Photochemical Electron Transfer across Surfactant Vesicle Bilayers mediated by 2,1,3-Benzothiadiazole-4,7-dicarbonitrile

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2,1,3-Benzothiadiazole-4,7-dicarbonitrile (BTDN) mediates the electron transfer from morpholine-4-ethanesulphonic acid to anthraquinone-1,5-disulphonate in the presence of positively charged micelles, or across the bilayer of vesicles of dioctadecyldimethylammonium bromide.

In recent years there has been considerable interest in the possibility of transferring electrons across membranes or simple bilayer structures such as those of surfactant vesicles. Such electron transfers would not only improve the efficiency of charge separation in linked redox systems, but would also allow the separation of the products of such systems. A particular attraction is the possibility of separating the sites of hydrogen and oxygen production in the photochemical decomposition of water.

A few successful systems for transmembrane electron transfer have been reported in which the bilayer head groups are generally zwitterionic (phospholipids) and the electron transfer agent is usually a photosensitive metal complex,[1—3] often chlorophyll.[3] An unusual example, in which the electron transfer mediator is a surface-active viologen molecule and the metal sensitiser is in the aqueous phase, has been reported,[4] as has a biphotonic process in which the electron is passed between metal complexes embedded in the near-surface regions of the bilayer by electron transfer agents such as butylallyloxazine.[5] Reports[6] of unmediated electron transfer across a bilayer were subsequently shown to be in error.[7] We now describe an unusual system, in which electrons are transported across a bilayer with *positively charged* head groups and the mediator is the simple organic molecule, 2,1,3-benzothiadiazole-4,7-dicarbonitrile (BTDN).[8]

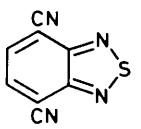
We have previously reported[9] that photolysis of BTDN in solutions containing cetyltrimethylammonium bromide (CTAB) micelles and EDTA (ethylenediaminetetra-acetic acid dianion) produces the corresponding anion radical $BTDN^{\cdot-}$ in yields up to 50%, that the product radical anion is confined within the micelle, and that it has a half-life of several days in the absence of oxygen. These results, together with lipid solubility of BTDN, suggest that it should be an ideal candidate for mediating electron transfer across a suitable bilayer structure or model membrane.

Since EDTA, at the concentrations required for successful electron transfer, causes coagulation of positively charged surfactant vesicles, it is necessary to use morpholine-4-ethanesulphonic acid (MES) as an electron donor. Photolysis of solutions containing BTDN, MES, and CTAB micelles produces $BTDN^{\cdot-}$. On addition of the disodium salt of anthraquinone-1,5-disulphonic acid (AQDS) the brown colour of $BTDN^{\cdot-}$ is immediately discharged and replaced by the yellow colour of the reduced form of the anthraquinone,† thus showing that $BTDN^{\cdot-}$ can act as a reducing agent and transfer its electron to an acceptor outside the micelle. Continuous photolysis of a solution containing MES, BTDN, CTAB, and AQDS causes formation of the hydroquinone ($AQDSH_2$) at a rate about twice that of a similar solution from which BTDN has been omitted [Figure 1, (a) and (b)].

† Detailed studies show that the anthraquinone product under these conditions is the hydroquinone $(AQDSH)_2$, formed by disproportionation of the semiquinone and double protonation of the resulting product.

Unilamellar vesicles were prepared[10] by sonication of dioctadecyldimethylammonium bromide (DODAB) in water containing MES (0.05 mol dm^{-3}). MES was removed from the outer water regions by eluting with water through a freshly prepared Sephadex G50 column to leave the vesicles with entrapped MES. AQDS and BTDN were then added to the outer water pools and the resulting solution was photolysed. Growth of reduced AQDS was monitored by visible spectroscopy and the results are shown in Figure 1 [(c) and (d)]. In the absence of BTDN, very little reduction of AQDS occurs, showing that neither MES nor AQDS leaks through the vesicle bilayer. In the presence of BTDN, $AQDSH_2$ is produced rapidly, thus indicating successful electron transfer across the bilayer mediated by BTDN.

To ensure that photolysis in the presence of BTDN was not causing leakage of either MES or AQDS through the vesicle bilayer, DODAB vesicles with entrapped MES and externally added BTDN and AQDS were prepared as before. These were photolysed until half the maximum yield of $AQDSH_2$ was achieved. The solution was then eluted through a 12 cm Sephadex G-50 (med) column and the fractions containing the



BTDN

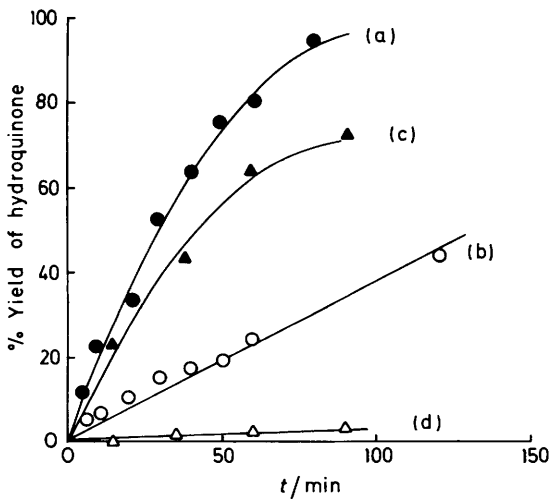


Figure 1. Yield for $AQDSH_2$ with time. (a) BTDN (3.3×10^{-4} M), acetate buffer (pH 5.6), CTAB (2.2×10^{-2} M), AQDS (3.3×10^{-4} M), MES (5.0×10^{-2} mol dm^{-3}); (b) as in (a) minus BTDN; (c) BTDN (3.3×10^{-4} M), AQDS (3.3×10^{-4} M), DODAB (2.0×10^{-3} M), MES (5.0×10^{-2} M); (d) as in (c) minus BTDN.

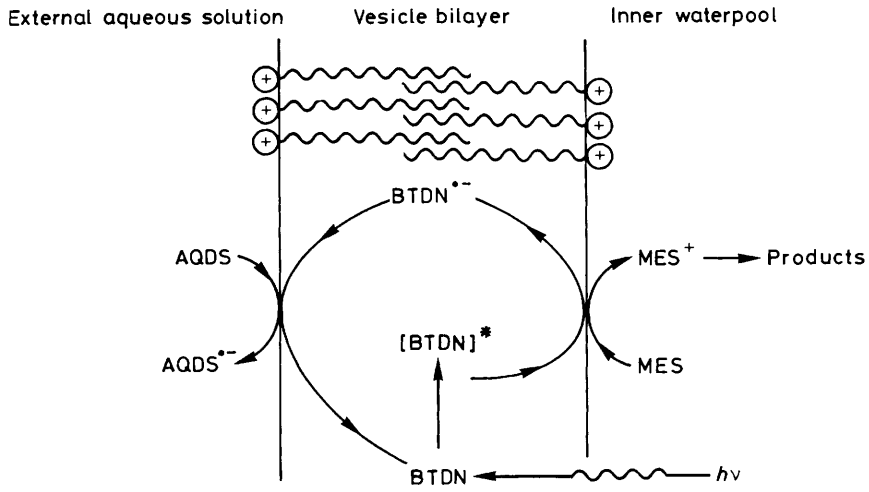


Figure 2. Possible scheme for the electron transfer across the vesicle bilayer mediated by BTDN.

vesicles and the bulk water from the experiment were collected. AQDS appeared in both fractions (it binds to the vesicle on account of its dinegative charge) but BTDN was largely in the bulk water. If leakage of the AQDS into the inner water pools had occurred, photolysis of the vesicle-containing fraction should have led to production of $AQDSH_2$, whilst if leakage of MES out to the bulk water had occurred, photolysis of the fraction containing the bulk water would have led to the formation of $AQDSH_2$. In practice, $AQDSH_2$ was not produced on photolysis of either fraction. However, when more BTDN was added to the fraction containing vesicles and the resulting solution was photolysed, $AQDSH_2$ was once again produced, indicating that the vesicles had retained their integrity and the MES was still entrapped within them.

A possible scheme for the electron transfer process is shown in Figure 2, but the exact electron transfer mechanism, *i.e.* whether it involves diffusion of $BTDN^{\cdot-}$ across the bilayer or a self-exchange reaction between $BTDN^{\cdot-}$ bound near the inner surface region of the bilayer and BTDN closer to the outer surface of the bilayer, that is, a promoted electron transfer mechanism,[2] awaits detailed flash photolysis studies.

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