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ELECTRON TRANSPORT ACROSS LIQUID MEMBRANES WITH AN ASYMMETRICALLY LOCATED ELECTRON MEDIATOR

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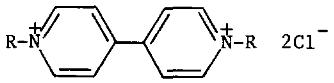
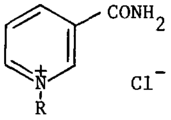
Summary: The addition of a surface active dipyridinium or nicotinamide chloride into a liquid membrane containing vitamin K_3 (VK_3), brought about a large enhancement in the rate of electron transport from $S_2O_4^{2-}$ to $Fe(CN)_6^{3-}$. The asymmetric location of this salt at one interface of the membrane was achieved by the use of a small pore-sized millipore filter.

Natural quinones of ubiquinones, plastoquinones and vitamin K's are essential link in mitochondrial and photosynthetic electron and proton transport. The biomimetic electron transport has been effected between aqueous reactants, separated by liquid membranes containing the above quinones.[1-4] The rates of electron transport are not large, mainly owing to the inefficient biphasic electron transfer between aqueous reactants and the quinone. Now, we have observed that the rate of biphasic electron transfer can be remarkably improved by locating an adequate surface active electron mediator at the interface of membrane.

We have investigated the effect of a surface active dipyridinium (**1**) ($E_0{}'$=*ca.*-0.4 V)[5] or nicotinamide chloride (**2**) (*ca.*-0.4 V)[6] on the rate of electron transport between $S_2O_4^{2-}$ (-1.13 V)[5] (Red phase) and $Fe(CN)_6^{3-}$ (+0.36 V)[5] (Ox phase) across a liquid membrane (M phase) containing VK_3 (+0.44 V), as developed by Lehn et al..[4] The system consisted of $Na_2S_2O_4$ (500 μmol)/phosphate buffer (pH 7.0) (50 mL) and $K_3Fe(CN)_6$ (250 μmol)/the same buffer (50 mL), separated by a liquid membrane: only VK_3 (40 μmol) or VK_3 (40 μmol) + **1**(**2**) (0.15 μmol)/Ph_2O-$Cl_2CHCHCl_2$ (10:3) (w/w)



(1a) R=C_6H_{13}
(1b) R=$C_{12}H_{25}$
(1c) R=$C_{16}H_{33}$



(2a) R=$C_{12}H_{25}$
(2b) R=$C_{16}H_{33}$

(0.07-0.12 mL) supported on a cellulose nitrate (pore diameter 0.025 μm) (VS) or fluorinert (0.2 μm) (FG) millipore filter (Millipore Ltd.).[7)] Equilibrations were conducted at 30°C and the aqueous phases were vibrated gently to facilitate mixing by argon bubbling. The electron transport from $S_2O_4^{2-}$ to $Fe(CN)_6^{3-}$ was determined spectrophotometrically by monitoring the decrease in the absorbance of $Fe(CN)_6^{3-}$ at 421 nm. In a blank membrane without VK_3 there was no detectable transport of electron across the membrane. The membranes containing VK_3, and VK_3 + 1(2) were found to produce the electron movement. In both cases a plot of a decreased amount (μmol) of $Fe(CN)_6^{3-}$ against time (hour) gave an almost straight line for an initial period of 2-3 hours, the slope of which indicates the rate of electron transport (μmol/h). Table I summarizes the results on rates of electron transport for each membrane examined. The membranes supported on a FG filter always exhibited larger rates as compared with those supported on a VS filter. The rates markedly increased by the addition of a catalytic amount of 1 or 2 into the membranes. 1,1'-Dihexyl-4,4'-dipyridinium chloride (1a) with a minor surface active property brought about 2- to 3-fold rate-enhancement. A further larger rate-enhancement was achieved by the use of more surface active 1,1'-dilauryl- (1b) and 1,1'-dicetyl-4,4'-dipyridinium chlorides (1c), and 1-lauryl- (2a) and 1-cetylnicotinamide chlorides (2b). The membrane containing only 1 or 2 transported no electron, indicating that these salts serve no electron carrier function by themselves. Therefore, it can be reasonably interpreted that 1 and 2 are located at the Red-M interface and mediate the biphasic electron transfer from $S_2O_4^{2-}$ to VK_3 to bring a large enhancement to the rate. The results of increased transport rates indicate that the electron mediators have turnover numbers of >600 h^{-1} in the electron transfer. Figure 1 represents a diagram for the electron transport from $S_2O_4^{2-}$ to $Fe(CN)_6^{3-}$ by the aid of the mediator.

The mediators can be also located at the Ox-M interface, but they do not mediate the electron transfer between the reduced VK_3 and $Fe(CN)_6^{3-}$. On the contrary, they should interfere with an access between the two reactants and decrease the rate of electron transfer. We have succeeded

Table I. Rates of electron transport from $S_2O_4^{2-}$ to $Fe(CN)_6^{3-}$ across various liquid membrane systems supported on a millipore filter.

Membrane component	Transport rate[a] (μmole/h)	Membrane component	Transport rate[a] (μmole/h)
None[b]	0	None[c]	0
VK$_3$[b]	30	VK$_3$[c]	22
VK$_3$ + 1a[b]	85	VK$_3$ + 1a[c]	35
VK$_3$ + 1b[b]	114	VK$_3$ + 1a[c,d]	20
VK$_3$ + 1c[b]	110	VK$_3$ + 1c[c]	58
VK$_3$ + 1c[b,d]	56	VK$_3$ + 1c[c,d]	20
1a, 1b, 1c[b]	0	1a, 1c[c]	0
VK$_3$ + 2a[b]	79		
VK$_3$ + 2b[b]	105		
2a, 2b[b]	0		

[a] Each value is the average of two or more independently determined rates (±5 % error). [b] Supported on a FG filter. [c] Supported on a VS filter. [d] The Ox phase was kept in contact with one side of the filter spread with a mixture of VK$_3$ and 1. In the other experiments the spread side was directed toward the Red phase.

in the preparation of membranes by using a small pore-sized VS filter with an asymmetric location of 1 (and 2) only at one (particularly Red-M) interface. This is evident from the fact that *ca.* 2.5-fold rate-enhancement was obtained when the Red phase was kept in contact with one side of the filter spread with a mixture of VK$_3$ and 1c, whereas *ca.* 10 % decrease in the rate was observed when the spread side was directed toward the Ox phase.[8] The similar asymmetric membrane was also attained by the use of 1a with a shorter alkyl chain.[9] On the other hand, a larger pore-sized FG filter could not obtain the membranes with a complete asymmetric location of the mediator, because it penetrated partially across the pore to reach the Ox-M interface. This was revealed by the observation that *ca.* 2-fold rate-enhancement was obtained even when the Ox phase was kept in contact with one side of the filter spread with a mixture of VK$_3$ and 1c.

The present finding offers a possibility for constructing a photosynthetic liquid membrane with an asymmetric location of photosensitizers at each interface to accomplish an efficient solar energy conversion.

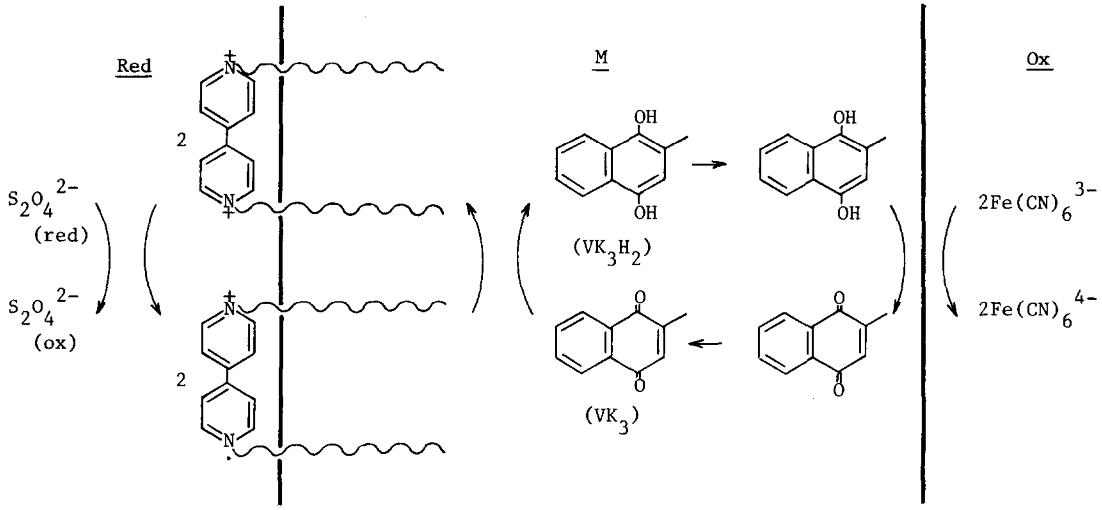


Figure 1. Diagrammatic representation for the electron transport from $S_2O_4^{2-}$ (Red phase) to $Fe(CN)_6^{3-}$ (Ox phase) across a liquid membrane (M phase) containing VK_3 + **1** supported on a VS filter.

References and Notes

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7. In a usual manner a solution containing the membrane components was spread on one side of the filter, and the spread side was directed toward the Red phase.
8. The rates of electron transport remained unchanged for each membrane whether it was instantly used or left for a few days after its preparation.
9. There is no clear explanation of the fact that the mediators cannot penetrate across the pore, whose diameter is *ca.* 4 times the longest dimension of the mediator.

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