Electron Transport by an Anthraquinone/Crown Ether Conjugate through an Organic Liquid Membrane controlled by Complexation with a Metal Cation

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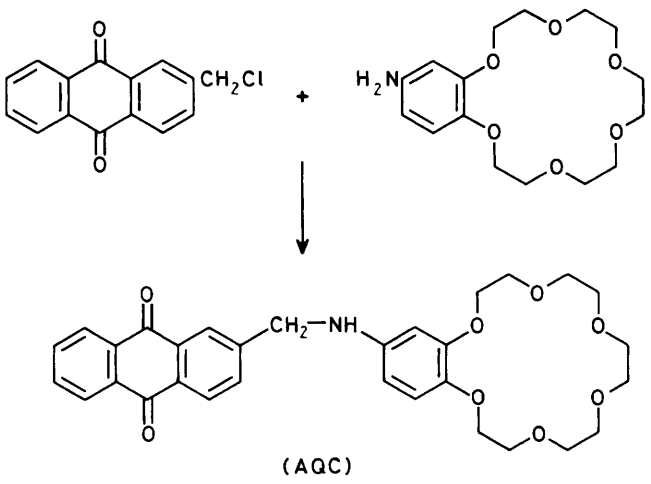
Anthraquinone/benzo-18-crown-6 conjugate was synthesized; its capability of transporting H^+ and electrons through a dichloromethane liquid membrane was modulated by the presence of K^+ ion in contact with the aqueous phases.

In signal and energy transductions which take place at a cell membrane, the flux of electrons and protons and/or other cations plays an essential role. Sometimes these types of transport are coupled with each other.[1] Various kinds of mediators have been applied to organic liquid and lipid membrane systems to reproduce and clarify the mechanism of coupled transport of ions and electrons across a biomembrane.[2,3] Coupled transport has also been investigated by simultaneous use of two independent mediators dissolved in an organic liquid membrane.[4] On the other hand, several



Scheme 1. Synthetic route to AQC.

kinds of crown ether derivatives which respond to light,[5,6] pH,[7,8] redox reactions,[9—11] and electrochemical processes[12—15] have been synthesized recently, and their effects in facilitating capture and transport of cations have been studied. In a previous study, a ferrocenyl group (as electron mediator) was bound to a crown ether unit (as cation-capturing group) and coupled transport of electron and cation through an organic liquid membrane was attempted.[16] However, because of the low solubility of the oxidized mediator in organic solvents, coupled transport was not achieved. In this paper, an anthraquinonyl group, which is neutral irrespective of its oxidation state and lipophilic, was chosen as electron mediator and bound to a crown ether unit. The resulting conjugate was investigated as a mediator of coupled transport of electrons and metal ions across an organic liquid membrane.

2-Chloromethylanthraquinone[17] reacted with 4′-aminobenzo-18-crown-6[18] to give 4′-(anthraquinon-2-ylmethylamino)benzo-18-crown-6 (AQC). The synthetic sequence is illustrated in Scheme 1. The product was purified by g.l.c. (LH 20) with MeOH as eluant, and identified by ^{1}H n.m.r. (90 MHz; $CDCl_3$; internal standard Me_4Si): δ 3.34—4.12 (m, 20H), 6.13—6.26 (m, 4H), 6.57 (s, 1H), 6.67 (s, 1H), 7.53—7.75 (m, 3H), and 8.06—8.37 (m, 4H).

A U-shaped glass tube (diam. 2 cm) was used for proton and K^+ ion transport across a CH_2Cl_2 membrane. The CH_2Cl_2 phase (20 ml) containing AQC (2 mM) separated the aqueous phase I (10 ml) containing potassium hexacyanoferrate(III) (1 mM) from the aqueous phase II (10 ml) containing ascorbic acid (10 mM). The redox process was monitored by measuring the amount of H^+ transported to the aqueous phase I.[19] The K^+ concentration was determined with a K^+-selective electrode (Horiba 8202-06T, Japan).

Figure 1 shows the time-dependence of the amount of H^+ in the aqueous phase I transported by AQC across the CH_2Cl_2 membrane. In the absence of $KClO_4$ in both aqueous phases, 0.13 μmol of H^+ was transported within 2 h. When $KClO_4$ (10mM) was added only to the aqueous phase II, electron transport was strongly enhanced. Thus, the amount of H^+ transported to the aqueous phase I increased to 0.66 μmol within 2 h. Conversely, the addition of $KClO_4$ (10 mM) to the aqueous phase I suppressed H^+ transport in either the presence or the absence of $KClO_4$ in the aqueous phase II. Such a modulation of electron and proton transport across the CH_2Cl_2 membrane on addition of metal ions to the contacting aqueous phases was not observed when 2-methylanthraquinone and benzo-18-crown-6 were mixed in the organic phase.

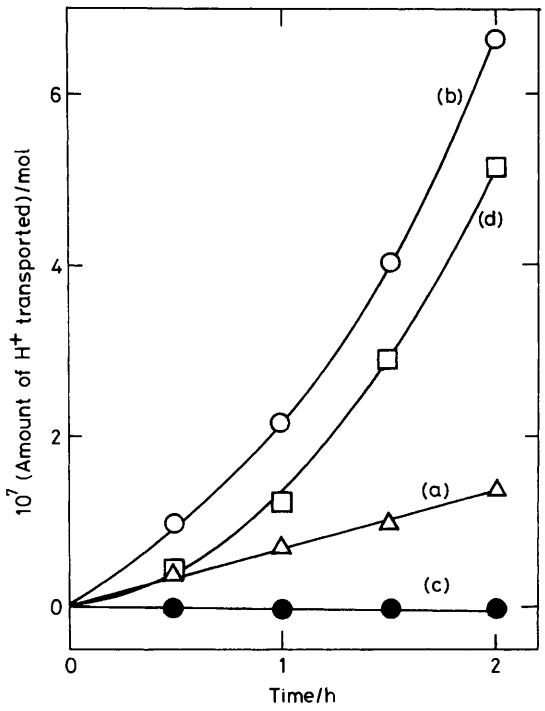


Figure 1. Amounts of H^+ transported to the aqueous phase I: (a) without $KClO_4$ in both aqueous phases; (b) with 10 mM-$KClO_4$ in the aqueous phase II; (c) with 10 mM-$KClO_4$ in the aqueous phase I; (d) with 10 mM-$KClO_4$ in both aqueous phases. Other ingredients: in aqueous phase I, 1 mM-potassium hexacyanoferrate(III); in aqueous phase II, 10 mM-ascorbic acid; in the dichloromethane phase, 2 mM-AQC.

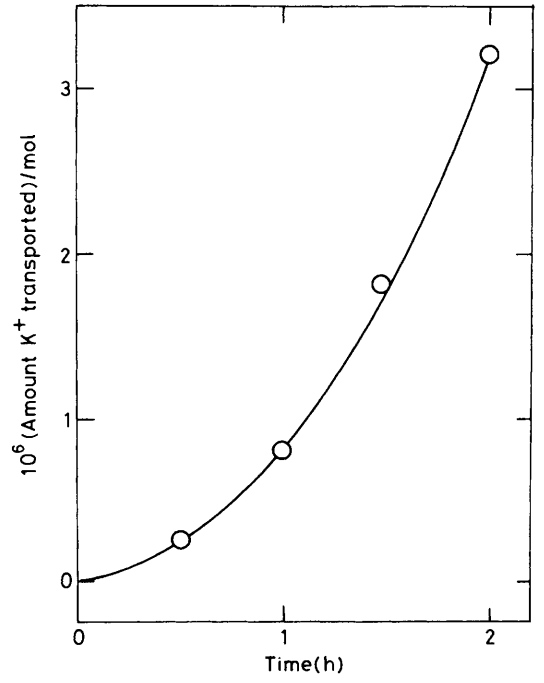


Figure 2. Amounts of K^+ transported to the aqueous phase I. Initial composition: in aqueous phase I, 1 mM-potassium hexacyanoferrate(III); in aqueous phase II, 10 mM-ascorbic acid and 10 mM-$KClO_4$; in the dichloromethane phase, 2 mM-AQC.

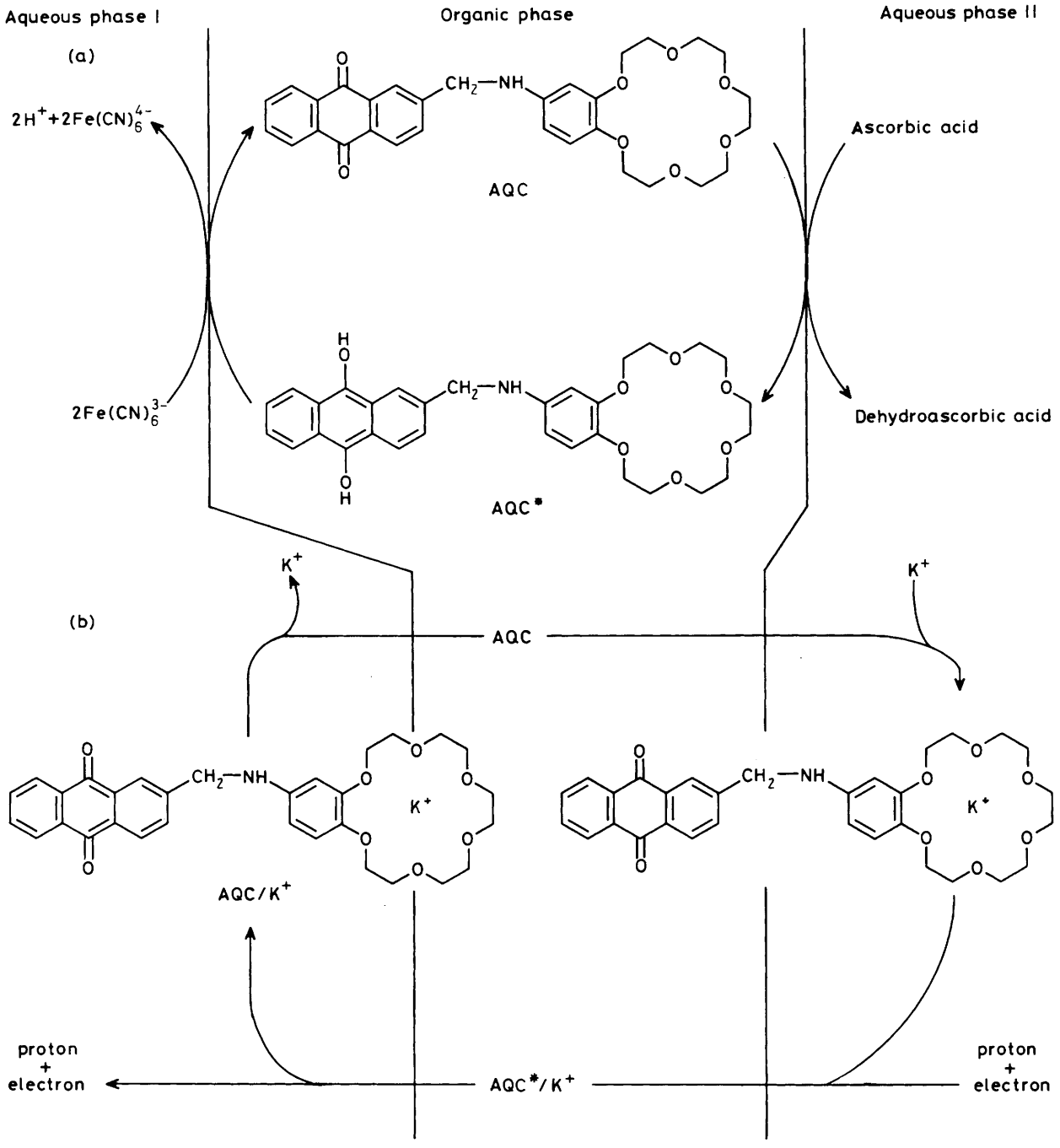


Figure 3. Diagram of electron, proton, and K^+ transport through a dichloromethane membrane by AQC (a) in the absence of K^+, (b) in the presence of K^+; AQC* represents the reduced state of AQC.

Thus the capability of the anthraquinone moiety in AQC to bring about electron and proton transport is clearly shown to be regulated by complexation with the metal ion of the crown ether moiety. This result was confirmed by the observation that H^+ transport to the aqueous phase I was not observed in the absence of hexacyanoferrate(III) in this aqueous phase, indicating that H^+ transport was carried out by the anthraquinone moiety according to a redox process and not by a secondary nitrogen moiety of the AQC ligand.

Since AQC efficiently transports H^+ when both aqueous phases contain the same amount of $KClO_4$, the effect of the concentration gradient across the CH_2Cl_2 membrane on cation transport should not be the primary reason for the enhanced electron transport.

Figure 2 shows the time dependence of the amount of K^+ transported to the aqueous phase I by AQC across the CH_2Cl_2 membrane in the presence of $KClO_4$ (10mM) in the aqueous phase II. The amount of K^+ transported was 3.2 μmol, which is larger than the amount of H^+ transported (0.66 μmol) under the same experimental conditions. It is therefore suggested that the enhancement of electron and proton transport on addition of K^+ ions to the aqueous phase II should be ascribed

to acceleration of the redox reaction occurring at the interface between the aqueous phase II and the CH_2Cl_2 membrane [Figure 3(b)]. The AQC molecule becomes more hydrophilic upon binding K^+ at the crown ether moiety, and more easily accessible to ascrobic acid in the aqueous phase. Electron and proton transport by AQC are in this way coupled with cation transport across the organic liquid membrane.

The application of AQC to coupled electron and cation transport across a lipid membrane will be a key experiment for the design and synthesis of artificial mediators for coupled electron and cation transport across a biological membrane.

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