum efficiency.

The formation of dimers and trimers in solutions of higher concentrations lead to fluorescence quenching. Formation of aggregates decreases the emission quantum yield of Rh6G by a combination of monomer–dimer energy transfer and absorp-

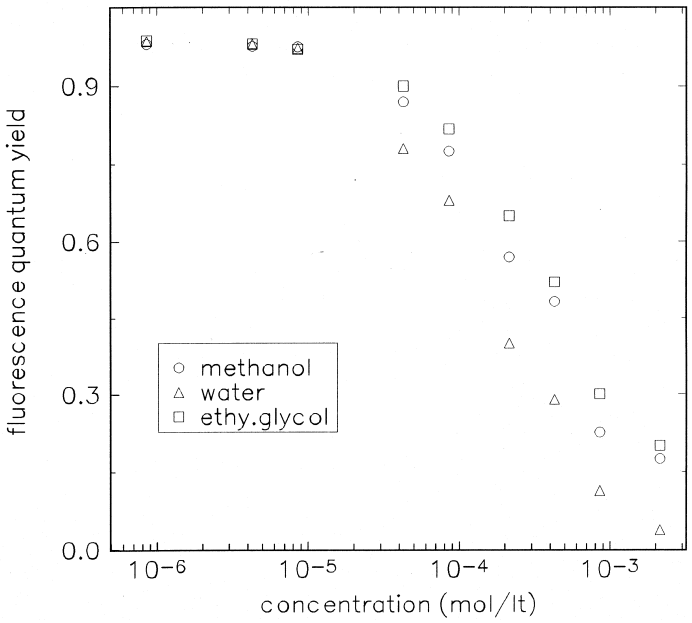

Fig. 4. The variation of Q_f with concentration of Rh6G laser dye in different solvents determined using pulsed thermal lens method.

tion of radiation by dimers. The nature of these aggregates has been extensively studied[37,38] as a result of this unique property of the dye solutions. The strength of the aggregation depends on the structure of the dye, the solvent, temperature, pressure and other factors. In earlier studies, the aggregates were attributed mainly to the dimer.[39,40] However, it has been proposed recently that higher aggregates consisting of three or more dye molecules exist in concentrated solutions. In the case of Rh6G in ethanol solution, the aggregates are supposed to involve the dimer, trimer and tetramer, whereas only the dimer and trimer are believed to exist in aqueous solution.[35] The decrease of quantum efficiency at higher concentrations is caused by Forster-type energy transfer to dimers. The equilibrium between monomer and dimer shift to the side of the latter with increasing concentration. The dimerization of laser dyes like RhB and Rh6G is severe enough to prevent laser action unless deaggregating agents like hexafluoroisopropanol or ammonyx LO is added to the solution.[35] In the present case, no such deaggregating agents were added and hence, significant reduction in fluorescence quantum yield can be expected due to aggregate formation at higher concentrations.

The dimer spectrum consists of two visibly separated bands, H and J. In that, it is similar to the dimer absorption spectrum of Rh6G in methanol[28,29] as well as in silica gel,[42] but differs from that in water where H and J bands overlap partially.[42] The H band of these dyes in water was observed to be larger than the J band while J band was found to be larger than H band in ethylene glycol solutions.[43] The H

class dimer is thought to be nonfluorescent, while the J class dimer is fluorescent. Molecules of RhB and Rh6G in water were proved to become nonfluorescent by dimerization, since these dimers show strong H absorption[44,45] whereas larger J band absorption was observed in the case of ethylene glycol. It should be noted that the presence of aggregates in concentrated donor–acceptor systems may influence significantly the courses of photophysical and photochemical processes, especially if they are conditioned by the nonradiative excitation transport. In that case, fluorescent aggregates play a role of additional acceptors acting as imperfect traps for the excitation energy.[46,47]

The values for Q_{f} in the aqueous solutions are lower and apparently more concentration-dependent than in the corresponding methanolic and ethylene glycol solutions. Two factors are responsible for such variation in Q_{f} values obtained. Firstly, the value of Q_{f} in aqueous solutions can be expected to be less than in methanol and ethylene glycol due to the strong quenching effect of water on fluorescence. Secondly, as in the case of the methanolic and ethylene glycol solutions, the inner filter effect can be expected to result in a decrease of Q_{f} with increasing concentration. These two effects would result in a curve for the aqueous Q_{f} values paralleling those of the methanolic and ethylene glycolic Q_{f} values. This appears to be true in the more dilute aqueous solutions, but at concentrations above $\simeq 5 \times 10^{-5}$ mol/l, there is a more rapid decrease in the value of Q_{f}. This rapid decrease is due to considerable formation of dimers in the aqueous solutions.

Penzkofer and Lu[48] were of the opinion that, in Rh6G:methanol solutions, ground state dimer formation is unstable and closely spaced pairs dominate the fluorescence behavior at higher concentrations. Within the lifetime of the excited monomer, an excited monomer and a ground state monomer come so near together that they interact mutually and form an excited quenching center. The strong radiationless deactivation of excitation in these quenching centers reduces the fluorescence emissions. A few authors disagreed with this argument and claimed that stable state dimers and higher aggregates are found in alcoholic solutions of Rh6G.[49] In the Rh6G–ethylene glycol system, the strong overlaps between all absorption and fluorescence bands enable forward and reverse energy transport between monomer and dimers. This phenomenon affects all the spectroscopic parameters including fluorescence quantum yields.[50]

The fluorescence yields reported here demonstrate that it is generally unjustified to assume that fluorescence parameters are minimally influenced by solvent. The absolute yield of Rh6G measured using this method show solvent varations of 1–15%, especially at higher concentrations, indicating that solvent–solute interactions play a measurable role in modifying unimolecular decay constants for excited singlet electronic states. It is interesting to note that the quantum yield of Rh6G is higher in ethylene glycol than in water or methanol. This suggests that the chromophore is fully rigid in the ground state and loosens up only after excitation, provided that the solvent is of low viscosity. In ethylene glycol, the viscosity is sufficiently high to prevent thermal equilibrium being reached during the radiative lifetime of

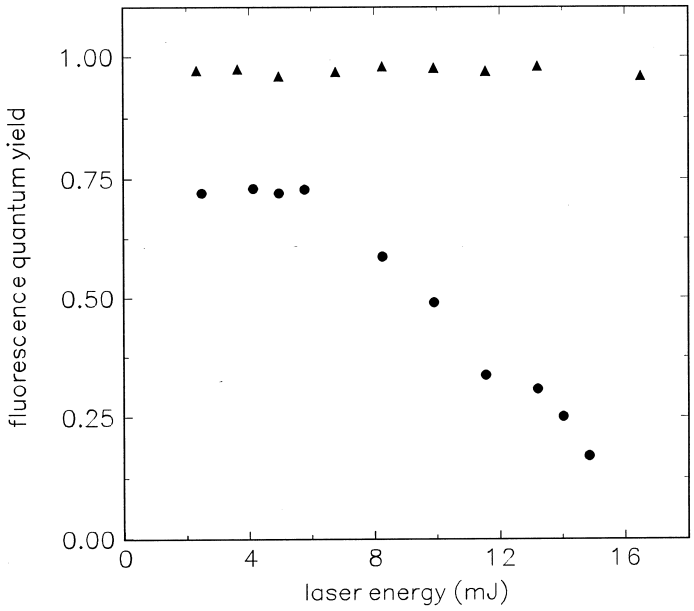

Fig. 5. The variation of Q_f with laser energy for Rh6G in methanol at different concentrations (▲ — 8.5×10^{-6} mol/l, • — 8.5×10^{-5} mol/l).

a few nanoseconds. Hence, the planarity of the ground state is not lost before light emission takes place.[35]

We have also studied dependence of absolute value of fluorescence yield on the laser energy of pulsed excitation source. When the rhodamine dyes are illuminated with the high intense pulses (532 nm) from the Q-switched Nd:YAG, nonlinear processes begin to appear.[11,51] The values of Q_f in Fig. 4 were measured at lower energy levels where a linear dependence of thermal lens signal on laser energy holds good. At higher intensities, a deviation from the linearity was observed due to different nonlinear processes like excited state absorption (ESA) and/or two photon absorption (TPA).[11,51] This is evident from the observed reduction in Q_f with increasing laser energy (Fig. 5). As the incident energy increases, the dye molecules populate higher excited levels. This, in fact, decreases the number of absorbing molecules in the ground state, thereby, reducing the effective number of emitted photons.

4. Conclusion

Dual beam thermal lens technique is successfully employed for the determination of absolute value of fluorescence quantum yield. For fluorescing materials like Rh6G, the thermal lens method is suitable for the evaluation of quantum efficiency since it requires no standard and is very convenient and useful, especially at higher concentrations, namely, near the fluorescence quenching regimes. Although it is difficult to

ascertain whether photothermal methods are more accurate than fluorescence measurements, the former are less sensitive to experimental errors. While fluorescence generally senses a narrow band of wavelengths and only a small part of the emitted photons, the photothermal methods are sensitive to the complementary part of the total fluorescence, which means that any change in the emission spectrum will influence the photothermal signal. However, changes in the fluorescence spectrum arising from the interaction of the emitted photons with the solution are expected not to affect the photothermal signal. However, in strongly absorbing medium, there exists an upper limit for pump beam power which gives a noise-free TL signal when dual beam TL technique is employed. This method also requires careful attention to all the possible photophysical processes associated with the relaxation of the fluorescent compound.

The fluorescence yields reported here demonstrate that fluorescence parameters are influenced by environment of the fluorescing molecule, processes like internal nonradiative conversion, excited singlet state absorption and aggregation of the dye molecule. These are strongly dependent on excitation source, solvent characteristics as well as concentration of the dye solution. Our results indicate that a higher fluorescence yield is obtained for Rh6G in ethylene glycol than in methanol or water. This quantum yield variation with solvent indicates that solvent–solute interactions play a measurable role in modifying unimolecular decay constants for excited singlet electronic states. The variation of quantum yield with concentration of the dye solution shows a decreasing tendency irrespective of the solvent used.

Acknowledgments

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