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# LED control of molecular interactions and phase transitions in soap films using photosurfactants : Supplementary informations

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## *CMC* of the cis-trans mixture as a function of the total concentration and trans ratio *R*

We explain now how the *CMC* evolves with the solution composition. Mysels[1,2] established the relation between the *CMC* and the properties of the pure surfactants for an ideal binary solution of ionic surfactants. It is valid in our system as binary solutions of surfactants with same polar head behave as an ideal mixture of adsorbed pure components[2]. The relation is given by:

$$\begin{cases} CMC^{\theta} = \dfrac{(cmc_{trans}\, cmc_{cis})^{\theta}}{x cmc_{cis}^{\theta} + (1-x) cmc_{trans}^{\theta}} \\ CMC^{\theta} = y\, cmc_{trans}^{\theta} + (1-y) cmc_{cis}^{\theta} \end{cases} \tag{1}$$

Where $y$ is the ratio of trans in the micelle phase, $x$ the ratio of trans in the monomer phase, $cmc_{trans}$ and $cmc_{cis}$ are the *CMC*s of the pure bodies without added salt, $\theta - 1$ is the effective degree of counter ions binding. For a given solution ratio $R$ at concentrations close to the formation of first micelles, $x \simeq R$ because almost no surfactant are in the micelles, and the *CMC* is given by $CMC^{\theta} \simeq \frac{(cmc_{trans}\, cmc_{cis})^{\theta}}{R cmc_{cis}^{\theta} + (1-R) cmc_{trans}^{\theta}}$. The *CMC* value (for $c \simeq CMC$) is highly nonlinear on $R$ and biased toward the most lipophilic surfactant because the first micelles are much enriched in the most lipophilic specie. However at total concentration much bigger than the *CMC*, most of the surfactants are in the micelles and $y \simeq R$, so that the *CMC* increases and is given by $CMC^{\theta} \simeq R\, cmc_{trans}^{\theta} + (1-R) cmc_{cis}^{\theta}$ : the CMC increases witht the total concentration in a binary mixture of surfactant.

We found experimentally[3] that the effective degree of counter ions binding is be close to 1, so we take $\theta = 2$. We measured the *CMC* at appearance of the first micelle by surface tension measurement for 3 different $R$, see Fig S1, and deduced from the eq S(1) the estimation of the pure bodies CMC : $cmc_{trans} \approx 1.6mM$ and $cmc_{cis} \approx 20mM$. We also plot on Fig S1 values of the CMC for the solutions of c=16mM (section 3 in the main text), that we estimate from the values of $\kappa_D^{-1}$ (Table 1 in the main text) using the theoretical formula $\kappa_D^{-1} = \left( \dfrac{\varepsilon_0 \varepsilon_r k_B T}{2q^2 CMC} \right)^{1/2}$ (derived in the main text). We would expect these CMC values to be higher, because for such a concentration the micelle phase is important and the CMC is between the blue and green curves ; however the values lie in the good range, and we observe a good qualitative trend (CMC decreases as $R$ increases) that validates our hypothesis.

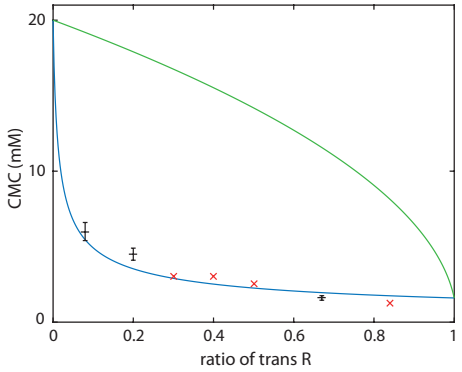


**Figure 1** Plot of the CMC as a function of $R$ the ratio of trans surfactants in the solution. In blue, the theoretical curve of the CMC when the first micelle appears. In green the theoretical curve of the CMC in the limit of high total concentrations of surfactants. The black crosses are the experimental evaluations of the CMC at appearance of first micelle (with which the theoretical curve is fitted) (the vertical segments are the error bars). The red crosses are the values of the CMC for solutions of c=16mM, deduced from the evaluations of $\kappa_D^{-1}$ (Table 1 in the main text) and from the theoretical value of $\kappa_D^{-1}$. (error comprised in the symbol size)

## Evolution of the surface and bulk composition under light stimulation

As the adsorption of micelles is negligible in front that of monomers, the flows between the interfaces and bulk are given by :

$$\begin{cases} \dfrac{d\Gamma_{trans}}{dt} = k_{ads}^{0trans} e^{-2arcsh\frac{\Gamma_{trans}+\Gamma_{cis}l_B}{2\kappa}} c_{mono}^{trans}(1-\omega_\infty^{trans}\Gamma_{trans}-\omega_\infty^{cis}\Gamma_{cis}) - k_{des}^{trans}\omega_\infty^{trans}\Gamma_{trans} - a\Gamma_{trans} + b\Gamma_{cis} \\ \dfrac{d\Gamma_{cis}}{dt} = k_{ads}^{0cis} e^{-2arcsh\frac{\Gamma_{trans}+\Gamma_{cis}l_B}{2\kappa}} c_{mono}^{cis}(1-\omega_\infty^{trans}\Gamma_{trans}-\omega_\infty^{cis}\Gamma_{cis}) - k_{des}^{cis}\omega_\infty^{cis}\Gamma_{cis} + a\Gamma_{trans} - b\Gamma_{cis} \end{cases} \tag{2}$$

$$\begin{cases} \dfrac{c_{trans}}{dt} = \dfrac{2}{h}\left(\dfrac{d\Gamma_{trans}}{dt} + a\Gamma_{trans} - b\Gamma_{cis}\right) - ac_{trans} + bc_{cis} \\ \dfrac{c_{cis}}{dt} = \dfrac{2}{h}\left(\dfrac{d\Gamma_{cis}}{dt} - a\Gamma_{trans} + b\Gamma_{cis}\right) ac_{trans} - bc_{cis} \end{cases} \tag{3}$$

Where $a$ and $b$ are the switch rates respectively from trans state to cis, and cis to trans, due to the light stimulation. These rates depend on the light wavelength, they are also proportionnal to the light intensity. We described them and determined their values in a previous work[4]. The concentrations in conformer trans and cis in the monomer phase are written $c_{mono}^{trans}$ and $c_{mono}^{cis}$. Their value is given by $c_{mono}^{trans} = xCMC$ (and $c_{mono}^{cis} = (1-x)CMC$), with $x = y(\frac{cmc_{trans}}{CMC})^\theta$, $(1-x) = (1-y)(\frac{cmc_{cis}}{CMC})^\theta$ [1]. At $c \gg CMC$ it is given by $c_{mono}^{trans} = Rcmc_{trans}{}^\theta CMC^{1-\theta}$, $c_{mono}^{cis} = (1-R)cmc_{cis}{}^\theta CMC^{1-\theta}$. These formulas are correct if the dynamics of exchange between the monomer phase and micellar phase equilibrate faster than the switch, which is the case. The total concentrations in the film at stationary state are given by:

$$\begin{cases} hc_{cis} + 2\Gamma_{cis} = n_0 \dfrac{a}{a+b} \\ hc_{trans} + 2\Gamma_{trans} = n_0 \dfrac{b}{a+b} \end{cases} \tag{4}$$

With $h$ the film thickness and $n_0 = 2(\Gamma_{trans}+\Gamma_{cis}) + h(c_{trans}+c_{cis})$ the total number of surfactant per unit surface of film (which remains constant during the stimulation). We notice that $R$ is independent of $h$, as long as the desorption of surfactants increase the volume concentration $c$ to $c \gg CMC$, which is the case in our situation.

## References


[1] K. J. Mysels and R. J. Otter, *Journal of Colloid Science*, 1961, **16**, 474–480.

[2] K. Ogino and M. Abe, *Mixed surfactant systems*, CRC Press, 1992.

[3] E. Chevallier, *Ph.D. thesis*, Université Pierre et Marie Curie-Paris VI, 2012.

[4] E. Chevallier, A. Mamane, H. Stone, C. Tribet, F. Lequeux and C. Monteux, *Soft Matter*, 2011, **7**, 7866–7874.