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Coupling of Electron Transfer to Ion Transport in Macromosaic Membrane System

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Electron transfer can be readily coupled to ion transport by a circulating current generated in a novel macromosaic membrane system as in a biological system. A circulating current in the system including an electron transfer membrane enhances ion transport and electron transfer through the membranes and a redox reaction causes ion transport or vice versa in this system.

Redox reaction is an electron transfer phenomenon and it can be readily coupled to ion transport in a novel membrane system. Redox reaction is coupled to ion transport in vivo on the basis of chemiosmotic coupling,1) but the mechanism has not been fully clarified until now. It is very difficult to realize the coupling phenomenon in an artificial membrane system, although there have been some reports on carrier mediated electron and cation symport across liquid membranes.2, 3) We will report in this paper a preliminary result of the coupling of redox reaction to ion transport in a new macromosaic membrane system consisted of an electron transfer membrane and ion-exchange membranes.

Figure 1(A) shows the scheme of ion transport across a mosaic membrane proposed by Sollner.4) A mosaic membrane has cation exchange regions and anion exchange regions, cations are permeated across the cation exchange regions, anions are permeated across the anion exchange regions, and consequently, circulating currents are generated across the membrane. The circulating currents in the mosaic membrane enhance ion transport and salts can be enriched under a pressure gradient by the mosaic membrane, which is called piezodialysis.5) The membrane is, however, difficult to be prepared because the opposite charged groups are arranged closely and alternately in the membrane. We have developed a macromosaic membrane system,6) where anion exchange membranes and cation exchange membranes are alternately arranged, and a circulating current is generated in the system as shown in Fig. 1(B). When all of the membranes in this system are cation exchange membranes or anion exchange membranes, ions are permeated through the imperfection of the membrane and the flux is very small. When cation exchange membranes and anion exchange membranes are arranged alternately, a circulating current generated in the cell causes a large ion flux.

If one of the anion exchange membranes in the system is replaced by an electron transfer membrane where ions can not be permeated but electrons can be permeated, electrons instead of anions are permeated across the membrane and a circulating current is generated in this new macromosaic membrane system as shown in Fig. 1(D). The flux of the symbol e$^-$ in the Figure means electron current in the membrane and net negative charge flux in bulk solution, which means, for example, the negative charge flux caused by the gap of the electric charge between hexacyanoferrate(III) ion and hexacyanoferrate(II) ion in the experiment of Fig. 2. In this system, a reduction reaction occurs in the compartment I, an oxidation reaction occurs in the compartment IV, and cations are transported across the cation exchange membranes to maintain the electric neutrality. Figure 2 shows the typical result of electron transfer between hexacyanoferrate(III) ion and hexacyanoferrate(II) ion caused by a concentration gradient of potassium chloride in the cell. Electrons were transported across an electron transfer membrane, that is, a thin platinum plate in this study and cations or anions were transported across ion-exchange membranes. The permeation experiment was carried out with a cell composed of four compartments, compartment I, II, III, and IV. Cation exchange membranes (Asahi Glass CMV membrane) were interposed between compartment I and II and between compartment III and IV, a platinum plate was interposed between compartment I and IV, an anion exchange membrane (Asahi Glass AMV membrane) was interposed between compartment II and III, and each membrane area was 7.0 cm^2. In compartment I, II, III, and IV, a mixed aqueous solution (70 cm^3) of 1.43 mmol dm^{-3} potassium hexacyanoferrate(III) and 1.43 mmol dm^{-3} potassium hexacyanoferrate(II), where total potassium concentration was 10 mmol dm^{-3}, 100 mmol dm^{-3} potassium chloride solution (70 cm^3), 10 mmol dm^{-3} potassium chloride solution (70 cm^3), and a mixed aqueous solution (70 cm^3) of 1.43 mmol dm^{-3} potassium hexacyanoferrate(III) and 1.43 mmol dm^{-3} potassium hexacyanoferrate(II) were pumped at a rate of 26 cm^3 min^{-1} from each reservoir, respectively. An aliquot of the solution in each compartment was collected at an interval and analyzed. Hexacyanoferrate(III) ion and hexacyanoferrate(II) ion were determined by the calculation from the absorbance of the solutions at 303 nm. The molar quantity of the reduced hexacyanoferrate(III) ion was equal to that of oxidized hexacyanoferrate(II) ion in both compartment I and IV and it was also

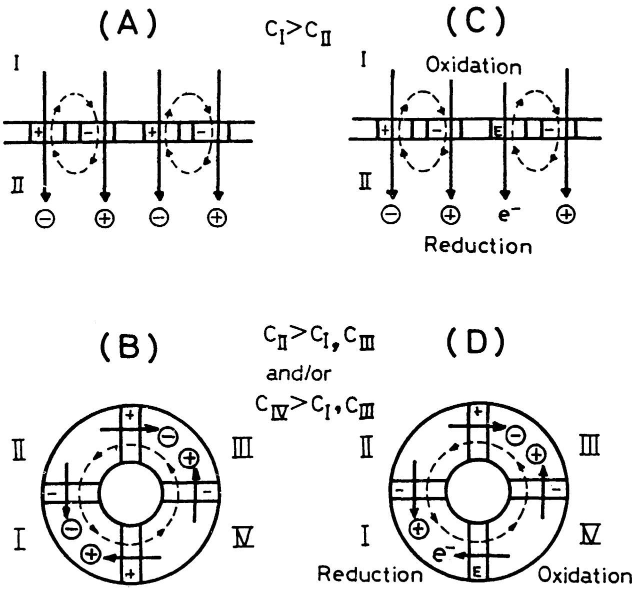

Fig. 1. Schematic circulating current in conventional mosaic membrane (A), in conventional macromosaic membrane system (B), and in novel mosaic membrane (C), in novel macromosaic membrane system (D): (+), anion exchange region or membrane; (-), cation exchange region or membrane; (E), electron transfer region or membrane; (---), circulating current; ⊕, cation flux; ⊖, anion flux; e$^-$, electron flux in membrane and net negative ion flux in bulk solution.

equal to the molar quantity of the potassium ion transported from compartment II to I and from compartment IV to III. The circulating current, which was caused by the concentration gradient of potassium chloride between compartment I and II and between compartment II and III, gave rise to the reduction reaction in compartment I and the oxidation reaction in compartment IV.

The circulating current, I relates to ion flux as follows.

$$I = nFSJ_s \qquad (1)$$

where n is the valence of the solute, F is the Faraday constant, S is the membrane area, J_s is the ion flux across a membrane. The circulating current relates to the total potential in this system, E_t and the total resistance, R_t as follows.

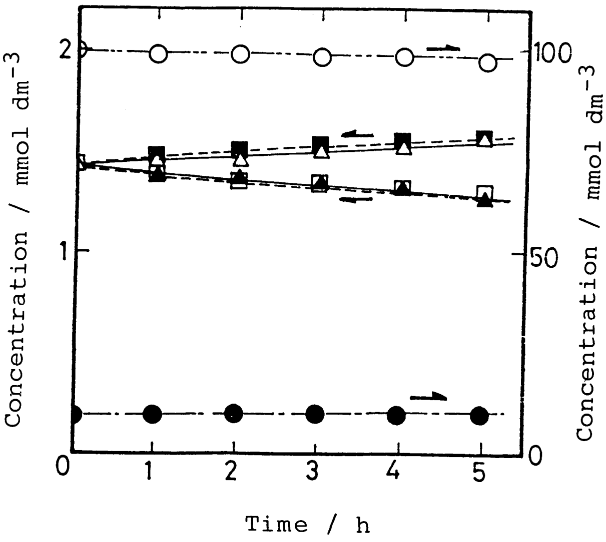

Fig. 2. Electron transfer coupled to ion transport: o, K^+ concentration in compartment II; ●, K^+ concentration in compartment III; △, ▲, concentration in compartment I; □, ■, concentration in compartment IV; △, □, $[Fe(II)(CN)_6]^{4-}$; ▲, ■, $[Fe(III)(CN)_6]^{3-}$.

$$I = E_t/R_t \qquad (2)$$

where E_t is expressed as the sum of the potential differences across the membranes and R_t is also expressed as the sum of the solution resistances and the membrane resistances as follows.

$$E_t = E_{I-II} + E_{II-III} + E_{III-IV} + E_{IV-I} - w_I - w_{IV} \qquad (3)$$

$$R_t = R_I + R_{II} + R_{III} + R_{IV} + 2R_C + R_A + R_E \qquad (4)$$

where E_{X-Y} is the potential generated between compartment X and Y, w_X is the overpotential generated on the compartment X side of the platinum surface in the step of electron transfer between hexacyanoferrate(III) and hexacyanoferrate(II) ions and platinum plate surface, R_X is the solution resistance in compartment X, R_A and R_C are the resistance of an anion exchange membrane and a cation exchange membrane, respectively, and R_E is the resistance of platinum plate, which can be negligible. The electromotive force calculated from the circulating current was about 30 % of the sum of the membrane potentials. The efficiency of the coupling of electron transfer to ion transport is low in this system, but this system simply simulate the chemiosmotic coupling.$^{1)}$ When there was a redox potential difference between compartment I and IV, a circulating current was also generated and drove the transport of potassium ion in this system. The coupling efficiency may be improved by some modification of the plate surface or by the introduction of enzyme-like materials to this system as in biological membrane system. The platinum plate can be substituted to other membrane prepared by some conducting polymer such as polyacetylene.$^{7)}$

Figure 1(C) shows electron and ion transport scheme in a novel mosaic membrane composed of ion exchange regions and electron transfer regions. In this Figure, the solutes are oxidized in the upper part and reduced in the lower part. The mechanism of electron and ion transports in this mosaic membrane is almost the same as that of biological membrane.$^{1)}$ A novel mosaic membrane containing electron transfer regions may be possible to be prepared but the macromosaic membrane system consisted of an electron transfer membrane and ion exchange membrane is much easier to be prepared. Electron transfer region or membrane is necessary to couple redox reaction to ion transport in both biological and artificial membrane system. If photo-reduction or photo-oxidation occurs in compartment I or IV in Fig. 1(D), an ion transport induced by the photo-energy can be realized in this system as in photosynthesis.

In this system, ion is transported in some compartments by the driving force of the redox reaction in other compartments which functions as a galvanic cell and the membrane potential developed in some compartments causes electrolysis in other compartments. Similar phenomena occur in phospholylation in biological membrane, where proton plays an important roll instead of metal cations.$^{8)}$ This system is very simple and will be applied to give rise to many reactions in membrane systems.

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