

MODIFICATION OF MOLECULAR PROPERTIES OF PROFLAVINE IN NON-IONIC MICELLAR AQUEOUS SOLUTIONS

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abstract: We studied the behavior of proflavine cationic dye (3,6- diaminoacridine) in non-ionic surfactants (Tween 20, Tween 60, Tween 80 and Triton X100). The determined CMC was practically the same in the presence or the absence of proflavine. The absorptivity ϵ_{444} is some higher comparative to the value obtained in water. The wide-line δH of NMR spectra are higher in the presence of proflavine than in its absence. These results suggested a possible interaction between proflavine monocation PFH^+ and these micelles. We determined also pK_a and found values some higher than that in water what confirms the interaction supposition too. Its nature is probably the hydrogen bonding between amino groups of PFH^+ and oxygen atoms of polyoxyethylenic chains, supported also by molecular orbital computation.

Introduction

Micelles provide various small environment which have considerable influence on molecular properties and chemical equilibria. Basic dyes are good choice for use as probes for micellar systems [1,2].

Bathochromic and hyperchromic modifications in the absorption spectrum of the dye indicate indeed the presence of interactions between this one and the micelles [3].

The ionic micelles were much more studied comparative to the non-ionic ones [4-8]. This is the reason for which we chose to study this problem in the present paper.

Experimental

We used as such proflavine $C_{13}H_{12}N_3.HSO_4$ (Serva Feinbiochemica Heidelberg) and the following non-ionic surfactants: Tween 20, Tween 60, Tween 80 and Triton X100 (Loba Chemie, Wien).

For CMC determination we used a wide-line NMR spectrometer IFA T-71 (10MHz), a Specord M40 Carl Zeiss Jena spectrophotometer and a Radelkis conductometer.

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The acidity constant pK_a of proflavine in these media was determined spectrophotometrically from the absorption spectra variation with pH .

The computation based on quantum mechanics was carried out using PC SPARTAN programs, version 1.5.

Results and Discussion

Our experimental CMC values for the above non-ionic surfactants, in the absence or presence of proflavine are summarized in Table 1.

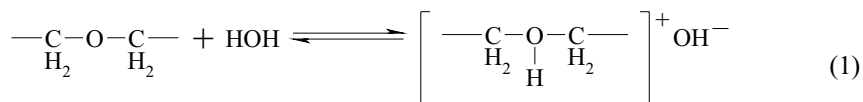
Table 1. CMC values of non-ionic surfactants.

Experimental method	$(CMC)_{Tween20} \times 10^3$ [g/dl]		$(CMC)_{Tween60} \times 10^3$ [g/dl]		$(CMC)_{Tween80} \times 10^3$ [g/dl]		$(CMC)_{Triton} \times 10^3$ [g/dl]	
	- PfH ⁺	+ PfH ⁺	- PfH ⁺	+ PfH ⁺	- PfH ⁺	+ PfH ⁺	- PfH ⁺	+ PfH ⁺
Conduct.	5.50	5.50	2.50	2.40	2.00	2.00	16.2	15.2
NMR	5.40	5.10	2.50	2.30	2.00	2.20	16.2	15.2
Spectroph.	–	5.50	–	2.30	–	2.00	–	16.2
Spectrofl.	–	5.60	–	2.40	–	2.00	–	15.8
Average	5.45	5.43	2.50	2.35	2.00	2.05	16.2	15.7

One observes that CMC ranged between $(2.0 \div 2.5) \times 10^{-3}$ g/dl for Tween 60 and 80 but it reaches a value of 5.45×10^{-3} g/dl for Tween 20. This result is in good agreement with the structure of these surfactants. Indeed, Tween surfactants are characterized by the formula: $C_{47}H_{91}O_{25}R$ in which $R = -C_{11}H_{23}$ for Tween 20, whereas for Tween 60 and Tween 80, R are very nearly, $-C_{17}H_{35}$ and $-C_{17}H_{33}$ respectively.

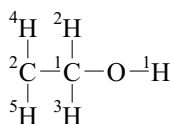
One observes also, that CMC is not influenced, in the limit of experimental errors by the presence of proflavine (in good agreement with micellar theory [9]).

One remarks too that it was possible to determine CMC conductometric although these micelles are non-ionic. Due to the hydrophilic end of polyoxyethylene chains, in water is established the following equilibrium by forming hydrogen bonding [10,11]:



It reveals the weak cationic character of these surfactants.

This cationic character at the end of the polyoxyethylene chains is sustained by the charge distribution (Table 2) determined by molecular orbital computation (at MNDO approximation level) for one oxyethylene group:


Table 2. Electronic charge distribution of polyoxyethylenic groups.

Surfactant	Charge [$\times 1,6 \times 10^{-19} \text{C}$]								
	${}_1\text{C}$	${}_2\text{C}$	O	${}_1\text{H}$	${}_2\text{H}$	${}_3\text{H}$	${}_4\text{H}$	${}_5\text{H}$	Σ
Tween 20	0.156	0.179	-0.332	0.185	-0.005	-0.005	0.001	0.001	0.180
Tween 60	0.137	0.166	-0.303	0.164	0.003	-0.031	0.007	0.020	0.163
Tween 80	0.155	0.167	-0.333	0.183	-0.001	-0.001	0.002	0.003	0.175
Triton X100	0.155	0.177	-0.332	0.185	-0.006	-0.006	0.001	0.001	0.175

As a consequence their hydrophil / lyophil ratio have values nearly to cationic HLB, namely ~ 15.5 .

We determined proflavine absorptivity ϵ at the absorption maximum ($\lambda=444\div 445$ nm) in these media and found $4.13 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ some higher than the value in water ($3.92 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$). This results suggest a possible interaction between proflavine and these non-ionic micelles. This affirmation is supported also by the spectral modification of proflavine with the increasing of micelle concentration. We exemplify by the absorption spectrum of proflavine ($2.14 \times 10^{-6} \text{ M}$) in water and Tween 80 respectively.

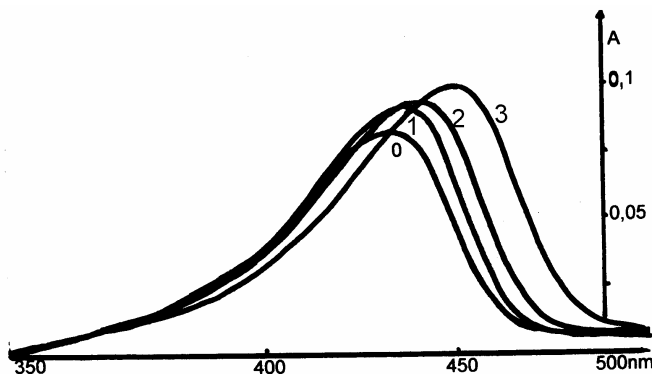


Fig.1: The absorption spectrum modification with Tween 80 concentration:
 0) 0 g/dl; 1) 9×10^{-4} g/dl; 2) $2,5 \times 10^{-3}$ g/dl; 3) 5×10^{-1} g/dl.

One remarks the shifting of the absorption spectrum towards the long wavelengths accompanied by the absorbance increasing. The same behaviour we found also in water-methanol mixtures so that we concluded that the interaction between proflavine and these non-ionic micelles may be ascribed to the hydrogen bonding formation.

We mentioned also that the initial value of δH NMR spectra obtained for pre-micellar concentrations is also some higher in the presence of proflavine, ascribed to the hydrogen bonding formation too.

We determined also the acidity constants pK_a of proflavine in these non-ionic micelles. In aqueous solutions it can exist in different protonations forms due to the three N atoms with aminic character. The prototropic equilibria are shifted according to pH:



In Fig. 2 we present the profile of proflavine absorption spectra in aqueous solutions of Tween 20 at various values of pH.

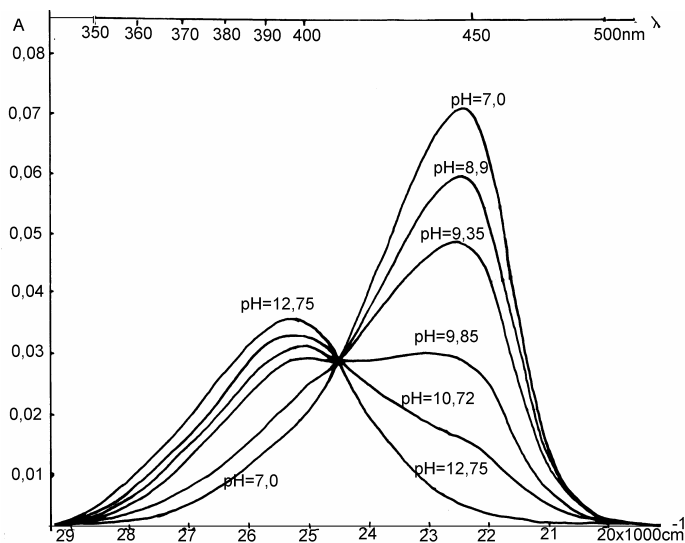


Fig. 2: The variation of proflavine ($1,917 \times 10^{-6} M$) spectra in Tween 20, $9 \times 10^{-3} g/dl$, at various values of pH.

One notices two absorption maxima: at 445nm absorbs the monocation PFH^+ whereas at 403nm the neuter form, separated by an isosbestic point at 403nm. By using the equation:

$$pK_a = pH - \log \frac{A - A_{\text{PFH}^+}}{A_{\text{PF}} - A} \quad (4)$$

were A_{PFH^+} is the absorbance of monocation and A_{PF} of the neuter proflavine.

We calculated with equ. (4) the following values of pK_a :

$$(pK_a)_{\text{Tween}20} = 10.64; (pK_a)_{\text{Tween}60} = 10.52; (pK_a)_{\text{Tween}80} = 10.72; (pK_a)_{\text{TritonX100}} = 10.81.$$

These pK_a values are some higher than that obtained in water (9.5). Such a result shows that proflavine molecule is stabilized in these non-ionic micelles interacting with these by hydrogen bonding formation between amino groups of PFH^+ and oxygen atoms of polyoxyethylenic chains.

In Fig. 3 we present the result of molecular orbital computation of interaction between the monocation proflavine molecule and Tween 20 molecule.

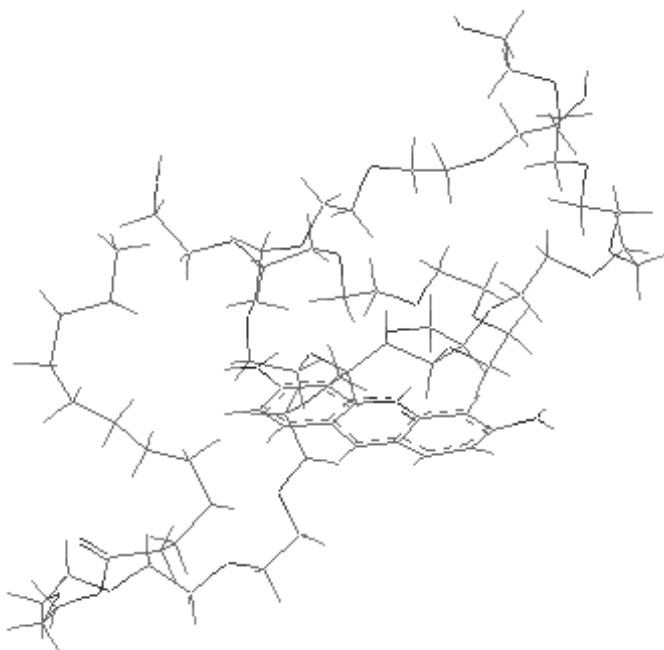


Fig. 3: *The results of molecular orbital calculation of the interaction between PFH⁺ and Tween 20.*

The hydrogen bonding between positive charged amino groups of the proflavine monocation and the polyoxyethylenic chains is determined by oxygen atoms with negative electric charge (Table 2).

Conclusions

The present study evidenced:

- CMC of the investigated non-ionic surfactants do not change in the presence of proflavine in the limit of experimental errors;
- the absorptivity ϵ_{444} of proflavine is some higher in these surfactants than in water;
- the absorption spectrum shifts toward long wave lengths accompanied by the increasing of absorbances with the increase of surfactant concentrations;
- the acidity constant pK_a is higher too comparatively to the value obtained in water;
- the wide-line δH of NMR spectra is some higher in the presence of proflavine;
- these experimental data suggest the existence of interactions between proflavine and these non-ionic surfactants most probably by hydrogen bonding;
- this last conclusion is also in good agreement with our molecular orbital computations.

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