

# Solvation-Shell Effect on the Cyanine-Dye Fluorescence in Binary Liquid Mixtures

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## *Photophysics / Cyanine Dyes / Binary Mixtures / Nanoclusters / Preferred Orientation*

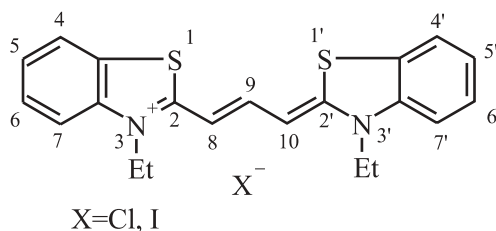
The steady-state fluorescence anisotropy and the relative quantum yield of fluorescence of cyanine dyes, 3,3'-diethyl-thiacarbocyanine iodide (DTCI) and chloride (DTCC), were measured in toluene/dimethyl sulfoxide (DMSO) liquid mixtures. It has been found that in toluene-rich mixtures the fluorescence quantum yield of DTCC is larger by about one order of magnitude than that of DTCI, the fluorescence quantum yields being the same for both cyanines in neat DMSO. Estimations based on the Perrin formula show that on decreasing DMSO volume fraction (less than 20 vol.%) the size of the preferential solvation shell around the DTCI increases up to 23 DMSO molecules at 3 vol.% DMSO as the solvation shell of DTCC does not vary. The influence of nearby solvent environment on the cyanine dye photophysics can be explained in terms of the Onsager model by taking into account the effect of the dynamic properties of DMSO solvation shell on the dye fluorescent rate constant.

## 1. Introduction

For decades, considerable effort has gone into the study of photophysical properties of cyanine dyes that show a wide variety of different mechanisms of the decay of electronically excited states. This interest was mainly provoked by the intensive use of these compounds in various applications, among other things, the creation of light emitting devices (for a recent review, see Ref. [1]). From this point of view, it might be important to find possible means of optimising fluorescence efficiency of these fluorophores.

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**Fig. 1.** The structural formula of 3,3'-diethyl-thiacarbocyanine chloride (DTCC) and iodide (DTCI).

Since the fluorescent decay of the electronically excited state in general competes with nonradiative relaxation processes, one might expect that the fluorescence quantum yield of dyes would increase as nonradiative processes are suppressed because of properly created nanoenvironment. In fact, Gao, Xiang, Feng, Tang, Chen and Xu [2] have observed the enhancement of fluorescence of a cyanine dye upon its adsorption on the surface of  $\text{TiO}_2$  colloids that is supposed to suppress the dye photoisomerisation. Our preliminary results [3] have shown that the quantum efficiency of nonradiative processes of a typical cyanine dye, 3,3'-diethyl-thiacarbocyanine iodide (TDCI), in toluene/DMSO liquid mixtures decreases by one order of magnitude as the volume fraction of DMSO significantly diminishes. Such an influence can be attributed to the effect of the DMSO nanocluster, produced by preferential solvation in the near vicinity of the TDCI molecule, and size of which can be modified by changing the composition of binary mixtures [4]. The interaction between the dye molecule and its polar solvation shell prevents the dye from structure changes that is determined by the size of the polar cluster. Controlling photophysical properties of fluorophores in binary mixtures by "fitting" the solvation shell looks promising at least from fundamental point of view.

In this communication we report that the DMSO nanocluster, produced by preferential solvation in toluene/DMSO mixtures, suppresses or enhances fluorescence of the cyanine dye depending on dye counterions, exchange of which leads to change in the nanocluster size. The rationalisation of this finding could be based on the suggestion that dynamic properties of the solvent environment of the fluorophore affect its fluorescence rate constant.

## 2. Experimental details

As a typical example, 3,3'-diethyl-thiacarbocyanine iodide (DTCI) and 3,3'-diethyl-thiacarbocyanine chloride (DTCC), whose chemical structures are shown in Fig. 1, were used in toluene/DMSO mixtures. The microheterogeneous properties of these mixtures were already studied earlier by means of optical spectroscopy (see [4] and references in it). The used solvents of spec-

**Table 1.** The viscosity of toluene/DMSO mixtures *versus* the DMSO volume fraction measured at room temperature.

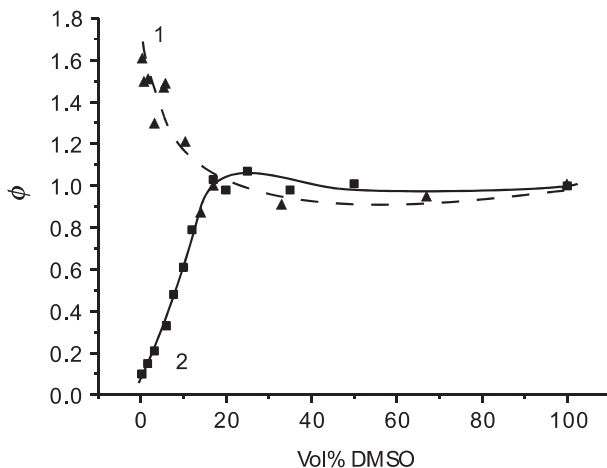
DMSO, vol. %	Viscosity, cP
0	0.617
0.30	0.596
0.83	0.596
1.60	0.604
2.40	0.611
3.20	0.619
6.25	0.651
12.50	0.710
17.80	0.771
25.00	0.855
50.00	1.202
100	2.222

**Table 2.** The quantum efficiency of non-radiative relaxation  $q$  and fluorescence life time  $\tau$  of DTCC in various toluene/DMSO mixtures.

DMSO vol. %	$q$	$\tau$ , ns
100	0.13	0.305
50	0.124	0.305
20	0.11	0.307
17	0.112	0.342
12	0.139	0.363
6	0.095	0.439
1.6	0.07	0.596

tropic grade (Uvasol<sup>®</sup>, Merk) were toluene with a dielectric constant of  $\epsilon = 2.4$ , a refractive index of  $n = 1.4969$  and a viscosity of  $\eta = 0.62$  cP, and dimethylsulfoxide (DMSO) with  $\epsilon = 49$ ,  $n = 1.4770$  and  $\eta = 2.22$  cP (data were taken from Ref. [5]). The viscosity of toluene/DMSO mixtures was measured by a capillary viscosimeter (see Table 1). The dye, DTCC, was purchased from Fluka and used without further purification; DTCC was obtained from the previous one by means of ion-exchange chromatography.

Steady-state fluorescence emission spectra and emission anisotropy of  $2.5 \times 10^{-6}$  M dye solutions were recorded by a Fluorolog-3 $\tau$  spectrofluorometer; and absorption spectra by a Cary 5E spectrophotometer. The lifetimes of fluorescence of DTCC were measured by Fluorolog-3 $\tau$  (see Table 2); those of DTCC were taken from Ref. [3]. All measurements were carried out at room temperature with freshly prepared samples. The relative quantum yield of dye fluorescence with respect to neat DMSO solution was determined by the procedure, described by Parker [6], that is based on the comparison of areas under



**Fig. 2.** The relative quantum yield of DTCC (1) and DTCI (2) solution in toluene/DMSO binary mixtures *versus* the volume fraction of DMSO.

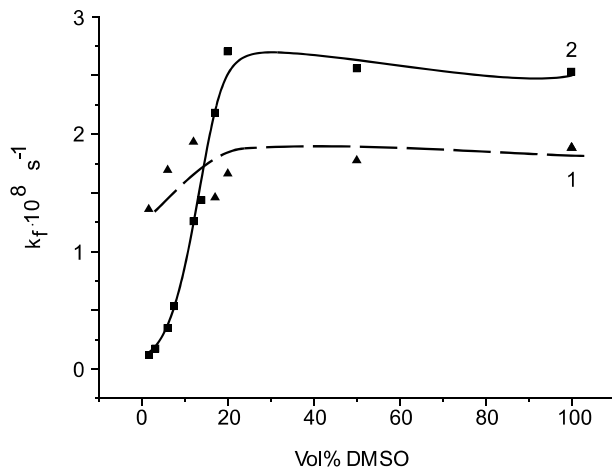
the corrected emission spectra curves. On doing so the corrections of the sample optical density at an excitation wavelength (about 564 nm) was also taken into consideration.

### 3. Results and discussion

The fluorescence of the dyes shows a peak at about 580 nm in neat DMSO that is shifted by about 10 nm to longer wavelengths as the DMSO volume fraction diminishes. Figure 2 shows the dependence of the relative quantum yield of DTCC and DTCC solutions upon DMSO volume fraction in mixtures with respect to those of the dyes in neat DMSO. In the range of 25 vol.% DMSO there is a slight increase in the DTCC fluorescence quantum yield followed by a steep decrease (by a factor of 10) with decreasing DMSO volume fraction. For DMSO volume fraction larger than 30 vol.%, the relative quantum yield is about unity; the absolute value of the DTCC fluorescence quantum yield in neat DMSO is 0.05 as measured with respect to an alcohol solution of Rhodamin B. After the iodine anion was changed by the chlorine one, the fluorescent quantum yield of the dye increased by a factor of *ca.* 1.5 on decreasing the volume fraction of DMSO in the same range; for large DMSO volume fractions, the fluorescence quantum yield of DTCC was approximately equal to that of DTCC.

Bearing in mind the classical Jablonski diagram, one can easily obtain the following formula for the fluorescence quantum yield  $\phi$  of a dye species:

$$\phi = (1 - q)k_f\tau, \quad (1)$$



**Fig. 3.** The fluorescence rate constant  $k_f$  of DTCC (1) and DTCI (2) species in toluene/DMSO binary mixtures versus the volume fraction of DMSO.

where  $k_f$  is the radiative (*i.e.*, fluorescence) rate constant,  $\tau$  is the lifetime of fluorescence, and  $q$  is the quantum efficiency of non-radiative transitions from high vibrational, “hot”, sublevels of the electronically-excited state  $S_1$  of the dye molecule. In fact this expression has a clear meaning: the quantum yield of fluorescence – the probability of emitting light after excitation in the excited state  $S_1$  – is equal to the product of probability of escaping non-radiative relaxation *via* “hot” sublevels of  $S_1$ , *i.e.*,  $(1 - q)$  and the probability of emitting light from vibronically-relaxed  $S_1$ , *i.e.*  $k_f\tau$ .

Recently, we have developed [3, 7] the technique of estimating the quantum efficiency  $q$  of cyanine dyes by comparison of their excitation and absorption spectra. Values of  $q$  for DTCI in various toluene/DMSO mixtures have been published in Ref. [3], those for DTCC are presented in Table 2. Since values  $\phi$  and  $\tau$  were also obtained experimentally,  $k_f$  values can be extracted by Eq. (1) as the function of DMSO volume fractions (see Fig. 3). For mixtures with volume fraction of DMSO larger than 20 vol.%, the fluorescence rate constant is about  $3 \times 10^8 \text{ s}^{-1}$  and  $2 \times 10^8 \text{ s}^{-1}$  for DTCI and DTCC compounds, respectively. Indeed, the value of DTCI fluorescence rate constant is close to values obtained in polar neat solvents [8]. For small toluene concentrations, therefore additional solvent-induced photo-reaction pathways of DTCI can be excluded. In the case of toluene-rich mixtures the fluorescence rate constant of DTCI diminishes (to  $\sim 10^7 \text{ s}^{-1}$ ) on decreasing DMSO volume fraction while that of DTCC remains almost the same. This findings show that a change in nano-environment of the dye molecule, caused by a variation of the binary-mixture composition, could modify the efficiency of the radiative transition of the fluorophore beyond a critical concentration mixture (20% vol. DMSO) and

**Table 3.** The fluorescence anisotropy of DTCl solutions in various toluene/DMSO mixtures.

DMSO vol. %	Anisotropy, <i>r</i>
3.2	0.1762
5	0.1505
6	0.1420
8	0.1375
10	0.1208
12	0.1238
15	0.1223
17	0.1261
20	0.1299
31	0.1390
50	0.1567
70	0.1723
90	0.1881
100	0.2002

**Table 4.** The fluorescence anisotropy of DTCC solutions in various toluene/DMSO mixtures.

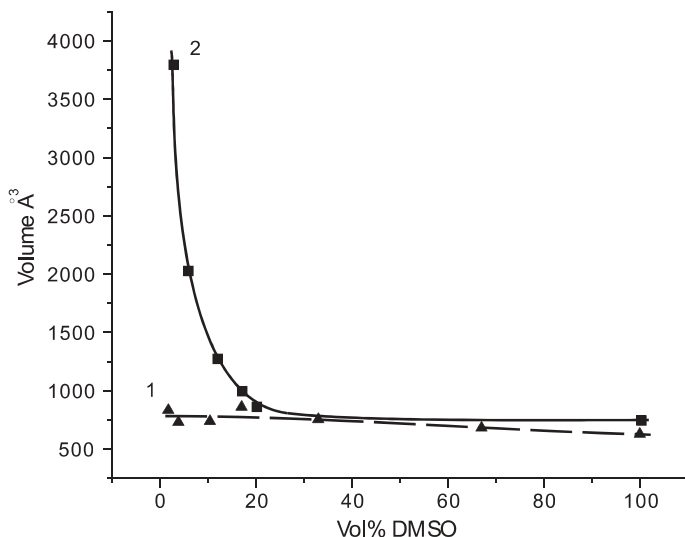
DMSO vol. %	Anisotropy, <i>r</i>
0.7	0.058
1.7	0.0627
3.5	0.0686
3.8	0.0686
10.4	0.0939
17.0	0.1181
33.0	0.1348
67.0	0.1663
100	0.1945

leads to some kind of “saturation behaviour” above this critical concentration value.

In the following we will qualitatively try to understand the reported experimental findings. Short lifetimes of the both dyes (300 ps in neat DMSO and up to 600 ps in toluene rich mixtures) allow the observation of relatively high emission anisotropy. The rotational depolarisation, determined experimentally (see Tables 3 and 4), can be described by the Perrin formula [9]

$$\frac{1}{r} = \frac{1}{r_0} \left( 1 + \frac{\tau k_B T}{V\eta} \right). \quad (2)$$

Here,  $r = (I_V - I_H)/(I_V + 2I_H)$  is the observed emission anisotropy (where  $I_V$  and  $I_H$  are the fluorescence components parallel and perpendicular to the



**Fig. 4.** The effective volume of the DTCC (1) and DTCC (2) species with its solvation shell in toluene/DMSO mixtures *versus* the volume fraction of DMSO.

electrical vector of the exciting light, respectively),  $r_0 = 0.372$  is the limiting fluorescence anisotropy measured in glycerol,  $\tau$  is the fluorescence lifetime of the dyes,  $k_B$  is the Boltzmann constant,  $T$  is the absolute temperature,  $\eta$  is the binary mixture viscosity and  $V$  is the effective volume of the solute (here the dye) with its solvent shell. Figure 4 shows the DTCC and DTCC effective volumes, calculated by Eq. (2), as a function of DMSO fraction in binary mixtures. In neat DMSO,  $V \approx 750 \text{ \AA}^3$  for the both species that is close to  $680 \text{ \AA}^3$ , the volume estimated from the chemical structure of the dyes. For DMSO volume fraction smaller than 20 vol.%, the DTCC effective volume significantly increases up to  $3800 \text{ \AA}^3$  at 3.2 vol.% DMSO; the DTCC effective volume is almost the same on diminishing the DMSO volume fraction. Note that the volume of a DMSO molecule is about  $120 \text{ \AA}^3$  as calculated from the solvent density, so that for a spherical model, this corresponds to a droplet with a radius of  $10 \text{ \AA}$  that contains about 26 molecules of DMSO. Thus in neat DMSO, the “slip” boundary condition (*i.e.*, the tangential forces between the solute and solvent are negligible) is obviously dominant which is in agreement with the results obtained for a similar cyanine dye in ethanol [10]. In mixtures with a small toluene content, the “stick” model (*i.e.*, solvent molecules drag against the motion of the solute) seems more appropriate.

In order to consider the observed results in a more quantitative fashion, it is useful to draw an analogy to energy transfer mechanism from the excited fluorophore to a nearby metal or dielectric surface [11, 12]. The excited dye molecule can be approximately considered as a classical harmonic oscillator

of angular frequency  $\omega_0$  and the radiative rate constant  $k_0$  found in free space. When this oscillator is placed into a cavity, the driving force associated with the reaction electric field of the cavity  $E_R$  should be taken into consideration:

$$\frac{d^2\mu(t)}{dt^2} + k_0 \frac{d\mu(t)}{dt} + \omega_0^2 \mu(t) = \left(\frac{e^2}{m}\right) E_R, \quad (3)$$

where  $\mu = \mu(t)$  is the dipole moment of the excited molecule. The reaction field of the cavity can be expressed on the basis of the Onsager formula for the reaction field [13]

$$E_R = \frac{\mu}{a^3} \frac{2(n^2 - 1)}{(2n^2 + 1)}, \quad (4)$$

where  $a$  is the characteristic size of the cavity (for simplicity, let us assume a sphere),  $n^2$  is the squared refractive index of media, in which the dye molecule is embedded, instead of its dielectric constant. Since we actually deal with the picosecond time scale, the applied Maxwell equation ( $n^2 = \varepsilon$ ) might be appropriate.

More generally, the reaction field of the cavity at a time point  $t$  can be written as a linear integral equation [14]:

$$E_R(t) = \frac{2(n^2 - 1)}{a^3(2n^2 + 1)} \int_0^\infty K(\tau) \mu(t - \tau) d\tau, \quad (5)$$

where  $\tau$  is a time delay and  $K(\tau)$  is a function of time that depends on the properties of the cavity; Eq. (5) reads that the reaction field at a certain point  $t$  depends only on the dipole moment of the dye molecule at the preceding rather than subsequent instants of time. Actually, the function  $K = K(\tau)$  describes the “memory” of the environment as decreasing rapidly with the delay time increases.

Indeed, from Eq. (3) it follows:

$$\frac{d^2\mu(t)}{dt^2} + k_0 \frac{d\mu(t)}{dt} + \omega_0^2 \mu(t) = \frac{2e^2}{ma^3} \frac{(n^2 - 1)}{(2n^2 + 1)} \int_0^\infty K(\tau) \mu(t - \tau) d\tau. \quad (6)$$

Assuming a solution of Eq. (6) in the form of

$$\mu(t) = \mu_0 \exp\left(-\frac{kt}{2} - i\omega t\right), \quad (7)$$

where  $\omega$  and  $k$  are the perturbed angular frequency and the emission rate constant, respectively, we find from Eq. (6) that

$$k = k_0 + k_1. \quad (8)$$



Here

$$k_1 = \frac{2e^2}{ma^3} \frac{(n^2 - 1)}{(2n^2 + 1)} \text{Im}K_{\omega}, \quad (9)$$

and

$$K_{\omega} = \int_0^{\infty} K(\tau) \exp(i\omega\tau) d\tau. \quad (10)$$

Note that Eqs. (9), (10) have been obtained with the constraint  $\tau k/2 \ll 1$ . The interaction with the Onsager cavity also causes a change in oscillation frequency but, as usual, in this case it might be regarded as negligible, *i.e.*,  $\omega^2 \approx \omega_0^2$ .

Equation (10) is quite a general result. In order to compare it with experimental data we need some suggestion about  $K(\tau)$ . Realistically, one may approximate it by a function

$$K(\tau) = \frac{1}{\tau_0} \exp\left(-\frac{\tau}{\tau_0}\right), \quad (11)$$

where  $\tau_0$  may be associated with a correlation time of the solvation-shell relaxation.

Substitution of Eq. (11) to Eq. (10) results in obtaining from Eq. (10) the following:

$$k_1 = \frac{2e^2}{ma^3} \frac{(n^2 - 1)}{(2n^2 + 1)} \frac{1}{\omega^2 \tau_0}. \quad (12)$$

Bearing in mind that the first Bohr radius is  $a_0 = \hbar^2/me^2 \approx 0.5 \text{ \AA}$ , the ionisation potential of hydrogen, *i.e.*, the Rydberg constant,  $R_{\infty} = e^2/2a_0 = me^4/2\hbar^2 \approx 13.6 \text{ eV}$ , one can rewrite Eq. (12) in a more convenient form:

$$k_1 = \frac{(n^2 - 1)}{(2n^2 + 1)} \left(\frac{2a_0}{a}\right)^3 \left(\frac{R_{\infty}}{\hbar\omega}\right)^2 \frac{1}{\tau_0}. \quad (13)$$

Assuming  $\hbar\omega \approx 2 \text{ eV}$ ,  $a \sim 5 \text{ \AA}$ , and taking as experimental value  $k_1 \sim 2 \times 10^7 \text{ s}^{-1}$  for TDCI in toluene-rich mixtures, one obtains from Eq. (13) that  $\tau_0 \sim 10^{-8} \text{ s}$ . This time seems much longer than the Debye rotational relaxation time of DMSO molecules in the nanocluster. However, it is the same order of magnitude as the characteristic time obtained by time-dependent Stokes shift of fluorescence in ionic solutions. According to Argaman and Huppert [15], this time is determined by an ion diffusion-motion in the near vicinity of the fluorescent probe. So, in the case of the  $\text{I}^-$  counterion in toluene-rich mixtures

(a large DMSO cluster), there exists a reasonable estimation of the correlation time

$$\tau_0 \sim \frac{(2R)^2}{D}, \quad (14)$$

where  $R = 10 \text{ \AA}$  is the radius of the DMSO cluster,  $D$  is the diffusion coefficient. One can use  $D \approx 3 \times 10^{-6} \text{ cm}^2/\text{s}$ ; this estimation is based on a typical value of an ion diffusion coefficient [15] with allowance made for viscosity. Thus it follows from Eq. (14) that  $\tau_0 \approx 10 \text{ ns}$ . In the case of the  $\text{Cl}^-$  counterion, the estimation by Eq. (14) is hardly valid but since the size of the cluster in such solutions is smaller and independent of mixture composition, the correlation time  $\tau_0$  should be shorter. This results in a larger value of  $k_f$  for the cyanine chloride in toluene-rich mixtures in accordance with experiment.

Thus, the above simple model is in a qualitative agreement with the experimental results obtained which leads to the conclusion that the dynamic properties of the preferential solvation shell, *i.e.* environment nanostructure, can affect the radiative decay of electronically excited states of cyanine dyes.

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