

Experimental study of solvent effect on the heat transfer characteristics of 4-[(4-aminophenyl)-(4-imino-1-cyclohexa-2,5-dienylidene) methyl] aniline hydrochloride – A concentration based study

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Abstract

The thermal diffusivity calculations of 4-[(4-aminophenyl)-(4-imino-1-cyclohexa-2,5-dienylidene) methyl] aniline hydrochloride were made for four distinct concentrations of dye dissolved in three solvents. The number of dye aggregates at higher concentrations produce more random collisions. Because of this, heat diffusion will be slower and a reduced thermal diffusivity value was observed. Due to the increased number of dye molecules, cluster formation can also occur at higher concentrations which further reduces the thermal transport through the media. Fourier-transform infrared spectroscopy (FTIR) showed the vibrational bonds of the dye in the three solvents. The dye dissolved in acetone showed higher diffusivity as compared to the other two solvents. Our studies revealed that thermal diffusivity of the dye under study is strongly solvent dependent as well as concentration dependent. The dye under study could be effectively used as insulators or heat sinks with proper choice of concentration and solvent.

Keywords

triaminotriphenylmethane dye, thermal blooming, thermal diffusivity, solvatochromism

1. Introduction

The thermal conductivity and thermal diffusivity (T_D) are two important parameters that characterize the heat transfer properties of a material. The speed at which a material heats up or cools down during thermal processing is influenced by the substance's thermal conductivity and thermal diffusivity. Conduction, convection, and radia-

tion are the three ways through which heat is transferred. Conduction is the primary mechanism for heat transfer in solid materials whereas convection plays a major role in liquids. In a heat exchanger both conduction and convection are involved. Different materials have different thermal conductivities, with metals typically being significantly greater conductors than non-metals. Thermal conductivity is a term used to describe how well a sub-

stance can conduct heat. There can be two types of heat transfer processes: steady-state and unsteady-state heat transfer. When a process is in a steady state, all the heat energy goes through the material without being heating it. Unsteady state heat transfer process is the process in which the temperature of a system or an object change as a function of time.

The thermal diffusivity is defined as the ratio of thermal conductivity to the product of specific heat and density (Eq. (1)).

$$T_D = \frac{k}{\rho c} \quad (1)$$

Thermal diffusivity, provides a measurement of how quickly the temperature will vary when it is heated or cooled. High thermal diffusivity materials will heat up or cool down quickly, whereas substances with a low thermal diffusivity will heat or cool slowly. Therefore, determining thermal diffusivity is crucial when thinking about unsteady-state heat transmission scenarios. Thermodynamic diffusivity can be measured experimentally or assessed based on an understanding of the individual properties.

Molecules are significantly more tightly packed in liquids than in gases. The molecular diffusion effect, or the random movement of molecules, is what mostly determines the heat conductivity of liquids. The flow of heat through liquids is impeded by the increased random movement of molecules. Molecular motions become more random as temperature rises which prevents heat diffusion through liquids. Therefore, thermal conductivity of liquids decreases with increasing temperature except in the case of pure water. Pure water's thermal conductivity first rises with increasing temperature and then falls. A substance with a high thermal diffusivity will also have a high thermal conductivity. The rate at which heat diffuses into the medium, increases with increasing thermal diffusivity. A low thermal diffusivity rating indicates that most heat is absorbed by the material and only a little quantity is transported further. Due to the numerous industrial heating and cooling issues, nonequilibrium heat transport is crucial.

Photothermal techniques have gained significant relevance among the numerous diffusivity calculation methods [1] because of their simplicity, dependability, reproducibility, and affordability [2]. The dual beam thermal lens approach, one of the photothermal techniques, is an effective way to determine the T_D of materials in solution [3] and in solid form [4]. This is a simple, precise, sensitive, and contactless approach that works with both low volume and low absorptivity samples [5–7]. This technique was used for the diffusivity calculations of dyes [7, 8], nanofluids [9–13], nanoparticle-dye samples [3, 14–16], biodiesel blends [17], DNA-dye samples [18], magneto-optical crystals [19] etc. Pharmacological application of the thermal lens technique was studied by swapna et.al. [20]. Thermal diffusivity of chloroform, hexane, heptane, acetone, and methanol was also measured by thermal lens technique [21].

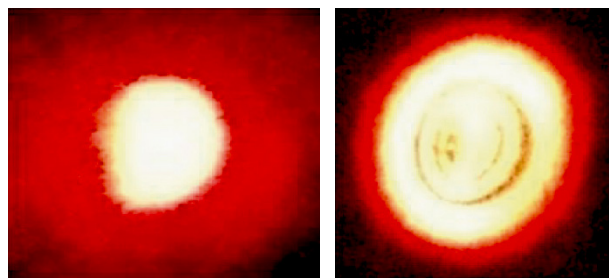


Figure 1. Thermal blooming of the probe beam

In this technique, the sample is excited by a Gaussian-profiled intensity modulated laser beam. The sample absorbs the intensity of the incident light, causing internal temperature changes that cause a gradient in the refractive index and the development of an induced lens. The induced lenses that are created are divergent ones since the majority of materials have negative temperature coefficients of resistance. To detect the created induced lens, a second laser beam-the probe beam-is used. The laser beam is diverged and extended in the far field as a result of this generated lens. This phenomenon is known as thermal blooming and is depicted in the Fig. 1.

Depending on the liquid environment of the sample under study, thermal blooming will vary and hence the T_D . Nature and properties of the solvent, intensity of the Gaussian beam, aggregation of the sample etc., are the crucial parameters determining the T_D of the sample. Thermal diffusivity value determines the applicability of a material as heat sinks or coolants. In this scenario the present work on calculation of T_D of the dye in different solvents requires attention. The impact of solvent on the dye's quantum efficiency has already been reported [22]. To the best of our knowledge, the influence of solvent and the concentration on the T_D of the dye under study is not yet carried out.

2. Experimental details

4-[(4-Aminophenyl)-(4-imino-1-cyclohexa-2,5-dienylidene) methyl] aniline hydrochloride, a magenta-coloured dye (molecular weight 337.85, molecular formula $C_{20}H_{20}ClN_3$) [7] was purchased from M/S Sigma Aldrich. This dye is commonly used for dyeing in textile industry and for the Staining of Bactria in medical field. Figure 2 illustrates the molecular structure of the dye.

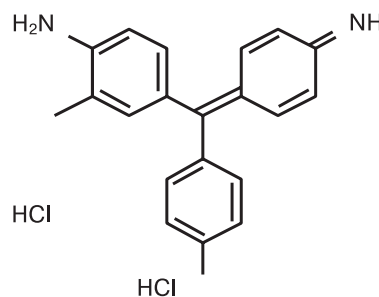


Figure 2. Molecular structure of the dye

The experimental set up is shown in Fig. 3 and is already reported [7]. With the use of a neutral density filter placed between the laser and the chopper, the output from the laser source in the current investigation was adjusted to 80 mW and is employed for the studies.

For making the stock solution, the powdered dye is weighed out and is then dissolved in the proper solvents. Different diluted concentrations were made from this stock solution. The solvents were purchased from M/S Sigma Aldrich. The sample names and concentrations are listed in Table 1.

Table 1. Molarity and sample names

Molarity (mol/L)	Distilled water	Ethanol	Acetone
10^{-5}	DW1	E1	A1
10^{-4}	DW2	E2	A2
10^{-3}	DW3	E3	A3
10^{-2}	DW4	E4	A4

3. Theory

The thermo-optic characteristics of the sample are found to be proportional to the measured probe beam intensity using the following expression.

$$I(t) = I_0 \left[1 - \frac{\theta}{1 + \frac{t_c}{2(t-t_0)}} + \frac{\theta^2}{2 \left(1 + \frac{t_c}{2(t-t_0)} \right)^2} \right]^{-1}. \quad (2)$$

Here t_c is the characteristic time constant and is defined as

$$t_c = \frac{\omega^2 \rho c}{4k}, \quad (3)$$

where ω is the beam radius, ρ is the density, c is the specific heat and k is the thermal conductivity. The parameter θ is related to the thermal power P_{th} and pump laser wavelength, λ by

$$\theta = \frac{P_{th} (dn/dt)}{\lambda k}, \quad (4)$$

where (dn/dt) is the temperature coefficient of refractive index of the sample. The t_c and θ can be obtained by fitting the experimental data to the Eq. (2). The T_D can then be calculated by

$$t_c = \frac{\omega^2}{4T_D}. \quad (5)$$

4. Results and discussions

The absorption spectrum of the dye in three solvents is measured with the corresponding solvent as the reference. The absorption peak is at 550 nm. It has previously been reported that the solvent has no effect on the dye's absorption peak wavelength but the absorption intensity (for a particular concentration in the three solvents) is varied because of the solvatochromic effects. The absorption spectra for the dye in ethanol for four different concentrations is shown in Fig. 4a. Similar is the concentration dependent variations for the other two solvents. The normalised absorption spectra for the dye in the solvents

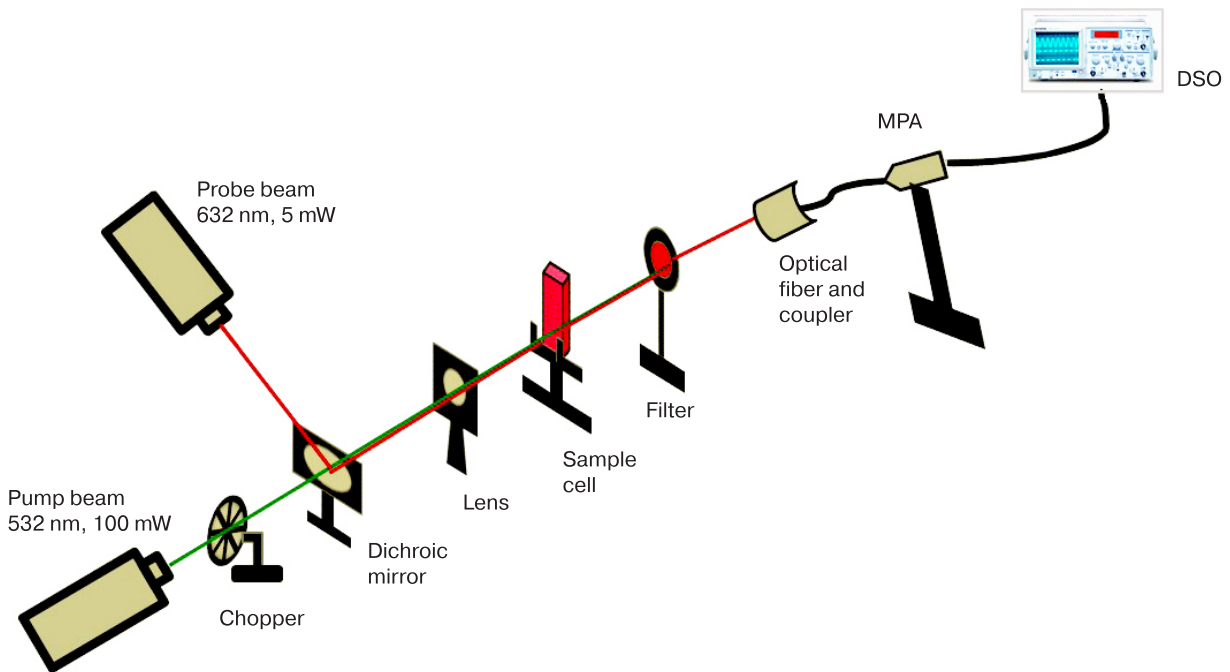


Figure 3. Experimental set up for the dual beam thermal lens approach

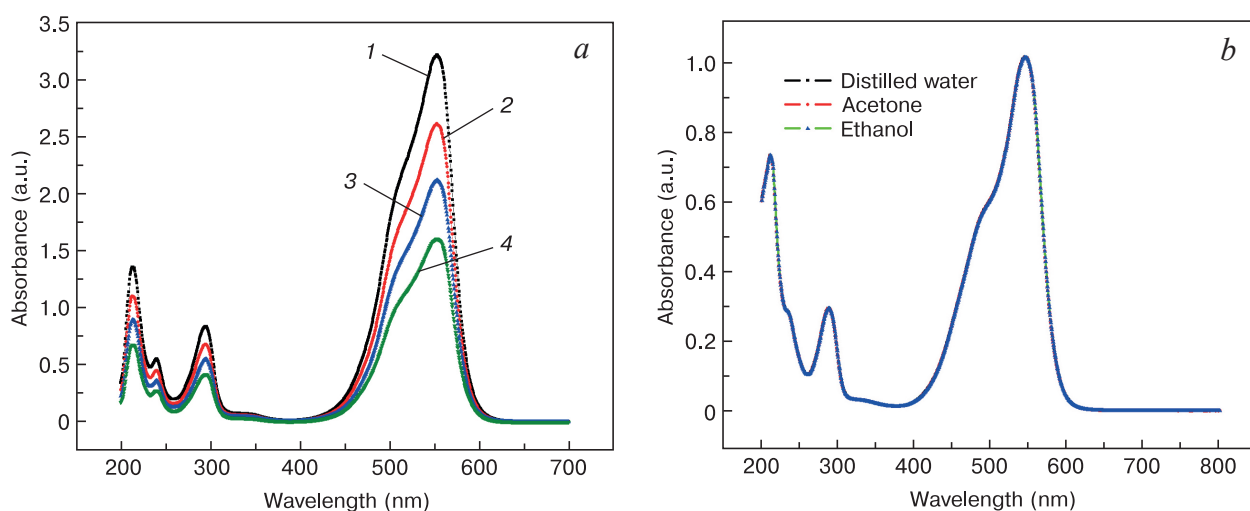


Figure 4. (a) Absorption spectrum of the dye in ethanol (3×10^{-4} mol/L (1), 2×10^{-4} mol/L (2), 8×10^{-5} mol/L (3), 2×10^{-5} mol/L (4)), (b) normalized absorption spectra of the dye in the solvents

are shown in Fig. 4b in order to examine the wavelength dependence of the dye in the solvents. The fourier-transform infrared spectroscopy (FTIR) spectrum of the dye in the three solvents and dye powder is depicted in Fig. 5.

Although the solvent has little effect on the absorption spectrum, the kind of solvent has a substantial effect on the fluorescence emission spectrum. The dye's

fluorescence emission wavelength changes depending on its concentration. The solvent properties are listed in Table 2.

Because of the solvatochromic effects, the dye's fluorescence emission spectra in the three solvents vary depending on intensity, much like the absorption spectrum did. Figure 6a depicts the dye's fluorescence emission

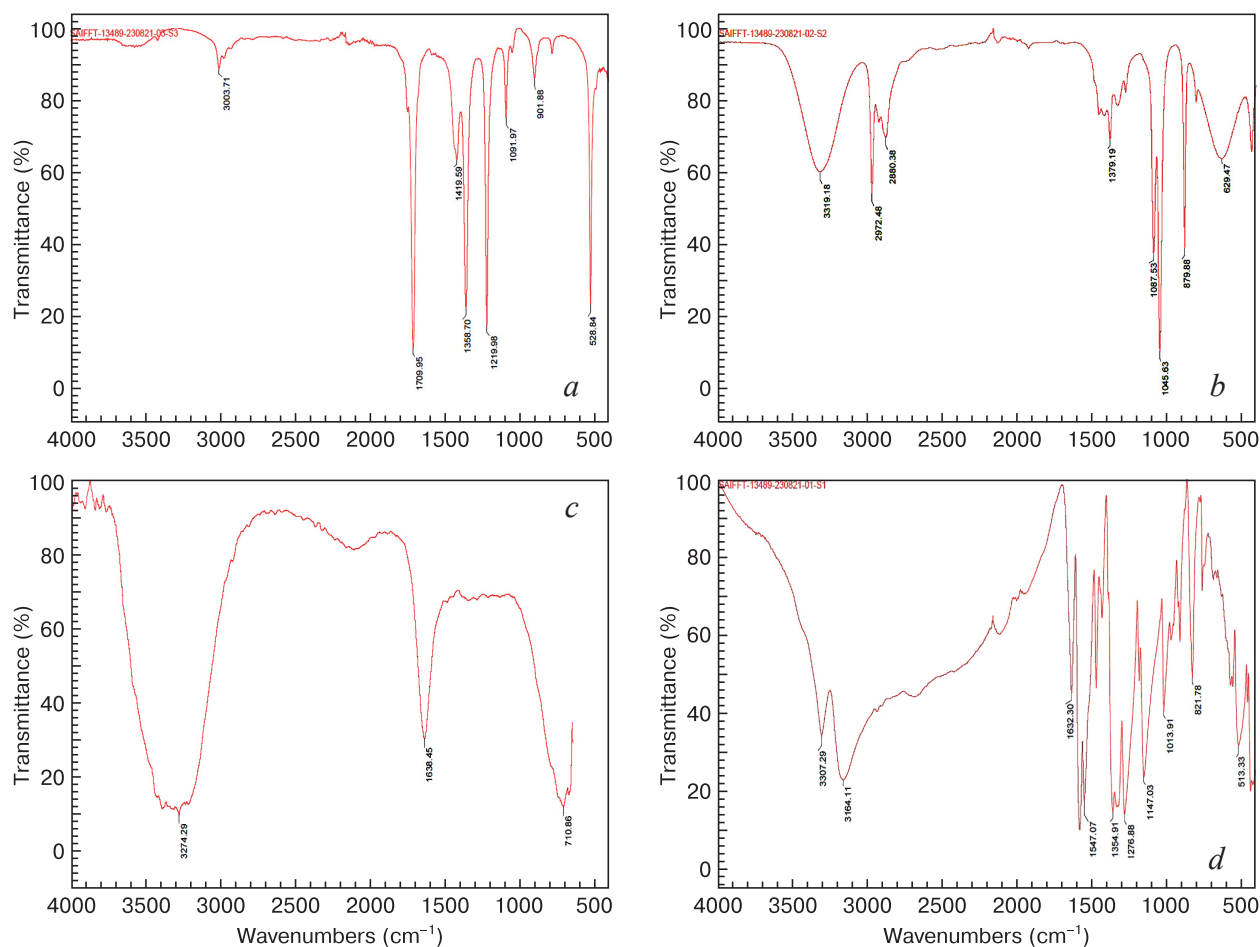
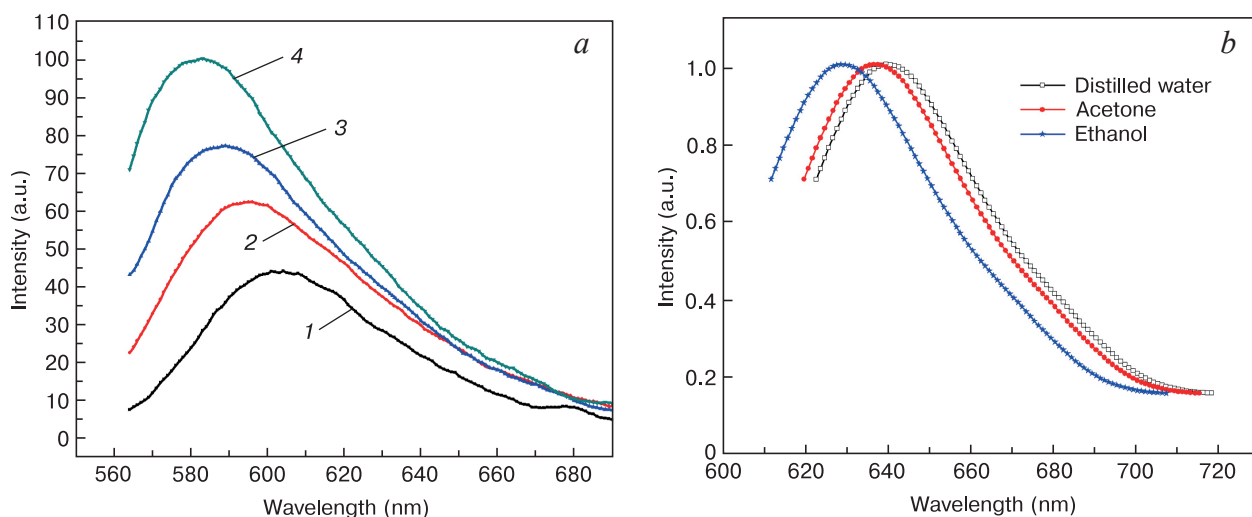


Figure 5. FTIR spectrum of the dye in acetone (a), ethanol (b), distilled water (c) and powder (d)

Table 2. Properties of solvents

Solvent name	Property					
	Solvent type	Polarity	Dielectric constant (ϵ)	Dipole moment (D)	Refractive index (n)	Viscosity (at 0 °C) (mPa·s)
Distilled water	Polar	9	78.3	1.85	1.33	1.787
	Protic					
Ethanol	Polar	5.2	24.3	1.69	1.35	1.720
	Protic					
Acetone	Polar	5.1	20.7	2.88	1.36	0.4013
	Aprotic					

**Figure 6.** (a) Fluorescence emission spectrum of the dye in ethanol (3×10^{-4} mol/L (1), 2×10^{-4} mol/L (2), 8×10^{-5} mol/L (3), 4×10^{-5} mol/L (4)), (b) normalized fluorescence emission spectrum of the dye in the solvents

spectra for four distinct concentrations of ethanol. The concentration-dependent variations for the other two solvents are similar. Figure 6b displays the dye's normalised fluorescence emission spectra for the three different solvents. A concentration-dependent red shift is visible in the peak fluorescence emission wavelength for a certain dye. It is owing to the energy misfortunes because of dissemination of vibrational energy, reallocation of electrons in the encompassing dissolvable atoms, reorientation of the dissolvable particles, and associations between the fluorophore and the dissolvable or the solute [16]. Table 3 lists the wavelength-dependent changes for the dye in the solvents at various concentrations.

Table 3. Fluorescence emission wavelength of the dye vs solvent and molarity

Sample name	Wave-length (nm)	Sample name	Wave-length (nm)	Sample name	Wave-length (nm)
DW1	600	E1	598	A1	590
DW2	618	E2	608	A2	605
DW3	640	E3	637	A3	620
DW4	668	E4	647	A4	638

The solvent dependent emission spectra can be related to refractive index, dipole moment and dielectric constant by the Lippert equation,

$$\bar{\nu}_A - \bar{\nu}_F = \frac{2}{hc} \Delta f \frac{(\mu_E - \mu_G)^2}{a^3} + \text{constant}, \quad (6)$$

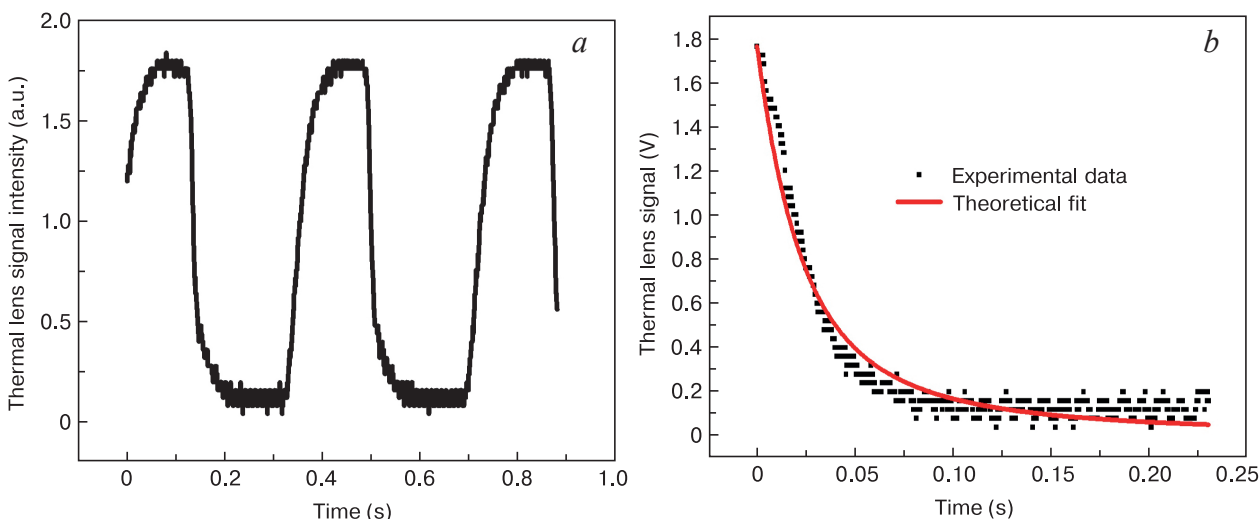
where

$$\Delta f = \frac{\epsilon - 1}{2\epsilon + 1} - \frac{n^2 - 1}{2n^2 + 1}. \quad (7)$$

The terms h , a and c corresponds to Plank's constant ($= 6.6256 \cdot 10^{-27}$ ergs), radius of the cavity where the fluorophore resides and speed of light ($= 2.9979 \cdot 10^{10}$ cm/s). ($\bar{\nu}_A$) and ($\bar{\nu}_F$) are wavenumbers (cm^{-1}) corresponding to the absorption and emission. The term (Δf) is the term for orientation polarizability. The energy difference between the ground and excited states decreases as the electrical and molecular polarizability increases [22]. Temperature and viscosity also plays a crucial part in the rate of solvent relaxation [22]. Greater orientation polarizability, which is brought about by an increase in the dipole moment, results from increased solvent polarity and causes a larger Stokes shift. [23].

Table 4. Thermal diffusivity and t_c of the dye vs solvent type and molarity

Sample name	t_c (s)	T_D (10^{-8} m ² /s)	Sample name	t_c (s)	T_D (10^{-8} m ² /s)	Sample name	t_c (s)	T_D (10^{-8} m ² /s)
DW1	0.1480	8.55	E1	0.1391	9.1	A1	0.0422	30
DW2	0.2801	4.52	E2	0.2751	4.6	A2	0.0452	28
DW3	0.5771	2.19	E3	0.3331	3.8	A3	0.0469	27
DW4	0.7031	1.80	E4	0.5503	2.3	A4	0.0974	13

**Figure 7.** Observed thermal lens signal for the dye in ethanol (a) and thermal lens decay curve (of the dye in ethanol) fitted (b)

Typical thermal lens signal observed in the DSO for the dye in ethanol is depicted in Fig. 7a. It is fitted in MATLAB and t_c and θ values are noted and is shown in Table 4. The decay curve fitted plot for the dye in ethanol is shown in Fig. 7b.

It is because of the solvation characteristics of the dye in different solvents, the diffusivity is varied. The dye is having maximum solubility in acetone and least solubility in distilled water. In the case of distilled water and ethanol, more aggregates will be created, which lowers the diffusivity in these solvents. The increased number of aggregates result in slower diffusion. Irrespective of the solvent, for higher concentrations, more aggregates will be formed. These increased number of aggregates not only produces extra random collisions but also produces a temperature rise. Because of this, heat diffusion will be slower and a reduced thermal diffusivity value is observed. There can also be cluster formation on higher concentrations. These clusters will further reduce the heat dissipation.

For the lifetime measurements, M/S Horiba Scientific's DeltaPro fluorescent lifetime system based on the TCSPC approach was utilised. Fluorescence intensity decay over time is given by

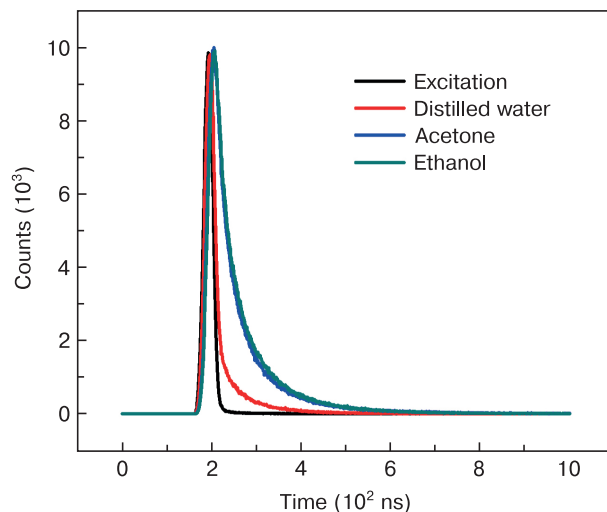
$$I(t) = I_0 \exp^{-t/\tau}, \quad (8)$$

where τ is the fluorescence lifetime, t is the time after the absorption and I_0 is the intensity at $t = 0$.

The fluorescence decay curve fitted using least square fitting algorithm is depicted in Fig. 8. Using the slope of the decay curve, the fluorescence lifetime was calculated. The measured average lifetime was shown in Table 5.

Table 5. Fluorescence lifetime of the dye in solvents

Solvent name	Lifetime (s)
Distilled water	$0.3 \cdot 10^{-9}$
Acetone	$2.35 \cdot 10^{-9}$
Ethanol	$2.45 \cdot 10^{-9}$

**Figure 8.** Lifetime decay curve fitted for the dye in the solvents

5. Conclusions

We have studied solvent and concentration dependency on the thermal diffusivity of the dye in three solvents using laser induced dual beam thermal lens technique. It was observed that the thermal diffusivity was decreased with increasing concentration irrespective of the solvent. This is attributed to the increased number of aggregates on higher concentrations and the solvatochromic properties of solvents. The Brownian motion of the dye particles

also plays a vital role in the thermal diffusivity. It was concluded that the dye studied could be effectively used as insulators or heat sinks with proper choice of concentration and solvent.

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