THE SITE OF SOLUBILIZATION OF BACTERIOPHEOPHYTIN IN CATIONIC MICELLES FROM STUDIES OF HEAVY-ATOM ENHANCED INTERSYSTEM CROSSING

S. Sadiq SHAH and Maurice W. WINDSOR
Department of Chemistry, Washington State University, Pullman, Washington 99164, USA

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From NMR spectroscopy and picosecond spectroscopic studies of the external heavy-atom effect on the excited singlet-state lifetime, we conclude that the porphyrin ring of BPh is situated in the vicinity of the polar head groups of CTAB at the micellar surface, while the phytyl chain lies within the hydrophobic innercore region of the micelle.

1. Introduction

Surfactant molecules in water undergo self-association, resulting in a colloidal aggregate called a micelle. Formation of micelles occurs over a narrow concentration range, characteristic for a given surfactant, called the critical micelle concentration (CMC). At concentrations close to CMC the micelles are roughly spherical in shape. Hydrophobic tails of the surfactant molecules form the non-polar innercore, while the polar head groups are directed towards the aqueous phase and constitute the charged micellar surface (fig. 1). Depending upon the type of surfactant (cationic or anionic), the surface charge can be negative or positive. A useful property of micellar media is that they offer a heterogeneous system, comprising a non-polar innercore and a polar bulk aqueous phase. This heterogeneity can be used to control the distance between and relative orientation of reactant molecules dissolved in the micellar system. These factors are determined by the site of solubilization and by the degree of hydrophobicity of the molecules.

During the past few years we have used the special properties of micellar media to study electron transfer reactions between model donor–acceptor systems of relevance to photosynthesis. Our studies are aimed at understanding the effect of the structured environment provided by the micelle on the forward and reverse electron transfer reactions. In particular, we have investigated the conditions required for improving the efficiency of the forward electron transfer (FET) step that leads to formation of the separated radical ion pair. We have also sought to exploit the electrostatic interactions between the micellar surface charge and the radical ions to prevent or inhibit the reverse electron transfer (RET) step that leads to recombination of the two radical ions. These studies, if successful, could lead to useful ways of capturing and storing solar energy in chemical form.

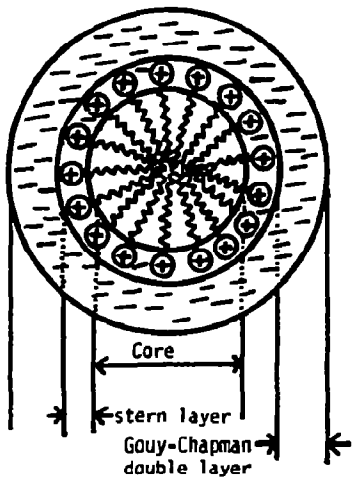

Fig 1. A cross section of a spherical cationic micelle where (−) represents the bromide counterion, (⊕) the polar head group and (∿∿) hydrocarbon chain of the surfactant molecule.

To explore such interactions, we have studied electron transfer from photoexcited bacteriopheophytin (BPh) to *p*-benzoquinone (BQ) in cetyltrimethylammonium bromide (CTAB) micelles [1,2]. Our results show that electron transfer from the lowest excited singlet state, BPh*, to BQ is more efficient in CTAB micelles than in homogeneous solutions at higher BQ concentration. This result can probably be ascribed in part to local enhancement of the concentration of BQ in the innercore of the micelle, but also in part to specific interactions between the reactants and products and the micellar surface. At low BQ concentrations the FET rates in homogeneous and micellar solutions are very similar (1.1×10^{10} M^{-1} s^{-1} and 1.5×10^{10} M^{-1} s^{-1}). Judging from the amplitude of the initial absorbance changes at 420 nm following the excitation, the observed yield of BPh^+ in CTAB is about a factor of two lower than that found in organic solvents [1]. The recombination rate for ions that do separate is about the same or slightly faster in CTAB micelles (2.3×10^{10} M^{-1} s^{-1}) than in a number of organic solvents (1.4×10^{10} M^{-1} s^{-1}). It seems reasonable to expect that, as soon as electron transfer occurs, the BQ^- anion would be drawn towards the positively charged inner micellar surface, thus increasing the relative distance between the charge-separated species. This should slow down the recombination rate. Nevertheless, we did not observe any reduction in the RET rate. How is this result to be explained? Perhaps the answer lies in the specific site of solubilization of the BPh within the micelle.

To learn more about the site of solubilization and thus perhaps explain the unexpectedly fast RET rate in micellar solution, we have used NMR spectroscopy and have also taken advantage again of the well-known external heavy-atom enhancement effect on intersystem crossing [3,4] that was used earlier in our laboratory in studying the BPh/BQ system in homogeneous solution [5]. For organic molecules containing π-condensed aromatic ring systems, heavy atoms, either as substituents or in the solvent, can cause enhanced intersystem crossing (ISC) from the lowest excited singlet state to the triplet manifold, thereby reducing the singlet lifetime. By observing the extent of reduction of the lifetime of BPh* in the presence of heavy counterions such as Br^-, we can infer how close the porphyrin ring system of BPh is to the bromide ions and thus the approximate location and orientation of BPh within the micelle.

2. Methods and materials

The sample solutions for picosecond studies were prepared by injection concentrated aliquots of BPh in ethanol into 0.1 M aqueous solutions of CTAB. In some experiments the concentration of heavy counterions, such as Br^-, at the micellar surface was increased by addition of aqueous sodium bromide solution to the micellar solution of BPh. In other experiments, the bromide counterions at the micellar surface were replaced by chloride ions by adding excess aqueous sodium chloride solution.

Excited singlet-state lifetimes of BPh were measured with the picosecond apparatus described elsewhere [5]. The excitation pulses at 530 nm had a duration of 8 ps and an energy, after one stage of amplification, of ≈ 1.0 mJ. A white continuum pulse of about the same duration as the excitation pulse was used to monitor the absorbance changes at 610 nm as a function of the delay time with respect to the excitation pulse.

The samples for NMR studies were prepared by injecting concentrated aliquots of BPh in deuterated acetone into 0.1 M CTAB solution in D_2O. The spectra were recorded on an NT200 Nicolet NMR spectrometer.

3. Results and discussion

The NMR spectrum (fig. 2) of 0.1 M CTAB solution shows resonance peaks at 0.91, 1.33, 1.83, 3.22, and 3.52 ppm corresponding to terminal $-CH_3$, $-(CH_2)_n-$, β-CH_2-, $-N(CH_3)_2$ and α-CH_2 protons, respectively. These resonance peaks remain unchanged in the presence of 5×10^{-5} M BPh. This result suggests that the main porphyrin ring of the BPh is not residing in the innercore or the Stern layer. If it were, chemical shifts would be expected due to the interactions between the porphyrin ring and the terminal methyl groups or the hydrocarbon chain of the surfactant molecules. Similar interactions have been reported previously [6]. One might also expect changes in the chemical shifts due to the interaction between the phytyl chain of the BPh and surfactant hydrocarbon tails [7,8]. But in view of the structural similarity of the phytyl chain and the surfactant hydrocarbon chain, hydrophobic interactions similar to those that occur between two surfactant hydrocarbon

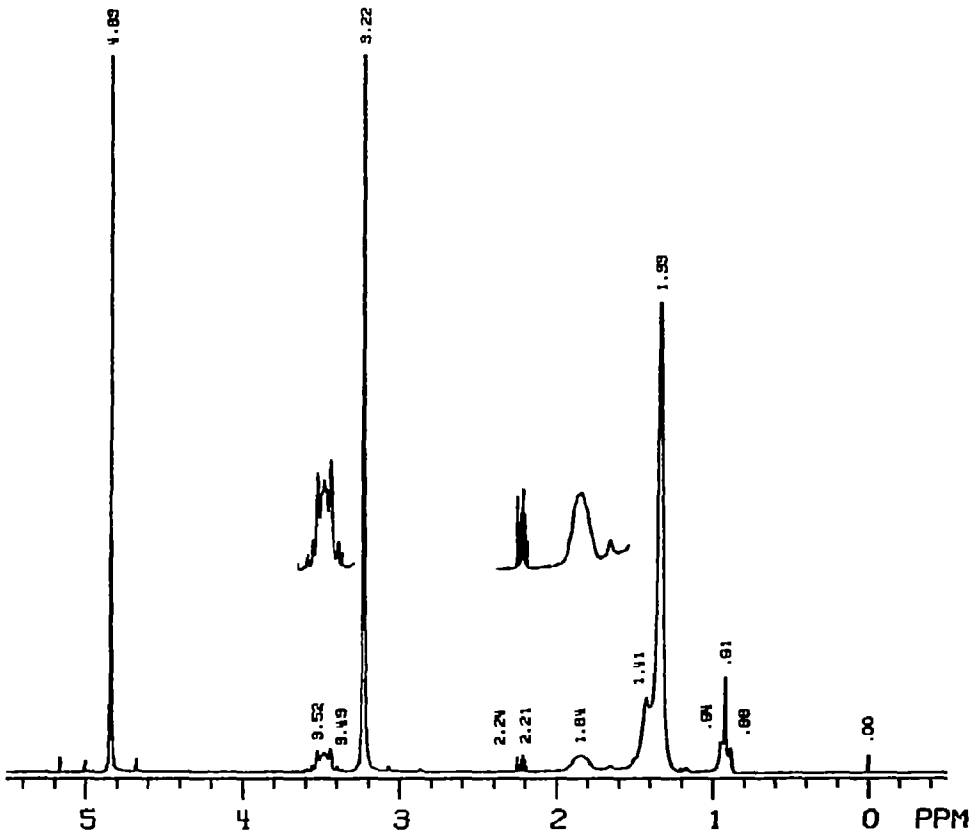

Fig 2 ^{1}H NMR spectrum of 0 05 M CTAB in D_2O in the presence of 5×10^{-3} M BPh Peaks at ≈ 3 5 and 3 43 correspond to the deuterated acetone used to dissolve BPh in CTAB

chains are to be expected. These would not lead to detectable further changes in the chemical shifts of the surfactant protons, in accord with our observations.

The excited singlet-state lifetimes of bacteriopheophytin (BPh*) in various homogeneous solutions and micellar systems were obtained by measuring the decay of the excited state absorbance at 610 nm (table 1). The lifetime (τ_s) in cyclohexane is 2.1 ± 0.2 ns, while in the presence of 3.8 M and 6.6 M methyl iodide it is reduced to 1.03 ± 0.33 and 0.78 ± 0.15 ns, respectively. We attribute this reduction of the singlet state lifetime to enhanced intersystem crossing from BPh* (singlet state) to BPh^T (triplet state) casued by an increase in spin–orbit coupling in the BPh molecule induced by nearby heavy atoms, in this case iodine [9].

Table 1
Lifetimes of BPh singlet at 610 nm

Solvent	τ (ps)
cyclohexane	2100 ± 200
cyclohexane + 3.8 M MeI	1030 ± 330
cyclohexane + 6 6 M MeI	780 ± 150
bromocyclohexane	1325 ± 150
CTAB (0.1 M)	2000 ± 300
CTAB + 0.1 M NaCl	1650 ± 220
CTAB + 0 033 M NaBr	440 ± 150
DAC	1500 ± 300

We find that the lifetime of BPh* in 0.1 M CTAB micelles is 2.0 ± 0.3 ns. Upon increasing the number of bromide counterions at the micellar surface/Gouy–Chapman layer by addition of NaBr to the solution to

bring the final concentration to 0.033 M NaBr in the sample, the observed BPh* lifetime is reduced to 440 ± 150 ps. Replacing the bromide counterions by a less efficient quencher, chloride ion, by adding NaCl to bring the final concentration to 0.1 M NaCl in the sample, increases the lifetime to 1650 ps. The greater quenching efficiency of bromide ions relative to chloride is apparent from the data in table 1. Very pronounced quenching occurs for bromide at a concentration only one-third of that at which relatively slight quenching occurs for chloride. Bear in mind that the bromide and chloride ions in the Stern layer are in dynamic equilibrium with those in the bulk aqueous phase. The addition of excess chloride, as in the system CTAB + 0.1 M NaCl, would be expected to replace most of the bromide ions in the Stern layer with chloride. This view is supported by the observation (table 1) that in micelles prepared from dodecylammonium chloride (DAC), in which chloride is of course the only counterion present, the lifetime of BPh* (1500 ps) is closely similar to that in the CTAB +0.1 M NaCl system (1650 ps).

It is apparent from the above results that the location of the BPh in the micelle must be such that the counterions can approach closely the π orbitals of the porphyrin ring in order to bring about the observed enhancement of intersystem crossing. It does not seem unreasonable to assume that the hydrophilic nature of the polar substituents, carbonyl and ester groups, on the main porphyrin ring, would preferentially solubilize the ring at the micellar surface. Thus chemical intuition and our quenching results lead to the same conclusion. Based on our NMR results, heavy-atom quenching studies, and the consideration of the structure of the BPh molecule (fig. 3) we propose, therefore, that the main porphyrin ring of BPh is oriented in such a way as to allow maximal interaction between the portion of the porphyrin ring containing the carbonyl and ester groups and the hydrophilic environment near the polar head groups at the micellar surface. The phytyl chain would lie within the innercore of the micelle, permitting the maximum possible hydrophobic interaction between the phytyl chain and the hydrocarbon tails of the surfactant molecules in the micelle. This proposed site of solubilization of BPh, with the porphyrin ring close to the micellar surface, would facilitate interaction between the π-electron cloud of the porphyrin ring and the

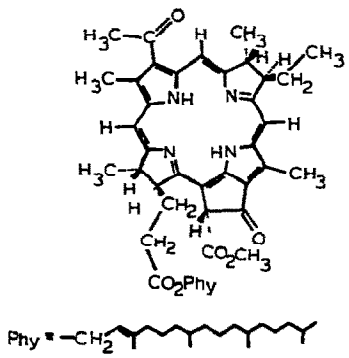

Fig 3. Structure of bacteriopheophytin, where "Phy" represents the phytyl chain

bromide ions at the surface of the micelle and is, therefore, consistent with our observations of heavy-atom quenching of the BPh* lifetime. Whether or not the porphyrin ring of the BPh is bent backwards, as suggested for chlorophyll in vesicles [10], cannot be deduced from our NMR and external heavy-atom effect results.

The model also helps to explain our earlier observation that the RET rate for the BPh/BQ system in micellar solutions is essentially unchanged from that observed in homogeneous solution in organic solvents [1]. We had anticipated that coulombic interactions between the charged micellar surface and the radical ions might serve to separate the ions physically and thus inhibit the reverse electron transfer step. We reasoned that, following the forward electron transfer step from triplet bacteriopheophytin, BPh^T, to benzoquinone in CTAB micelles, the negatively charged BQ^- radical ion would be held in place in the positively charged BPh^+ cation to be forced by electrostatic repulsion out into the aqueous phase. Nevertheless, no reduction of the RET rate was observed. It is clear now that we did not earlier place enough emphasis on the possible strength of the hydrophobic interaction between the phytyl chain of the BPh and the hydrocarbon tails of the surfactant molecules that make up the micelle. The magnitude of this hydrophobic interaction will be greatly influenced by the orientation of the BPh molecule within the micelle. In turn, the orientation will be affected by the hydrophilic interactions between the polar substituents in the porphyrin ring and the micellar surface.

In the case of BPh, it is known that the $-COOCH_3$ ester group and the phytyl side chain (fig. 3) lie on opposite sides of the plane of the porphyrin ring [11]. Thus, if the $-COOCH_3$ group is located at the micellar surface, the phytyl tail would be thrust strongly into the innercore of the micelle, rather than lying, for example, along the inside surface of the Stern layer. Under these conditions, the hydrophobic effect could be stronger than the coulombic repulsion between the cationic porphyrin ring and the positively charged micellar surface, effectively immobilizing the BPh^+ cation and keeping it in close proximity to the BQ^- anion and thus facilitating reverse electron transfer.

Further studies of the use of micellar media to control hydrophobic and coulombic interactions between appropriate donor–acceptor systems are in progress, with the goal of finding systems in which forward electron transfer is enhanced while reverse electron transfer is either prevented or inhibited [12].

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References

[1] S S. Shah, D Holten and M.W. Windsor, Photobiochem. Photobiophys 1 (1980) 361.
[2] D. Holten, S.S. Shah and M.W. Windsor, Picosecond phenomena, Vol 2, Springer Series in Chemical Physics, Vol. 14 (Springer, Berlin, 1980) p. 317.
[3] S.P McGlynn, T Azumi and M. Kinoshita, The triplet state (Prentice-Hall, Englewood Cliffs, 1969) p 307.
[4] M Kasha, J. Chem. Phys 20 (1952) 71.
[5] D Magde and M.W. Windsor, Chem. Phys Letters 27 (1974) 31
[6] K.A. Zacharisse, N V Phuc and B. Kozanklewicz, J. Phys. Chem. 85 (1981) 2676
[7] M.J Minch and S S. Shah, J. Org. Chem. 44 (1979) 3252.
[8] C Wolff and M. Grätzel, Chem. Phys Letters 52 (1977) 542.
[9] D Holten, M. Gouterman, W.W. Parson, M.W. Windsor and M G Rockley, Photochem. Photobiol. 23 (1976) 415
[10] J. Luisetti, H Mohwald and H.J. Galla, Biochem Biophys Res Commun. 78 (1977) 759
[11] D Mauzerall, in. The photosynthetic bacteria, eds R K. Clayton and W.R. Sistrom (Plenum Press, New York, 1978) ch 11
[12] S.S. Shah, D Holten and M W. Windsor, unpublished work