

ELECTRONIC SUPPLEMENTARY INFORMATION

FLUORESCENCE QUENCHING OF 1-PYRENE-CARBOXALDEHYDE BY THE IODIDE ION IN THE PRESENCE OF ANIONIC (SDS) AND CATIONIC (CTAC) MICELLES: A QUANTITATIVE TREATMENT

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1.-Appendix 1

DEDUCTION OF EQUATIONS 6 AND 21

The purpose of this appendix is to justify equations 6 and 21, that is, the equations for $(K_{SV})_{obs}$ and a_b/a_f in the case where the fluorophore and the quencher are distributed between the continuous phase and the receptor. In this case, an equilibrium constant K_Q can be defined with an analogous meaning to the equilibrium constant K , of the fluorophore. Using K_Q , the following equations arise:

$$[Q_f] = \frac{1}{1 + K_Q[M]}[Q] \quad (a) \quad (A1-1)$$

$$[Q_b] = \frac{K_Q[M]}{1 + K_Q[M]}[Q] \quad (b)$$

It should be noted that this case is different to the case of anionic micelles. On the one hand, $[Q_f]$ cannot be considered a constant and $\approx [Q]$, because the concentration of the quencher in solution depends on the concentration of the receptor (see equation A1-1a). On the other hand, not all the quenchers bound to the receptors, $[Q_b]$, are able to produce quenching of R_b^* . Only the quencher located at micelles also containing R_b^* are effective because, obviously, quenchers bound to receptors that do not contain excited fluorophore do not produce quenching. In relation to this, equation A1-1b may be misleading. According to this equation, $[Q_b]$ increases with $[M]$, however, the average number of quenchers per micelle decreases when $[M]$ increases. In fact, this number is given by:

$$\langle Q \rangle = \frac{[Q_b]}{[M]} = \frac{K_Q[Q]}{1 + K_Q[M]} \quad (A1-2)$$

Both $[Q_f]$ and $\langle Q \rangle$ depend on the concentration of the receptor and decrease when $[M]$ increases. This fact changes the expression of $(K_{SV})_{obs}$, that now must be reformulated as:

$$\begin{aligned} (K_{SV})_{obs}[Q] &= \frac{(K_{SV})_f [Q_f] + (K_{SV})_b \frac{a_b}{a_f} K[M] \langle Q \rangle}{1 + \frac{a_b}{a_f} K[M]} = \\ &= \frac{(K_{SV})_f \frac{[Q]}{1 + K_Q[M]} + (K_{SV})_b \frac{a_b}{a_f} K[M] \frac{K_Q[Q]}{1 + K_Q[M]}}{1 + \frac{a_b}{a_f} K[M]} \end{aligned} \quad (A1-3)$$

Hence:

$$(K_{SV})_{obs} = \frac{(K_{SV})_f + (K_{SV})_b K_Q \frac{a_b}{a_f} K[M]}{\left(1 + \frac{a_b}{a_f} K[M]\right) (1 + K_Q[M])} = \frac{(K_{SV})_f + (K_{SV})_b K_Q K_{app} [M]}{1 + [K_Q + K_{app}] [M] + K_Q K_{app} [M]^2} \quad (A1-4)$$

$$\frac{a_b}{a_f} = \frac{(\varphi_b)_Q \varepsilon_b}{(\varphi_f)_Q \varepsilon_f}.$$

That is equation 6. Equation A1-4 (or 6) deserves some comments. The first point is to emphasize that this equation is the counterpart of equation A1-5 for the rate constant of processes in which ground state reactants participate.¹

$$k_{obs} = \frac{k_f + k_b K_{R1} K_{R2} [M]}{(1 + K_{R1} [M]) (1 + K_{R2} [M])} \quad (A1-5)$$

However, in the case of photochemical reactions, $K_{app} = K \cdot a_b/a_f$ appears instead of K .

In order to employ equation A1-4, $(K_{SV})_f$, $(K_{SV})_b$ and a_b/a_f must be known. But now, a_b/a_f depends on both the concentration of the quencher (in solution) and the concentration of the receptor, according to equation A1-2. The determination of $(K_{SV})_f$ does not present any difficulties. However, in order to obtain $(K_{SV})_b$ and a_b/a_f , the rate constants of the radiative, non-radiative and the quenching processes for the bound reactant must be known. These constants can be determined from fluorescence decay and emission quantum yield measurements, in the absence and presence of the quencher according to the following equations:

$$\begin{aligned}(\varphi_f)_0 &= \frac{(k_r)_f}{(k_r)_f + (k_{nr})_f} \\(k_{df})_0 &= (k_r)_f + (k_{nr})_f\end{aligned}\tag{A1-6}$$

$$\begin{aligned}(\varphi_f)_Q &= \frac{(k_r)_f}{(k_r)_f + (k_{nr})_f + (k_q)_f[Q]} \\(k_{df})_Q &= (k_r)_f + (k_{nr})_f + (k_q)_f[Q]\end{aligned}\tag{A1-7}$$

Using the same procedure in the presence of a given concentration of receptor, high enough to produce a situation in which all the fluorophores are bound to the receptors, the result will be:

$$\begin{aligned}(\varphi_b)_0 &= \frac{(k_r)_b}{(k_r)_b + (k_{nr})_b} \\(k_{db})_0 &= (k_r)_b + (k_{nr})_b\end{aligned}\tag{A1-8}$$

$$\begin{aligned}(\varphi_b)_Q &= \frac{(k_r)_b}{(k_r)_b + (k_{nr})_b + (k_q)_b \langle Q \rangle} = \frac{(k_r)_b}{(k_r)_b + (k_{nr})_b + (k_q)_b \frac{K_Q[Q]}{1 + K_Q[M]}} \\(k_{db})_Q &= (k_r)_b + (k_{nr})_b + (k_q)_b \langle Q \rangle = (k_r)_b + (k_{nr})_b + (k_q)_b \frac{K_Q[Q]}{1 + K_Q[M]}\end{aligned}\tag{A1-9}$$

Hence, $(k_q)_b$ can be obtained if K_Q is known. Once $(k_q)_b$ is obtained, the determination of $(K_{SV})_b$ is straightforward:

$$(K_{SV})_b = k_{qb} \tau_{0b} = \frac{k_{qb}}{k_{db}^{Q \neq 0}} \quad (\text{A1-10})$$

Finally, a_b/a_f for each concentration of quencher and micelle, will be given by:

$$\begin{aligned} \frac{a_b}{a_f} &= \frac{(\varphi_b)_Q \varepsilon_b}{(\varphi_f)_Q \varepsilon_f} = \frac{\frac{(k_r)_b}{(k_r)_b + (k_{nr})_b + (k_q)_b \langle Q \rangle} \varepsilon_b}{\frac{(k_r)_f}{(k_r)_f + (k_{nr})_f + (k_q)_f [Q_f]} \varepsilon_f} = \\ &= \frac{\frac{(k_r)_b}{(k_r)_b + (k_{nr})_b + (k_q)_b \frac{K_Q [Q]}{1 + K_Q [M]}} \varepsilon_b}{\frac{(k_r)_f}{(k_r)_f + (k_{nr})_f + (k_q)_f \frac{[Q]}{1 + K_Q [M]}} \varepsilon_f} \end{aligned} \quad (\text{A1-11})$$

that is equation 21.

2.- Appendix 2

ON THE MEANING OF $(K_{SV})_f$ IN MICELLAR SOLUTIONS: A GENERALIZATION OF THE TREATMENT

As mentioned in section 3.2, I_f is different from the emission intensity in the absence of a surfactant. This indicates some interactions of the monomers with the pyal. Indeed the Stern-Volmer constant at the cmc, to which $(K_{SV})_f$ corresponds, is different from the value in the absence of surfactant ($(K_{SV})_s = 50 \text{ mol}^{-1} \text{ dm}^3$). This implies that the monomers can be considered as *receptors*, in the sense that they interact with the pyal and change its properties. According to this, a micellar solution should be considered as a system containing two different receptors, monomers and micelles.

This question will be considered with some detail, because it is relevant not only in the case of micellar solutions. It is also of interest for the cases of biological receptors, such as DNA, that present different binding sites to which the ligands bind with different affinities.¹

Consider the case of a solution containing two receptors m and M and the fluorophore. The emission intensity will be given by:

$$I = \frac{I_s + I_m K'_m [m] + I_M K'_M [M]}{1 + K'_m [m] + K'_M [M]} \quad (\text{A2-1})$$

In this equation K'_m and K'_M represent the (true) binding constant of the fluorophore to m and M, respectively, and I_m and I_M the corresponding emission intensities. I_s is the emission intensity of the free fluorophore, that is, in the solvent.

For the observed Stern-Volmer constant, one can write:

$$(K_{SV})_{\text{obs}} = \frac{(K_{SV})_s + (K_{SV})_m \frac{a_m}{a_s} K'_m [m] + (K_{SV})_M \frac{a_M}{a_s} K'_M [M]}{1 + \frac{a_m}{a_s} K'_m [m] + \frac{a_M}{a_s} K'_M [M]} \quad (\text{A2-2})$$

Equations A2-1 and A2-2 are the generalization of equations 4 and 7, respectively.

Now consider that the receptor m is present at constant concentration (the cmc in the case of micellar solutions). In this case equation A2-1 can be written as:

$$I = \frac{\frac{I_s + I_m K'_m [\text{cmc}]}{1 + K'_m [\text{cmc}]} + \frac{I_M K'_M [M]}{1 + K'_M [M]}}{1 + \frac{K'_M [M]}{1 + K'_m [\text{cmc}]}} \quad (\text{A2-3})$$

This equation can be expressed as equation 4, if one takes:

$$K = \frac{K'_M}{1 + K'_m[\text{cmc}]} \quad (\text{a})$$

(A2-4)

$$I_f = \frac{I_s + I_m K'_m[\text{cmc}]}{1 + K'_m[\text{cmc}]} \quad (\text{b})$$

Equations A2-4 give the meaning of the parameters I_f and K appearing in equation 4.

On the other hand, following a similar procedure it can be shown that equation A2-2, in the present case, can be reduced to equation 7 if:

$$(K_{SV})_f = \frac{(K_{SV})_s + (K_{SV})_m \frac{a_m}{a_s} K'_m[\text{m}]}{1 + \frac{a_m}{a_s} K'_m[\text{m}]} \quad (\text{A2-5})$$

and

$$\frac{a_b}{a_f} = \frac{\frac{a_M}{a_s} (1 + K'_m[\text{cmc}])}{1 + \frac{a_m}{a_s} K'_m[\text{cmc}]} = \frac{\frac{a_M}{a_s}}{\frac{1 + \frac{a_m}{a_s} K'_m[\text{cmc}]}{1 + K'_m[\text{cmc}]}} = \frac{\frac{a_M}{a_s}}{\frac{a_{\text{cmc}}}{a_s}} = \frac{a_M}{a_{\text{cmc}}} \quad (\text{A2-6})$$

In this equation $a_{\text{cmc}} = \varphi_{\text{cmc}} \varepsilon_{\text{cmc}}$ and is given by

$$a_{\text{cmc}} = \frac{a_s + a_m K'_m[\text{cmc}]}{1 + K'_m[\text{cmc}]} \quad (\text{A2-7})$$

Of course a_{cmc} is different from a_m , because this latter parameter refers to a situation in which the fluorophore would be completely bound to the monomer and a_{cmc} corresponds to the cmc.

Figure S1

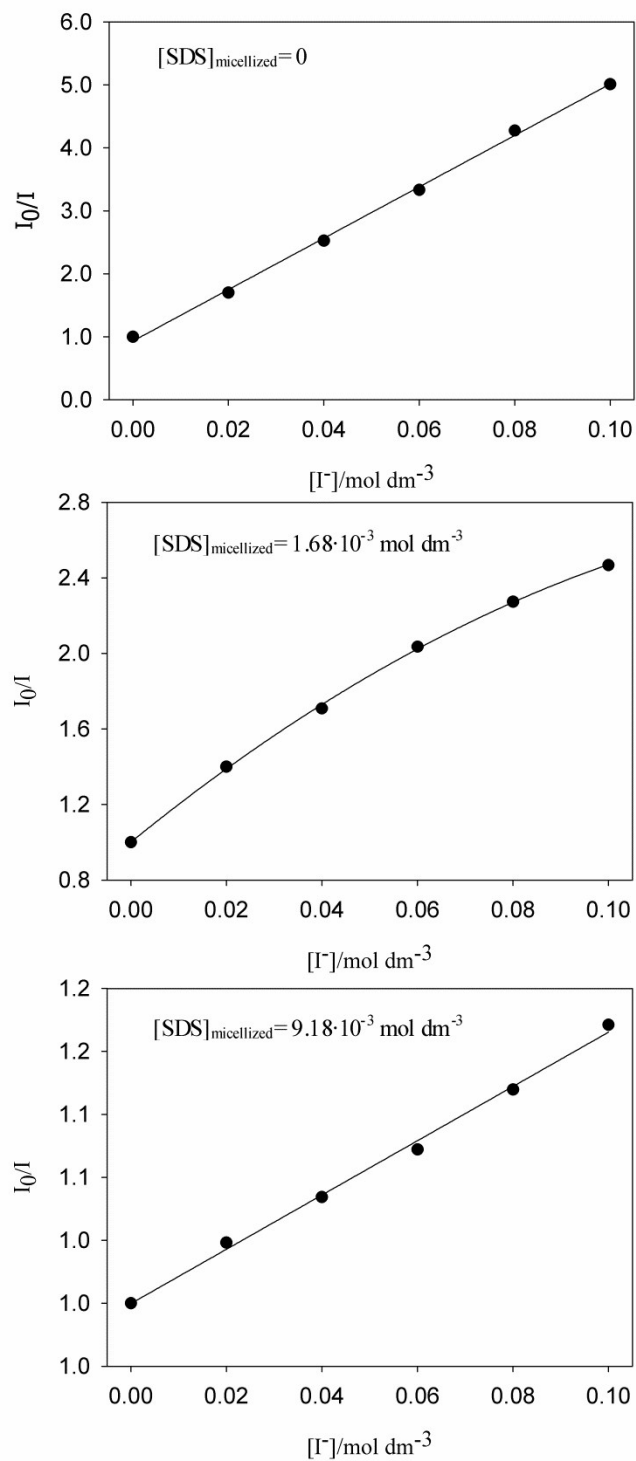


Figure S1: Stern-Volmer plot for the quenching of 1-pyrene-carboxaldehyde by iodide ion in micellar solutions of SDS at several micelles concentrations.

1. M. J. Hannon, *Chem. Soc. Rev.*, 2007, **36**, 280–295.