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Nonradiative Relaxation of Thiacarbocyanine Dyes in Binary Mixtures

N. Kh. Petrov,[1,3] M. N. Gulakov,[1] M. V. Alfimov,[1] G. Busse,[2] B. Frederichs,[2] and S. Techert[2,3]

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It was found that preferential solvation of cyanine dyes in binary mixtures can strongly affect both their isomerization and aggregation; the comparison of absorption and fluorescence excitation spectra might be a useful tool for studying these nonradiative processes.

KEY WORDS: preferential solvation; binary mixtures; cyanine dyes.

In binary mixtures, a solvent composition in the near vicinity of a solute molecule can differ from that in the bulk if the solute interacts differently with each of the solvent components. The production of such microheterogenicity is called preferential solvation [1]. It is well known that preferential solvation might strongly affect physicochemical processes involving charged particles or species with a large dipolar moment. Since cyanine dyes in solution usually exist as ions or ion pairs, one might expect that preferential solvation in binary mixtures could facilitate aggregation of dyes [2]. The purpose of this short communication is to demonstrate that preferential solvation in binary mixtures also can influence on photoisomerisation of cyanine dyes as their usual relaxation mechanism [3].

As a typical example, 3,3′-diethyl-9-methylthiacarbocyanine iodide (Dye I), purchased from Acros was used without further purification (its chemical structures is shown in Fig. 1) in toluene/DMSO mixtures. Toluene and dimethylsulfoxide (DMSO) are of spectroscopic grade (Uvasol, Merk). Fluorescence emission and excitation spectra were recorded by a Fluorolog-3 spectrofluorometer (Jobin Yvon-Spex, France) and corrected according to manufactory specifications. Absorption spectra were measured by a Cary 5E spectrophotometer. Concentration of the dye was about 2×10^{-6} M. All measurements were carried out with 10 mm cells at room temperature with freshly prepared samples.

When the DMSO volume fraction diminishes in toluene/DMSO mixtures, the absorption peak of Dye I solution shifts to the longer wavelengths (∼20 nm) with respect to that in neat DMSO; some representative absorption curves are shown in Fig. 2. It significantly increases in magnitude for DMSO volume fraction less than 8 vol.% after a slight decrease in the range from 50 to 10 vol.%. It is worth noting that in toluene rich mixtures, a quite distinct isobestic point appears at about 555 nm, which is destroyed as DMSO volume fraction becomes larger than 10 vol.%. Figure 3 shows typical excitation and fluorescence spectra of Dye I. There is only one fluorescence peak at about 580 nm that slightly shifts to longer wavelengths (∼10 nm) with respect to neat DMSO as the DMSO volume fraction becomes as small as 0.33 vol.%.

We shall elucidate the relaxation of electronically excited states of the dye by the comparison of their absorption and excitation spectra, using the concept generally outlined by Parker [4]. The fluorescence-excitation spectrum is defined as the dependence of fluorescence intensity I, detected at a given wavelength, upon wavelengths of exciting light λ. In dilute solutions it is

$$I \approx 2.3 \cdot \varphi \cdot I_0 \cdot [\varepsilon(\lambda) \cdot c \cdot l]. \qquad (1)$$

[1] Photochemistry Center, Russian Academy of Sciences, 119421 Moscow, Russia.
[2] Max-Planck-Institut für biophysikalische Chemie, Abteilung Spektroskopie und Photochemische Kinetik, 37077 Göttingen, Germany.
[3] To whom corresponding should be addressed. E-mail: npetrov@photonics.ru

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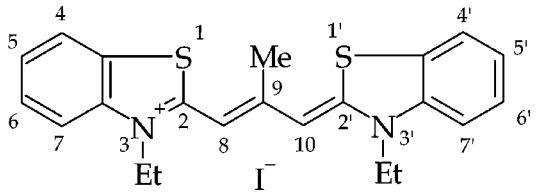

Fig. 1. The structural formula of 3,3′-diethyl-9-methylthiacarbocyanine iodide (Dye I).

Here, φ is the fluorescence quantum yield independent of excitation wavelengths, I_0 is the intensity of exciting light, $\varepsilon(\lambda)$ is the molar extinction coefficient, c is the fluorophore concentration and l is the optical depth. By definition, Abs $(\lambda) \equiv \varepsilon(\lambda) \cdot c \cdot l$, the optical density or absorbance, that is directly recorded by a spectrophotometer. If I_0 is corrected for its dependence upon exciting light wavelengths and nonradiative processes are negligible, the fluorescence-excitation spectrum is a replica of the absorption spectrum In other words, a properly scaling excitation spectrum should coincide with the corresponding absorption spectrum. Therefore, a significant deviation from absorption profile indicates the existence of a nonradiative channel of relaxation.

Taking into account nonradiative processes in a more precise manner, we rearrange the extinction coefficient as follows

$$\varepsilon(\lambda) = \varepsilon^{f}(\lambda) + \varepsilon^{nr}(\lambda), \tag{2}$$

where $\varepsilon^{f}(\lambda)$ is the cross section of the fluorescent excited state and $\varepsilon^{nr}(\lambda)$ is the cross section of the excited state which relaxes nonradiativly. Then, we have by definition

$$\mathrm{Abs}(\lambda) = [\varepsilon^{f}(\lambda) + \varepsilon^{nr}(\lambda)] \cdot c \cdot l, \tag{3}$$

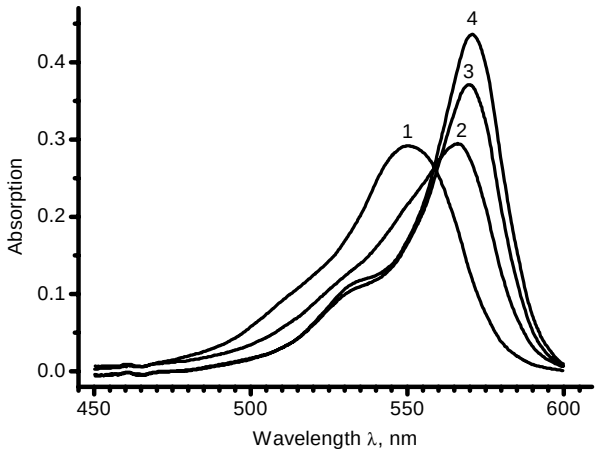

Fig. 2. Absorption spectra of dye solutions in toluene/DMSO mixtures: neat DMSO (1), 7.7 vol.% DMSO (2), 3.2 vol.% DMSO (3), 1.6 vol.% DMSO (4).

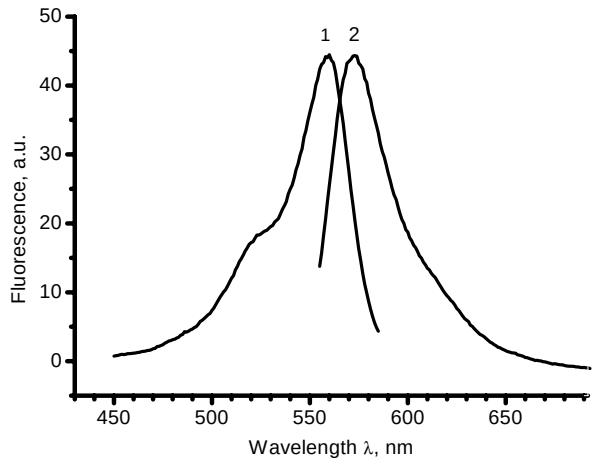

Fig. 3. Excitation, $\lambda_{em} = 615$ nm, (1) and fluorescence, $\lambda_{exc} = 565$ nm, (2) spectra of dye solution in neat DMSO.

and

$$I \approx 2.3 \cdot \varphi \cdot I_0 \cdot [\varepsilon^{f}(\lambda) \cdot c \cdot l], \tag{4}$$

Further, subtracting from Eq. (3) a properly scaled Eq. (4), one always can obtain

$$\mathrm{Act}(\lambda) \equiv \varepsilon^{nr}(\lambda) \cdot c \cdot l, \tag{5}$$

which is a measure of the efficiency of nonradiative processes as a function of excitation-wavelengths and can be called the action spectrum of nonradiative relaxation. In practice, in order to expand the total optical density into a fluorescent and nonradiative terms, one should find a scaling factor independent of wavelengths so that the excitation spectrum profile will be as close as possible to the absorption spectrum curve but *never exceed the latter* (just because $\varepsilon^{nr}(\lambda) \geq 0$ for any wavelength). Assuming the Rullière model for the particular case of cyanine-dye isomerization [5], one might expect that $\varepsilon^{nr}(\lambda) \ll \varepsilon^{f}(\lambda)$ for the long wavelength tail of the absorption band of cyanine dyes.

Figure 4 shows such action spectra, obtained by above defined procedure, for various toluene/DMSO mixtures. Clearly, there exist two characteristic spectral bands in the range of 545 nm, and of 570 nm. The values of the former band decreases as the DMSO volume fraction becomes less than 50 vol.%. For volume fractions as small as 3.2 vol.% these bands almost disappear. As the DMSO volume fraction decreases further, a new narrow peak around 570 nm arises, indicating that for toluene rich mixtures there exists a new deactivation route.

For cyanine-dye polar solutions, it is widely accepted [3] that, *trans-cis* isomerisation is the main deactivation channel of the S_1 excited state. Its radiationless quantum

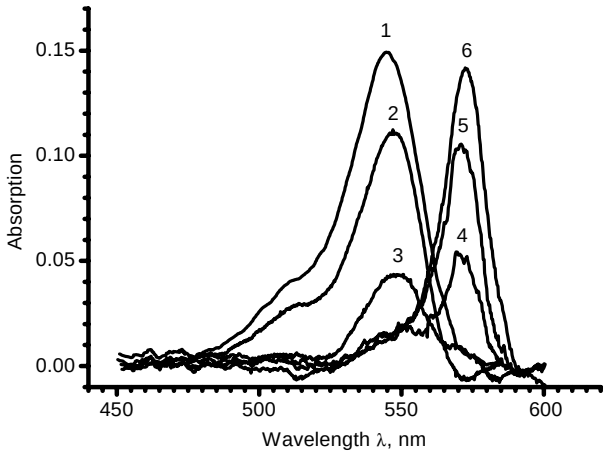

Fig. 4. Action spectra of dye solutions in toluene/DMSO mixtures: neat DMSO (1), 20 vol.% DMSO (2), 7.7 vol.% DMSO (3), 3.2 vol.% DMSO (4), 1.6 vol.% DMSO (5), 0.33 vol.% DMSO (6).

efficiency can be directly estimated as a ratio of the area under the action-spectrum curves to that of corresponding absorption spectra (see Table I). As the volume fraction of DMSO diminishes, it monotonely decreases from, $q \approx 0.38$ for neat DMSO to ≈ 0.1 for the 7.7 vol.% DMSO mixture, then for DMSO volume fractions less that 3.2 vol.% the radiationless quantum efficiency increases. So it means that the transformation of the dye solvation shell upon varying the mixture composition suppresses the process of isomerisation (see ref. [6]).

The narrow peak at 570 nm, which arises for DMSO volume fractions $\leq$3 vol.%, may be attributed to aggregation facilitated by preferential solvation in binary mixtures. In toluene rich mixtures, polar microclusters of DMSO can attract dye molecules, producing aggregates e.g. dimers. The production of dimers in DMSO microclusters surrounding the dye molecules, solvation shells, can result in an effective quenching of the excited state The observation of the isobestic point at about 555 nm, which become clear-cut for small volume fraction of DMSO, is also in agreement with this assumption.

Table I. The Radiationless Quantum Efficiency of Dye I, q, for Various Volume Fraction of DMSO with Toluene Mixture

DMSO (vol.%)	q
100	0.62
50	0.36
20	0.30
7.7	0.09
3.2	0.11
1.6	0.14
0.33	0.14

In conclusion, preferential solvation of cyanine dyes in binary mixtures can strongly affect both their isomerisation and aggregation; the comparison of absorption and fluorescence excitation spectra might be a useful tool for studying such nonradiative processes.

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