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Solvent effect on fluorescence lifetime of Rhodamine 6G

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Abstract

Fluorescence lifetime τ and absorption spectra of Rhodamine 6G (R6G) at different concentrations have been measured in a variety of solvents, such as methanol, ethanol n-propyl-, n-butyl and t-amyl alcohols, acetonitrile and water etc. The variation of τ for R6G in these solutions (except H_2O) at 10^{-4} md. is related linearily to the ability of solvent to form hydrogen-bonding. This finding in combination with the absorption measurement leads us to a suggestion that the influence of solute-solvent interaction via hydrogen-bonding on aggregation between R6G molecules is responsible for observed solvent effect on fluorescence lifetime.

Introduction

The xanthene dyes, in particular Rhodamine 6G(R6G), have been widely used in solution as an efficient active medium in organic dye lasers[1]. However, most of discussions on the dynamic behaviour of excited singlet state of these molecules have up to now involved only the experimentally observed absorption,emission spectra and quantum yield of fluorescence rather than the rates of decay processes. It is known that the fluorescence decay for R6G has a marked dependence on concentration and temperature in alcoholic and aqueous solutions[2~5]. But there is little information concerning the solvent effect on the fluorescence decay[6, 7].

In this work we present fluorescence lifetime data for R6G in a variety polar solvents: methanol, ethanol, propy land butyl-alcohol, glycerol, aceto-nitrile and water; these data are combined with absorption measurements to ascertain the nature of solvent effect on fluorescence decay for Rhodamines. The results obtained indicate that the influence of hydrogen-bonding between Rhodamine dyes and solvent on the aggregation of dyes seems to be a likely factor responsible for the solvent effect observed.

Experiment

In our experiment the commercial laser dye R6G was used without further purification. Solutions were prepared using reagents of spectroscopic grade and the doubly-distilled water was used as a solvent for aqueous solution.

The absorption spectra of various R6G solutions were recorded using a Specord UV

VIS type spectrophotometer. The fluorescence lifetimes for R6G were determined for the decay of fluorescence intensity monitored on Sp-7x nanosecond fluorescence spectrometer (Applied Photophysics Ltd. BK.) in which the nondegassed dye solution, contained in a 1 cm square quartz cuvette, was excited with a nsec (337 nm) light pulse of low intensity ($\sim 10^{+7}$ photon/rad.) from a repetitive discharge lamp, filled with nitrogen. The fluorescence signals were detected by the time-correlated single photon counting technique. The decay curves of fluorescence were analyzed by a nonlinear, least square fitting procedure on a PDP11/05 computer. Fluorescence lifetimes τ were extracted from these data with deconvolution analysis, in which the shift in response time of equipment has been taken into account, and the results were checked by weighted error distribution. The accuracy in fluorescence lifetime measurement in present work was estimated to be within ± 0.15 nsec[18].

Results

1. Fluorescence lifetime

The decay of fluorescence of R6G in all solvents used was found to be an exact exponential and may be characterized by the fluorescence lifetime τ, the time at which the intensity of fluorescence has decreased by a factor of 1/e. The measured τ for R6G at three concentrations in various solvents are summarized in Table 1. These data are in qualitative agreement with the values reported in literature[9~12], and the slight discrepancy between them can be attributed to the difference in measurement techniques, purity of samples used and/or the excitation conditions.

Table 1　Absorption maxima and fluorescence lifetimes for Rhadamine 6G as a function of solvents

Solvents (α)[a]	Absorption maximum[d] (cm^{-1})	Fluorescence Lifetime τ (n sec.)		
		1×10^{-5} mol	1×10^{-4} mol	1×10^{-3} mol
Methanol (0.99)	18581	4.17	6.81	11.03
Ethanol (0.85)	18519	4.74	6.00	10.65
n-Propyl alcohol (0.77)	18450	4.58	6.21	11.72
n-Butyl alcohol (0.71)[b]	18450	4.52	5.75	11.91
t-Amyl alcohol (0.44)[c]	18315	4.22	5.01	—
Glycerol (0.79)	18382	4.11	6.13	—
Acetonitrile (0.29)	—	—	3.66	—
Water (1.02)	18587	4.59	4.90	—

a. solvent paramter in parenthesis.

b. parameter for t-butyl alcohol.

c. parameter for ethylene glycol.

d. absorption maximum in 1×10^{-3}, 1×10^{-4} and 1×10^{-5} mol solutions.

The data given in Table 1 show that the τ is not influenced noticeably by the nature of solvents in diluted ($\leqslant 10^{-5}$ mol) and concentrated ($\geqslant 10^{-3}$ mol) solutions, but in intermediate concentrations ($\sim 10^{-4}$ mol) it is changed with changing of solvents. The dependence of τ on the properties of solvents, such as polarity, viscosity, dielectric constant etc, was less regular. However we found that the variation of τ for R6G in these solutions (but not in water) was successfully correlated with the Kamlet-Taft parameter[13] α, an empirically derived constant reflecting the ability of solvent molecule to donate a hydrogen-bond. Least square analysis of this correlation provided the following expression relating the fluorescence lifetime τ and the hydrogen-bonding parameter α of solvents (correlation coefficient, r, is included):

$$\tau = 2.834 + 4.082\alpha, \qquad (r = 0.964).$$

2. Absorption spectra

Observed absorption spectra of R6G in a series of alcohols and in aqueous solution are shown in Fig. 1. Absorption spectra of R6G in all solutions used are a superposition of two components: the absorption band with maximum at 530～550 nm, and secondary band, which is detectable only as a small shoulder on～500 nm. According to the literatures[14,15] these bands may be assigned to the "monomeric" and aggregated R6G molecules, respectively. Absorption maxima of "monomeric" R6G in solution shifts to blue with the increase of the hydrogen-bonding ability of solvents and the magnitude of the shift in a given solution remains practically unchanged as the concentration changed from 10^{-5} mol to 10^{-3} mol. The location of the secondary absorption band is identical in various solutions but this small shoulder becomes somewhat better defined, particularly in aqueous solution, with the increase of the hydrogen-bonding ability of solvents, the total concentration of R6G being kept the same.

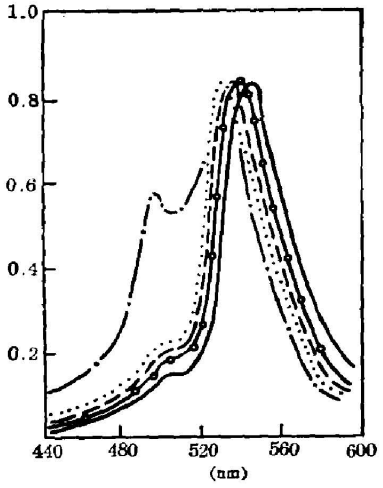

Fig. 1 Absorption Spectra of Rhodamine 6G in Various Solvents
(····Methanol; ----Ethanol; ∘∘∘∘n-Propyl and n-Butyl alcohol; ——Glycerol; -·-·Water)

Discussion

The linear variation of τ versus α suggests that the solvent effect on fluorescence lifetime for R6G is closely related in some way to the hydrogen-bonding between the dye and solvent molecules, rather than the total influence of solvent properties, as proposed by Alobaidi et. al[7].

It is generally believed that changes in fluorescence lifetime could in principle be the result of variation in either radiative or non-radiative decay parameters. In the case

of xanthene dyes. Martin[16] has shown that the effect of hydrogen-bonding between the dye and solvent molecules is mainly on the $S_1 \rightarrow S_0$ internal conversion rate which increases exponentially upon decreases in the energy gap between the initial and final state of transitions. Thus, the enhancement of non-radiative deactivation of excited state via internal conversion might be accompanied by the shift of absorption band of monomeric R6G to longer wavelengths. The well-known red shift of absorption maximum in consequence of the decrease of energy gap, on decrease in hydrogen-bonding ability of solvent was reproduced in our experiment (Fig. 1). But the variation of energy gap does not seems to be an important factor responsible for observed relationship between the τ and α, as shown in Fig. 2. The fluorescence lifetimes for R6G in methanol and water are different at 10^{-4} mol, but the spectral shifts in both solutions are the same. On the other hand, in dilute (10^{-5} mol) solutions, fluorescence lifetimes τ in all alcohols are almost identical despite the fact that the spectral shifts differ depending on the α of solvent used. Therefore we are led to disagree with the statement that the observed variation of fluorescence lifetime for R6G in different solutions is related to the change in relaxation rate by intramolecular processes.

On the other hand, taking into account the fact discovered in the present absorption measurements that accompanying the decrease in hydrogen-bonding ability of solvent in alcoholic solution is an increase in absorbance of aggregated R6G together with the consideration that aggregated R6G Mn ($n=2, 3, 4, \cdots$) was found to be effective in deactivation of fluorescent R6G, M^*, by the bimolecular process[4,5,14,17]

$$M^* + Mn \rightarrow M + Mn^* (n=2, 3, 4, \cdots),$$

we might infer that the observed solvent effect on fluorescence lifetime for R6G is probably governed by the influence of solute-solvent interaction via hydrogen-bonding on R6G aggregation. Thus, since hydrogen-bonding between R6G and solvent molecules would, for example, create a steric hinderance for aggregating with another R6G, such as in alcoholic solutions, where the alkyl substituent of the solvent molecule hydrogen-bonded in complex R6G-solvent would obstruct the approaching of another R6G (or R6G-solvent complex) to it, the higher the hydrogen-bond forming ability α of solvent molecule is, the smaller is the concentration of aggregated R6G. As a consequence, is longer the fluorescence lifetime in this solution. This inference indeed is consistent with the picture observed by us in a series of alcoholic solutions. The fact that fluorescence lifetime of R6G in aqueous solution is shorter than those in alcohols with the same α values, accordingly, might be related to the properties of water molecule, which does not hinder the aggregation of R6G hydrogen-bonded with H_2O.

On the basis of the above mentioned inference concerning the nature of solvent effect on fluorescence lifetime for R6G it is expected that this solvent effect appears only within a certain concentration range, in which the difference in the state of aggregation

of R6G is governed by different α's of solvents. Otherwise, the change in fluorescence lifetime accompanied by the changing of the hydrogen-bonding ability α of solvent would diminish, or even become undetectable. That is the reason why fluorescence lifetime for R6G in solvents with different α values approaches almost the same value when the solution is diluted to such concentration (e. g$\sim 10^{-5}$ mol) at which the aggregated R6G, practically, becames negligible (Table 1). The absence of noticable dependence of fluorescence lifetimes on parameter α of solvents in concentrated R6G solutions (e. g$\sim 10^{-3}$ mol) where the difference in concentration of aggregated R6G governed by the difference in hydrogen-bond donating ability of solvents becomes less important as compared with the total concentration of aggregated R6G in solutions, may be considered as an additional experimental evidence for the inference mentioned above.

All of these taken together leads us to the conclusion that the solvent effect on the observed decay time of fluorescent R6G in proton donating solvents, e. g. water, alcohols, etc; may be attributed to the influence of solute-solvent interaction via hydrogen-bonding on the formation of aggregated Rhodamine 6G which appears to be an important quencher responsible for acceleration of fluorescence decay by excitation transfer mechanism. This solvent effect, however, seems to be dependent on the total concentration of Rhodamine 6G.

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溶剂对若丹明 6G 荧光寿命的影响

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提　　要

采用时间相关单光子计数技术测量了若丹明 6G 在不同溶剂中的荧光寿命。实验结果表明：在若丹明 6G 浓度为 10^{-4} 克分子/立升条件下，它的荧光寿命和溶质分子生成氢键的能力呈线性函数关系。据此，并参照溶剂对若丹明 6G 吸收光谱影响的实验结果，可以认为，溶剂对若丹明 6G 荧光寿命的影响主要是通过在溶质和溶剂分子间生成氢键，从而影响了若丹明 6G 分子发生缔合的容易程度所致。

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* 参加部分实验工作的还有马纫兰同志

光学薄膜专题讨论会在黄山召开

在上海光学仪器研究所的积极努力支持下，中国光学学会光学薄膜专业委员会专题讨论会于 1982 年 8 月 31 日至 9 月 6 日在黄山召开。

出席这次会议的有来自全国各高等院校、科研单位、工厂企业的 76 名代表。会议特邀复旦大学物理系王迅副教授作题为“表面物理、表面分析技术及其与光学薄膜的关系”的报告；贾玉润副教授作题为“薄膜光学性质的测量”的报告；清华大学韩丽英副教授作题为“激光干涉法测量薄膜的光学参数”的报告。他们的报告，受到了与会代表的热烈欢迎。

这次会议采用专题讨论的方式进行。重点讨论光学薄膜的监控和测量方面的工作，包括：宽光谱扫描监控；石英晶体振荡监控和其它监控方法；椭圆偏振测试 n、k、d；散射、吸收与低反射测试和常规测量等六个专题。代表们就科研工作中所取得的成果、发现的问题、解决的方法以及与专题有关的见闻，进行了广泛的交流、讨论。会议开得生动活泼，富有成效。

会议建议：(1) 集中全国椭圆偏振仪进行统测，并在上海、北京设立高精度薄膜参量测试点。(2) 加强石英晶体振荡膜厚监控仪的研制工作，提高质量并加以推广应用。

会议还就专业委员会明年的活动计划进行了初步研究，并增选了专业委员会秘书。

（赵竞满）