

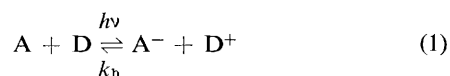
Effects of Hydrophobic Association and Interfacial Surface Potential on the Photosensitized Reduction of Anthraquinone Sulphonate in Positively Charged Micelles and Vesicles

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Photoinduced reductions of anthraquinone sulphonates in positively charged micelles and vesicles are affected by the interfacial surface potential and the nature of the counter ion of the electron acceptor; with a surfactant counter ion, close association of the electron acceptor with the charged interface is achieved, effective control of the photosensitized electron transfer process is accomplished, and the photoreduction of the quinone proceeds with a quantum yield of $\phi = 2.6 \times 10^{-1}$.

Photosensitized electron transfer reactions [equation (1)] are currently of interest as a means of solar energy conversion.^{1,2} A basic limitation of these reactions is the recombination process of the photoproducts that prevents their accumulation and further utilization. Several charged interfaces such as micelles,³ polyelectrolytes,⁴ and colloids⁵ have been suggested as an environment to stabilize the photoproducts. In these interfacial systems electrostatic attractive and repulsive interactions of the interface with oppositely charged photoproducts retard their recombination. Recently, it was demonstrated that the extent of stabilization of the photoproducts correlates with the interfacial surface potential.⁶

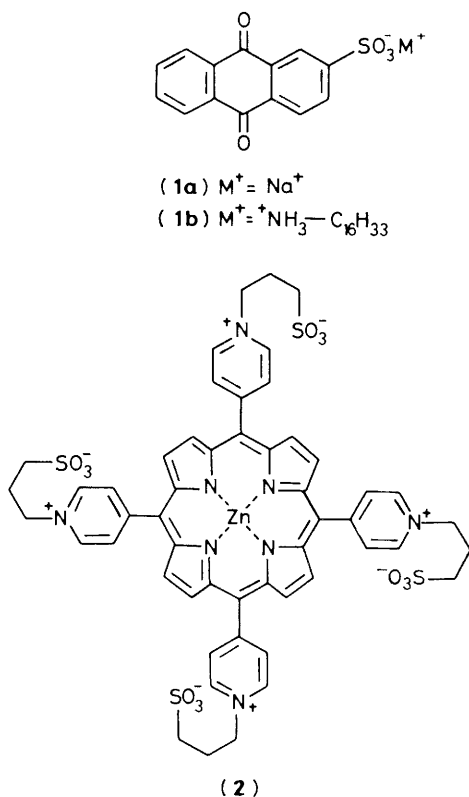


The binding characteristics of photoactive reagents with charged interfaces have been examined. These measurements imply that only a fraction of the photoactive reagent is in close association with the charged interface, while most of it is partitioned in the electrical double layer of the interface.⁶

Therefore, only a fraction of the photoproducts experience effectively the interfacial electric potential against the recombination reaction. Thus, enforcement of one of the photoproducts to the interfacial surface is expected to enhance substantially the effectiveness of the electrostatic interactions in photosensitized electron transfer reactions.

Here we report the photosensitized reduction of anthraquinone sulphonates, AQS⁻ (1) in positively charged hexadecyltrimethylammonium bromide (CTAB) micelles and didodecyldimethylammonium bromide (DODB) vesicles, using a water soluble neutral sensitizer Zn-TPPyS^o (2) and cysteine (Cy-SH) as the ultimate electron donor.

The sensitizer (2) was prepared by the reaction of *meso*-tetrapyrrolylporphyrin with 1,3-propanesultone, followed by refluxing the zwitterionic porphyrin ligand with zinc acetate in water. The system is composed of the sensitizer (2) (1.0×10^{-5} M), (1a) (2.0×10^{-3} M), and Cy-SH (2×10^{-3} M). Illumination of a deaerated aqueous solution of these components ($\lambda > 400$ nm), pH = 4.2, results in an inefficient photoreduction of AQS⁻ to the corresponding hydrosemi-quinone radical, AQHS^{•-}. The photoreduction of AQS⁻



was followed spectroscopically and the estimated quantum yield is $\phi = 1.0 \times 10^{-2}$ [Figure 1(a)]. Illumination of the same components in a 1.3×10^{-2} M CTAB solution results in a 5-fold enhancement in the photoreduction rate of (1a), $\phi = 5.4 \times 10^{-2}$ [Figure 1(b)]. This enhancement is attributed to electrostatic interactions of the intermediate photoproducts with the positively charged interface. The oxidized sensitizer, Zn-TPPyS⁺, is repelled by the interface with which AQHS⁻ is associated. Consequently, the recombination rate is retarded and the subsequent oxidation of cysteine is facilitated.

The similar photosensitized reduction of (1a) with positively charged DODB vesicles instead of micelles has been investigated. With this interface the photoreduction of (1a) is 2-fold enhanced as compared with that in CTAB micelles, $\phi = 1.0 \times 10^{-1}$ [Figure 1(c)]. This enhancement is attributed to the higher surface potential of the charged vesicles (*ca.* +100 mV *vs. ca.* +70 mV for the micellar interface).[†] Consequently, the photoproducts are further stabilized against the recombination process, owing to the higher electrostatic barrier introduced by the vesicular interface.

A significant effect on the photosensitized reduction of anthraquinone sulphonate is observed when (1a) is substituted by hexadecylammonium anthraquinone-2-sulphonate, (1b), in the CTAB micelles. Illumination of a 1.3×10^{-2} M CTAB micellar solution that contains (1b) (2×10^{-3} M), the sensitizer (2) (1×10^{-5} M), and cysteine (2×10^{-3} M), results in the extremely efficient formation of AQHS⁻ ($\phi = 2.6 \times 10^{-1}$) [Figure 1(d)]. Thus, using a negatively charged electron acceptor with a surfactant counter ion results in a 26-fold enhancement in the quantum yield as compared to the homogeneous aqueous solution of the respective quinone

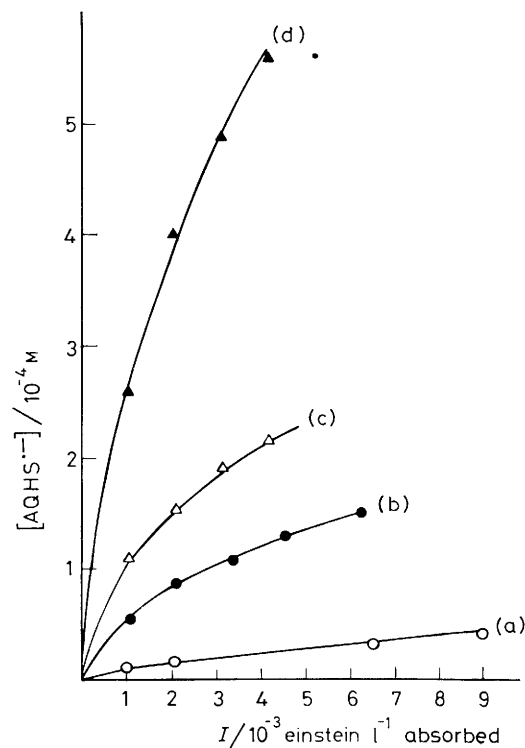


Figure 1. Progress of the photosensitized reduction of anthraquinone-2-sulphonate, AQHS⁻, as a function of absorbed light [the electron acceptor is (1a) unless otherwise stated]: (a) in homogeneous aqueous phase; (b) in 1.3×10^{-2} M CTAB micelles; (c) in DODB vesicles; (d) in 1.3×10^{-2} M CTAB micelles with (1b) as the electron acceptor.

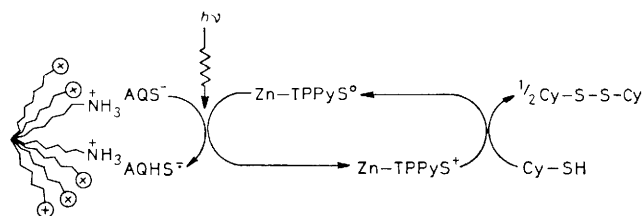


Figure 2. Schematic function of CTAB micelles in controlling the photosensitized reduction of anthraquinone sulphonate *via* hydrophobic association and electrostatic interactions.

with Na⁺ as counter ion. Furthermore, the photoproduction of (1b) is *ca.* 5-fold enhanced as compared with that of (1a) in CTAB micelles, and 2.5-fold higher than that of (1a) in DODB vesicles. This enhancement is attributed to the participation of the surfactant counter ion of the electron acceptor in its fixation on the micellar surface (Figure 2). The surfactant ion is associated with the micellar aggregates. Consequently, the electron acceptor is associated with the micellar surface, and thus the intermediate photoproducts experience effectively the electrostatic interactions.

In conclusion, the results demonstrate that the association of a photoproduct with a micellar interface by means of a surfactant counter ion significantly enhances the rate of the photoinduced electron transfer reaction. The interfacial surface potential affects the effectiveness with which the recombination rate can be controlled and the location of photoproducts in the interfacial electrical field seems to be important in controlling the electrostatic interactions. Thus, interfaces characterized by a high surface potential to which

[†] The surface potentials were determined by flow dialysis. For experimental details see ref. 6.

one of the photoproducts is strongly bound by covalent or hydrophobic interactions, seems a productive route to follow in order to increase the quantum yields of photosensitized reactions.

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