Chemical Methodologies

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Semi-empirical Estimation of Rhodamine 6G's Fluorescence Lifetimes from Fluorescence Quenching Data

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ARTICLE INFORMATION

ABSTRACT

The fluorescence quenching of rhodamine 6G by hydroquinone in methanol, water and dimethylsulphoxide (DMSO) is explored. A combination of solvent parameter could be necessary to explain solvatochromism in rhodamine 6G as the consideration for solvent refractive index alone is insufficient. Stokes' shifts ranged between 25 and 29 nm. Rhodamine 6G's fluorescence was effectively quenched by hydroquinone within the quencher's concentration (0.01 to 0.05 M) which was used in this work, and the quenching data were in conformity with the Stern-Volmer's model. Stern-Volmer's constants (K_{SV}) were 47.1, 29.6 and 14.8 M^{-1} in methanol, water and DMSO respectively. These values, together with the calculated bimolecular rate constants (k_D) in the respective solvents, were used in the semi-empirical estimation of the fluorescence lifetimes (τ_F) of rhodamine 6G in the individual solvents. The τ_F determined values (3.78, 3.89 and 4.36 ns in methanol, water and DMSO respectively) are comparable with literature values.

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Graphical Abstract
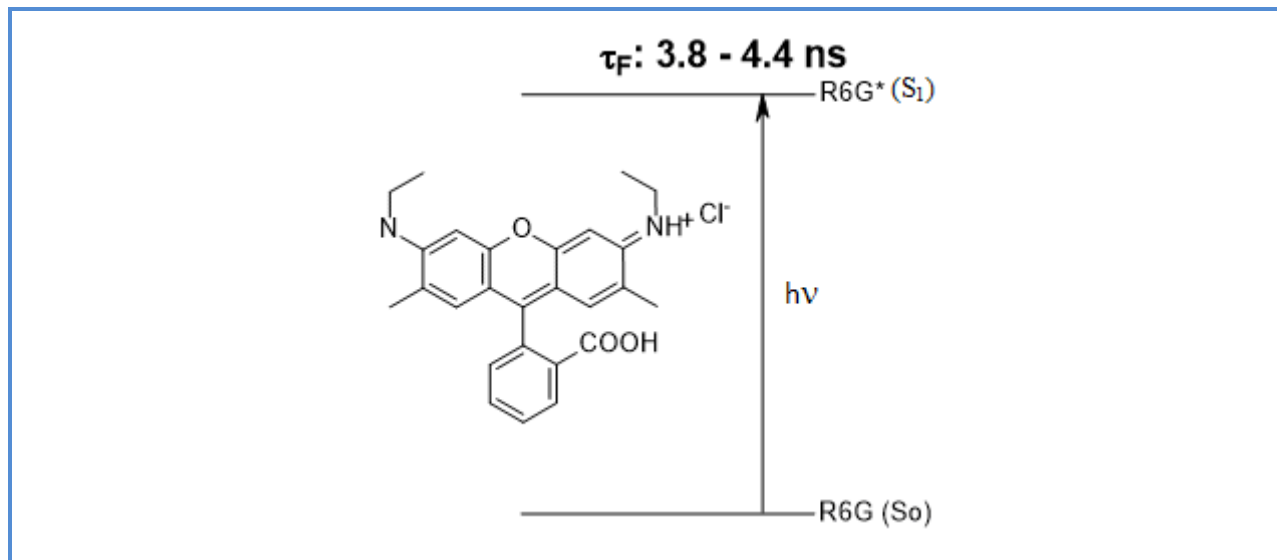
Introduction

Rhhodamine 6G (R6G) is a cationic, lipophilic and highly fluorescent member of the rhodamine dye family. It is one of the most commonly utilized dyes, as it has found use in many areas or endeavor, including photosensitization [1-3], non-linear optics [4-6] and as a gain medium in dye lasers [7, 8]. Once excited, an absorbing species could lose its excitation energy in a variety of ways; non-radiative processes compete with fluorescence in deactivating the excited state. Aside internal conversion and intersystem crossing, notable among non-radiative deactivation processes are collisions of the excited molecule with solvent and quencher molecules.

Once excited, a fluorophore loses its excitation energy as photoluminescence (fluorescence); however, the excitation energy could be intercepted by the use of an appropriate fluorescence quencher and channeled toward eliciting a secondary photophysical or photochemical process.

The modes of fluorescence quenching include excited state reactions, energy transfer, complex-formation and collisional quenching. In recent past, we have reported works involving collisional quenching of macrocycle fluorescence by benzoquinone and hydroquinone in aqueous and non-aqueous media [9, 10]. Two forms of fluorescence quenching are known as viz: dynamic and static quenching. Be it dynamic or static, molecular contact between the fluorophore and quencher is a basic requirement. For purely dynamic quenching, the quencher must diffuse to the fluorophore during the lifetime of the latter's excited state. Upon contact, the fluorophore's excitation energy is intercepted, and it returns to the ground state via a non-radiative deactivation pathway (without emission of a photon). In general, dynamic quenching occurs without any permanent change in the

fluorophore's identity. In static quenching a non-fluorescent complex is formed between the fluorophore and the quencher.

Photosynthesis is a process by which light energy is captured by green plants and other organisms, and transformed into chemical energy. Green plants consist of chlorophylls, quinones and other materials; it is supposed that chlorophyll acts as the absorber while quinone acts as an energy transducer. The energy transducing tendencies of quinones is due to their ease of oxidation and reduction. The fluorescence-quenching tendency of benzoquinone is well-documented in the literature [9], particularly with porphyrin and phthalocyanine derivatives. However, literature is rather scanty on the use of hydroquinone for the same purpose. This work explores the fluorescence quenching of R6G by hydroquinone (HQ) in aqueous and non-aqueous solvents. The obtained quenching data shall then be exploited in the estimation of the fluorescence lifetimes of R6G.
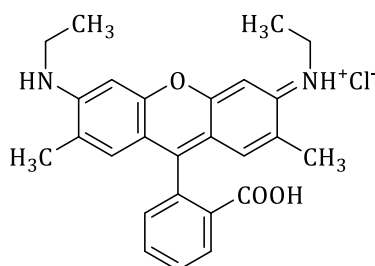
Figure 1. Structure of Rhodamine 6G (R6G)

Experimental

Materials and Equipment

Rhodamine 6G (R6G) and hydroquinone were purchased from Aldrich. Solvents-dimethylsulphoxide (DMSO) and methanol (MeOH) were obtained from SAARCHEM; water was freshly distilled. UV–visible spectra were recorded on a Shimadzu 2550 UV-Vis spectrophotometer. Fluorescence emission spectra were recorded on a Varian Eclipse spectrofluoremeter.

Fluorescence quenching by hydroquinone

A study of the fluorescence quenching of the various R6G was carried out by the addition of increasing concentrations of HQ to a fixed concentration of the complex, and the concentrations of HQ in the resulting mixtures were 0, 0.008, 0.016, 0.024, 0.032 and 0.040 M. The fluorescence spectra of R6G complexes at each HQ concentration were recorded, and the changes in fluorescence intensity with HQ concentration were related by the Stern-Volmer plot, Eq. 1.

$$\frac{I_0}{I} = 1 + K_{SV}[HQ] \tag{1}$$

Where I_0 and I are R6G fluorescence intensities in the absence and presence of quencher (HQ), respectively; [HQ] is the concentration of the quencher, and K_{SV} is the Stern-Volmer constant. The ratios I_0/I were calculated and plotted against [HQ] according to Eq. 1. K_{SV} is determined from the slope, and is also the product of the bimolecular quenching constant (k_Q) and the fluorescence lifetime τ_F, i.e.

$$K_{SV} = k_Q.\tau_F \tag{2}$$

The bimolecular rate constant for diffusion-controlled reactions (k_D) is related to the bimolecular quenching constant (k_Q) by Eq.3:

$$k_Q = fk_D \tag{3}$$

where f is the collision efficiency.

The bimolecular rate constant (k_D) can be obtained from the Einsten-Smoluchowski relationship:

$$k_D = 4\pi N_A(D_{R6G} + D_{HQ})(R_{R6G} + R_{HQ}) \tag{4}$$

Where N_A is the Avogadro's number; D_{R6G} and D_{HQ}, the diffusion coefficients of R6G and HQ respectively. R_{R6G} and R_{HQ} are the radii of R6G and HQ respectively.

The diffusion coefficient D is given by the Stokes' equation (Eq. 5).

$$D = \frac{kT}{6\pi\eta R} \tag{5}$$

Where k is the Boltzmann constant; T, the absolute temperature; η, the solvent's viscosity and R, the R6G (or HQ) radius.k_Q values which can be determined from Eq. 3 using the calculated k_D value, provided that f is known. From the values of k_Q, the values of τ_F can then be calculated according to the relation

$K_{SV} = k_Q.\tau_F$

$R_{R6G}$is assumed to be equal to the dyes' Onsager cavity radius, and can be obtained from molecular volume, as given by Suppan's equation [11]:

$$a = \sqrt[3]{\frac{3M}{4\pi\rho N}} \tag{6}$$

Where M is the molecular weight of R6G (479.02 g mol^{-1}),ρ, its density (1.26 g cm^{-3} [12]) and N, the Avogadro's number. This treatment resulted in an R_{R6G} value of 5.32 x10^{-10} m. The literature value of the HQ's radius is 3.90 x10^{-10} m [10].

Results and discussion

Ground state electronic absorption and fluorescence spectra

Figure 2 shows the UV-Vis spectra of R6G in three solvents – methanol, water and DMSO. The spectral signals are sharp near the wavelength of maximum absorption which can be regarded as the characteristic of monemeric species. The molecules exhibit monomeric behavior up to a concentration of 10^{-1} mol dm^{-3} in methanol and DMSO(that Beer's law was obeyed). In water, however, deviation from Beer's law was observed at a concentration as low as 10^{-5} mol dm^{-3}. At high temperature, interaction between neighboring dye molecules results in aggregation which can be viewed as a deviation from Beer's law.
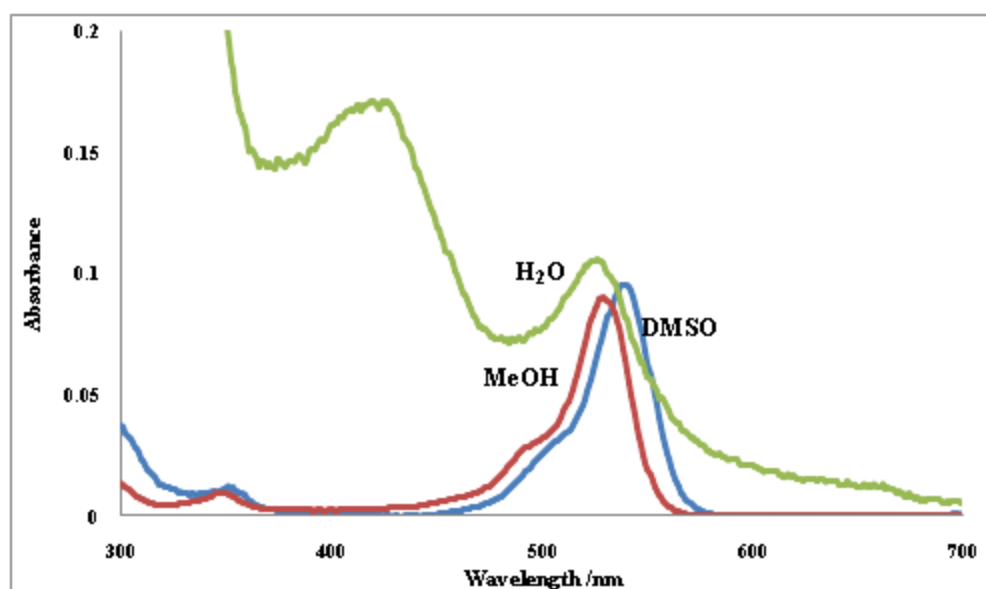
Figure 2. Absorption spectra of R6G ($\sim 1 \times 10^{-6}$ M)) in water, methanol and DMSO.

The observed trend in the variation of band position (wavelength of maximum absorption, λ_{max}) with solvent is usually attributed to solvent refractive index, with the band position expected to shift bathochromically as solvent refractive index increases. Therefore, as expected, DMSO, having the highest refractive index value exhibits the longest λ_{max}. However, in Table 1, water and methanol exhibit almost the same λ_{max} in spite of a clear difference in their refractive indices.

Table 1. Electronic absorption and fluorescence data for R6G in three solvents

	n	λ_{max} (Abs) /nm	Log ε	λ_{max} (Ems) /nm	$\Delta\lambda_{Stokes}$ /nm
Methanol	1.326	528	5.12	553	25
Water	1.332	527	5.01	556	29
DMSO	1.479	539	5.11	565	26

This discrepancy demonstrates that a combination of solvent parameter could be necessary to explain solvatochromism in R6G. Solvent parameters such as aromaticity, polarity and coordinating power have been shown to exert significant effects on the band positions of organic and coordination entities [13, 14]. Figure 3 shows the absorption and fluorescence emission spectra of R6G in methanol, with Stokes' shifts ranging between 25 and 29 nm.

The absorption and fluorescence excitation (spectra not shown) spectra are in close agreement, suggesting that the absorbing species is also the fluorescing species.
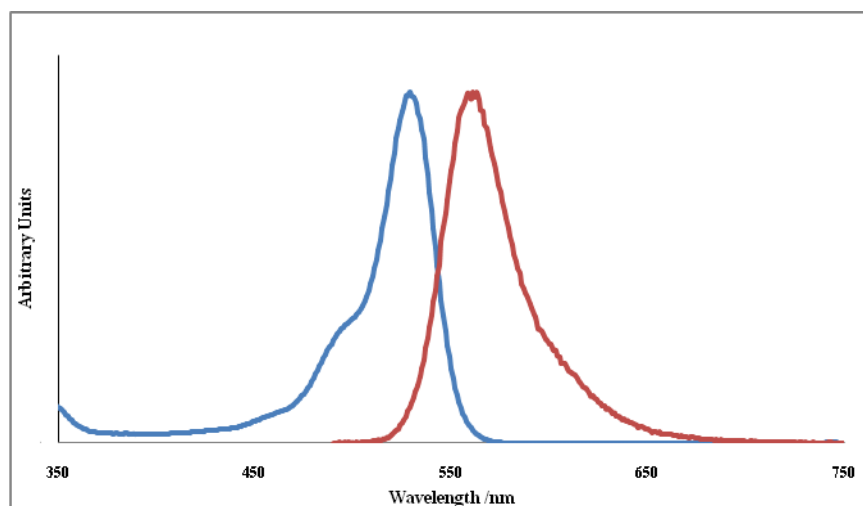
Figure 3. Absorption and fluorescence spectra of R6G in methanol

In addition, the fluorescence emission spectrum is a mirror image of its absorption spectrum (Figure 3). This also rules out the presence of R6G-R6G molecular aggregation at the concentration used for fluorescence studies.
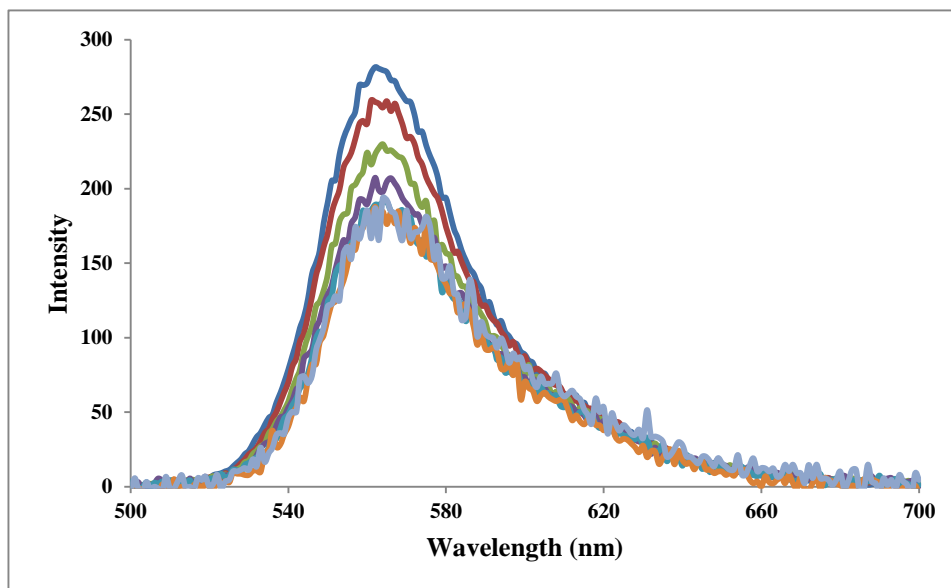
Fluorescence quenching by hydroquinone (HQ)

Figure 4 demonstrates the fluorescence quenching of R6Gby HQ, in DMSO. Stern-Volmer's plot (Eq. 1) gave a straight line (Figure 5), which implies an exclusively dynamic quenching. In addition, there was no modification to the absorption spectrum of R6G in the presence of HQ, ruling out the existence of static quenching. The operational quenching mechanism, therefore, involves a diffusion-controlled collisional interaction between R6G and the HQ molecules; and under this situation, *f*, the quenching efficiency (Eq. 3) is assumed to be $\cong 1$.
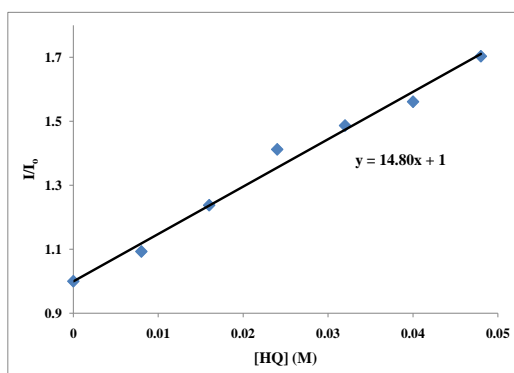
Table 2. Data for R6G fluorescence quenching by hydroquinone in three solvents

	$10^4.\eta/\text{kg m}^{-1}$	$D_{R6G}/10^{-10} \text{ m}^2 \text{ s}^{-1}$	$D_{HQ}/10^{-10} \text{ m}^2 \text{ s}^{-1}$	$k_D/10^{10} \text{ M}^{-1} \text{ s}^{-1}$	K_{SV}/M^{-1}	$^\dagger\tau_F/\text{ns}$
Methanol	5.44	6.77	10.3	1.25	47.1	3.78 (4.07)
Water	8.90	4.14	6.28	0.76	29.6	3.89 (4.03)
DMSO	19.90	1.85	2.81	0.34	14.8	4.36

† Values in parentheses are from literature [15].

Figure 4. Fluorescence quenching of R6G by hydroquinone (HQ) in DMSO.

y = 14.80x + 1

Figure 5. Stern-Volmer plot for the fluorescence quenching of R6G by hydroquinone (HQ) in DMSO.

Values of Stern Volmer's quenching constant (K_{SV}) in the three solvents are listed in Table 2. These K_{SV} values and the calculated k_Q values were used to compute the fluorescence lifetimes (τ_F) of R6G in the various solvents (Eq. 2, Table 2). The τ_F values are comparable with literature values [15], attesting to the validity of this treatment.

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