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An emulsion dye laser

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A laser dye which is insoluble in water has been dissolved in hexane and emulsified in a water matrix. When pumped with a nitrogen laser, this mixture was observed to lase. The emulsion is superior to a simple hexane solution because the excellent thermo-optical properties of the water matrix help prevent refractive-index gradients from degrading laser performance. This is a useful characteristic for flash-pumped dye lasers, laser-pumped dye lasers, and liquid filters. Another type of solvent system, a critical solution, is also discussed. For certain dyes, a critical solution has even better thermo-optical properties because of its ability to absorb heat as it undergoes a liquid-liquid phase transition.

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If pumping deposits heat unevenly in the active medium of a laser, beam quality will be degraded by the resulting refractive-index gradients. These gradients can refract light sufficiently to increase divergence, destroy spectral purity, decrease power, and in severe cases quench laser action.[1] Gradients begin to form less than 1 μsec after pump energy is deposited, and they last until thermal homogeneity has been restored. The severity of the formation of these gradients depends on the thermo-optical properties of the liquid, namely, the specific heat C_p and the refractive-index change with temperature dn/dT. Water has the best thermo-optical properties of any common solvent. Because of extensive hydrogen bonding it has a high heat capacity (4.184 J/°K cm^3) and a low $dn/dT (1.0\times 10^{-4}\,\text{deg}^{-1}$ at 25 °C and $0.2\times 10^{-4}\,\text{deg}^{-1}$ at 0 °C). Unfortunately, many laser dyes are insoluble in water, and some organic solvent must be used. All organic solvents are at least eight times worse than water when judged on the basis of refractive-index change per joule of heat added to a cubic centimeter of the liquid.

A new approach to this problem is to dissolve the dye in an orgainc solvent and then emulsify this solution into water. The average dye concentration can be high enough to lase, and the small droplets rapidly transfer excess heat to the water matrix, thus maintaining excellent thermo-optical properties. In this paper, we report the operation of such an emulsion dye laser. The emulsion was made from a hexane solution of BBOQ (4,4‴-di(2-butoctoxy-1)-*p*-quaterphenyl) emulsified in a glycerine/water mixture. A 50-KW nitrogen laser was used for pumping.

The most serious threat to the operation of such a laser is light scattering at the laser wavelength by the small droplets. This can be minimized by matching the refractive index of the two phases. Because both the scattering and rate of heat transfer depend on droplet size, we next present calculations to show that small droplets are preferred. It is assumed that the average concentration of the dye in the emulsion is near $10^{-3}M$ and that the minimum amount of organic solvent has been used to achieve this concentration.

For droplets of radius r, large compared to the wavelength of light, and with refractive indexes fairly well matched to the matrix, Mie scattering occurs.[2] The fractional decrease in intensity of transmitted light I/I_0 due to scattering by N spherical droplets of radius r is given by

$$I/I_0 = \exp[-8\pi^3 N l r^4 (n_2 - 1)^2 \lambda^2]. \tag{1}$$

Here, l is the length of the light path, λ is the wavelength of interest, and n_1 and n_2 are the refractive indexes of the two phases.

To take full advantage of Eq. (1), we must describe N more fully. If one assumes that a given volume of dye solution V_1 will remain emulsified in some initial volume V_2 of the aqueous phase, then the possible number of droplets per unit volume is

$$N = \frac{3V_1}{4\pi r^3 (V_1 + V_2)}. \tag{2}$$

Substituting this into Eq. (1) we obtain

$$I/I_0 = \exp[-6\pi^2 r l V (n_1/n_2 - 1)^2/\lambda^2], \tag{3}$$

where V is the volume fraction of the organic phase. From Eq. (3) it is clear that to minimize scattering one should minimize the path length l, the volume fraction V, the droplet radius r, and the refractive-index mismatch. The path length is a matter of laser design and will not be discussed further here. To minimize the volume fraction one must select an organic solvent in which the laser dye is very soluble so the average concentration can be brought up to the threshold for laser action. Care must be taken to avoid dye concentrations high enough to cause dimerization or other quenching processes. Droplet radius is a function of the emulsifying technique and the intrinsic tendency of the organic solvent to form emulsions in water. It should be noted that extremely small droplets (micelles) are formed by soaps and detergents, and that dye molecules in these micelles have been shown to lase.[3] Also, microemulsions (droplets smaller than the wavelength of light) can be formed by the proper choice of components.[4] They scatter even less light than the macroemulsion used in this work, and so they should make excellent laser dye solvents. We selected a macroemulsion to provide a more severe test of the emulsion laser. Our scattering equations do not apply to small droplets and micelles, but it should be kept in mind that for some dyes they may be better than the droplets of a macroemulsion.

The refractive-index mismatch plays a decisive role in the scattering. It causes the exponential part of Eq.

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TABLE I. Candidate solvents for emulsion lasers.

Solvent	Refractive Index $n_{D,20^\circ C}$	$\left(\frac{dn}{dT}\right)\times 10^4$	Water solubility in aq, 25 °C	aq in 25 °C
Water	1.3330	0.8	NA	NA
Methyl formate	1.34332	4.4	23	...
2-Methylbutane	1.35373	5.8	0.0048	0.0097
Ethyl formate	1.35994	4.4	11.8	17.0
Methyl acetate	1.3614	...	24.	8.
2-Methylpentane	1.37145	4.6	0.0014	...
Ethyl acetate	1.37239	4.9	8.08	2.94
n-hexane	1.37486	5.4	0.00095	0.0111
Glycerol	1.4746	2.4	infinite	infinite

(3) to overwhelm the gain of the active medium; no laser action is possible. Because laser dyes have such high gain, slight mismatches are not serious. Nevertheless, if there is no mismatch, there is no scattering. The organic solvent must be selected to have a refractive index near that of water, but must not be miscible with water or no emulsions can be formed. Promising candidates are listed in Table I.

The BBOQ emulsion laser was prepared in the following manner. A saturated solution of BBOQ(4, 4‴-di(2-butoctoxy-1)-*p*-quaterphenyl) in *n*-hexane was prepared to obtain the maximum concentration of dye into the emulsion. Glycerol was mixed with water in the ratio 35 : 65 wt% to match the refractive index of the *n*-hexane. Equal volumes of the two solutions were mixed in a blender at high speed for 2 min. Although the emulsion separated into two phases after about 10 min, it was stable long enough to be tested for laser action. Emulsifiers and surfactants can be used to stabilize the emulsion for much longer periods, but they must not absorb the laser or the pump light. Microemulsions are stable indefinitely, or in the worst cases, for months. When our emulsion was pumped in a 10-mm quartz fluorimeter cell by a 50-kW nitrogen laser beam, lasing was observed perpendicular to the incident pump light.

An advantage of the emulsion dye laser is that any water-insoluble dye can be emulsified into a mixture which is largely water and therefore has good thermo-optical properties. A solvent with even better thermo-optical properties is a critical solution operated near its lower critical solution temperature (LCST). If the temperature is raised even slightly, the solution breaks into two phases and this transition absorbs much of the added heat without allowing very much temperature increase. An example of such a critical solution is a 45 : 55 wt% mixture of triethylamine in water. Its LCST is 18.5 °C. The apparent heat capacity of such a solution over a 12 °C range near the LCST is approximately eight times that of pure water.[3] The peak apparent heat capacity is even higher.

There are a number of other organic liquids which form critical solutions with water,[5] each with its own lower critical solution temperature. The properties of the single phase are such that most laser dyes are more soluble in it than in pure water, so both excellent thermo-optical properties and good dye solubility are realized with certain critical solutions.

If a laser based on such a solvent is to continue operation after phase separation has produced droplets, then some other material must be added to bring the refractive index of the droplets to that of the matrix or light scattering will quench laser action. In small quantities, such an additive decreases the LCST and probably slightly changes the apparent specific heat of the liquid, but neither is a serious effect in laser operation.

In summary, to minimize optical distortion in liquid lasers, water near its freezing point should be used. The next best choice is water at some higher temperature. If the lasing material (such as an organic dye) is insoluble in water, it may be possible to retain many of water's thermo-optical properties by emulsifying a dye-saturated organic solvent into the water. We have observed laser action from such an emulsion when the refractive indexes of the two liquids are matched. Finally, if the dye is soluble in a critical solution such as triethylamine in water, thermo-optical properties will be improved by heat absorption at the LCST as the phases separate. It should be noted that these same solvents will improve the thermo-optical properties of liquid filters and liquid saturable absorbers, thus minimizing beam distortion.

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