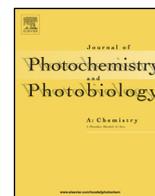




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Photophysics and photochemistry of mercurochrome in reverse micelles



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ABSTRACT

The photophysics of the xanthene dye 2',7'-Dibromo-5'-(hydroxymercurio)fluorescein disodium salt (merbromine, mercurochrome) (Mcr) was studied in reverse micelles (RMs) of sodium 1,4-bis (2-ethylhexyl) sulfosuccinate (AOT) and benzylhexadecyldimethylammonium chloride (BHDC). In the reverse micellar media both the absorption and emission spectra of the dye present a red shift with respect to water. It is concluded that MCr in both reverse micellar systems is localized in the interface. In BHDC due to the positive charge at the interface and the negative charge of the dye, it remains anchored to the interface irrespective of the water content of the RMs. On the other hand in the case of the negative interface of AOT the photophysical properties tend to those in homogeneous water solution as the water content increases. For small size AOT RMs the dye resides in the interface co-micellizing with the surfactant, although more exposed to water than in the case of BHDC. Special interest was assigned to the effect of confinement on the triplet state properties. The triplet state decay kinetics and absorption spectra were determined by laser flash photolysis. The triplet lives longer in RMs than in homogeneous solvents. The compartmentalization of the dye precludes the auto-quenching which shorts the lifetime in homogeneous solvents. Furthermore, the quenching by electron donors and acceptors was investigated. Two aliphatic amines were used as electron donors. The hydrophilic triethanolamine (TEOA) is localized in the water pool, and the triplet quenching is more efficient than in homogeneous solvents. The apparent quenching rate constant for TEOA in AOT is one order of magnitude higher than BHDC. On the other hand the quenching by dipropylamine (DPA) which is located in the bulk organic solvent is much less efficient. The quenching by TEOA in RMs can be understood in terms of an exchange mechanism between micelles. As electron acceptor 1,4-benzoquinone (BQ) was employed, and the value in BHDC is two orders of magnitude higher than in AOT. These divergences most likely arise from different partitions of the quenchers in the reverse micellar systems.

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1. Introduction

Reverse micelles (RMs) are frequently considered as self-organized nano-reactors. In these systems, the reactants are confined within a small region, a few nanometers in size, and the reactivity and products properties of different processes may differ dramatically from those in homogeneous solutions. In the interior of RMs the local properties like polarity, viscosity and pH are vastly different from those in homogeneous medium [1]. Consequently, the physical and chemical properties of confined molecules may undergo dramatic changes in these systems. These changes are also useful to characterize the so-called microenvironmental

properties, including local polarity (micropolarity) and local viscosity (microviscosity) of micellar systems. The photophysics of dyes provides a useful tool for investigate these properties [2] and the information gained in this way is very important from both an applied and a fundamental point of view [3]. For example, these studies are of interest with regard to micellar systems as a reaction medium because they affect both the kinetics and the mechanism of a specific reaction [4,5]. They are as well important in many applications of electronic energy transfer, which may include photosensitized reactions and the micelle enhanced emission detection in analytical techniques [6]. In these systems donor, acceptor and micelle concentrations may be high enough to allow considerable energy transport between neighboring micelles. On the other hand, the understanding of the interactions between ionic dyes and charged surfaces is of interest in numerous applications ranging from the design of electronic devices to the

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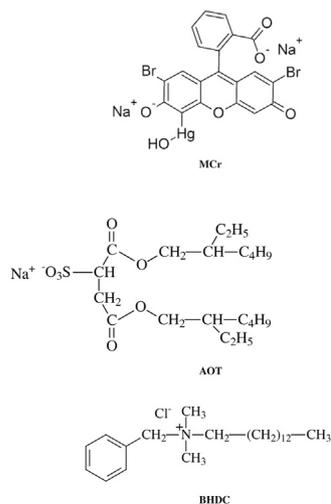
characterization of drug-delivery systems. RMs are also particularly appropriate to the synthesis of nano-scale materials. In the last years there has been a continuing interest in reverse micellar systems where polar solvents other than water are used [7,8]. This is in part due to potential application in nanomaterial synthesis when the synthesized material should have solubility in nonaqueous medium for further applications [9]. Recently we employed RMs formed by the cationic surfactant benzyl-hexadecyl-dimethylammonium chloride (BHDC) to synthesize latex nano particles of polyacrylamide using a dye as visible photosensitizer of polymerization [10].

In this paper we present a study of the photophysics and photochemistry of the xanthene dye 2',7'-dibromo-5'-(hydroxymercuro) fluorescein disodium salt, commonly known as merbromin or mercurochrome (MCr) in reverse micelles formed by sodium 1,4-bis (2-ethylhexyl) sulfosuccinate (AOT)/heptane or BHDC/benzene. In Scheme 1 the structures of the dye and surfactants are shown. The photophysics of xanthene dyes were investigated in normal [11–14] and reverse micelles [15,16] generally by means of fluorescence spectroscopy. Reorientation of xanthene dyes in the interior of AOT was studied [17] and it was found that the water content of the reverse micelles has an important effect on the rotational dynamics of the probe. However, the photophysics and photochemistry of MCr in homogeneous and micro-heterogeneous systems was much less studied than other xanthene dyes.

MCr is often used as an antiseptic and antibacterial substance. At pH values ranging from 5.5 to 10.0 proved to be highly fluorescent with a quantum yield of 0.2 [18]. However, the presence of heavy atoms in the molecule gives rise to an efficient intersystem crossing and a high room temperature phosphorescence emission signal can be observed when mercurochrome is immobilized on a solid support [19]. It was shown that MCr is a relatively efficient sensitizer for photodynamic action via singlet oxygen generation with a quantum yield of 0.14 in methanolic solution [20] and 0.23 in water (buffer pH 7) [15]. Unlike eosin, MCr is extremely resistant to light; it does not fade even when exposed to strong visible irradiation [21]. This makes this dye a very suitable choice for applications as sensitizer requiring long irradiation periods.

2. Experimental

Mercurochrome was obtained from Aldrich and was used without further purification. Sodium 1,4-bis (2-ethylhexyl)



Scheme 1. Chemical structures of the dye and surfactants.

sulfosuccinate (AOT) from Sigma was dried under vacuum over P₂O₅. *n*-Heptane, benzene, methanol and water were from Sintorgan (HPLC grade) and used as received. The surfactant benzylhexadecyldimethylammonium chloride (BHDC) from Fluka was twice recrystallized from ethyl acetate and dried under vacuum. Triethanolamine (TEOA) and Dipropylamine (DPA) both from Aldrich, were purified by vacuum distillation before use. 1,4-Benzoquinone (BQ) from Aldrich was purified by sublimation.

Reverse micelles solutions were prepared by dissolving the surfactant in the organic solvent, *n*-heptane for AOT and benzene in the case of BHDC. The surfactant concentration was varied between 0.05 M and 0.2 M in both cases. A small amount of MCr dissolved in water (buffer pH 8) was added to these micellar solutions, so that the final total analytical concentration of the dye was less than 10⁻⁶ M. The micellar water content, $w = [H_2O]/[Surfactant]$, was adjusted by adding water (buffer pH 8) up to desired ratio. It is not possible to work at $w > 20$ in BHDC because at room temperature the solutions become cloudy. The aggregation number of BHDC in benzene is in the range from 100 ($w = 10$) to 400 ($w = 20$) [22], while for AOT in *n*-heptane it goes from 60 at $w = 6$ to 500 at $w = 30$ [23]. Accordingly, the mean occupation number of the dye is < 0.1 in all cases. In the quenching experiments small aliquots of a concentrated aqueous solution of the quencher were added to the RMs. In the case of DPA the amine was added as the pure compound.

Absorption spectra were obtained on a Hewlett Packard 6453E diode array spectrophotometer. Fluorescence spectra were measured with a Horiba Jobin Yvon Fluoromax-4 spectrofluorometer in air equilibrated solutions. Fluorescence quantum yields were determined relative to 4,5 dibromofluorescein 0.01 M in KOH/ethanol [24]. Fluorescence lifetimes were determined by time-correlated-single-photon-counting (SPC) with a FL 900 Edinburgh Instruments equipped with a PicoQuant sub-nanosecond pulsed LED emitting at 498 nm. The fluorescence decays were analyzed by a deconvolution method provided by Edinburgh Instruments. The quality of the fitting was judged by the reduced chi-square (χ^2) values and the distribution of the weighted residuals. In all cases a mono-exponential fit was satisfactory, the χ^2 value was close to unity and the weighted residuals were distributed randomly along the spanned time interval.

Transient absorption measurements were carried-out by excitation at 532 nm using a laser flash photolysis equipment as previously described [25]. The samples were deoxygenated by bubbling during 15 min with organic solvent-saturated high purity argon.

3. Results and discussion

3.1. Absorption and fluorescence

The absorption and fluorescence spectra in water, methanol and RMs are shown in Figs. 1 and 2 respectively.

In Table 1 the photophysical parameters of the dye in different media are collected. It is well-known that the maxima in the absorption and fluorescence spectra of xanthene dyes are red shifted as medium polarity decreases. Furthermore, fluorescence lifetime increases as solvent polarity decreases [26]. Therefore, the photophysical parameters in AOT presented in Table 1 point to the dye molecules located in a region of micropolarity lower than water although due to the negative charge it is expected to be located in the water pool of the RMs. The absorption and fluorescence parameters in BHDC are an indication that MCr is sensing a region of polarity lower than MeOH. This can be explained by the negative dye molecules anchored to the interface in the positive palisade (the layer immediately below the micellar surface) of the RMs. On the other hand in AOT at low w the dye is in close proximity with

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