

Refractive Indices and Thermo-Optical Properties of Dye Laser Solvents

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Abstract. By measuring the wavelength tuning of a distributed feedback dye laser, solvent refractive-index changes as small as 0.0002 may be determined. This technique hence allows precise measurement of refractive-index dependence on temperature (dn/dT) and therefore enables the thermo-optical properties of solvents used in dye lasers to be assessed. In addition to single component solvents, the thermo-optical properties of solvent mixtures and additives are reported here. The refractive-index change with temperature (dn/dT) is related to solvent density change with temperature ($d\rho/dT$) through molecular polarizability.

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A major limitation on achieving high-power, spectrally narrow and spatially coherent radiation from dye lasers lies in the formation of refractive-index gradients due to non-uniform heating by the pump radiation in the region of optical gain. Pump radiation is converted into heat in the dye solution by two processes; radiationless deactivation of molecules in excited states, the proportion of which determines the dyes fluorescence efficiency, and through the Stokes shift since the emitted photons are less energetic than the absorbed photons. Typically about 25% of incident light is converted into heat, within a confined area. In high-power cw and pulsed dye lasers the formation of such refractive-index gradients acts as a thermal lens with severe consequences for output power [1], cavity stability [2], spatial coherence [3], and minimum linewidth obtainable [4]. Further, the effect has been shown to be a major limiting factor in narrow linewidth operation of distributed feedback dye lasers (DFDL) [5]. The quantity dn/dT , the rate at which solvent refractive-index changes with temperature, is a most useful parameter in assessing a solvent thermo-optically. Accurate values of dn/dT for a wide range of dye laser solvents, solvent mixtures and solvents with additives are reported here for the first time.

1. Experimental Method

The DFDL, originally reported by Shank (1971), is a simple device for producing tunable dye laser radi-

ation. The two pump beams, obtained from the same laser, are caused to intersect in the cell containing the dye solution. An interference pattern is produced along the axis of the dye cell, the period of which is dependent only on the free-space wavelength of the pump laser, λ_p , and the angle of intersection, θ . This interference causes Bragg backscattering of radiation with a wavelength in the solvent equal to twice the grating period, thus providing frequency selective feedback. As a result the free-space wavelength at which the dye laser oscillates is given by

$$\lambda_d = \frac{n\lambda_p}{\sin\theta}, \quad (1)$$

where n is the solvent refractive index at wavelength λ_d . As can be seen from (1), this wavelength can be tuned by altering n , λ_p , and θ . The pump laser used was a frequency-doubled Nd:YAG laser (Quantel YG480), which was slow Q-switched to produce narrow-linewidth (single longitudinal mode) pulses of duration 12 ns and energy 1 mJ at a wavelength of $\lambda_p = 532$ nm. In order to determine dn/dT for a solvent the change of lasing wavelength λ_d was measured, using a high-resolution monochromator (Rank Hilger Monospek 1000) giving resolution down to 0.01 nm, as the dye solvent temperature was changed by using a refrigerator unit in the circulator system. Equation (1) was then used to deduce the associated change in refractive index. The DFDL wavelength was normally

around 600 nm. DF DL linewidth, and shot to shot fluctuation of DF DL wavelength were less than the resolution limit set by the monochromator. This technique was first demonstrated by McIntyre and Dunn [6]. In the tables of results to follow, where a numerical value of dn/dT is quoted for a particular temperature this represents a least squares fit over the range $\pm 2^\circ\text{C}$ around that temperature. Since n is recorded every 0.5°C each fit utilizes nine data points. Errors quoted in brackets are the standard deviation of the fit to the data. Values of dn/dT are quoted for 20 and 5°C representing room-temperature and cooled dye-laser operation, respectively.

2. Background

The Lorentz-Lorenz formula [7] relates the mean polarizability α to the refractive index n and the number of molecules per unit volume N by

$$\alpha = \frac{3}{4\pi N} \frac{n^2 - 1}{n^2 + 2}. \quad (2)$$

Using the molar refractivity A , which is essentially the total polarizability of a mole, (2) may be written as

$$\frac{n^2 - 1}{n^2 + 2} = \frac{A}{W} \rho, \quad (3)$$

where W is the molecular weight, and ρ the density. For a mixture of liquids, the refractive index of the mixture is given by

$$\frac{n_m^2 - 1}{n_m^2 + 2} = \left(\frac{A_1}{W_1} f_1 + \frac{A_2}{W_2} f_2 \right) \rho_m = \left[\frac{A}{W} \right]_m \rho_m, \quad (4)$$

where n_m and ρ_m represent the refractive index and density, respectively, of the mixture. A_1 , A_2 and W_1 , W_2 represent the molar refractivities and molecular weights of molecules type 1 and 2. f_1 and f_2 are the fractions, by mass, of molecules of type 1 and 2. Refractive index and density are functions of temperature (T), but molar refractivity is expected to be independent of temperature, so that we have

$$\frac{n_m^2(T) - 1}{n_m^2(T) + 2} = \left[\frac{A}{W} \right]_m \rho_m(T). \quad (5)$$

Hence assuming that the refractivity of a liquid is constant, dn/dT may be estimated from the density, refractive index and $d\rho/dT$, by differentiating (5) with respect to temperature to find

$$\frac{dn_m}{dT} = \left[\frac{A}{W} \right]_m \frac{(n_m^2 + 2)^2}{6n_m} \frac{d\rho_m}{dT}. \quad (6)$$

However, since

$$\left[\frac{A}{W} \right]_m = \frac{1}{\rho_m} \frac{n_m^2 - 1}{n_m^2 + 2},$$

(6) may be expressed in terms of the macroscopic properties of density and refractive index.

3. Results

Solvents for dissolving organic dyes may be divided into three main categories: a) Simple organic solvents, e.g., methanol, ethanol, ethylene glycol, and mixtures of them; b) Water based solvents, e.g., pure water or water based solutions such as ammonyx LO. Using a) and b) together yields a third class of dye laser solvent i.e., c) Mixtures of water based solvents and organic solvents, e.g., ethylene glycol/ammonyx LO. The need for this class of solvent, as will become apparent shortly, is to combine good solubility of the laser dye with good thermo-optical characteristics.

3.1. Organic Solvents

The most commonly used dye-laser solvents are contained in this class, e.g., methanol, ethanol, ethylene glycol, benzyl alcohol and propylene carbonate. Figure 1 shows the variation of refractive index with temperature for ethylene glycol and methanol which are typical of this group. Since the dn/dT 's of these organic solvents are, to within 10% independent of temperature, results are quoted as a straight line fit over the temperature range of $5\text{--}25^\circ\text{C}$. Results of all the organic solvents we measured are found listed in Table 1, and show that the dn/dT 's of these organic solvents are much higher than that of water. These liquids, unlike water, have a normal density/temperature behaviour, i.e., their density decreases linearly, by

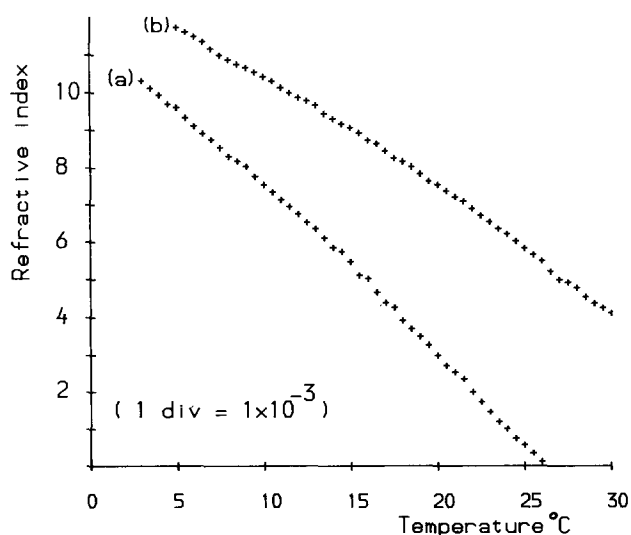


Fig. 1. Refractive index against temperature of *a* methanol, and *b* ethylene glycol. Vertical axis divisions correspond to a change in refractive index of 1×10^{-3} . Methanol had the largest dn/dT of any of the solvents measured

Table 1. Measured values of dn/dT (over range 5–25 °C) for organic solvents. For convenience refractive index data for the individual solvents is given in brackets, and is taken from CRC [8] tabulated values

Solvent	$n(20\text{ °C})$	dn/dT [-1 $\times 10^{-5}\text{ K}^{-1}$] (5–25 °C)
Methanol	(1.327)	46.8(1.1)
Ethanol	(1.360)	43.8(0.4)
Ethylene glycol	(1.431)	30.6(0.3)
Benzyl alcohol	(1.540)	42.0(0.4)
Propylene carbonate	(1.421)	38.0(0.4)
50/50 BA/PC	(1.471)	42.0(0.5)

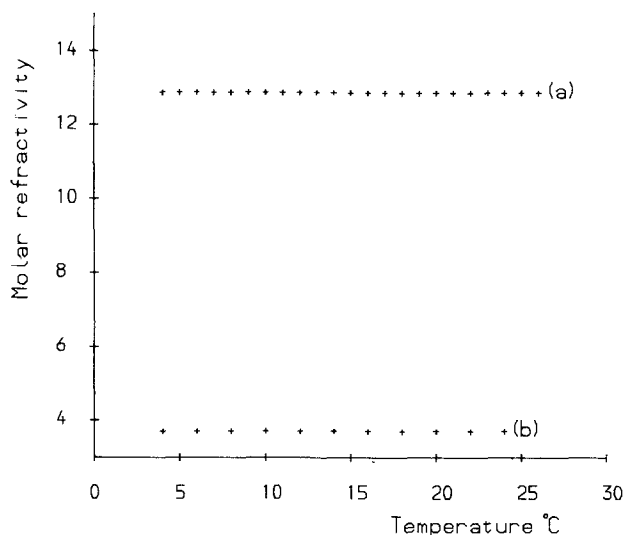


Fig. 2. Molar refractivity against temperature for *a* ethanol, and *b* water. In both cases the refractivity is constant to 1 part in 10^4

expansion, with increasing temperature. In order to verify that the temperature dependence of refractive index is due solely to the temperature dependence of density, as implied by (5), we have plotted in Fig. 2a, A as a function of temperature deduced from our measured values of $n(T)$ and CRC tabulated values of density [8] for ethanol. The constancy of A with temperature verifies this assumption. Its value of 12.9 is close to that expected from the addition of generally accepted atomic refractivities [8], which gives 13.2.

3.2. Water Based Dyes

Water-based solvents are generally regarded as superior in their thermo-optical properties since dQ/dT and hence from (6) dn/dT is small in comparison with other liquids. Furthermore the density of water increases until 4 °C, the temperature at which the density

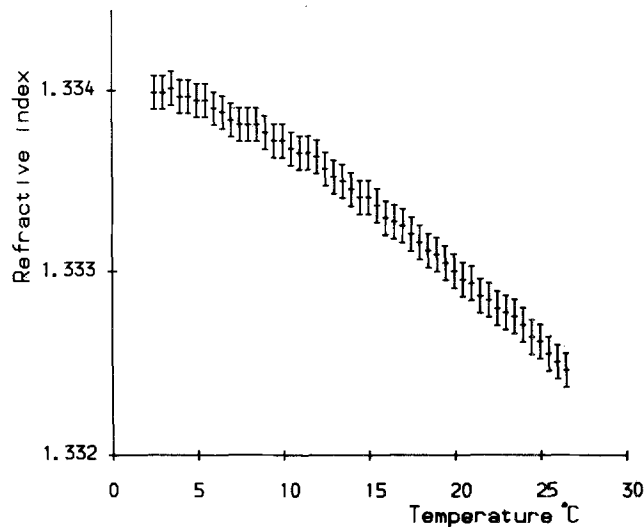


Fig. 3. Refractive index against temperature of pure water. Vertical axis divisions correspond to a change in refractive index of 1×10^{-3} . Around 4 °C refractive index is constant i.e. $dn/dT=0$

is at a maximum, i.e. dQ/dT equals zero. Thus for small changes in temperature around 4 °C, dn/dT may be expected to be zero, although there is some doubt about the exact temperature at which this occurs [9]. It is this particular property, exhibited only by water, that makes it the best solvent thermo-optically. Figure 3 shows the measured refractive index versus temperature profile for water and it can be seen that around 4 °C there is no detectable change in refractive index with temperature. The molar refractivity A of water is plotted as a function of temperature on Fig. 2b using our measured values of refractive index and CRC [8] values for density. As is the case of ethanol, the refractivity is constant, with $A=3.71$. This compares very well with the tabulated values of 3.72 [7, 8]. However dye lasers based on aqueous solutions exhibit low efficiencies. This is due to the association of dye molecules to produce dimers, whose absorption spectra lie in the absorption region of the lasing monomers and also frequently overlap their fluorescence band hence reducing the fluorescence efficiency. In organic solutions dimerization is slight and hence the efficiency is much improved. It is possible however to suppress this process of dimerization by the addition of organic compounds to water [10–13]. This class includes the two soaps ammonyx LO (lauryl dimethylamine oxide) [10, 11], Triton-X100 [12], and the much simpler compound urea $\text{CO}(\text{NH}_2)_2$ [13], and indeed in our DF DL we have observed an increase in efficiency using these products. What has been misunderstood however is their effect on the temperature dependence of refractive index. To this end we have characterized the effects of the addition of both ammonyx LO and urea.

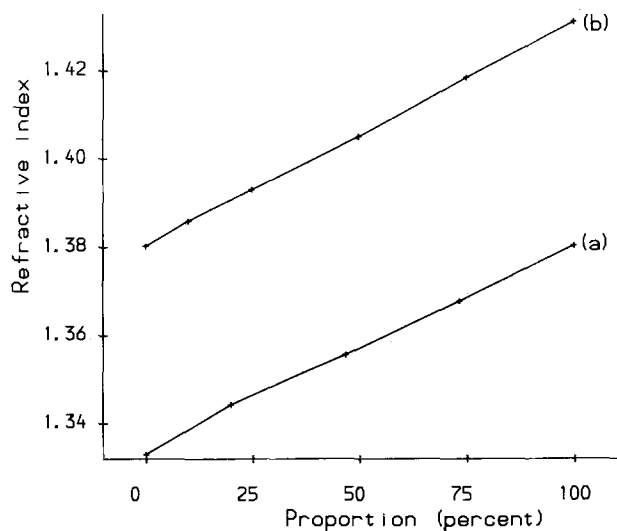


Fig. 4. Refractive indices for *a* water/ammonyx LO series, and *b* ammonyx LO/ethylene glycol series. 0% represents pure water in *a*, and pure ammonyx LO in *b*

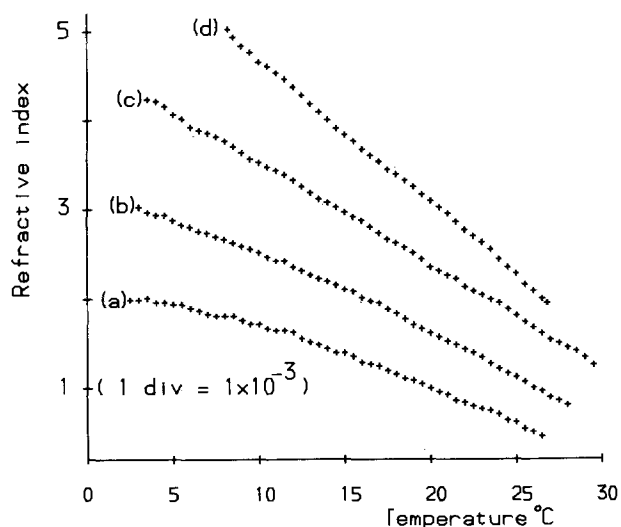
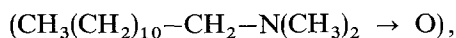


Fig. 5. Refractive index against temperature of *a* pure water, *b* 75% water 25% ammonyx LO, *c* 50% water 50% ammonyx LO, *d* 100% ammonyx LO. Vertical axis divisions correspond to a change in refractive index of 1×10^{-3} . As ammonyx LO is added the dn/dT of the solvent is increased in proportion to the amount added

i) *Ammonyx LO/Water Series*. The ratio of liquid ammonyx LO [30%, by mass lauryl dimethylamine oxide



70% water] to water was varied in this experiment from 0 to 100% by volume and two features of refractive index measured, namely: *a*) bulk index (the refractive index at 20 °C) for different proportions of ammonyx LO and water; and *b*) temperature de-

Table 2. Measured refractive index n versus temperature for ammonyx LO

Temperature [°C]	Refractive index
26.0	1.3793
24.0	1.3796
22.0	1.3800
20.0	1.3803
18.0	1.3806
16.0	1.3809
14.0	1.3812
12.0	1.3816
10.0	1.3819
8.2	1.3822

Table 3. Measured molar refractivity for mixtures of water and ammonyx LO

Substance	Mol.-wt.	Refractive index	Density [g/cc]	A from (5)
Water	18.0	1.333	0.98	3.71
Ammonyx LO	24.9	1.380	0.96	6.00
Lauryl amine oxide	229.0	—	—	74.10

pendence of refractive index dn/dT for particular mixes. Results to part (*a*) are given in Fig. 4*a*. These show that the measured bulk index is equal to the ratio by volume of ammonyx LO times its refractive index ($n(20^\circ\text{C})=1.380$) plus the ratio by volume of water times its refractive index ($n(20^\circ\text{C})=1.333$), as is to be anticipated on the basis of simple proportionality. Note that we were unable to cool the solution to less than 8.2 °C due to its high viscosity. Results to part (*b*) are given in Fig. 3, for pure water, and Fig. 5 for varying proportions of ammonyx LO. Since ammonyx LO is a commonly used solvent the refractive index/temperature relation is listed more fully in Table 2. The effect of the addition of lauryl dimethylamine oxide to water may be explained using (4). To determine the molar refractivity of the ammonyx LO active ingredient (lauryl dimethylamine oxide) Eq. (4) is solved using the following values: $n_m=1.380$, $W_1=18$ g, $W_2=229$ g, $f_1=0.7$, $f_2=0.3$, $\rho_m=0.96$ g cc^{-1} and $A_1=3.71$ to give A_2 , the molar refractivity of the lauryl dimethylamine oxide molecule, as 74.1. This last figure may be checked by the usual procedure of the addition of the refractivities of the constituent atoms [7, 8], which gives $A=72.63$, in good agreement with our experimentally obtained value. Results are shown fully in Table 3. The molar refractivity A versus temperature was obtained using refractive index and

density values which were experimentally obtained as a function of temperature for the mixture of 1:1 by volume of ammonyx LO: water. The density/temperature measurement for this mix showed that $d\rho/dT$ was always non zero. As was observed previously with ethanol and water, the molar refractivity of the mixture was independent of temperature, to greater than 1 part in 10^{+4} showing that the refractive-index behaviour is due solely to the change in the density with temperature, the addition of ammonyx LO acting to suppress the agglomeration of water molecules which normally leads to a density minimum. Since the dn/dT of pure ammonyx LO is similar to that of a normal liquid (Fig. 5d), i.e. no flat portion in dn/dT , the addition of ammonyx LO will degrade the thermal properties of water in proportion to the amount added. On the basis of these results, the commonly used proportions of 1.5 to 4% ammonyx LO [11, 14] produce only a slight degradation in the thermal properties.

The use of ammonyx LO at much higher concentrations has been reported, e.g. 18% [15] or 20% [16] have been used, and indeed 100% ammonyx LO [1] has been proposed as solvents with claimed good thermal properties for use in high-power dye lasers. However, as can be seen from Fig. 5, at these concentrations there is a significant increase in the dn/dT compared with water with consequent degradation of thermal properties.

ii) *Water/Urea Series.* Viktorova et al. [13] reported an observed increase in fluorescence efficiency from ~ 0.4 in water to ~ 0.7 on addition of 40% by mass of urea, while still retaining the good thermo-optical properties of water. Figure 6 shows the measured effect on dn/dT of the addition of 10% and 30% urea, compared with pure water. As can be seen from Fig. 6 the effect of adding 30% urea to water is substantial. This mixture has a dn/dT approaching that of organic solvents, hence rendering it poor thermo-optically. An empirical expression for the refractive index of the solution is;

$$n_m = n_{\text{water}} + \beta P, \quad (7)$$

where P is the proportion by weight of urea, and β , which is a function of temperature is given by

$$\beta = 0.1308 - (5.084 \times 10^{-4} T)$$

for the range 0–30 °C, where T is the temperature in °C. While no density/temperature measurements were made for the water plus urea solution we strongly suspect that the effect is similar to the addition of ammonyx LO to water as described in the previous subsection.

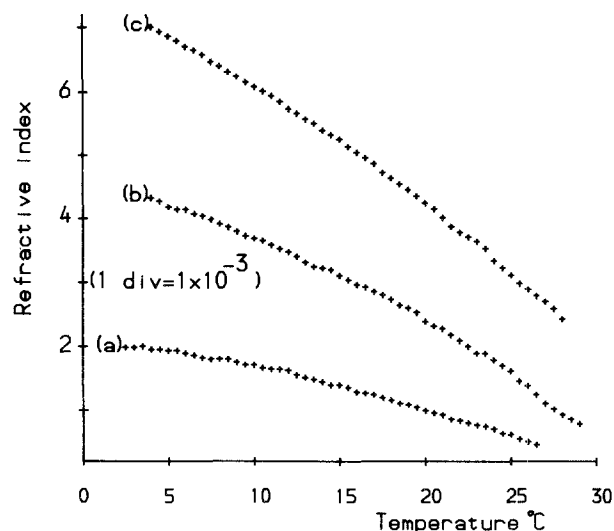


Fig. 6. Refractive index against temperature of *a* pure water, *b* water with 10%, by mass, urea, and *c* water with 30%, by mass, urea. Vertical axis divisions correspond to a change in refractive index of 1×10^{-3}

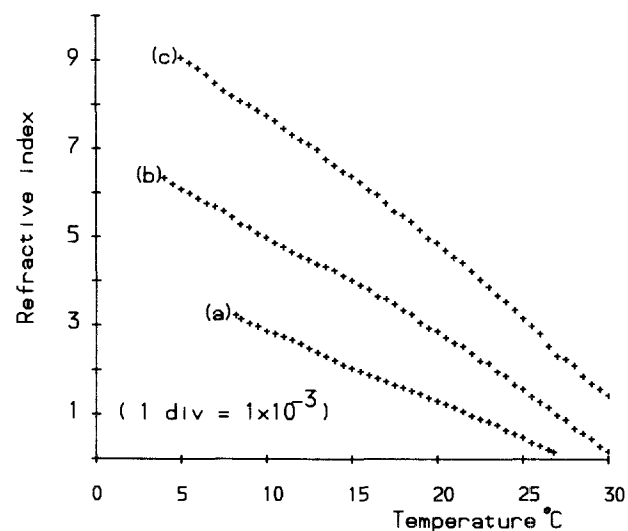


Fig. 7. Refractive index against temperature of *a* ammonyx LO, *b* 75% ammonyx LO 25% ethylene glycol, and *c* 100% ethylene glycol. Vertical axis divisions correspond to a change in refractive index of 1×10^{-3} . As expected the mixtures of these two solvents have index properties (n , dn/dT) inherited from the parent solvents

3.3. Solvent Mixtures

In this class are mixtures of water based solvents, mixtures of organic solvents, or mixtures of water based and organic solvents. In Sect. 3.1 the solvents benzyl alcohol and propylene carbonate were combined in equal proportions to observe the resultant dn/dT . This experiment shows that, to a good approximation, the index properties (n , dn/dT) of mixtures are given by an average of the index properties of the

parent solvents weighted in proportion to their percentages in the mixture. It has been claimed [1] that by adding 25% ethylene glycol to an ammonyx LO solution that the desired flat spot in the dn/dT of water may be preserved, although shifted to higher temperatures (10°C). However, since we had observed a non-zero dn/dT in ammonyx LO, and a larger dn/dT in ethylene glycol we did not expect a zero dn/dT for any combination of ammonyx LO/ethylene glycol. The results of this experiment are shown on Fig. 4b for the bulk indices (20°C) and Fig. 7 for dn/dT 's, and as with other solvent mixtures, show that the bulk index and the dn/dT for a particular solvent mix is simply inherited from the parent solvents in proportion to their percentages in the mixture. This combined with the evidence of the water/ammonyx LO series allows us to conclude that the effect of mixing two or more liquids is simply to add proportionally their bulk indices and dn/dT 's.

4. Conclusion

We have measured, using the technique first described by McIntyre and Dunn [6], the refractive indices of most commonly used dye laser solvents. The results of these measurements are tabulated in Tables 1 and 2. From these it can be seen that dn/dT is smaller for water than for organic solvents, and furthermore that dyes dissolved in water which is cooled to 4°C represents the best obtainable solvent, since dn/dT is zero at this temperature, in terms of thermo-optical properties. It has been recognized [10] that organic additives generally improve the quantum efficiency of dyes dissolved in water. The effect of these additives on dn/dT and hence the thermo-optical properties is reported here for the first time and, contrary to previous claims, it is found that an additive superimposes an additional dn/dT on that of water. For liquid mixtures the resultant dn/dT is simply the proportional average of the parent dn/dT 's. For the temperature range of interest the molecular polariza-

bility of liquid molecules is seen to be constant hence indicating that the changes in refractive indices reported are derived from density change with temperature. Thus if density/temperature measurements are available, dn/dT , and hence the thermo-optical suitability, may be inferred. Since water is unique in its $d\rho/dT=0$ at around 4°C it still remains the best solvent thermo-optically, despite attempts to engineer superior ones.

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