Short Communication

Fluorescence quantum yield of pyrene-1-carboxaldehyde in protic solvents

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1. Introduction

The exocyclic carbonyl group of pyrene-1-carboxaldehyde (PyCHO) gives rise to n,π^* singlet and triplet states close in energy to the π,π^* states. It is highly likely that this situation plays a key role in the marked solvent dependence of PyCHO fluorescence [1 - 3]. However, additional quantitative data, mainly quantum yields and lifetimes, are needed to identify the detailed photophysical mechanism. In the work of Kalyanasundaram and Thomas [4] on the suitability of PyCHO as a probe for micellar polarity, new data have been reported on the fluorescence intensity of methanol–water mixtures. Although no quantum yields were determined a steady increase in the fluorescence intensity with increasing water content, from 10 to 90% water, was reported. Moreover, we have published recently [5] a quantum yield for PyCHO in oxygen-free water of 0.98 ± 0.08, *i.e.* six times higher than the value of 0.15 reported [1] for the yield in pure methanol. Very recently [6] the use of PyCHO as a polarity probe has been questioned; these authors also included some lifetime and quantum yield measurements for a number of solvents, with a yield of 0.41 for PyCHO in pure water and of 0.10 for PyCHO in pure methanol. Without joining the controversy about the use of fluorescence maxima as a polarity probe [6], it would be necessary, in order to reconcile these quantum yields with previous evidence [4], for the fluorescence intensity in methanol–water mixtures to increase with increasing water content up to a certain value and then to decrease abruptly to the value in pure water. In addition, the published fluorescence quantum yield [6] of PyCHO in pure water differs widely from that found by us. The experiments reported here were designed to clarify this point. It is shown here that the unusual fluorescence intensity variation just described has nothing to do with the photophysics of PyCHO; it is simply an artefact probably produced by slow aggregation of the aldehyde in water.

2. Experimental

PyCHO (Aldrich) was recrystallized from AR ethanol. Methanol (Riedel, less than 0.1% H_2O) and water were not degassed in this work. Absorption

spectra were obtained in 10 cm quartz cells. The quantum yields, recorded on an SLM photon-counting spectrofluorimeter, were based on a value of 0.51 for quinine sulphate (Aldrich) in 0.1 N H_2SO_4 [7]. The aldehyde concentrations in mixed solvents, described as nominal, were obtained by dilution from a 10^{-4} M methanol solution. No thermal or photochemical reaction products were detected. Additional experimental details have been given elsewhere [5].

3. Results and discussion

The behaviour of the fluorescence intensity of nominally 5×10^{-6} and 10^{-7} M PyCHO in methanol–water mixtures is shown in Fig. 1. The parameter S is the area under the corrected emission spectrum normalized to $S = 0.07$ for pure methanol. Thus S is directly proportional to the quantum yield of the emitting species at the exciting wavelength. There is a marked dependence of S on the aldehyde concentration that cannot be explained by changes in the extinction coefficient of the solubilized PyCHO. Moreover, the fluorescence intensity of the samples with higher water content depends on the time elapsed from the preparation of the solution, as can be seen in Fig. 2. These phenomena are consistent with an aggregation [8] of the aldehyde due to its very low solubility in water. Depending on the initial concentration the aggregates either remain in suspension or sediment with time. Although the low optical densities involved did not allow us to identify the aggregates in the absorption spectrum, they could be detected by an increase in the scattered light of the mixtures. We also included in Fig. 1 the quantum yield of 10^{-7} M PyCHO for three different solvent compositions, the spectra being recorded immediately after preparing the samples. These values, the average of several determinations, show the marked increase in the emission efficiency of PyCHO in going from pure methanol to pure water.
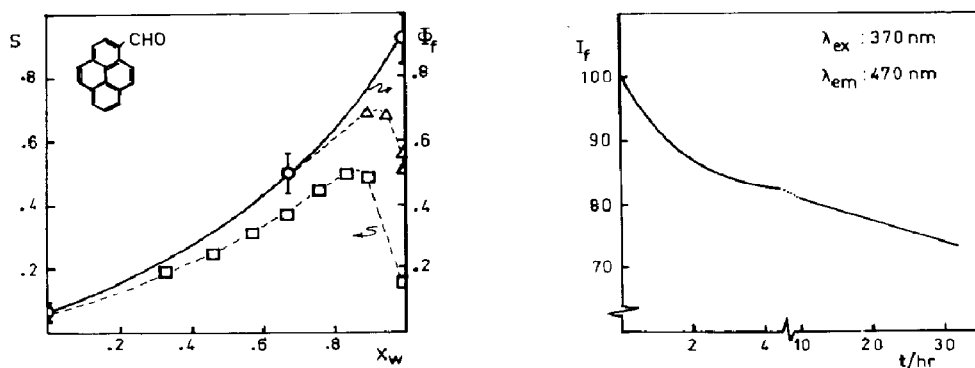

Fig. 1. The area S under the corrected fluorescence spectrum of PyCHO in methanol–water mixtures vs. the water mole fraction X_W. Nominal concentrations are 5×10^{-6} M ($\square$) and 10^{-7} M ($\triangle$). The fluorescence quantum yields ($\bigcirc$) of 10^{-7} M solutions correspond to the right-hand axis. See text for details.

Fig. 2. The time dependence of the fluorescence intensity of a 10^{-7} M solution of PyCHO in water.

This large increase could be related to the supression of radiationless channels and/or to an increased radiative rate constant. With the published fluorescence lifetimes [5, 6] and the quantum yields reported here, a radiative rate constant in water 5 times higher than that in methanol can be estimated; the radiationless rate constant is 30 times smaller in water. The direction of this change is consistent with an increase in the energy of singlet and triplet n,π^* states by hydrogen-bonding interactions with the solvent. However, the magnitude of the change appears to be too large to be explained just by this kind of interaction. After all, methanol and water are both good hydrogen-bonding solvents. Probably the considerable stabilization of the emitting state [1] by dipolar interaction is also contributing in the same direction. This would be made possible by a large contribution of charge transfer components to the first singlet, reflected also in the fluorescence wavelength shift [4] and in the excited state protonation rate [5].

4. Conclusions

The experimental determination of the fluorescence quantum yield of PyCHO in methanol–water mixtures is complicated by the tendency of this compound to aggregate. However, values of Φ_f of 0.98 in oxygen-free water and 0.07 in methanol could be determined. This large change in the emitting efficiency was explained as a consequence of the lowering of the intersystem crossing rate in water by two mechanisms: an increase in energy of the n,π^* singlet and triplet states due to increased hydrogen-bonding interactions and a stabilization of the first π,π^* singlet state by dipolar solvent molecules.

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