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Photophysics of safranine-O and phenosafranine in reverse micelles of BHDC

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ABSTRACT

The photophysics of safranine-O (3,7-diamino-2,8-dimethyl-5 phenyl phenazinium chloride, SF) and phenosafranine (3,7-diamino-5-phenyl phenazinium chloride, PSF) was investigated in reverse micelles (RMs) of the cationic surfactant benzyl hexadecyl dimethylammonium chloride (BHDC). The excited singlet state properties were measured by absorption and fluorescence spectroscopy. All the measurements indicate that both dyes are localized in the interface, sensing a medium of lower polarity than water. Stokes' shift increases and fluorescence quantum yield decreases with increasing the water content, but never reach the values or pure water. The triplet state properties of the dyes in RMs were investigated by laser flash photolysis. The maximum of the T–T absorption spectra in RMs confirms that, in spite of their positive charge, the dyes remain at the interface co-micellizing with BHDC. The triplet lifetime is much longer in the RMs than in homogeneous organic solvents. The two dyes present a different dependence of their photophysical properties with the water content. The two methyl groups in the ring of SF produce a stronger preference of the dye for a hydrophobic environment, and consequently a deeper location in the interface closer to the organic phase. A remarkable difference is observed in the triplet quenching by aliphatic amines. While the quenching by hydrophobic tributylamine is much lower in BHDC/benzene RMs than in a homogeneous solvent, the hydro soluble triethanolamine is near two orders of magnitude more effective in the RMs than in homogeneous solution. This is explained by the different local concentration of the amines in the interface.

1. Introduction

Reverse micelles (RMs) and microemulsions have attracted considerable interest in recent years because they can provide "nano-sized reactors" for chemical, photochemical and biological reactions [1]. In reverse micelles a solute can be located in a variety of microenvironments. The simplest approach is to consider the system as composed by two pseudophases: the bulk solvent and the microaggregates formed by the surfactant molecules and the entrapped water. However, a three pseudophases model is more often preferred, comprising the bulk solvent, the surfactant–water interface and the water pool. Moreover, four different probable locations for a small molecular probe in a reverse micelle have been proposed. In this model two interfacial regions are distinguished, the bulk solvent/micelle interface and the interior surfactant/water pool interface [2]. The three governing factors for solubilization are electrostatic, hydrophobic, and specific interactions of the RM interface with the solubilized molecules. The localization of the solute will depend also on the water/surfactant ratio since several interface properties, such as microviscosity and micropolarity, are influenced by this parameter [3]. In many cases a dye molecule was used as a probe to characterize reverse micelles and to investigate the effect of the surfactant and dye molecular structure on its localization in the microheterogeneous system [4,5].

Most of the photophysical and photochemical studies in reverse micellar systems have been carried out using the anionic surfactant Aerosol OT (AOT, sodium bis (2-ethylhexyl) sulfosuccinate) [2]. This surfactant forms reverse micelles in a variety of organic solvents and is able to support high water contents, up to $w = 50$ ($w = [H_2O]/[\text{surfactant}]$). On the other hand, cationic surfactants have been much less explored. In particular, benzyl hexadecyl dimethylammonium chloride (BHDC) is the most employed cationic surfactant for RMs and microemulsion studies [4(a),6]. In this case the positive interface offers a different microenvironment and consequently diverse properties of the solubilized substrate. BHDC reverse micelles are less stable than those of AOT and the range of w is limited to w <25–30 depending on the organic solvent. It has been shown that truly reverse micelles are formed at BHDC concentrations higher that 0.02 M in benzene [7]. It was also shown that in these systems, hydrophobic and electrostatic effects of the interface can control the course of a photochemical reaction [8].

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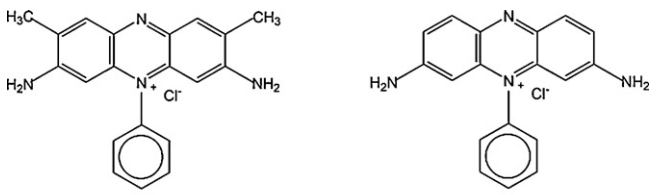

Scheme 1.

We have previously investigated several photoinitiating systems for vinyl polymerization operating in the visible region based on synthetic dyes [9,10]. In particular the phenazinium dye safranine-O (3,7-diamino-2,8-dimethyl-5-phenylphenazinium chloride, SF), which absorbs around 500 nm, was used as sensitizer and several aliphatic amines were employed as co-initiators (hydrogen donors) [9]. This system was found to be highly efficient for the free radical polymerization of vinyl monomers and it was also shown to be useful for photopolymerization in aqueous media [11]. The addition of a third component (diphenyliodonium salt) improved the efficiency of the system SF–triethanolamine in aqueous photopolymerization of acrylamide [12]. The deactivation mechanism of the excited states of SF, and the related dye phenosafranine (3,7-diamino-5-phenyl phenazinium chloride, PSF), in the presence of aliphatic and aromatic amines have been the subject of several studies of our group [13–16]. Therefore, it was of interest to explore the possibility of using these photoinitiator systems in reverse micelles. To this end we have undertaken an investigation of the photophysical properties of SF and PSF in reverse micelles of BHDC. These two dyes differ in terms of methyl substitution on the planar phenazinium skeleton (Scheme 1). Differential extent of hydrophobicity due to the presence of methyl substitution may cause a different location of the dyes in the reverse micellar system, and in turn different photophysical behaviour. SF was widely employed to characterize normal micelles [17], to investigate the kinetics of electron transfer reactions in these media [18] and in studies DNA–dye interactions [19]. On the other hand, similar studies employing PSF are very much scarce. In RMs absorption and fluorescence emission spectra of SF were determined in order to understand the localization of the dye in the microheterogeneous domains and to determine the properties of the microenvironment where the dye is located. Most of these studies were carried out in AOT–heptane solutions. Since the interfacial region is composed by the negative heads of the surfactant, it is expected that the positive dye will remain either close to the hydrated heads or oriented toward the bulk organic phase. From fluorescence studies Bose et al. [5] suggested, that at low *w* values SF does not penetrate into the reverse micellar core, rather it binds at the interfacial region. These authors also compare the photophysics of SF and PSF in AOT RMs. The fluorescence quenching of SF by AgCl nanoparticles has been investigated in the W/O microemulsion medium at different $[H_2O]/[AOT]$ ratios by Pramanik et al. [20]. The fluorescence quenching of SF by the inorganic ions Fe^{2+}, $[Fe(CN)_6]^{3-}$ and Cu^{2+} was studied in AOT RMs and microemulsions in various non-polar solvents [21]. Chaudhuri et al. [22] studied the luminescence behaviour of PSF in RMs of AOT in heptane. They concluded that the photophysical properties of the dye do not reach those in pure water even at high w.

All these studies of the photophysics of SF and PFS in RMs have been based on the absorption and fluorescence emission spectra and lifetime measurements. The effect of organized media on the triplet state of these dyes has received much less attention. The effect of microheterogeneous media, polyelectrolytes and normal SDS micelles, on the triplet state of the dye was investigated by Pastre and Neumann [23]. To our knowledge the triplet state properties of these dyes in RMs have not yet been reported. Since most of the applications of SF and PSF involve the triplet state and its electron transfer reactions with electron donors, it is of interest to study these processes in RMs.

2. Material and methods

2.1. Materials

Safranine-O and phenosafranine from Aldrich (≥85%) were recrystallized from ethanol. BHDC was two times recrystallized from ethylacetate and dried under vacuum. Benzene and methanol were from Sintorgan (HPLC grade) and used as received. Water was purified through a Millipore Milli-Q system. Reverse micelles solutions were prepared by the addition of a small amount of the dyes dissolved in water to a 0.05 M BHDC/benzene solution. The water:micelle content, $w = [H_2O]/[\text{surfactant}]$, was varied by adding neutral water. The final analytical concentration of the dye was *ca.* 5×10^{-6} M. Since the aggregation number of BHDC in benzene at $w = 15$ is *ca.* 500 [24], at the surfactant concentration used the mean occupation number of the dye was less than 0.05. The aliphatic amines triethanolamine (TEOA) and tributylamine (TBA) were commercially available and were purified by standard procedures when necessary.

2.2. Measurements

Absorption spectra were obtained by using a Hewlett Packard 6453E diode array spectrophotometer. Fluorescence spectra were measured with a Spex Fluoromax spectrofluorometer in air equilibrated solutions. Fluorescence lifetimes were determined by using the time-correlated-single-photon-counting technique with a FL 900 Edinburgh Instruments equipped with a PicoQuant subnanosecond pulsed LED emitting at 495 nm. Fluorescence quantum yields were determined relative to those of the dyes in MeOH [25,26]. Transient absorption measurements were carried out by excitation at 532 nm using a laser flash photolysis equipment as previously described [27]. The samples were deoxygenated by continuous bubbling with high purity argon. All measurements were carried out at 30 °C.

3. Results and discussion

3.1. Singlet state properties

Absorption and fluorescence spectra of SF and PSF are highly dependent on the polarity of the solvent [25,26]. In water solutions, SF shows absorption and emission maxima centred at ~520 nm and ~586 nm, respectively. A red shift in the ground-state absorption and a blue shift in the emission band of both dyes are observed when the solvent polarity decreases. In BHDC reverse micelles the spectral characteristics depend on the water content. The absorption spectra are more sensitive to the value of *w* than the fluorescence emission spectra. The absorption maximum of safranine is blue shifted from 548 nm at $w = 2$ to 539 nm at $w = 20$. On the other hand, the fluorescence emission spectrum remains unchanged in position ($\lambda_{max} = 572$ nm) but decreases in intensity as shown in Fig. 1.

It is to be noticed that in homogeneous solvent the absorption maxima for SF are at 529 nm in MeOH and 537 nm in 2-propanol [25]. The fluorescence emission maxima are at 564 and 562 nm in MeOH and 2-propanol, respectively. Similarly, for PSF the emission changes only 2 nm on going from $w = 2$ to $w = 20$ while in the same interval the absorption changes by more than 12 nm. Fluorescence lifetime and quantum yields of the dyes present a small