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4-Hydroxycoumarin Derivatives in Micelles: An Approach to Detect a Structural Transition Using Fluorescent Viscosity Probes

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The spectroscopic behavior of three coumarin derivatives was investigated in water and in different micellar media. In SDS, the fluorescence intensity of two of the dyes increased upon addition of sodium chloride. This effect was tentatively related to a sphere-to-rod transition occurring in the micelles.

KEY WORDS: Coumarin; micelle; sphere-to-rod transition; fluorescence.

There is a considerable current interest in the study of micellar organization and dynamics, because the general principles underlying the formation of micelles are common to other supramolecular assemblies, such as bilayers, liposomes, and biological membranes. It is now well established that in dilute solutions, the shape of the charged micelles varies from sphere to rod in the presence of an increased salinity. It has been suggested that hydrocarbon chains are more ordered in rod-like micelles than in spherical micelles, thus leading to a higher microviscosity. Besides classical methods such as light scattering and nuclear magnetic relaxation, several fluorescence techniques based on electron transfer, energy transfer, and red-edge effect have been used to explore many important aspects of this system [1]. The present work was aimed at determining whether some new fluorescent compounds, which proved to be sensitive to microviscosity variations, are able to report on the structural transition of the micellar assembly.

The molecules used in this work were two original 4-hydroxycoumarin derivatives (HCD), bearing an ethyl furoate (**1**) or a benzodioxanyl (**2**) substituent in the 3-position (Scheme 1). They were compared to **3**, which is deprived of a substituent in this position.

The spectroscopic and photophysical properties of compounds **1** to **3** in organic solvents have been the subject of a previous paper [2]. It was shown that molecule **1** displayed excellent fluorescence properties, very weakly altered by its environment. In this molecule, intramolecular hydrogen bond was formed between the hydroxyl group in the 4-position and the hydrogen atom of the furoate group. This H-bond made the structure planar and led to good conjugation of the electron system. In contrast, **2** emitted with lower efficiency and shorter lifetimes than **1**, but was extremely sensitive to factors that affect the rotation of the benzodioxanyl substituent. The behavior of these probes was also investigated in water (1.3% ethanol) [3]. It was shown that all three compounds were ionized at pH 5.4, and no aggregation was detected below 10^{-5} M. In this medium, the spectroscopic properties of **1** and **2** were found to be quite close, because the intramolecular hydrogen bond, which stabilizes **1** in organic solvents, was disrupted.

Dyes **1** to **3** (1×10^{-5} M) were introduced in anionic

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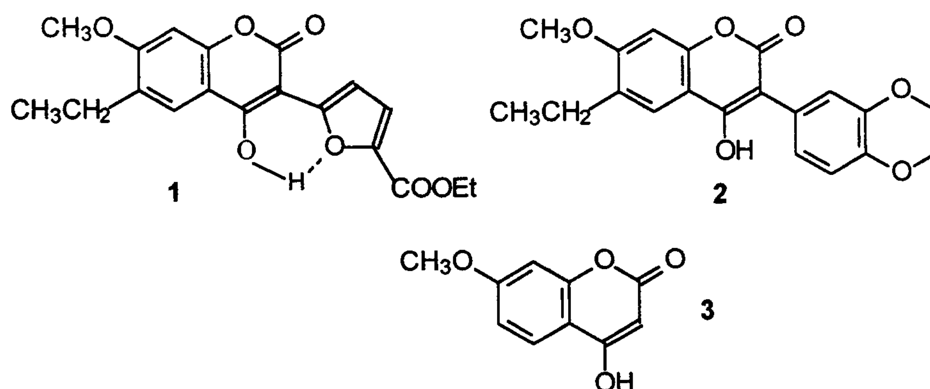

Scheme 1. Chemical structure of 4-hydroxycoumarin derivatives **1–3**.

(sodium dodecylsulfate, 10^{-1} M), cationic (cetyltrimethylammonium bromide, 10^{-2} M), and neutral (Triton X100, 10^{-2} M) micelles. The surfactant concentration was around 10 times higher than the critical micelle concentration. The spectroscopic characteristics obtained in these media are reported in Table I. The UV/vis absorption spectrum of **2** and **3** hardly varied from water to surfactant solutions. In contrast, the spectrum of **1** was strongly shifted to the red, and the molar absorption coefficient was markedly increased in the same conditions. It can be noted that the absorption maximum of **1** in CTAB and TX100 was very close to that obtained in ethanol [3] and in other organic solvents [2]. Therefore, it seems that in micellar medium, the hydrogen bond takes place in **1** just like in organic solvents.

Concerning the fluorescence behavior, it was checked for the three dyes in the presence of micelles that the excitation spectrum was similar to the corresponding absorption spectrum, and that the emission spectrum was unchanged when varying the excitation wavelength. The presence of micelles led to a blue shift of the spectra for **1** and **2**, accompanied by an increase in the fluorescence quantum yield, which was moderate in SDS but multiplied by 10 for **1** in TX100. The probes therefore experimented a medium of lower proticity than water, and their behavior was reminiscent of that encountered for their neutral form in organic solvents.

In SDS, small variations were encountered with respect to water. Probably the probes remained at the exterior of the micelle, because of electrostatic repulsion between the negatively charged HCD and the surfactant anionic groups. However, a little amount of neutral probes interacted with the micelle and can account for the weak spectroscopic effect observed. For CTAB and TX100 micelles, the insertion of the neutral form of the dye between the surfactant polar heads is more likely to take

Table I. Spectrophotometric Characteristics of Dyes **1**–**3**, in Deionized Water (1.3% ethanol) in the Presence and Absence of Surfactants

	Water, pH 5.4				SDS			
Dye	λ_{abs} (nm)	ε (M^{-1} cm^{-1})	λ_{em} (nm)	Φ	λ_{abs} (nm)	ε (M^{-1} cm^{-1})	λ_{em} (nm)	Φ
1	318, <u>338</u>	25000	440	3.6×10^{-2}	320, <u>348</u>	27200	438	4.3×10^{-2}
2	316	24400	446	2.2×10^{-3}	316	24100	442	3.6×10^{-3}
3	286, <u>302</u>	10500	349	7.3×10^{-3}	286, <u>302</u>	9600	344	5.2×10^{-3}
	CTAB				TX100			
Dye	λ_{abs} (nm)	ε (M^{-1} cm^{-1})	λ_{em} (nm)	Φ	λ_{abs} (nm)	ε (M^{-1} cm^{-1})	λ_{em} (nm)	Φ
1	320, <u>362</u>	30600	434	3.1×10^{-1}	322, <u>362</u>	31600	434	3.6×10^{-1}
2	318	20200	440	1.0×10^{-2}	318	21000	436	1.5×10^{-2}
3	288, <u>302</u>	8400	352	1.3×10^{-2}	302	9400	–[a]	–[a]

[a] Maximum absorption wavelength λ_{abs}, molar absorption coefficient ε, maximum emission wavelength λ_{em}, fluorescence quantum yield Φ, ε was measured at the underlined wavelength (maximum absorption of the most intense band) a: The fluorescence data of **3** in TX100 were not recorded because of the strong fluorescence of TX100 in the same region.

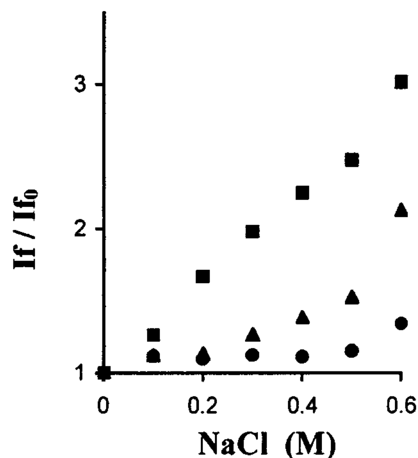

Fig. 1. Relative increase in the fluorescence intensity of compounds **1** (■, λ_{ex} = 398 nm), **2** (▲, λ_{ex} = 350 nm) and **3** (●, λ_{ex} = 276 nm) (1×10^{-5} M) in SDS (6.9×10^{-2} M) upon addition of NaCl (from 0–0.6 M).

place. This location is commonly found for heterocyclic dyes [4].

The variation of the optical properties upon addition of sodium chloride in SDS solutions was investigated. It was firstly checked that, in the absence of micelles, increasing NaCl concentration until 0.6 M in aqueous solutions of the three dyes had no effect on the absorption or fluorescence spectra. In contrast, when adding 0.6 M NaCl into SDS micellar solutions of the dyes (1×10^{-5} M), the fluorescence intensity was multiplied by 3 and 2.1 for **1** and **2** (Fig. 1). A much weaker effect was observed with **3**. No effect was detected on the absorption spectrum of **1, 2** and **3**, suggesting that no interaction took place in the ground state.

The increase in fluorescence intensity was only observed in the simultaneous presence of micelles and sodium chloride. It has been reported that the addition of salt did not change the amount of neutral dyes extracted by the micelles [5]. So, one hypothesis is that probes **1** and **2** were sensitive to a variation of the compactness of the micelle, which underwent a sphere-to-rod transition. The increased microviscosity could prevent the substituent in the 3-position from rotating, so that thermal deactivation was reduced. This hypothesis is in line with the weak effect observed for **3**.

The spectroscopic effect was stronger for **1** than for **2**. This can be explained by the fact that probes **1** and **2** can occupy slightly different locations within the micelles. Actually, the lipophilicity parameter calculated for the substituent in the 3-position revealed that the benzodioxanyl group was more hydrophobic (log P = 2.22) than the ethylfuroate group (log P = 1.52).

Work is presently underway to test this hypothesis. In particular, lifetime measurements could allow a discrimination to be made between an increase in the incorporation of the probes and their stabilization in a compact medium. Comparison must also be done with CTAB micelles, for which the probes show higher affinity.

EXPERIMENTAL

The hydroxycoumarin derivatives were prepared as previously described [2]. SDS, CTAB, and Triton X100 were purchased from Acros. There were used as obtained, except SDS, which was recrystallized in 95% ethanol and dried at 115°C for 4 h. Absorption spectra were recorded on a Hewlett-Packard 8452A diode array spectrophotometer. Corrected steady-state fluorescence spectra were obtained with a Photon Technology International (PTI) Quanta Master 1 spectrofluorometer. The fluorescence quantum yields were determined using coumarin 6 in ethanol (Φ = 0.78) as standard.

Solutions were prepared by first dissolving HCD (7.6×10^{-4} M) in absolute ethanol. Then, 40 μL of these solutions were added to 3 ml deionized water or surfactant solution. Final concentrations were 10^{-5} M HCD and 1.3% ethanol. All solutions were kept and measured in thermostatted cells at 26°C.

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