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Cation-regulated Viologen-mediated Transmembrane Electron Transfer

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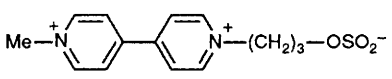
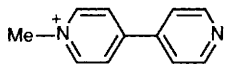
A chemically switchable microheterogeneous redox system exhibiting vectorial charge transfer has been developed by asymmetrically organizing viologens across dihexadecylphosphate vesicle bilayers.

We will describe a microheterogeneous system wherein oxidation–reduction across a bilayer membrane is controlled by addition of a lipophilic ion to the system. Because transmembrane charge transfer occurs only in the presence of an added ion, this system is of interest to the field of molecular electronics;[1] *i.e.*, the lipophilic ion provides a switching mechanism controlling electron conduction across the bilayer.

Methyl viologen (MV^{2+}) was entrapped within dihexadecylphosphate (DHP) vesicles by sonicating the DHP in 20 mM Tris–HCl, 200 μM *N,N'*-dimethyl-4,4'-bipyridinium dichloride ($MVCl_2$) at pH 8.0, followed by removal of external MV^{2+} by cation exchange chromatography (Chelex 100). The internal MV^{2+} concentration was then determined spectrophotometrically.[2] Varying amounts of 1-methyl-1'-sulphanatopropyl-4,4'-bipyridinium[4] (MSV^+) chloride (**1**) were then added to the vesicle suspension. After purging the solution of oxygen by bubbling with argon, an anaerobic solution containing excess sodium dithionite ($S_2O_4^{2-}$) was added. Immediate one-electron reduction of the viologen to the radical ensued, but only to an extent equal to the concentration of externally added MSV^+. After several minutes, about 60% of the total viologen in a system containing equimolar internal MV^{2+} and external MSV^+ was reduced and no further changes occurred over a period of 5 min. If an anaerobic solution of 1-methyl-4,4'-bipyridinium (MB^+) (**2**) was then added in slight molar excess, the remainder of the viologen was reduced within a few minutes. One-to-one correspondence was observed between the number of electrons allowed to flow into the vesicles and the number of MB^+ ions added to the bulk aqueous phase. The additional viologen radical formed upon adding 10, 21, and 31 μM MB^+ to systems containing equimolar internal MV^{2+} and external MSV^+ was 12, 21, and 31 μM, respectively. Although the stoicheiometry of electron flow was independent of the concentration of external MSV^+ (6—50 μM), the rate of internal MV^{2+} reduction increased with increasing MSV^+, indicating that the latter functioned as a transmembrane redox mediator. The close 1 : 1 correspondence of MB^+ added to MV^{2+} reduced is demonstrated in Figure 1, where viologen reduction attending MB^+ addition is monitored spectrophotometrically at 546 nm.



(1)



(2)

Since charge transfer across the bilayer is electrogenic, compensatory ion movement is necessary to maintain electroneutrality.[2] We have shown that externally bound MV^{2+} mediates reduction of MV^{2+} occluded within DHP vesicles.[3] Because MV^+ was the only lipophilic ion in that system, it co-migrated with the electron in 1 : 1 stoicheiometry. In the present case, reduced MSV is uncharged and cannot dissipate the electrical gradient generated by transmembrane charge displacement. Therefore, in the absence of ions capable of penetrating the bilayer, a membrane potential quickly developed which blocked further reaction. Adding MB^+, which has no redox chemistry under these conditions

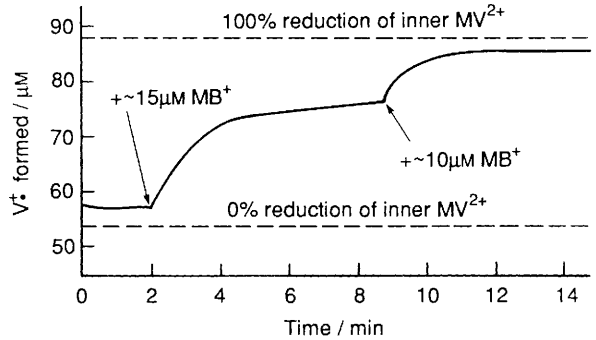
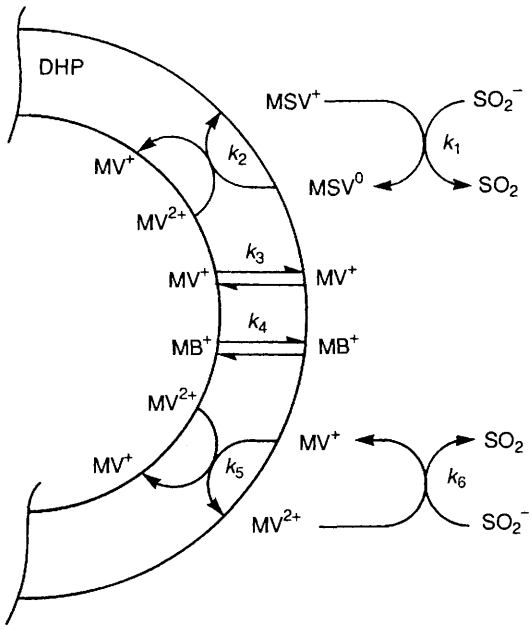


Figure 1. Effect of anaerobic addition of MB^+ upon 4 mM suspensions of DHP vesicles containing initially 34 μM internal MV^{2+} and 53 μM MSV^+ plus 0.4 mM $Na_2S_2O_4$ in the external medium (20 mM Tris–HCl, pH 8.0, 23 °C).



Scheme 1. Proposed mechanism for transmembrane oxidation–reduction: The k_2—k_5 steps are electrogenic and must be balanced such that overall electroneutrality is maintained; $^2k_5$ arises as a consequence of electroneutral MV^+–MB^+ exchange ($k_3 + k_4$).

but does have high intrinsic permeability towards bilayer membranes,[4] provided a mechanism for collapsing the electrical gradient, thereby allowing transmembrane redox to proceed to completion.

Cation-exchange chromatography was used to probe further the nature of transmembrane translocation of the viologens and MB^+ ion attending charge transfer. When a 4 mM suspension of DHP vesicles in 20 mM Tris–HCl buffer, pH 8.0, containing initially 36 μM occluded MV^{2+}, and 31 μM and 48 μM external MSV^+ and MB^+, respectively, was passed over a Chelex 100 column, it was found that 34 μM viologen (corrected for dilution), but no MB^+, co-chromatographed with the vesicles. These results support earlier conclusions that the MV^{2+} dication is impermeable to the DHP membrane on the experimental timescale.[2—4] Following $S_2O_4^{2-}$ reduction and reoxygenation, chromatographic and spectrophotometric analyses[2] indicated that only 14 μM viologen (corrected for dilution) was present within the vesicles, although now ~20 μM MB^+ was also internally localized. Oxygen is freely membrane permeable; consequently, it oxidizes viologen radicals on both sides of the membrane without generating a membrane potential. Since MV^{2+} is membrane impermeable, its transmembrane distribution at the end of the reductive half-cycle is 'frozen' upon oxygenation. The demonstration of dithionite reductant-dependent accumulation of MB^+ within the vesicle establishes that it is actively taken up in response to electrogenic transmembrane oxidation–reduction; further, the loss of compartmented MV^{2+} following reduction indicates that electroneutral MB^+–MV^+ transmembrane ion exchange also occurs on the reaction timescale.

The salient reaction characteristics have been incorporated into the mechanism given in Scheme 1. By manipulating the electrostatic charge of a redox mediator through chemical derivatization and asymmetrically distributing it across a bilayer membrane possessing appropriate mediator diffusion characteristics, it has been possible to vectorially couple transmembrane ion and electron flow. This behaviour illustrates the potential for developing switchable electron-conducting membranes exhibiting rectification. Replacement of the membrane-permeable ion by a gated ion channel or lipophilic ion-generating system will provide a means for reversibly switching the membrane between conducting and nonconducting states.

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