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Thermo-optical properties of some common laser-dye solvents

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Abstract

We have used a laser interferometric method to determine the refractive index of some laser dye solvents with a high accuracy 5.8×10^{-4}. The determination of refractive index (n) was performed by counting the interfering fringes (N) as a function of the incidence angle of the laser beam. The absolute refractive index of pure water, Dimethylsulfoxide (DMSO), and deferent mixtures, P (percentage), (25%, 50%, and 75% of DMSO) of them were measured. The relation between the bulk refractive index (n_m) of these mixtures are plotted as a function of the investigated portions (P). The temperature behavior (dn_m/dt) of these refractive indices were studied carefully within a temperature range (from 20°C to 80°C). It was found that both the refractive index (n_m) and temperature behavior of the refractive indices (dn_m/dt) of that different mixtures of the investigated solvents are the average index properties of the parent solvents. Also, we did a fitted imperical relation to formulate the relation between n_m, P, and t $N_m = ap^b t^c$; with an imperical constants a, b, and c. According to the equation we recalculated n_m of the solvent mixtures and we found an agreement with a very little difference.

Keywords: Refractive index; Laser-dye solvents; Thermo-optical properties

1. Introduction

When the pump laser beams are incident upon the dye solution it will be absorbed causing a heat change in the solution. The density of the solution will change tending to change the refractive index (n) of the solution. The formation of the refractive-index gradients due to non-uniform heating by the pump radiation in the region of the optical gain give a major limitation on achieving high power, spectrally narrow and spatially coherent radiation from the lasers. There are two mechanisms by which the pump radiation is converted into heat in the dye solution [1]:

1. Radiation-less de-activation of molecules in excited states, the proportion of which determines the dyes fluorescence efficiency; and
2. The Stokes Shift ($1-\nu_{laser}/\nu_{pump}$) since the emitted photons are less energetic than the absorbed photons.

Also, the environmental temperature cause the same effects like the ones caused by the pump radiation conversation into heat in the solution. The inhomogeneous heating causes an inhomogeneous distribution of the refractive index of the dye solution which causes a thermal lensing effect which in turn influences the stability of the optical system and reduces the maximum pump power. In addition, the temperature change of the laser dye will defocus the laser beam when $dn/dt < 0$ or focus the beam when $dn/dt > 0$. The rate of change of the refractive index (dn/dt) with temperature of the solvent is a most useful parameter to achieve the thermo-optical properties of a solvent. The accurate value of $|dn/dt|$ is essential to determine the dependence of the critical pump intensity $P_{crit.}$ [1,2] which is given as

$$P_{crit.} \leq \frac{\sqrt{2\pi}\rho c}{(4\delta[1-\exp(-yl)]|dn/dt|\exp(2y^2/\omega_A^2)(\nu\omega_A/S)} \quad (1)$$

where:

S	Stability range of the unperturbed dye laser resonator,
δ	Percentage value of the pump power which is converted into heat,
ρ	Density,
l	Thickness of the jet stream,
ν	Flow velocity, and
ω_A	Beam radius of the focused pump laser.

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The values of both n and (dn/dt) of the mixtures are studied carefully by using Mach–Zehnder interferometer (MZI) with a high degree of accuracy and are reported in the present paper.

2. Experimental

The Mach–Zehnder interferometer (MZI) was used as an accurate measurement technique to determine the refractive index (n) of the solvent [3]. The refractive index of both pure water and the dimethyl sulfoxide (DMSO) was determined at the ambient temperature and then as a function of temperature. The solvent mixture was done from DMSO and pure water with different percentages (P). The refractive index of the different mixtures were measured at different temperatures. The sample was contained within a rectangular quartz cell in one of MZIs arms. The light source of the interferometer is the He–Ne laser at 632.8 nm wavelength. The cell was fixed on the base plate of a spectrometer to enable us to change the incident angle of laser beam with a small fraction of degree for 10 min. The whole range of the incidence angle was 5°–30° with step 30 min measured at both right and left side of the beam to reduce the error as much as possible. The solvent refractive index was determined with a high degree of accuracy 5.8×10^{-4}. By counting the number of the interfering fringes (N) produced as a function of the incidence angle (φ) of the expanded laser beam, one can determine the refractive index (n) of the given sample by the graphical representation [4] of the following relation;

$$n = \frac{(t - N\lambda)(1 - \cos\varphi) + (N^2\lambda^2/2t)}{t(1 - \cos\varphi) - N\lambda} \quad (2)$$

where:

φ	Angle of incidence,
N	Number of fringes,
t	Cell thickness (10 mm)
λ	Wavelength of the laser source (632.8 nm).

The term $N^2\lambda^2/2t$ can be neglected [5] as it is very small.

In order to determine the value of (dn/dt) for a solvent the change of the number of fringes was measured as the dye solvent temperature was changed by using a thermal heating unit. Eq. (1) was used to deduce the associated change in refractive index (Δn). At normal incidence of the laser beam ($\varphi = 0$) one can use the neglected term of Eq. (2) at temperature T_1 and then at temperature T_2. One can count the change in the number of fringes (ΔN) which cross the field of view corresponding to the change of sample temperature (Δt). Therefore, the change of the refractive index (Δn) is determined as a function of the number of fringes which has been changed (ΔN) as follow;

$$(\Delta n) = \left(\frac{\Delta N}{2t}\right)\lambda \quad (3)$$

3. Theoretical background

3.1. Mean-polarizability and dielectric constant

The mean polarizability (α) can be determined as a function of refractive index (n) of a sample in accordance to the following relation:

$$\alpha = \left(\frac{3}{4\pi M}\right)\left(\frac{n^2 - 1}{n^2 + 2}\right) \quad (4)$$

Where, M is the number of molecules per unit volume.

By using the Maxwell's relation between the dielectric constant (ε) and the refractive index (n) for a non-polar material which gives:

$$\varepsilon = n^2 \quad (5)$$

Therefore, one can rewrite Eq. (4) as:

$$\alpha = \left(\frac{3}{4\pi M}\right)\left(\frac{\varepsilon + 1}{\varepsilon + 2}\right) \quad (6)$$

that is, the mean polarizability (α) can be determined as a function of either (n) and (M) or (ε) and (M).

For a polar material one can use the following equation to calculate the dielectric constant (ε) and the permanent dipole moment (μ_0) of the molecule under investigation [6]:

$$\left(\frac{\varepsilon - 1}{\varepsilon + 2}\right) - \left(\frac{n^2 - 1}{n + 2}\right) = \frac{3\varepsilon(n^2 + 2)}{(2\varepsilon + n^2)(\varepsilon + 2)}\left(\frac{4\pi M\mu_0^2}{9kT}\right) = \left(\frac{4\pi M\mu_0^2}{9kT}\right) f(\varepsilon, n^2) \quad (7)$$

with

$$f(\varepsilon, n^2) = \frac{3\varepsilon(n^2 + 2)}{(2\varepsilon + n^2)(\varepsilon + 2)}$$

where μ_0, is the permanent dipole moment of the molecule and k, the Boltzmann's constant.

3.2. Molar refractivity (A)

The molar refractivity (A) is essentially the total polarizability of a mole for the substance [7], being defined as:

$$A = \left(\frac{4\pi}{3}\right) N_{\mathrm{Avo}}.\alpha \quad (8)$$

where $N_{\mathrm{Avo.}}$, is the Avogadro's number.

For a mono-atomic substances it is called atomic refractivity.

In terms of the molecular weight (W), the density (ρ) and the refractive index (n) of the substance, one can write the molar refractivity (A) in the form:

$$A = \left(\frac{W}{\rho}\right)\left(\frac{n^2-1}{n^2+2}\right) \tag{9}$$

The quantity:

$$\ddot{r} = \left(\frac{n^2-1}{n^2+2}\right)\left(\frac{1}{\rho}\right)$$

is called the specific refraction of a substance, for a given substance r is independent of ρ. Therefore [8]:

$$A = rW \tag{10}$$

3.3. Molar refractivity of a mixture

The molar refractivity of a mixture of two substances is equal to the sum of the contributions due to each substance. Thus, if two liquids of refractivities A_1 and A_2 are mixed, and if a unit volume of the first liquid contains N_1 molecules and of the second N_2 molecules, then the molar refractivity of the mixture will be:

$$A = \left(\frac{N_1A_1 + N_2A_2}{N_1 + N_2}\right) \tag{11}$$

Finally, we consider the dependence of the molar refractivity A of a compound on the atomic refractivities of its constituent atoms. If the molecule consists of N_1 atoms of refractivity A_1 and of N_2 atoms of refractivity A_2, etc., then obviously

$$A = N_1A_1 + N_2A_2 \tag{12}$$

3.4. (n_m) of a mixture

For a mixture of different liquids, the refractive index of that mixture (n_m) is given by [9];

$$\left(\frac{n_m^2-1}{n_m^2+2}\right) = \left[\frac{A_1}{W_1}f_1\right] + \left[\frac{A_2}{W_2}f_2\right]\rho_m = \left(\frac{A}{W}\right)_m \rho_m \tag{13}$$

where:

A_1 and A_2	Molar refractivities of molecules of types 1 and 2
W_1 and W_2	Molecular weights of molecules types 1 and 2
f_1 and f_2	Fractions, by mass, of molecules of types 1 and 2
n_m	Refractive index of the mixture, and
ρ_m	Density of the mixture.

3.5. Temperature behavior (dn/dt)

Both the density and the refractive index are functions of temperature (t), but molar refractivity is expected to be independent of temperature [10], So that we have:

$$\left(\frac{n_m(T)-1}{n_m^2(T)+2}\right) = \left(\frac{A}{W}\right)_m \rho_m(T) \tag{14}$$

If we assume that the refractivity of a liquid is constant, (dn/dt) may be estimated from the density, refractive index and ($d\rho/dt$), from the above equation one can get;

$$\left(\frac{dn_m}{dt}\right) = \left(\frac{A}{W_m}\right)\left(\frac{n_m^2+2}{6n_m}\right)\left(\frac{d\rho_m}{dT}\right) \tag{15}$$

But,

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

Therefore, the macroscopic properties of both density and refractive index of the liquid can be used to determine (dn_m/dt) according to Eq. (15).

4. Results and discussion

The DMSO solvent is one of the strong organic solvents for laser dyes. Both water and DMSO belongs to the three main categories of solvents for dissolving organic dyes. These categories are [1,2,10]:

1. Water-based solvents, for example, pure water or water-based solutions such as DMSO,
2. simple organic solvents, for example, methanol, ethanol, ethylene glycol, DMSO, and mixture of them and,
3. mixture of water-based solvents and organic solvents, that is, the using the above mentioned methods together produce this third class of laser dye solvent.

The importance of this class of solvent is to get a high solubility of the laser dye and a solubility of the laser dye and a suitable thermo-optical characteristics.

4.1. Water based solvents

Water-based laser dye solvents are considered as excellent solvents because their thermo-optical characteristics. In a comparison with the other liquids one can note the smaller value of ($d\rho/dt$) and consequently a smaller value of (dn/dt) as shown from Eq. (15). It is known that the water has a maximum density at about 4°C which tends to ($d\rho/dt = 0$). Therefore, if the temperature of the water about 4°C is changed with small fraction one can expect that (dn/dt) = 0, but there is some doubt about the exact temperature at which this occurs [9]. This particular property of water shows why it is considered as the best solvent thermo-optically. The method of determination of the refractive index (n) of water is shown in Fig. 1. *The obtained value of (n) is* shown in Table 1.

Fig. 2 shows the dependence of the measured refractive index (n) as a function of temperature for pure water. It was shown that around 4°C there is a very little change in

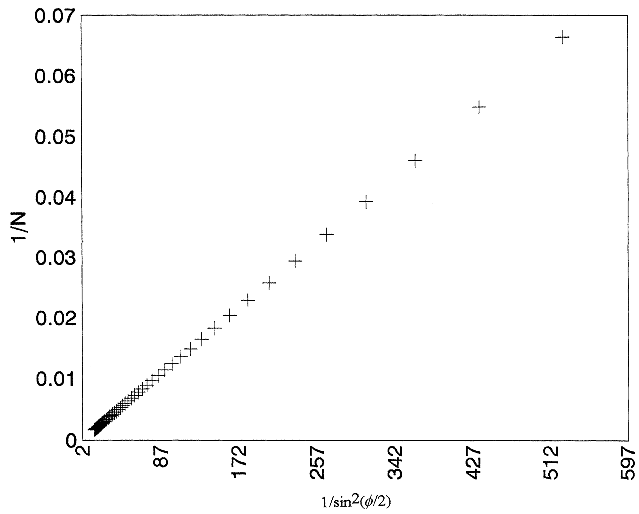

Fig. 1. The relation between number of fringes (N) and the angle of incidence (φ) to determine the refractive index (n) of pure water.

Table 1

P (%)	n_{exp}	$n_{th.}$	$(dn/dt)_{exp}$	$(dn/dt)_{th.}$
0	1.3326	–	1.55×10^{-4}	–
25	1.3687	1.35939	1.28×10^{-4}	1.19×10^{-4}
50	1.4047	1.40743	1.020×10^{-4}	1.033×10^{-4}
75	1.4475	1.43632	1.395×10^{-4}	1.386×10^{-4}
100	1.4768	–	1.19×10^{-4}	–

refractive index with temperature [10]. This result agrees with some other author [11]. We have used our measured value of the refractive index (n) of water and the tabulated value of CRC [12] for density (ρ) at different temperatures to calculate the molar refractivity (A) of water. The value (A) of water was plotted against the temperature on Fig. 3. The molar refractivity of water is constant at a value 3.71 which compares very well with the other authors [10,12,13].

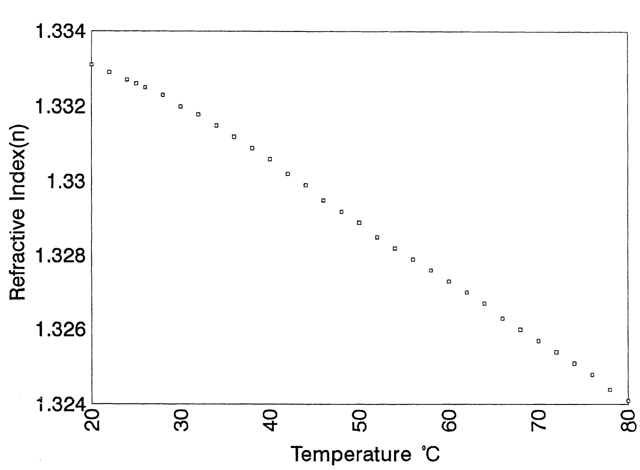

Fig. 2. Thermal behavior of the refractive index of pure water for the determination of dn/dt.

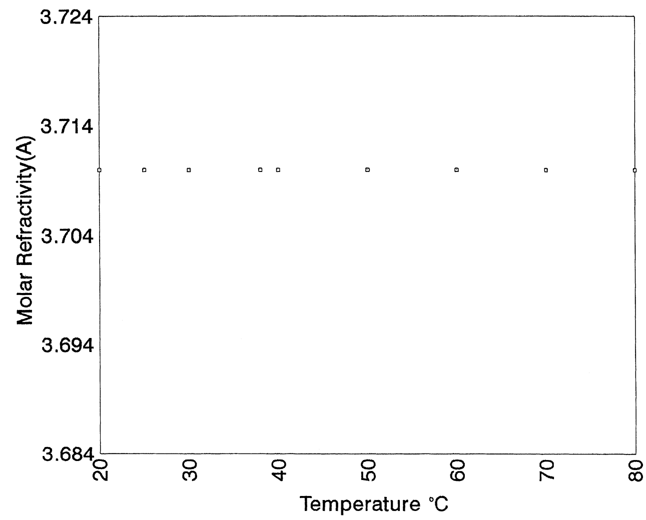

Fig. 3. The relationship between molar reflectivity (A) and temperature (t) of water.

Because the tendency of dye molecules to form dimers the dye laser based on aqueous solutions has a low efficiency. The absorption spectra of that formed dimers lie in the absorption region of the lasing monomers and also frequently overlap their fluorescence band hence reducing the fluorescence efficiency. In case of use of organic solutions the dimerization is slight and the efficiency of the dye laser produced is much better. Therefore, to reduce the dimerization process one should add some organic compounds to water.

4.2. DMSO organic solvent

The DMSO is one of the strongest organic solvents which belongs to the class (2) of leer dye solvent. The determination of the refractive index of DMSO is shown in Fig. 4

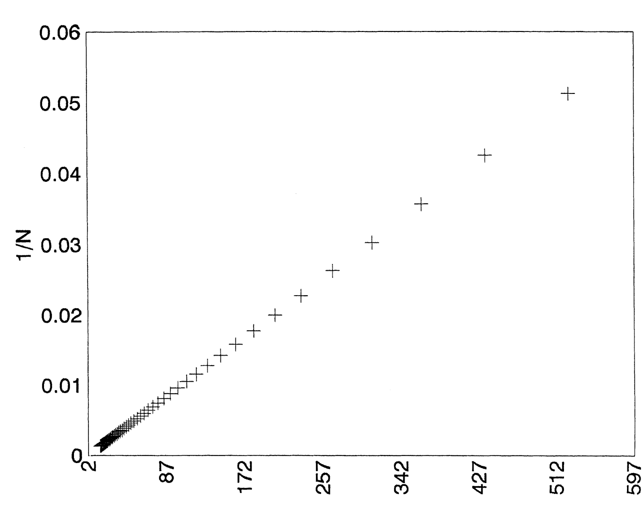

Fig. 4. Determination of the refractive index (n) of dimethylsulfoxide (DMSO) by using MZI method.

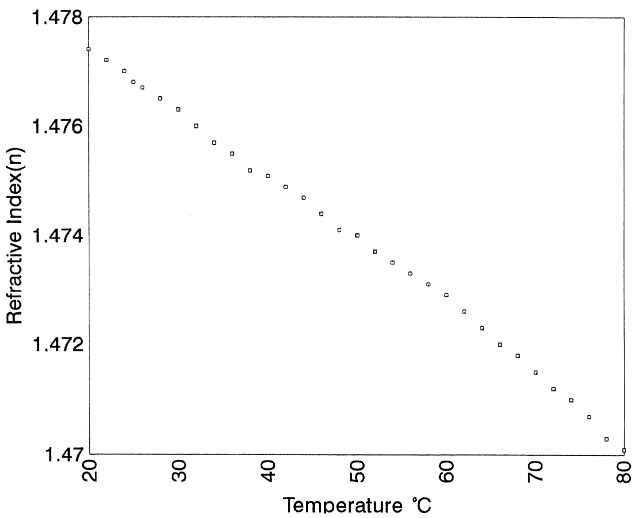

Fig. 5. Thermal behavior of the refractive index of DMSO.

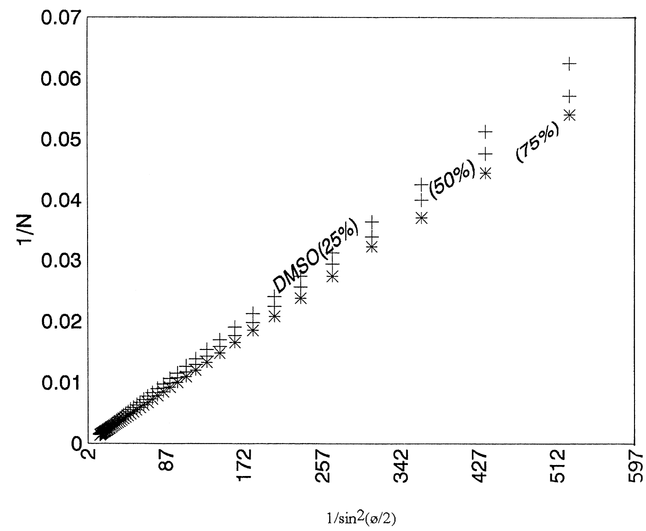

Fig. 6. Determination of the refractive index of different portions (percentages) 25%, 50%, and 75%.

with the value given in Table 1. The temperature behavior of the refractive index for this solvent within a temperature range (20°C–80°C) is shown in Fig. 5. The value of (dn/dt) is given in Table 1. This kind of organic liquid does not have the same behavior like water since it has a normal density-temperature behavior, that is, their density decreases linearly by expansion, with increasing temperature.

4.3. Solvent mixtures

The third class of laser dye solvents could include mixtures of water-based solvents, or mixtures of water-based and organic solvents. In this class we added DMSO to water with different proportion within the range (0%, 25%, 50%, 75% and 100% DMSO). During the determination of the number of interfering fringes of a such mixture ($N_{\rm m}$) we had found that, at the same angle of laser beam incidence (φ),

$$N_m = N_{s1}P_1 + N_{s2}P_2$$

where $N_{\rm s1}$ and $\rm N_{s2}$, are number of the interfering fringes of the solvents 1 and 2, and P_1 and P_2, are the portions of the two mixed solvents.

The refractive index of each percentage is determined as shown in Fig. 6 and the relation between percentages (P) and the refractive index ($n_{\rm m}$) is plotted on Fig. 7 from which one can evaluate that there is a direct proportionality between the refractive index and the refractive index ($n_{\rm m}$) of the mixture and the percentage of the organic solvent (DMSO) which had been added to the water. The temperature behavior of the mixtures are plotted on one diagram shown in Fig. 8. From Fig. 9 one can estimate that the index properties (n and dn/dt) of a mixture is given by an average of the index properties of the parent solvents. Since we had observed a non-zero (dn/dt) for both water and DMSO one cannot expect a zero (dn/dt) for any combination of water and DMSO. The results of this experimental work are shown in Fig. 7 for bulk refractive index $n_{\rm m}$ and Fig. 8 for (dn/dt's) of the mixed solvents. These results also show that both the bulk index and (dn/dt) for solvent mixtures are inherited from the parent solvents in proportion to their percentages in the mixture. Therefore, one can expect that the effect of mixing two or more liquids is simply to add proportionally their bulk indices and (dn/dt).

We did an imperical relation to formulate the refractive index of a mixture ($n_{\rm m}$) with both portions (P) and temperature (t) as follows:

$$n_m = aP^b t^c$$

with, $0\% < P < 100\%$, $20°C \le t \le 80°C$ and a, b and c are imperical constants.

$a = 1.44133$, $b = 5.0107 \times 10^{-2}$, and $c = 3.3962 \times 10^{-3}$

By using this formula we calculated the refractive index

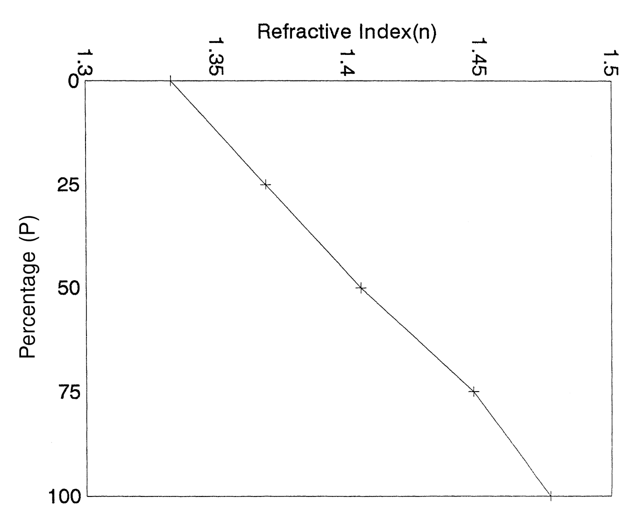

Fig. 7. The relation between portion (percentage) 0%, 25%, 50%, 75%, and 100% and refractive index (n).

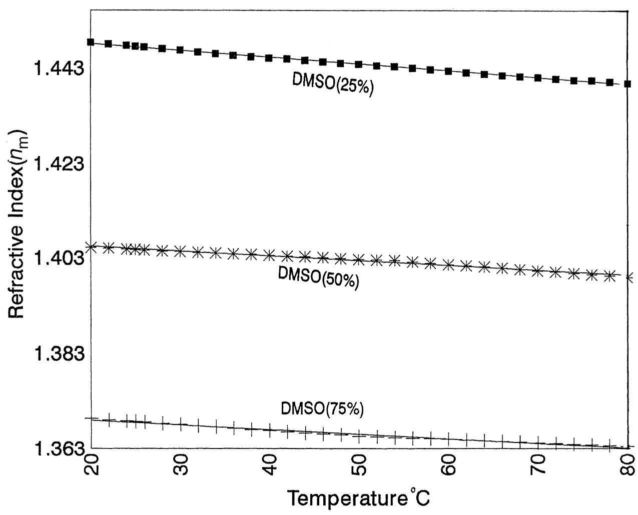

Fig. 8. Temperature behavior of refractive index of the three different portions 25%, 50%, and 75% DMSO.

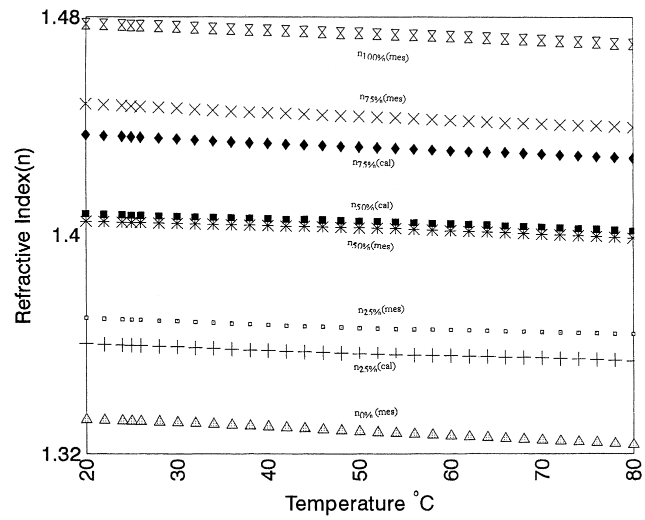

Fig. 9. Comparisons between measured and calculated values of refractive index versus temperature for different portions of DMSO.

($n_{m\ cal.}$) at different temperature for each portion and compared it with the measured indices as shown on Fig. 9.

5. Conclusions

By using MZI, we measured the absolute refractive indices for two solvents which belongs to the most commonly used laser dye solvents. Also, we measured the temperature behavior of the refractive indices for both pure water and DMSO in the temperature range from 20°C to 80°C with an accuracy better than 5.8×10^{-4}. The quantum efficiency of dyes dissolved in water is improved by adding the organic additives [1]. The effect of these additives on (dn/dt) and hence thermo-optical properties is reported here and 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 parents (dn/dt).

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