EFFECT OF SOAP ON THE FLUORESCENT LIFETIME AND QUANTUM YIELD OF RHODAMINE 6G IN WATER

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Addition of the soap ammonyx LO to a solution of 2×10^{-4} M rhodamine 6G in water lengthens the fluorescent lifetime from 3.8 to 5 nsec, and increases the relative quantum yield by ≈ 1.5. Concentrations of soap and solute are those commonly used in cw rhodamine dye lasers. Comparisons are made with rhodamine 6G in ethanol solutions.

It is well known that addition of a soap [1] † to a rhodamine 6G solution in water significantly lowers the threshold for cw lasing action. Addition of soap presumably results in the removal of dimers [1, 2] in rhodamine solutions, a result verified by changes in absorption and emission profiles. Indeed the addition of 1.5% ammonyx LO by volume to a 2×10^{-4} M rhodamine in water solution makes the sample appear noticeably yellower. We report that addition of soap to the rhodamine–water solution also results in lengthening the fluorescent lifetime and increasing the quantum yield, a result consistent with the reduction of the critical power for cw dye laser operation.

The technique of Mack [3] was used to measure fluorescent lifetimes. Samples were excited at 3472 Å with picosecond pulses derived by frequency doubling a mode-locked ruby laser. Fluorescence was detected with a Hadron 105C S20 photodiode connected to a Tektronix 519 oscilloscope. The time resolution of this system was 0.6 nsec. Great care was taken to avoid stimulated emission without a cavity [4] by expanding the incident laser beam to a large size.

Relative quantum yields [5] among rhodamine 6G solutions were calculated from the total areas under their fluorescence spectra. To measure relative quantum efficiencies quasimonochromatic exciting light at 5000 ± 50 Å was focused on solutions contained in 1-cm long cuvettes and was observed to be absorbed within ≈ 1 mm for the solutions studied. Fluorescence was collected at an angle of 40° with respect to the front surface of the cuvettes into a Jarrell–Ash $\frac{1}{2}$ meter Ebert scanning spectrometer. A photomultiplier (RCA 7265) located at the exit slit of the spectrometer measured the intensity at all spectral wavelengths. Fluorescence spectra were then

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† The active medium was a 2.5×10^{-4} M solution of rhodamine 6G with 1.5% triton-X-100.

Table 1
Fluorescent lifetime and relative quantum yields of rhodamine 6G in different solvents

Solvent	Rhodamine 6G concentration (M)	Lifetime (nsec)	Q_r a)
water	2×10^{-4}	3.8 ± 0.45	0.45 ± 0.05
water and 1.5% ammonyx LO	2×10^{-4}	5.0 ± 0.5	0.69 ± 0.07
ethanol	10^{-1}	≤ 0.6	
ethanol	2×10^{-2}	1.8	
ethanol	2×10^{-3}	4.2	
ehtanol	2×10^{-4}	4.8	1.0
ethanol	1×10^{-5}	3.1	
ethanol	4×10^{-6}	3.1	

a) $Q_r = Q/Q_{\text{ethanol}\,2 \times 10^{-4}\,M}$.

constructed taking account of variations of spectral responses of the spectrometer and photomultiplier but not self-absorption.

Rhodamine 6G was purified by the solvent extraction technique and solutions of 2×10^{-4} M in water were prepared with and without soap. Solutions of rhodamine 6G in ethanol were prepared to study the dependence of the lifetime on the rhodamine 6G concentration.

Fluorescent lifetime and relative quantum yield results are shown in table 1. The lifetime of rhodamine 6G in water increases from 3.8 to 5 nsec with the addition of 1.5% ammonyx LO to the solution. For rhodamine 6G in ethanol the litetime is very short at high concentrations, reaches a maximum at a concentration of about 2×10^{-4} M, and then decreases slightly at lower concentrations. Such lifetime–concentration dependences are known, and data for fluorescein are given in Pringsheim [6]. Relevant parameters determining the lifetime–concentration dependence in rhodamine solutions are self-quenching and dimer formation.

The substantial increase of the fluorescent lifetime and quantum yield of rhodamine 6G in water upon adding soap helps in part to explain why the cw dye and N_2 3371 Å pumped dye laser behaves so favorably to this addition.

We found for our preparations that the addition of the soap increased the lifetime of the rhodamine 6G in water by a significant amount in two days. Presumably the rate at which the dimers break up into monomers depends on the method of mixing the solution.

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