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Fluorescence emission of pyrene in surfactant solutions

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ABSTRACT

The systematic description of the complex photophysical behaviour of pyrene in surfactant solutions in combination with a quantitative model for the surfactant concentrations reproduces with high accuracy the steady-state and the time resolved fluorescence intensity of pyrene in surfactant solutions near the *cmc*, both in the monomer and in the excimer emission bands. We present concise model equations that can be used for the analysis of the pyrene fluorescence intensity in order to estimate fundamental parameters of the pyrene–surfactant system, such as the binding equilibrium constant *K* of pyrene to a given surfactant micelle, the rate constant of excimer formation in micelles, and the equilibrium constant of pyrene–surfactant quenching. The values of the binding equilibrium constant $K_{TX100} = 3300 \cdot 10^3\ M^{-1}$ and $K_{SDS} = 190 \cdot 10^3\ M^{-1}$ for Triton X-100 (TX100) and SDS micelles, respectively, show that the partition of pyrene between bulk water and micelles cannot be ignored, even at relatively high surfactant concentrations above the *cmc*. We apply the model to the determination of the *cmc* from the pyrene fluorescence intensity, especially from the intensity ratio at two vibronic bands in the monomer emission or from the ratio of excimer to monomer emission intensity. We relate the finite width of the transition region below and above the *cmc* with the observed changes in the pyrene fluorescence in this region.

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1. Introduction

Pyrene has been used for more than 50 years as fluorescent probe par excellence for microheterogeneous systems such as micelles [1–13], polymers [14–16], proteins [17–19], peptides [20] and biological membranes [18,21–23]. The sensitivity of the pyrene fluorescence intensity to the solvent polarity is widely used for the determination of the *cmc* of micellar systems [3,12,13,24–30]. Therefore, it is surprising that there is still no established procedure to extract a *cmc* value from pyrene fluorescence data that can be related to basic properties of the micellar system and thus be compared to results obtained from other techniques. Currently, ad hoc graphical procedures are used, such as the intersection of straight lines drawn through the experimental data at low and high surfactant concentrations or the fit of arbitrary functions that have no foundation on the well-known fluorescence properties of pyrene in micellar systems. In order to obtain a *cmc* value consistent with other techniques it is necessary to use a common definition of the *cmc* that is based on the surfactant concentration and then to deduce the response of the pyrene fluorescence to the changes in the micellar solution around the *cmc*. The difficulty to do this lies mainly in the first part, the definition of the *cmc* and the necessary model for the concentrations of monomeric and micellized surfactant around the *cmc*. Many excellent theoretical and numerical descriptions of surfactant self-aggregation [31–37] allow now to understand and to predict the properties of micellar systems, but they are still too complex to be used as models for the analysis of experimental data. As a practical solution we proposed recently a manageable model for the surfactant concentration derived from a few empirically established properties of micellar solutions around the *cmc* [38]. This model reproduces with high precision the concentrations of monomeric and micellized surfactant around the *cmc* and allows one to deduce unified descriptions for several properties that depend on these concentrations. We obtained consistent *cmc* values from different surfactant properties such as electrical conductivity, surface tension, NMR chemical shifts, absorption, and self-diffusion coefficients, and also from the fluorescence intensity and the mean translational diffusion coefficient of several fluorescent dyes in surfactant solutions [38,39]. In this contribution we combine this concentration model with the well-known photophysics of pyrene in order to obtain a manageable procedure for the analysis of the fluorescence intensity of pyrene in micellar solutions.

The photophysical behaviour of pyrene in microheterogeneous systems is complex and has been the object of many detailed studies and reviews. The fluorescence spectrum of pyrene shows characteristic vibronic bands around 370–400 nm, whose absolute and relative intensities, width and positions depend sensitively on the polarity of the microenvironment [3,26,40–45]. The pyrene fluorescence emission can be quenched due to the diffusion controlled formation of excimers with a characteristic emission band at longer wavelengths around 500 nm [24,40,46–49]. The time dependence of the pyrene fluorescence intensity after pulsed excitation follows Stern–Volmer quenching kinetics in pure water but has a much more complex behaviour in microheterogeneous environments [26,49–53]. Although pyrene is highly hydrophobic and only sparingly soluble in pure water, it still follows a partition equilibrium between the aqueous phase and the micellar pseudophase with a partition equilibrium constant that is high but not infinite [27,39].

The ratio of the fluorescence intensities of the first and third vibronic bands of pyrene (I_I/I_{III}-ratio) increases characteristically with increasing polarity of the probe environment and defines the so called "py-scale" [42,44]. The passage of the hydrophobic pyrene from the aqueous phase to the apolar micellar pseudophase with increasing surfactant concentrations results in a sigmoidal decrease of the I_I/I_{III}-ratio around the *cmc*. Although visually very suggestive, there is no one special point of the sigmoid which can be directly assigned to the *cmc* of the solution, especially not the centre of the sigmoid. Zana et al. [27] gave a special solution for the limiting case of zero *cmc* taking into account the partition equilibrium of pyrene between aqueous and micellar phase. Aguiar et al. proposed to use the relative width of the sigmoidal as a criterion for the selection of one of two possible *cmc* values: the centre of the sigmoid in the case of nonionic surfactants and the intersection of two straight lines drawn through the rapidly changing part and the horizontal part at high concentrations for ionic surfactants with higher *cmc* values [30]. This leads to *cmc* values that are in agreement with those obtained with other techniques. However, this phenomenological approach does not take into account the partition equilibrium of pyrene and does not relate the sigmoidal model and its parameters with more fundamental physical properties of the system under study. It is not clear why any of the two selected concentrations should represent the same *cmc* as determined with other techniques.

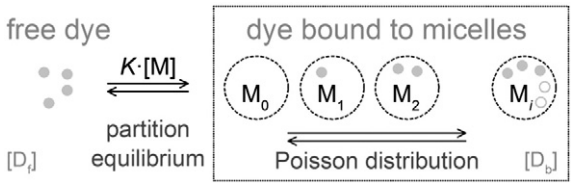
Pyrene excimer formation is another property that is highly sensitive to the formation of the first micelles around the *cmc* [8,52,54,55]. Due to the low solubility of pyrene in pure water, the efficiency of excimer formation is low at surfactant concentrations below the *cmc*. The same is true at high surfactant concentrations where there is a very low probability to find more than one pyrene molecule in a micelle. However, at the *cmc* the pyrene molecules are crowded into the first few micelles so that excimer formation is favoured and leads to a relatively strong peak in the excimer fluorescence intensity. Again, this peak does not coincide with the *cmc* itself and the quantitative analysis of the excimer fluorescence for the determination of the *cmc* has not been fully achieved yet.

Misra et al. interpret the fact that the excimer peak appears at concentrations below the *cmc* as evidence for the formation of pre-micellar aggregates and the gradual decrease of the I_1/I_3-ratio as a progressive increase of the micellar size [56]. As we will show here, both observations can be readily explained taking into account the partition equilibrium of pyrene and the finite size of the transition region around the *cmc* without the need for pre-micelles or a stepwise growth of micellar size.

A full description of the dependence of the pyrene fluorescence intensity and decay on the surfactant concentration near the *cmc* has to take into account several processes (Scheme 1): (1) the concentration of monomeric surfactant and micelles for a given total surfactant concentration (the surfactant-concentration model), (2) the partition equilibrium of pyrene between bulk water and micelles, (3) the distribution of bound pyrene among the micelles, (4) the quenching of pyrene due to excimer formation and (5) the interaction of pyrene with monomeric surfactant. We will combine these processes step by step and then apply the resulting equations to experimental data.

2. Theory

We distinguish three dominant fluorescent pyrene species in a micellar solution: free pyrene in the aqueous phase emitting as monomer (D_f), and pyrene bound to micelles emitting as monomer (D_{bm}) or emitting as excimer (D_{be}) (see Fig. SI2 in the SI). We ignore the very weak contribution of the excimer formed by free pyrene in water.



Scheme 1. Processes controlling the dependence of the pyrene fluorescence intensity and decay on the surfactant concentration near the *cmc*. The dye (D_f) partitions between bulk water and micelles with binding equilibrium constant *K*. The distribution of the bound dye (D_b) among the micelles leads to different local dye concentrations in micelles M_i with occupancy *i*. Not shown here is the quenching of free dye by surfactant molecules and the formation of dye excimers in the micelles.