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FLUORIMETRIC CHARACTERIZATION OF THE INTERACTION OF 3-CARBOXY-5,6-BENZOCOUMARINIC ACID WITH MICELLES

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The interaction of 3-carboxy-5,6-benzocoumarinic acid (BzCum) with cationic cetyl trimethylammonium bromide (CTAB), anionic sodium dodecyl sulfate (SDS) and nonionic *p-tert*-octylphenoxy polyoxyethanol (TX-100) surfactants has been studied by steady state fluorescence. In order to evaluate the binding constants for the fluorophore-surfactants interaction, two of the most important characteristics of the micelles, the critical micellar concentrations (cmc) and aggregation number (N_{agg}), were determined in our experimental conditions, i.e. phosphate buffer with pH=10.

INTRODUCTION

Micelles are self-organized molecular assemblies of amphiphilic molecules that consist of a hydrophobic core and a hydrophilic shell. The core of a micelle is essentially "dry", being formed by hydrocarbon chains (hydrophobic tail) with polar and/or charged head groups (hydrophilic head) projecting outward into the bulk water.[1] Depending on the nature of head group, micelles can be negative, positive or uncharged. The shell of the micelles is called Stern layer if the micelle is ionic or palisade layer if the micelle is non-ionic. The interest for micelles resides in the fact that they can mimic biological systems. The water molecules that are tightly bound to the surfactant head groups of the micelles resemble the hydrophilic pockets of enzymes and have high viscosities, low mobilities and polarities.[2]

The coumarins represent a widely studied class of compounds with many applications.[3] They are used in foods, cosmetics, tobacco and also as anticoagulants, antioxidants, immunomodulatory agents, laser dyes, ionophores, fluorescence markers and probe molecules for the examination of electron transfer processes and ultrafast solvation effects. In our previous studies the photophysical properties and the behavior in electron transfer processes of a new fluorescent coumarin derivative, the 3-carboxy- 5,6-benzocoumarinic acid, BzCum (Fig. 1) were analyzed in organic solvents, in aqueous media, in hydrophobic cavities offered by cyclodextrins and in the presence of aromatic amines in acetonitrile.[4-7] This study is just a preliminary step for the characterization of photoelectronic transfer into the system coumarins-amines in organized media as micelles and cyclodextrins. Since BzCum is a weak acid ($pK_a = 4.6$)[4] it can exist in water in two forms, i.e. protonated and unprotonated form. In order to simplify the system we have chosen to work in buffered solutions with pH=10 which can assure the prevalence of a single species, the carboxylate one. Obviously the basic pH is in accordance with our further intention to analyze the fluorescence quenching of BzCum by amines in micelles, assuring the availability of the electrons pairs of nitrogen atom. A perfect candidate for this task seems to be a cationic surfactant (CTAB) that insures strong interaction through electrostatic forces. However, for the sake

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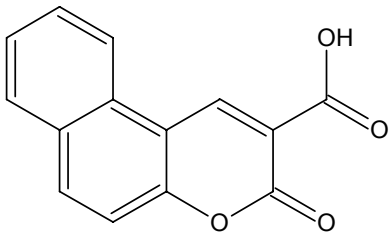
of comparison we have chosen to work as well with an anionic and a nonionic surfactant. Therefore, the aim of this paper is to characterize the interaction of the anionic form of BzCum with CTAB, SDS and TX-100 micelles in terms of binding constants. For this purpose we have evaluate also two of the most important characteristics of the micelles i.e. the critical micellar concentrations (cmc) and the aggregation numbers (N_{agg}).

A)

BzCum



B)

CTAB: $CH_3(CH_2)_{15}N^+(CH_3)_3\ Br^-$

SDS: $CH_3(CH_2)_{11}OSO_3^-Na^+$

TX-100: $CH_3\text{-}C(CH_3)_2\text{-}CH_2\text{-}C(CH_3)_2\text{-}C_6H_4\text{-}O\text{-}(CH_2\text{-}CH_2\text{-}O)_n\text{-}H$, n = 9-10

Fig. 1 – Structure of BzCum (A) and of the surfactant molecules (B).

RESULTS AND DISCUSSION

1. Fluorescence spectra

The anionic form of BzCum in water at pH 10 exhibits a single, broad fluorescence band with a maximum at 438 nm. At first, the addition of surfactant causes an enhancement of the fluorescence intensity, the effect being most significant for CTAB (Fig. 2) and TX-100 (Fig. 3). Further increase in the CTAB concentration induces a drastic suppression of the fluorescence intensity (Φ = 0.01, comparing with Φ = 0.27 in buffered solution pH=10) and a hypsochromic shift of the band of 8 nm. In the presence of the other two surfactants we also found a decrease of the fluorescence intensity, very small for SDS (Fig. 4) and quite important for TX-100, but no shift of the band was observed even at high surfactant concentration. Although in the most reported cases the inclusion of a fluorophore within the micellar environment determines an enhancement of the fluorescence intensity due to the binding of the probe in a less polar site as compared to the pure aqueous phase,[8] the opposite situation is also know (for example in the case of 2-benzoyl benzimidazole[9] and 7-ethoxy-coumarin and 7-ethoxy-4-methylcoumarin[10]). A decrease of the fluorescence intensity was also observed in our previous study on the interaction of BzCum with cyclodextrins in buffered solutions. The fluorescence suppression has been rationalized in terms of an increased probability of the $S_1 \rightarrow T_2$ intersystem crossing process upon inclusion as compared to the situation in polar media, as suggested by Wagner et al. who explained the fluorescence decrease for 7-methoxycoumarin upon inclusion into the cyclodextrins cavity on this basis.[11] It was found that this probability is even greater for the dissociated form of BzCum as compared to the acidic one.[6]

2. Determination of cmc

Cmc represents the concentration of surfactant above which the micelles begin to form spontaneously. The cmc values of surfactants in pure water are well known, being determined from different physical properties such as conductivity[12], surface tension,[13,14] absorbance,[14] fluorescence intensity[14] etc. But it is also known that the presence of electrolytes tends to reduce them.[15] In order to find the cmc values of the surfactants in our experimental conditions, i.e. phosphate buffer that assures a pH = 10, we have plotted the normalized fluorescence as a function of the surfactants concentrations. The plots present multiple breakpoints (Fig. 5). Multiple breakpoints,

generally two or three, were also previously reported and they have been assigned to multiple cmc's.[8,16] Although the interpretation of multiple cmc's is not yet clear, quite often the lower value (cmc_1) is assigned to a phase with premicellar aggregation, the second one (cmc_2) is considered as showing the formation of micellar units, while the higher value (cmc_3) corresponds to some change in the shape of the micellar units.[8] Some of these literature data are summarized in Table 1, together with our data for BzCum. Our values are in good accordance with the values reported by De Paula *et al.* for CTAB and SDS in phosphate buffer pH 7.4 (NaCl 0.9 % w/w).[22] However, using a pyrene solution and following the variation of the polarity index (i.e. I_1/I_3) with the surfactant concentration we have found that the ccm value of TX-100 in phosphate buffer pH 10 is 0.08 mM (data not show). This means that what we considered to be the critical premicellar concentration (ccm_1) is actually the critical micellar concentration (ccm_2).

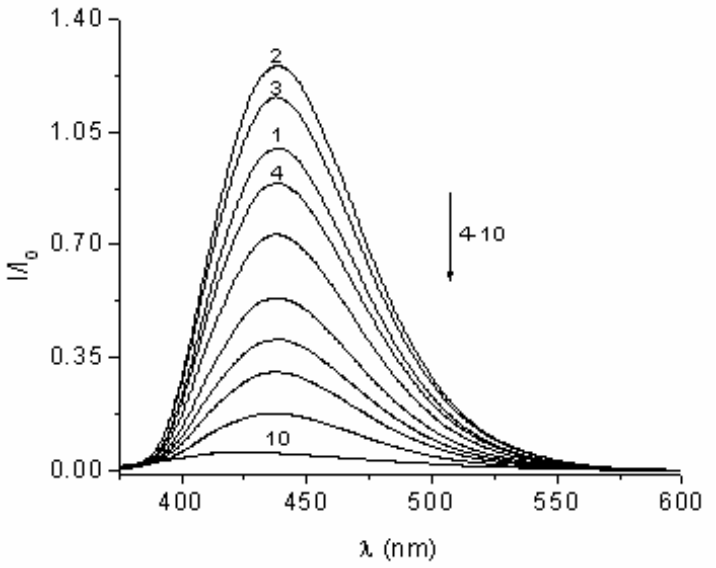


Fig. 2 – Normalized fluorescence spectra of BzCum (2.76×10^{-5}M) in the presence of different CTAB concentrations. [CTAB]: (1) 0 M; (2) 3.65×10^{-5} M; (3) 7.25×10^{-5} M; (4) 1.43×10^{-4} M; (5) 1.78×10^{-4} M; (6) 2.46×10^{-4} M; (7) 3.14×10^{-4} M; (8) 4.28×10^{-4} M; (9) 8.08×10^{-4} M; (10) 1.47×10^{-2} M. λ_{ex} = 360 nm.

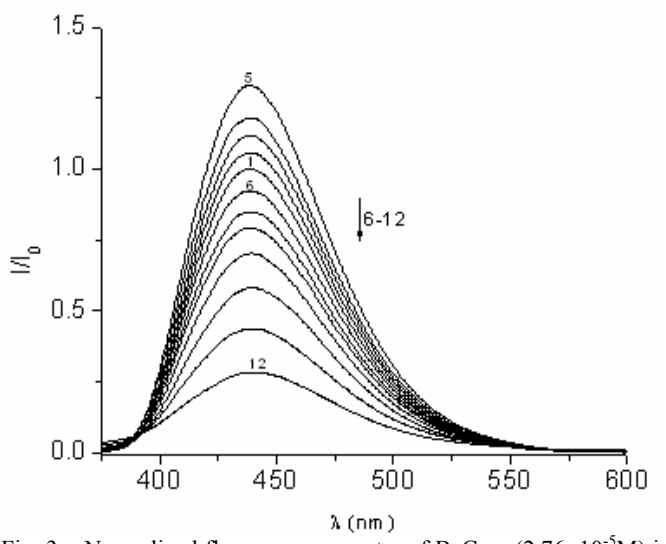


Fig. 3 – Normalized fluorescence spectra of BzCum (2.76×10^{-5}M) in the presence of different TX-100 concentrations. [TX-100]: (1) 0 M; (2) 2.23×10^{-5} M; (3) 3.37×10^{-5} M; (4) 1.51×10^{-4} M; (5) 8.09×10^{-4} M; (6) 5.03×10^{-3} M; (7) 7.08×10^{-3} M; (8) 8.96×10^{-3} M; (9) 1.3×10^{-2} M; (10) 2.1×10^{-2} M; (11) 3.66×10^{-2} M; (12) 1.85×10^{-1} M; λ_{ex} = 360 nm.

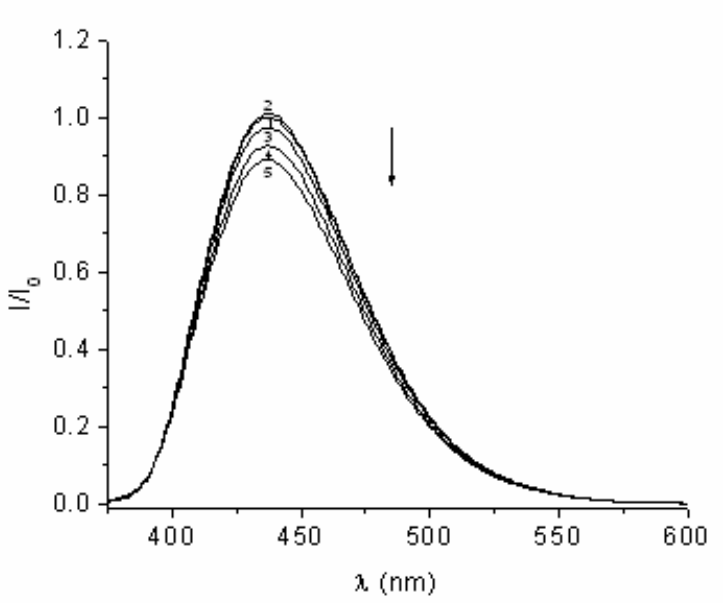


Fig. 4 – Normalized fluorescence spectra of BzCum (2.76×10^{-5}M) in the presence of different SDS concentrations. [SDS]: (1) 0 M; (2) 4.06×10^{-3} M; (3) 9.81×10^{-3} M; (4) 1.95×10^{-2} M; (5) 2.92×10^{-2} M; λ_{ex} = 360 nm.

The case of BzCum-CTAB interaction needs a special discussion. The drastic suppression observed in the presence of CTAB is in fact in the range cmc_1-cmc_2 values, i.e. in the premicellar region. In literature, the spectral changes of ionic dyes with oppositely charged ionic surfactant below their cmc has been attributed to various types of interactions as dye-surfactant salt, ion-pair, dye-rich induced micelles, induced self-aggregates of dye, aggregation of dye–surfactant complex and change in chromophore microenvironment.[23-27] Since there was no experimental prove for the aggregation of BzCum we believe that the possible type of interaction consists in the formation of an ion-association complex. Liu *et al.*[28] have suggests the same explication for the interaction of 9-anthracenecarboxylic acid with cationic surfactant (cetylpyridinium chloride and CTAB) at pH 8.5. Based on this interaction they have proposed a new quantitative method for cationic surfactants assay.

Table 1

Compared cmc values of used surfactants in water and buffered solution

Medium	Cmc values from literature, in water (mM)				Determined cmc values, at pH 10 (mM)		
	cmc_1	cmc_2	cmc_3	References	cmc_1	cmc_2	cmc_3
CTAB	0.20-0.30	0.65-1.00	1.60-1.95	16, 17, 18	0.038	0.37	1.12
TX-100	0.25-0.30	1.00-1.35	4.30-7.30	16, 17, 19	0.098	0.83	7.24
SDS	1.40-3.00	5.00-8.20	12.00-15.40	17, 20, 21	-	4.00	9.70

3. Steady-state fluorescence anisotropy

Fluorescence anisotropy may be correlated with the extent of restriction generated by micellar environment on the dynamic of fluorophore and thus it can give a cloud about the probable location of the probe in the constrained media.[8]

For BzCum in buffered water (pH 10) the measured anisotropy fluorescence value is 0.021, whereas in the presence of surfactants above their cmc the values are: 0.035 for SDS, 0.041 for TX-100 and 0.155 for CTAB. This increase of the fluorescence anisotropy in micelles compared with the bulk solution confirms that the probe molecules are residing inside the micelles, the rotational diffusion of the probe being decreased owing to the constraints imposed by the micelles. However, the changes in fluorescence anisotropy are significantly larger for CTAB than for SDS and TX-100. Such results suggest that the BzCum is dipped more inside in CTAB micelle than in TX-100 and SDS.

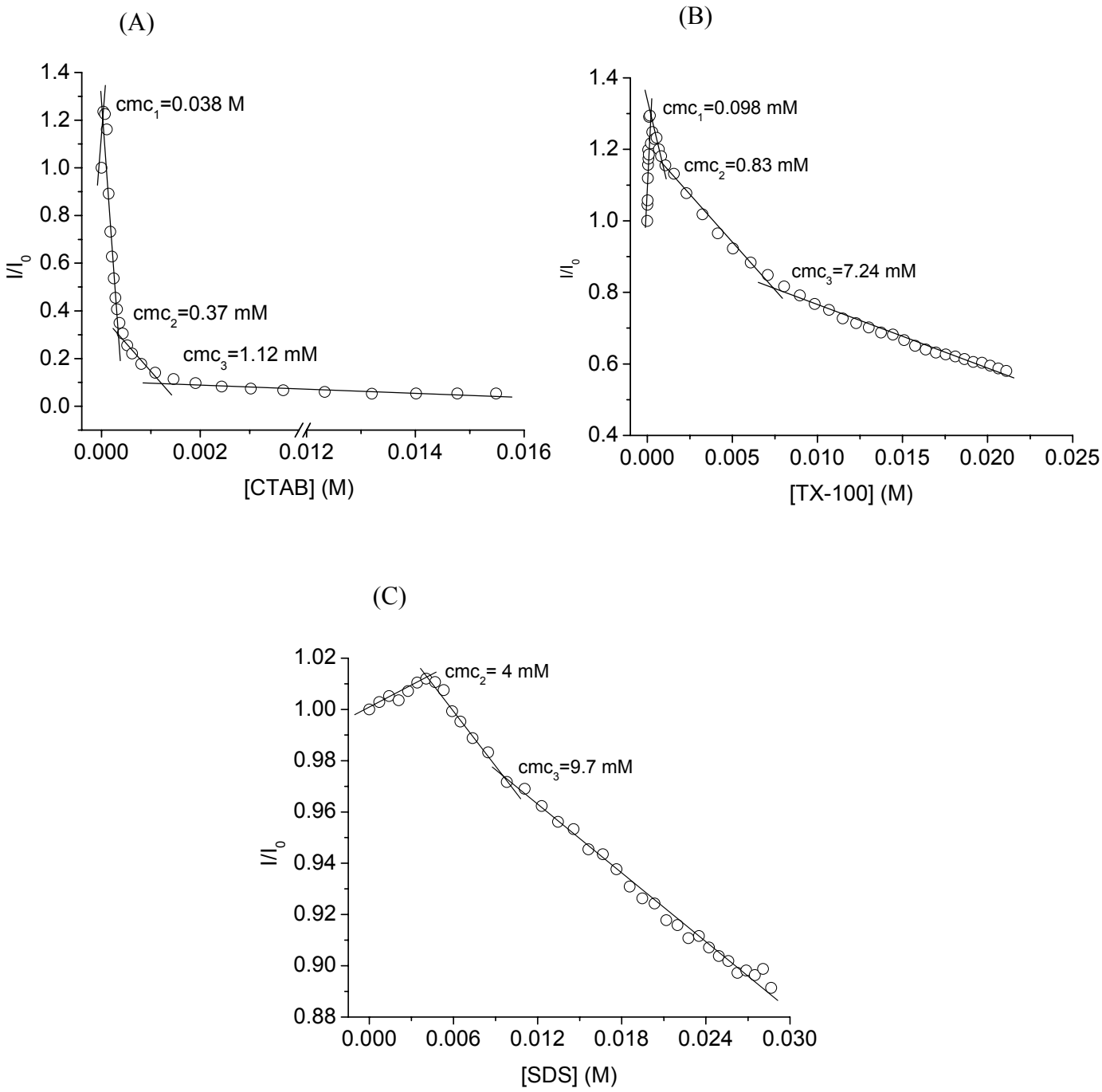


Fig. 5 – Variation of normalized fluorescence of BzCum as a function of CTAB (A), TX-100 (B) and SDS (C) concentrations.

4. Determination of the aggregation number

The aggregation number, *i.e.* the average number of surfactant molecules in a micelle unit, was determined using a static fluorescence quenching method proposed for the first time in 1978 by Turro and Yekta.[29] This method is based on the assumptions that the Poisson distribution describes the distribution of the probe and quencher in micelles and thus the emitting species is completely quenched when it occupies a micelle containing at least one quencher molecule. In other words, the probe emits only from the micelle that does not contain a quencher molecule.[29] In these conditions, the ratio I/I_0, where I and I_0 are the probe fluorescence in the presence and in the absence of the quencher, respectively, is related to the micelle concentration

[M] and to the quencher concentration [Q] according to the equation:

$$\frac{I}{I_0} \quad e^{\frac{[Q]}{[M]}} \tag{1}$$

The micelle concentration is expressed by:

$$[M] \quad \frac{[S]\ cmc}{N_{agg}} \tag{2}$$

with [S] the surfactant concentration under experimental conditions. Combining eqs. (1) and (2) we find:

$$\ln(\frac{I_0}{I}) \quad [Q]\frac{N_{agg}}{[S]\ cmc} \tag{3}$$

Eq. (3) indicates that the plot of $\ln(I_0/I)$ vs. [Q] leads to a straight line and from its slope we can evaluate the aggregation number.

As a fluorescent donor we have used the pyrene molecule. Most often the quenchers of pyrene fluorescence are alkylpyridinium chloride,[30] benzophenone,[31] dimethylbenzophenone[32] and *N*,*N*-dibutylaniline.[33] In our experiments cetylpyridinium chloride (CpCl) was the hydrophobic quencher in CTAB and SDS media. As regarding the use of CpCl as quencher of pyrene in TX-100 micelles the literature data are controversial. There are some authors that consider that the high microviscosity of Tritons micelles requires the use of very efficient quenchers and CpCl does not fulfill this requirement.[33] However, in a very recent study Das *et al.*[34] have quenched pyrene fluorescence with CpCl in TX-100 micelles in formamide. Thus we have decided to use benzophenone as quencher in the case of TX-100 micelles medium. In all experiments we have kept constant the concentrations of surfactant and pyrene (1.97×10^{-6} M) and varied the quencher concentrations for each determination (Fig. 6). The quencher concentration was in the range 0 to at most 0.14 mM for CpCl (much below its own cmc) and 0 to at most 0.24 mM for benzophenone. These values assure the Poisson distribution for which the ratio [pyrene]/[M] and [Q]/[M] must be less than 0.01 and 0.9, respectively.[35]

Earlier reports[15] have showed that the aggregation number of micelles depends on the surfactant concentration. Therefore, in order to determine the aggregation number we have carried out many sets of experiments at different surfactant concentrations above their cmc. As an exemple, in the inset (A) of Fig. 6 are plotted the $\ln(I_0/I)$ vs. [Q] at two TX-100 concentrations, *i.e.* 10 mM and 92 mM, the points being fitted with eq. (3). Since the cmc values are known, the aggregation numbers were determined and they are given in Table 2.

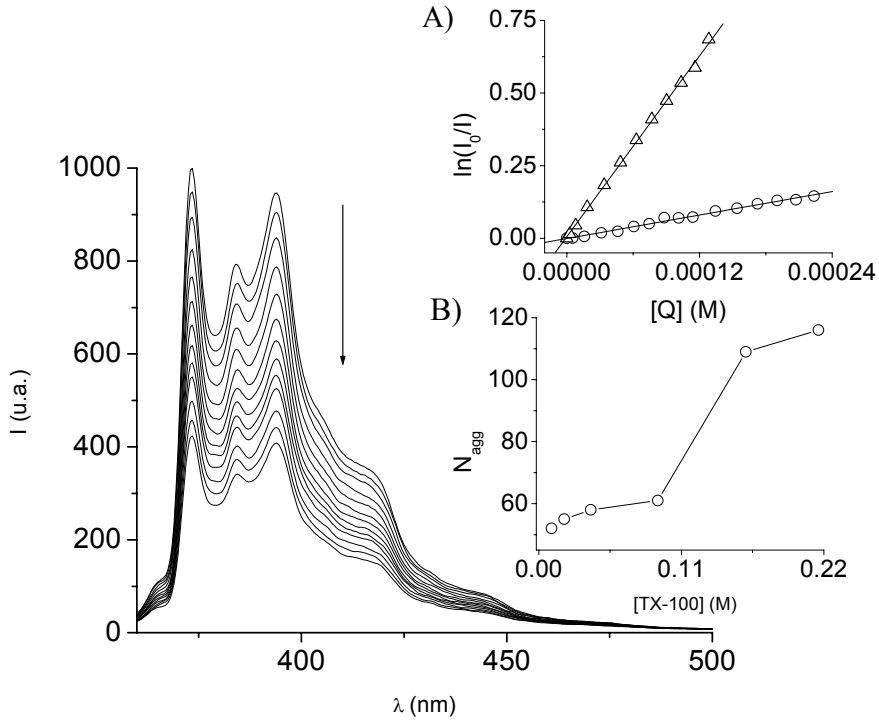


Fig. 6 – Fluorescence quenching of pyrene in TX-100 10 mM by various concentrations of benzophenone. Inset (A) plot of the $\ln(I_0/I)$ for pyrene in the presence of different benzophenone concentrations in 10 mM (Δ) and 92 mM (○) Tx-100. The solid lines represent the fits using Eq. (3). Inset (B) the dependence of the aggregation numbers of TX-100 with the surfactant concentration in buffered solutions.

Table 2

Aggregation number values in buffered solutions (pH=10) estimated at different surfactant concentrations

Medium	$N_{ag\ g}$ measured in buffered solution	N_{agg} in water
CTAB (3 /10 / 20 mM)	64/ 68/72	58[36], 60[37], 92[38]
TX-100 (10/ 20/ 40/92/160/216 mM)	52/55/58/61/108/116	64[33], 86[39], 100[40]
SDS (20 /25 /30mM)	78/ 90/ 84	55[29], 62[21]

The values from Table 2 shows that for CTAB and SDS there is not a significant variation of N_{agg} in the range of the used surfactant concentration and therefore a mean aggregation number of 68 and 84, respectively, where further considered for concentration estimation. For concentrations of TX-100 less than 92 mM, where there are small variations of N_{agg} (inset B Fig. 6), an average value of 57 will be further used, whereas for the experimental point at 160 mM we will use the value 108.

5. Estimation of the dye-micelle binding constant

The fluorescence suppression of BzCum in the micellar media can be rationalized in terms of binding of fluoprophore with the micelle. The interaction of the dye molecule (*Dye*) with the micelle (*M*) can be described by the following equilibrium:

$$Dye + M \leftrightarrow Dye\text{-}M$$

The binding constant K associated to this equilibrium is K = [*Dye-M*]/([*Dye*][*M*]) where [Dye-M] represent the concentration of the micellar phase complex, [*Dye*] the concentration of the dye in aqueous phase and [*M*] the concentration of the micelle calculated using eq. 2.

In order to evaluate the strength of the binding, i.e. to determine the binding constant from the fluorescence intensity data, non-linear or linear regression models can be used. Although the non-linear models are preferably over the linear [41] we have tried both models.

The non-linear regression equation used has a similar expression with that of dye-cyclodextrin inclusion equilibrium for a 1:1 complex:

$$\frac{I}{I_0} \quad \frac{1 \ (I_{11}/I_0) \ K \ [M]}{1 \ K \ [M]} \qquad (4)$$

where I_0 and I_{11} are the fluorescence intensities of the dye in absence of the micelle and of the 1:1 dye-micelle complex, respectively. The best fits for TX-100 and SDS, with the parameters I_{11} and K, are presented in Fig. 8 and the parameters values are summarized in Table 3. In the case of CTAB, due to the abrupt variation of I/I_0 with the micelle concentration, the fit with eq (4) is doubtful (Fig. 8).

Table 3

Binding constants of the BzCum-micelle systems.

Micelle	From equation (4)				From equation (5)		
	$K \times 10^{-3}$ (M^{-1})	I_{11}/I_0	F-stat	r^2	$K \times 10^{-3}$ (M^{-1})	F-stat	r^2
CTAB	1928 ± 213	0.04 ± 0.001	6394	0.998	715 ± 14	3287	0.994
TX-100	3.01 ± 0.14	0.21 ± 0.02	2068	0.990	2.95 ± 0.02	1664	0.988
SDS	0.70 ± 0.08	0.37 ± 0.06	5379	0.995	0.67 ± 0.01	3592	0.993

For the second procedure, i.e. the linear regression, we have followed the method described by Almgren et al.[42] According to this method

$$\frac{I \quad I_0}{I \quad I_0} \quad 1 \quad \frac{1}{K[M]} \qquad (5)$$

where I_0, I, and I_∞ are the fluorescence intensities of BzCum in the absence of the surfactant, in micellar solutions and under conditions of complete micellization, respectively. In fact, I_∞ from eq (5) has the same meaning as I_{11} from eq (4) and therefore we have used instead of I_∞ the fitted I_{11} values. This procedure was needed especially for SDS in which case the experimental values do not reach a plateau (Fig. 8). The plot of $(I_\infty - I_0)/(I - I_0)$ vs. $1/[M]$ gives straight lines (Fig. 7). From the slopes, the binding constants have been determined and the values are also listed in Table 4.

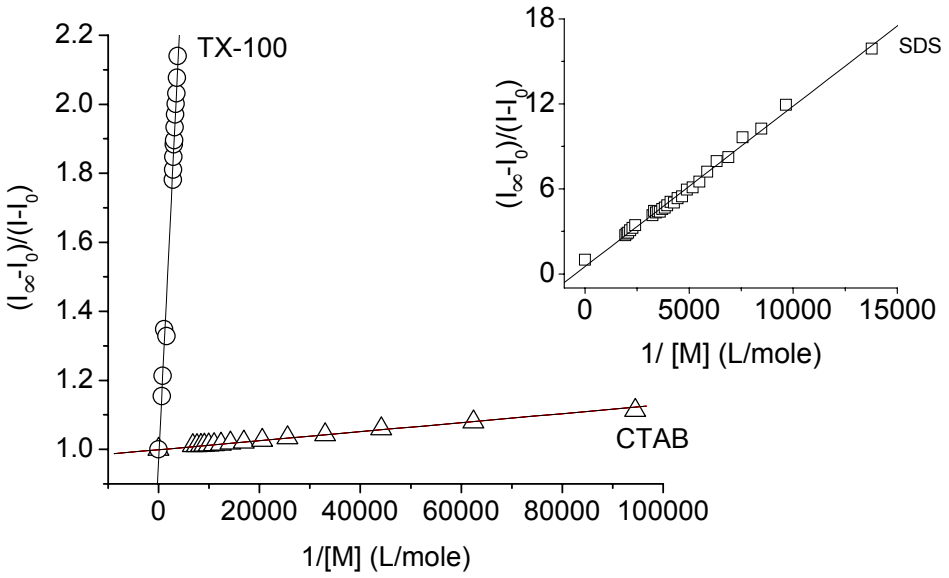


Fig. 7 – Plot of $(I_\infty-I_0)/(I-I_0)$ versus $1/[M]$ for BzCum in CTAB (Δ), Triton-X (○) and SDS (□) at pH=10. The lines corresponds to the linear fits using eq. (5).

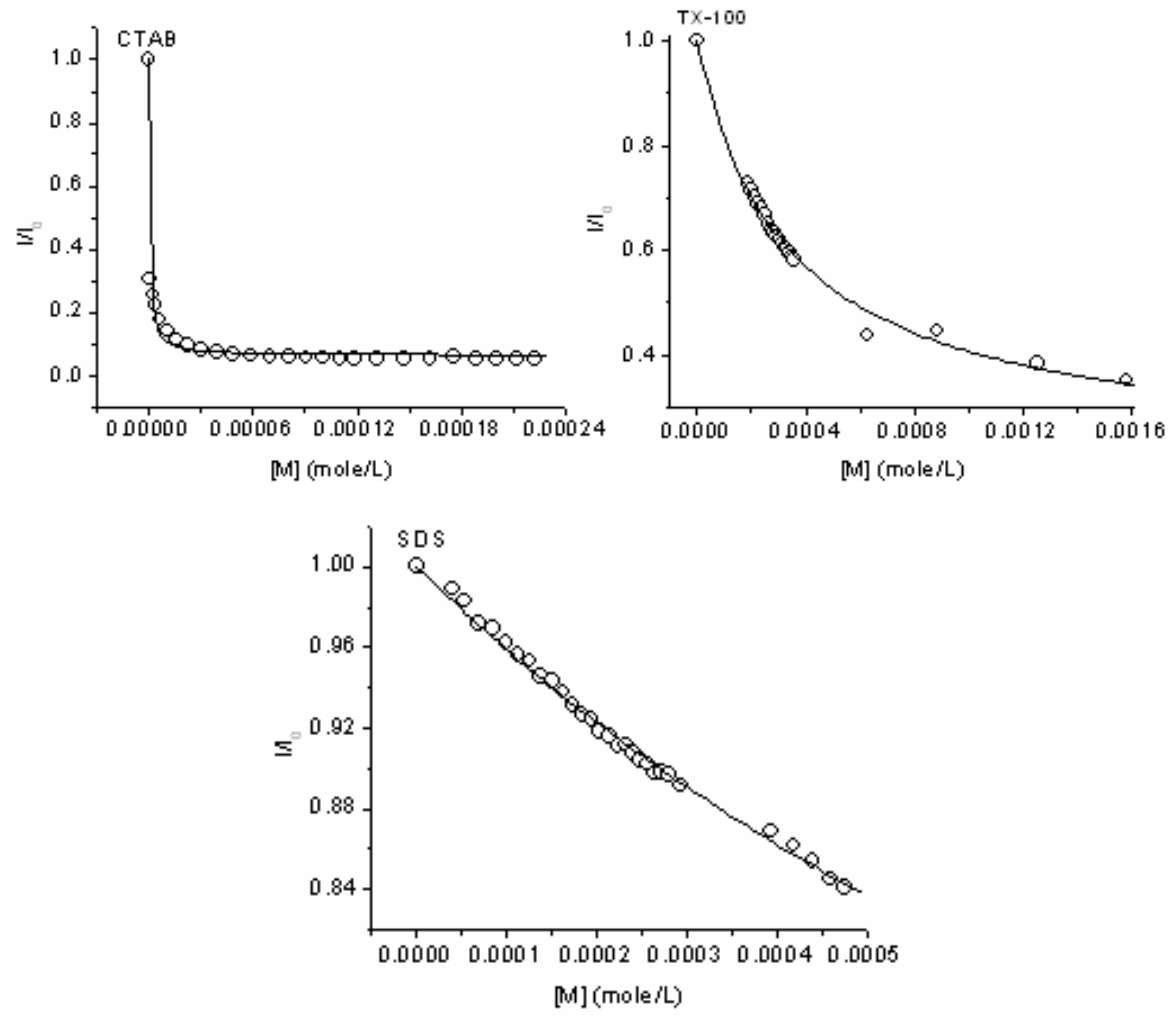


Fig. 8 – Best fit of the plot of the normalized intensity versus micelle concentration using eq. (4).

For the second procedure, i.e. the linear regression, we have followed the method described by Almgren et al.[42] According to this method

$$\frac{I - I_0}{I - I_0} \quad 1 \quad \frac{1}{K[M]} \qquad (5)$$

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From Table 4 we can observe that, excepting CTAB, there is a satisfactory agreement of the K values obtained by both methods and that the binding constants follow the order: CTAB >> TX-100 > SDS. There are two possible types of interactions between BzCum and micelles: hydrophobic and electrostatic.[43] Thus, stronger binding between the negatively charged fluorophore and the positively charged CTAB micelle is not a surprising result and indicates the dominance of the electrostatic interaction. However, there is a binding between BzCum and negatively charged SDS micelles too, which means that in this case the hydrophobic interaction predominates over the electrostatic repulsion.[43]

EXPERIMENTAL

The surfactants CTAB (Fluka), TX-100 (Sigma-Aldrich), SDS (Fluka), CpCl (Sigma) were used as received. The steady state measurements were performed using a JASCO FP-6300 spectrofluorometer equipped with a thermostatic rectangular cell holder fixed at 25^0C. According to the maximum in the absorption spectrum of BzCum, the excitation wavelength was set at 360 nm. The slits for both the excitation and emission monochromators were 5 nm. All the experiments were made in phosphate buffered (Sigma-Aldrich) solutions with pH=10 prepared with double distilled water. The fluorescence quantum yields were estimated using quinine sulphate in H_2SO_4 1N as standard (Φ=0.55). For determination of aggregation number in the preparation of solutions we have followed the procedure described by Li *et al.*[44] The fluorescence anisotropy (r) values was determined as:

$$r \quad \frac{I_{VV} - GI_{VH}}{I_{VV} - 2GI_{VH}}$$

where I_{VV} and I_{VH} represent the vertically and horizontally polarized emission intensities, respectively, following instrumental excitation with vertically polarized light and G is a correction factor which detects the instrumental sensitivity of the polarization direction of emission. G has the expression $G = I_{HV}/I_{HH}$, where I_{HV} and I_{HH} represent the vertically and horizontally polarized emission intensities obtained by excitation with horizontally polarized light.[45]

CONCLUSIONS

In this work we have analyzed the interaction of the anionic form of 3-carboxy-5,6-benzocoumarinic acid with some of the most commonly used cationic, anionic and nonionic surfactants. We have found that the binding constants followed the order CTAB >> TX-100 > SDS. Although in the presence of CTAB the value of the binding constant is larger than for the other used surfactants, there is the inconvenient brought by the fact that the fluorophore is totally quenched. Thus, for our future studies of the photoinduced electron transfer from amines to BzCum we will use TX-100 or SDS as restricted media and we will check up the possibility to use another cationic surfactant.

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REFERENCES

1. A. Mallick, P. Purkayastha and N. Chattopadhyay, *J. Photochem. Photobiol.C: Photochem. Reviews,* **2007**, *8*, 109-127.
2. A. Sarkar, P. Banerjee and S. C. Bhattacharya, *J. Colloid Interface Sci.*, **2009**, *329*, 160-166.
3. R. O'Kennedy and R.D. Thornes, "Coumarins: Biology, Applications and Mode of Action",Wiley, Chichester, UK, 1997.
4. C. Tablet, A. Jelea and M. Hillebrand, *J. Photochem. Photobiol. A: Chem.*, **2006**, *183*, 89–97.
5. C. Tablet and M. Hillebrand, *J. Photochem. Photobiol. A: Chem.*, **2007**, 73–79.
6. C. Tablet and M. Hillebrand, *Spectrochim. Acta Part A*, **2008**, *70*, 740–748.
7. Tablet, M. Fifirig and M. Hillebrand, *Rev. Roum. Chim.,* **2008**, *53*, 113-117.
8. A. Mallick , B. Haldar, S. Maiti and N. Chattopadhyay, *J. Colloid Interface Sci.*, **2004**, *278*, 215–223.
9. P. Chowdhury, T. Pratim and S. Chakravorti, *J. Luminesc.*, **2008**, *128*, 1113-1120.
10. T. Moriya, *Bull. Chem. Soc. Jpn.*, **1988**, *61*, 585-587.
11. B.D. Wagner, S.J. Fitzpatrick and G.J. McManus, *J. Incl. Phenom.,* **2003,** *47*, 187–192.
12. D. López-Díaz and M. M. Velázquez, *Chem. Educator*, **2007**, *12,* 327–330.
13. G. D'Errico, D. Ciccarelli and O. Ortona, *J. Colloid Interface Sci.*, **2005**, *286*, 747–754.
14. P. Banerjee, S. Chatterjee, S. Pramanik and S. C. Bhattacharya, *Colloids and Surfaces A: Physicochem. Eng. Aspects*, **2007**, *302*, 44–50.
15. E. Feitosa, M. R. Savério Brazolin, R. M. Zumstein Georgetto Naal, M. P. Freire de Morais Del Lama, J. R.

Lopes, W. Loh and M. Vasilescu, *J. Colloid Interface Sci.*, **2006,** *299*, 883–889.
16. A. Mallick and N. Chattopadhyay, *Biophys. Chem.*, **2004,** *109*, 261-270.
17. A. Mallick, B. Haldar, S. Maiti and N. Chattopadhyay; *J. Colloid Interface Sci.* **2004,** *278*, 215–223.
18. S. Kundu and N. Chattopadhyay, *Chem. Phys. Lett.*, **1994,** 228, 79.
19. S. Basu, *J. Photochem. Photobiol. A.*, **1991,** *56*, 339.
20. N. Chattopadhyay, R. Dutta and M. Chowdhury, *J. Photochem. Photobiol. A*, **1989,** *47*, 249.
21. P. Mukerjee and K. J. Mysels, "Critical Micelle Concentration of Aqueous Surfactant Systems", NSRDS-NBS 36, US. Government Printing Office, Washington,.D.C., 1971.
22. R. de Paula, A.E. da Hora Machado and J.A. de Miranda, *J. Photochem. Photobiol. A:Chem*, **2004,** *165*, 109-114.
23. B. Gohain and Robin K. Dutta, *J. Colloid Interface Sci.*, **2008,** *323*, 395.
24. B. Gohain, P.M. Saikia, S. Sarma, S.N. Bhat and R.K. Dutta, *Phys. Chem. Chem. Phys.*, **2002**, *4*, 2617.
25. M. Sarkar and S. Poddar, *J. Colloid Interface Sci.*, **2000,** *221*, 181.
26. R. V. Pereira, Marcelo Henrique Gehlen, *Spectrochim. Acta Part A*, **2005**, *61*, 2926.
27. S. Sarma and R. K. Dutta, *Spectrochim. Acta Part A*, **2006,** *64*, 623.
28. J. Liu, X. Wang and L. Wang, *Microchim. Acta*, **2005**, *151*, 123.
29. N.J. Turro and A.Yekta, *J. Am. Chem. Soc.,* **1978**, *100*, 5951-5952.
30. S.E. Burke, M.P. Rodgers and R. Palepu, *Molec. Phys.*, **2001**, *99*, 517-524.
31. W. Brown, R. Rymden, , J. van Stam, M. Almgren and G. Svensk, , *J. Phys. Chem.*, **1989**, *93***,** 2512.
32. M. Vasilescu, A. Caragheorgheopol and H. Căldăraru, *Adv.Colloid Interface Sci.*, **2001**, *89-90*, 169-194.
33. M. Wolszczak and J. Miller, *J. Photochem. Photobiol. A:Chem*, **2002**, *147*, 45.
34. J. Das and K. Ismail, *J. Colloid Interface Sci.*, **2009,** *337*, 227.
35. S.A. Moore and R. M. Palepu, *Molecular Physics*, **2006,** *104*, 3155-3159.
36. O. Pastor, E. Junquera and E. Aicart, *Langmuir*, **1997,** *14*, 2950.
37. G. Saroja, B. Ramachandan, S. Saha and A. Samanta, *J. Phys. Chem. B* , **1999,** *103*, 2906.
38. K. Weidemaier, H.L. Tavernier and M.D. Fayer, *J. Phys. Chem. B* **1997,** *101*, 9352.
39. M. Kumbhakar, T. Goel, T. Mukherjee and H. Pal, *J. Phys. Chem. B*, **2004**, *108,* 19246-19254.
40. M. Kumbhakar, S. Nath, T. Mukherjee and H. Pal, *J. Chem. Phys.*, **2004**, *120*, 2824.
41. R. Bruce Martin, *J. Chem. Edu.*, **1997**, *74*, 1238.
42. M. Almgren, F. Grieser and J. K. Thomas, *J. Am. Chem. Soc.,* **1979**, *101*, 279.
43. A. M. Wiosetek-Reske and S. Wysocki, *Spectrochim. Acta Part A*, **2006**, *64*, 1118.
44. W. Li, Y.-C. Han, J.-L. Zhang and B.-G. Wang, *Colloid Journal,* **2005***, 2*, 159–163.
45. J.R. Lakowicz, "Principles of Fluorescence Spectroscopy", Plenum, New York, 1983, p. 112.