

Supporting material for "Control of spontaneous spirals formation in a zwitterionic micellar medium"

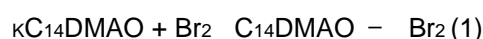
Federico Rossi^{*} Rosario Varsalona[†] Nadia Marchettini[‡] Maria Liria
Turco Liveri[§]

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1 CTC formation constant

Starting from the measurements of the absorbance ($\lambda = 271.5$ nm) of an acidic solution of C₁₄DMAO and molecular bromine, we want to calculate the equilibrium constant

(K) of the process



We postulate, in fact, that the zwitterionic surfactant could be considered an analogue of an aliphatic amine, *i.e.* a *n*-donor equivalent, therefore when in solution with an acceptor (Br₂) can form a CTC complex. In order to describe the analytical approach to the problem we can define few variables as follows:

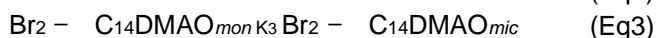
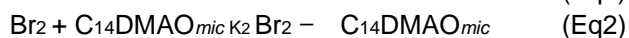
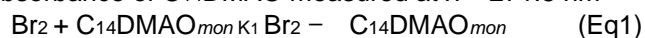
^{*} Dipartimento di Chimica, Università di Siena, Siena, E-mail: f.rossi@unisi.it

[†] Dipartimento di Chimica, Università di Palermo, Palermo

[‡] Dipartimento di Chimica, Università di Siena, Siena [§] Dipartimento di Chimica, Università di Palermo, Palermo, E-mail: tliveri@unipa.it

$a_0 = [\text{Br}_2]_0$ the analytic concentration of Br_2 $d_0 = [\text{C}_{14}\text{DMAO}]_0$ the analytic

ϵ_a the molar extinction coefficient of Br_2
 ϵ_d the molar extinction coefficient of C_{14}DMAO
 ϵ_x the molar extinction coefficient of the CTC
 a_t the absorbance of the solution at equilibrium measured at $\lambda = 271.5$ nm
 a_{0a} the analytic absorbance of Br_2 measured at $\lambda = 271.5$ nm
 a_{0d} the analytic absorbance of C_{14}DMAO measured at $\lambda = 271.5$ nm



concentration of C_{14}DMAO $x = [\text{Br}_2 - \text{C}_{14}\text{DMAO}]_{eq}$ the concentration of the complex at the equilibrium

For the sake of simplicity, the optical path length l has been omitted from the relations among experimental absorbances and the absorbing species, being always equal to 1 cm. If we assume the constancy of the activity coefficients for diluted solutions, the equilibrium (formation) constant can be expressed as the ratio between products and reactants.

$$[\text{Br}_2 - \text{C}_{14}\text{DMAO}]_{eq}$$

$$K = (2)$$

$$[\text{Br}_2]_{eq}[\text{C}_{14}\text{DMAO}]_{eq}$$

1.1 Non interfering spectra

If the absorption spectrum of the CTC do not overlaps with the spectra of the reactants in the wavelength region where the CTC has the absorption maximum, a simple method can be used to determine K . Equation 2 can be rewritten as

x

$$K = (3)$$

$(a_0 - x)(d_0 - x)$ remembering that

$x = a_t/\epsilon_x$ where a_t is the absorbance of the solution at equilibrium
measured at $\lambda = 271.5$ nm and ϵ_x is the molar extinction coefficient
of the CTC

complex, equation 3 yields

$$a_t = (a_0 + d_0) + \frac{a_0 d_0}{\epsilon^2} \quad (4)$$

$$\frac{a_t}{\epsilon x} = \frac{a_0 + d_0}{z} + \frac{a_0 d_0}{z^2} \quad (5)$$

by plotting y against z for several experiments with different a_0 and/or d_0 , from a linear fitting we obtain m and b , which ultimately give

$$\frac{1}{\epsilon x} = \frac{1}{z} + \frac{m}{z^2} \quad (5)$$

and

$$K = \frac{m}{b + a m^2} \quad (6)$$

1.2 Interfering spectra

In the case where the absorption of the complex overlaps with the one of the donor and the acceptor, a different approach should be used. The measured absorbance at the equilibrium can be expressed as the sum of the single absorbances of the species absorbing at $\lambda = 271.5$ nm

$$a_t = a_a + a_d + a_x \quad (7)$$

and if the Lambert-Beer law holds for all the species

$$a_t = \epsilon_a a + \epsilon_d d + \epsilon_x x$$

or

$$a_t = x(\epsilon_x - \epsilon_a - \epsilon_d) + \epsilon_a a_0 + \epsilon_d d_0 \quad (8)$$

We can also introduce a quantity to give an estimation of the deviation from additivity in the mixture

$$a_c = a_t - \frac{a^0}{ad} - a^0 \quad (9)$$

or

$$a_c = x(\epsilon_c) \quad (10)$$

being

$$\epsilon_c = \epsilon_x - \epsilon_a - \epsilon_d \quad (11)$$

Equation 4 can now be rewritten as

$$\frac{a_0 d_0}{1 + a_c} = (a_0 + d_0) + \frac{\epsilon_c}{K} \quad (12)$$

Analogously to the case of non interfering spectra, the values of ϵ_c and K can be inferred by fitting equation 12 for several experiments. Finally, the molar extinction coefficient of the CTC can be calculated through equation 11. When the coefficient ϵ_c is large, the term a/ϵ_c^2 can be neglected.

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The values of a_a , a_d , ϵ_a and ϵ_b can be measured with *ad hoc* experiments, by separately recording the spectra of $[Br_2]_0$ and $[C_{14}DMAO]_0$ in acidic solutions. Depending on the experimental conditions, an iterative procedure may be used to improve the reliability of the results. In this case a first value of K is calculated by fitting equation 12, the constant is then used to calculate x through equation 3 and a new value of ϵ_c is calculated from equation 10 and inserted in equation 12. An arbitrary change to K is then made and the whole procedure is repeated until the correlation coefficient for the fitting of equation 12 becomes constant.

1.3 Monomers and Micelles

In our experimental conditions we could not perform measurements below the surfactant cmc, because in the presence of bromine a slow precipitation process takes places and spectrophotometric acquisitions are not possible. On the one hand this fact con

firmly the strong association between Br₂ and C₁₄DMAO but, on the other hand, it does not permit a precise quantification of K for monomers and consequently for the micelles. However, when [C₁₄DMAO] is larger than cmc, the precipitate is rapidly solubilized, meaning that the Br₂- C₁₄DMAO_{mon} adducts participate to the micellization process. The behavior of the system in our experimental conditions,

can be sketched	ϵ_a	the molar extinction coefficient of Br ₂
	ϵ_d	the molar extinction coefficient of C ₁₄ DMAO
with the scheme	ϵ_x	the molar extinction coefficient of the CTC
Eq1–Eq3	a_t	the absorbance of the solution at equilibrium measured at $\lambda = 271.5$ nm
analogous to that	$a_0 a$	the analytic absorbance of Br ₂ measured at $\lambda = 271.5$ nm
for other systems, like Br ₂ - AOT (see ref. 41 in the manuscript).	$a_0 d$	the analytic absorbance of C ₁₄ DMAO measured at $\lambda = 271.5$ nm

According to the pseudophase model, the nonlinear equation 13 can be used to fit experimental data

$$\epsilon_{C1} + \epsilon_{C2}K_3[d_n]$$
$$\epsilon_{app} = (13)$$

$1 + K_3[d_n]$ where $\epsilon_{app} = a_t/a_0$, ϵ_{C1} is the molar extinction coefficients of the monomeric adduct, ϵ_{C2} is the molar extinction coefficients of the micellar adduct and $[d_n]=[C_{14}DMAO]-cmc$. The nonlinear fitting procedure yields the value of K_3 which gives an estimation of the ratio between K_1 and K_2 through the relation $K_2 = K_1K_3[cmc]$.

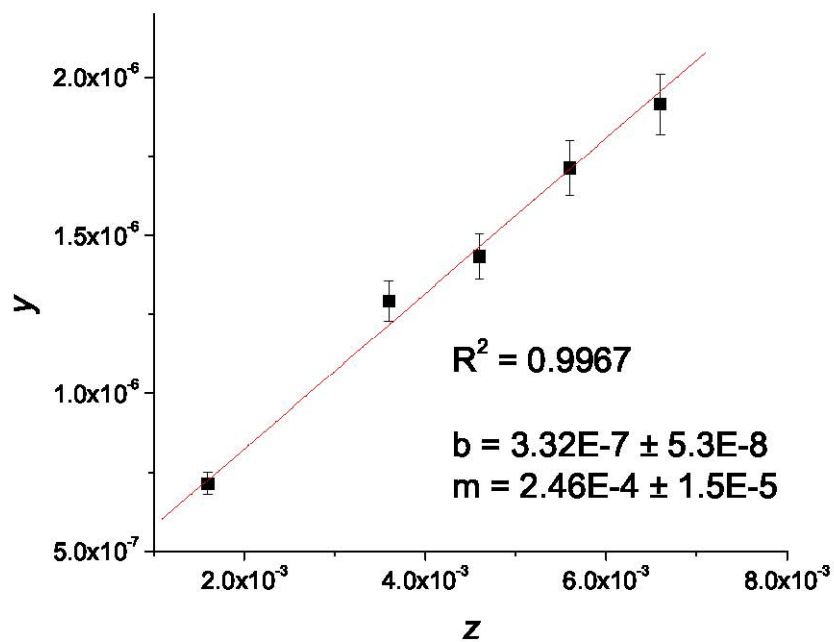
1.4 Experimental Results

Without experiments below the cmc it is not possible to calculate the exact value for the constants K_1 and K_2 , nevertheless we applied to the collected data all the procedures previously described. From the spectra reported in the manuscript we

built the graphs depicted in figures 1 and 2. To data reported in Fig. 1 we applied equations 4 and 12, while to those reported in Fig. 2 we applied equation 13. All the the fitting parameters are reported in the figures. Because the absorption of Br₂ and C₁₄DMAO is weak but non zero at $\lambda = 271.5$ nm, we applied both the procedures for non interfering and interfering spectra and the constants were found to be very similar, $K = 542 \pm 30 \text{ mol}^{-1} \text{ dm}^3$ ($\epsilon = 4166 \pm 30 \text{ cm}^{-1} \text{ mol}^{-1} \text{ dm}^3$) calculated by means of equation 4 and $K = 575 \pm 36 \text{ mol}^{-1} \text{ dm}^3$ ($\epsilon = 4405 \pm 35 \text{ cm}^{-1} \text{ mol}^{-1} \text{ dm}^3$) from equation 12. Finally, from equation 13 we found that $[K_2]/[K_1] = 1.35 \times 10^{-2}$, meaning that the interaction of Br₂ is stronger with the monomers rather than with the micelles. The K values, evidently, account for both the monomeric and micellar form of the surfactant and they represent a rough description of the behavior of our system; nevertheless they can be successfully used for simulations and for giving a general idea of the dynamics which causes the appearance of an induction period in the BZ/C₁₄DMAO system.

2 The Belousov-Zhabotinsky reaction with acetone

In order to check the proposed mechanism of bromine removal by its interaction with the surfactant, we added acetone (Ac, Merck used as received) to the BZ reactive mixture as bromine scavenger. Figure 3 effectively shows that the system moves towards a global oxidized state upon increasing the ketone concentration. The oscillations become progressively faster with a smaller amplitude, meaning that the catalyst is preferentially in the oxidized form (ferriin). Anyway, acetone is not able to induce a real induction period where oscillations are temporary suppressed, but, when [Ac] is too high, oscillations never take place and the systems remain in an oxidized stationary state.



3 Figures

Figure 1: Fitting of experimental data to the equations 4 and 12; $[Br_2] = 6.0 \times 10^{-4} \text{ mol dm}^{-3}$, $[H_2SO_4] = 0.3 \text{ mol dm}^{-3}$, $1.0 \times 10^{-3} \text{ mol dm}^{-3} < [C_{14}DMAO] < 6.0 \times 10^{-3} \text{ mol dm}^{-3}$, $t \sim 24^\circ \text{C}$.

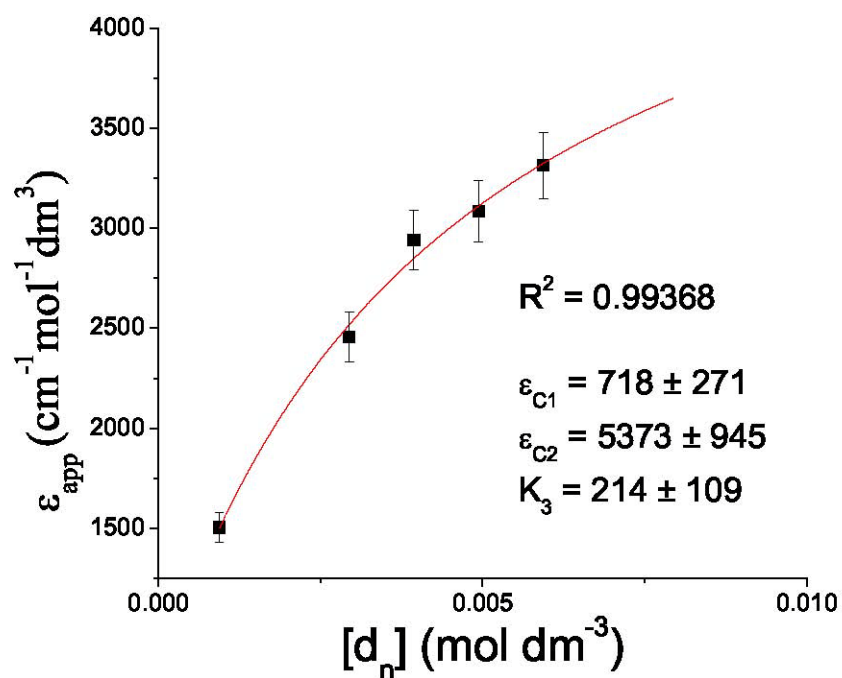


Figure 2: Fitting of experimental data to the equation 13; $[\text{Br}_2] = 6.0 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{H}_2\text{SO}_4] = 0.3 \text{ mol dm}^{-3}$, $1.0 \times 10^{-3} \text{ mol dm}^{-3} < [\text{C}_{14}\text{DMAO}] < 6.0 \times 10^{-3} \text{ mol dm}^{-3}$, $t \sim 24^\circ \text{C}$.

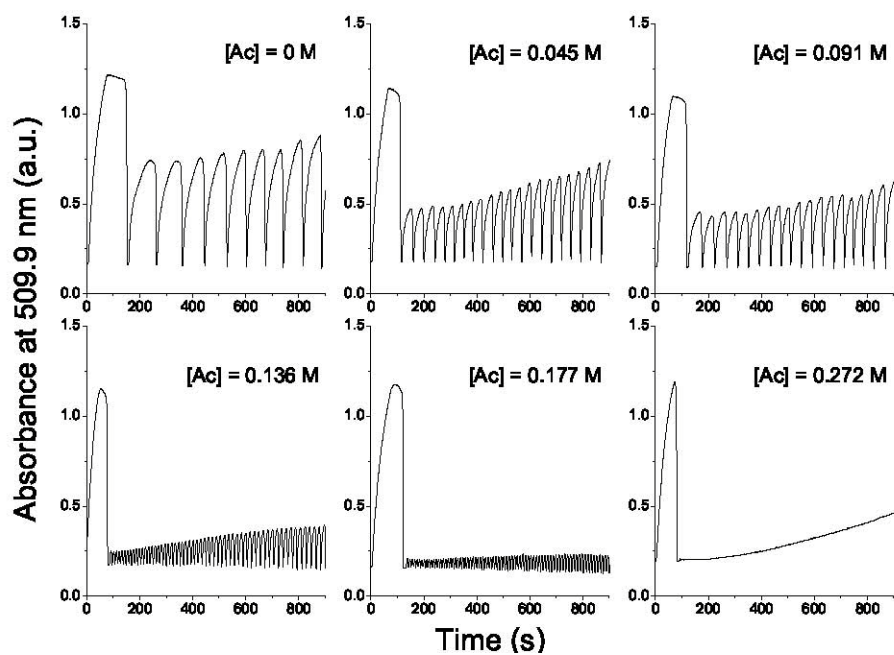


Figure 3: Spectrophotometric time series of a BZ reaction in the presence of increasing amount of acetone (as reported in each panel); $[MA] = 0.03 \text{ mol dm}^{-3}$, $[NaBrO_3] = 0.12 \text{ mol dm}^{-3}$, $[ferroin] = 3.0 \times 10^{-3} \text{ mol dm}^{-3}$, $[H_2SO_4] = 0.30 \text{ mol dm}^{-3}$. $t \sim 24^\circ \text{C}$.