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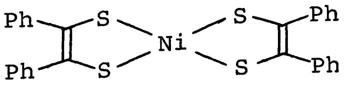
ION TRANSPORT THROUGH LIQUID MEMBRANE DRIVEN BY REDOX POTENTIAL. MULTI-COMPONENT ION CARRIER AS A MEDIATOR

Akira OHKI, Makoto TAKAGI, and Keihei UENO
Department of Organic Synthesis, Faculty of Engineering,
Kyushu University, Hakozaki, Higashi-ku, Fukuoka 812

A new-type of ion transport system driven by redox potential was presented. Nickel bisdithiolene complex, which undergoes the redox reaction of (**1**-Ni^0) $\rightleftharpoons$ (**1**-Ni^-), transported anions through a diphenyl ether liquid membrane by use of a lipophilic cation as a co-carrier.

Recently, several studies have examined the devices to transport selected ions through a liquid membrane with the aid of an electron carrier which is driven by a redox potential difference between two aqueous solutions.[1)] Shinbo *et al.* have reported an anion transport system in which N,N,N',N'-tetramethyl-*p*-phenylenediamine (TMPD) served as both an electron carrier and an anion carrier,[2)] and Grimaldi *et al.* have described a cation transport system by use of nickel bisdithiolene complex (**1**) as both an electron carrier and a cation carrier.[3)] These systems are important not only in modeling some of the physio-chemical processes of biomembranes but also in giving some applications in analytical and separation chemistry.



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In all of the systems hitherto reported, a single ion carrier has been used, and hence the ions to be transported should have the charge opposite to the electron carrier. However, this restriction can be removed, in principle, by constructing a multi-component carrier system in which another kind of lipophilic ions are employed in the membrane phase as a co-carrier in addition to the electron carrier. We would like to verify this in this communication by showing that **1** can be made to transport anions instead of cations by the combined use of a lipophilic cation as a co-carrier.

Figure 1 shows the apparatus used in the present study. The cell was consisted of two compartments, W_{ox} and W_{red}, each 150 ml capasity, which were separated by a plastic film-supported liquid membrane of effective area 28 cm^2. A micro-porous polypropylene film, Duragard 2500 (thickness, 25 µm; porosity, 45 %; maximum pore size, 0.4 x 0.04 µm; Polyplastics Limited) was used as a support, on which a diphenyl ether solution (*ca.* 0.04 ml) containing carrier compounds was applied.

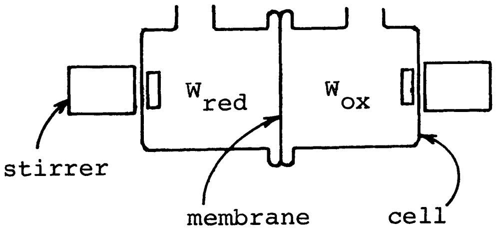

Fig. 1. Schematic representation of the apparatus.

In a typical run, W_{red} initially contained an aqueous solution of 20 mM (1 M = 1 mol/dm^3) sodium dithionite, 44 mM phosphate buffer (pH 7.0), and 10 mM sodium thiocyanate, while W_{ox} contained an aqueous solution of 10 mM potassium hexacyanoferrate (III), 44 mM phosphate buffer (pH 7.0), and 10 mM sodium thiocyanate. The both solutions were deoxygenated with argon. The membrane phase (diphenyl ether solution) contained 5 mM each of **1** and methyltrioctylammonium chloride ($MTOA^+ \cdot Cl^-$, Aliquat 336S). The aqueous solutions were stirred at 28 °C under argon atmosphere. Aliquots of the solutions were taken periodically and analyzed. The concentration of hexacyanoferrate (III) was determined by an absorption photometry at 420 nm, and that of thiocyanate by a conventional method.4)

Figure 2 shows the change in the concentrations of hexacyanoferrate(III) and thiocyanate in W_{ox} phase along with that of thiocyanate in W_{red} phase against time. It is evident that the concentration of hexacyanoferrate(III) and that of thiocyanate in W_{ox} phase decreased in the same amount as the time elapsed, the process being accompanied by the increase in thiocyanate concentration in W_{red} phase, again in the same amount. The decrease in the hexacyanoferrate(III) resulted in the formation and accumulation of hexacyanoferrate(II) ion in the same solution, and it is obvious that electrons were

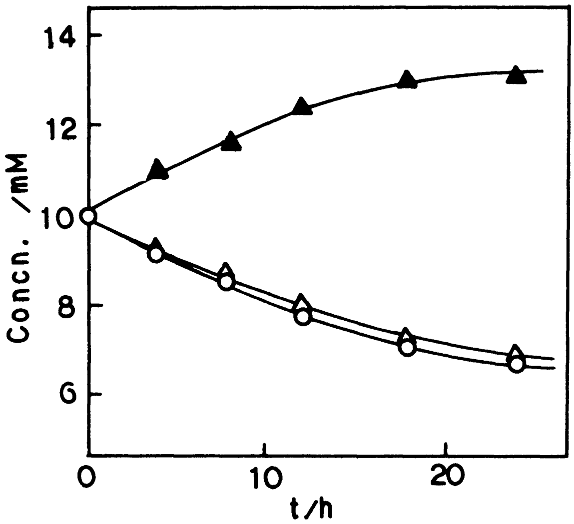

Fig. 2. Change in concentration of hexacyanoferrate(III) (○, in W_{ox}) and thiocyanate (△, in W_{ox}; ▲, in W_{red}) against time.

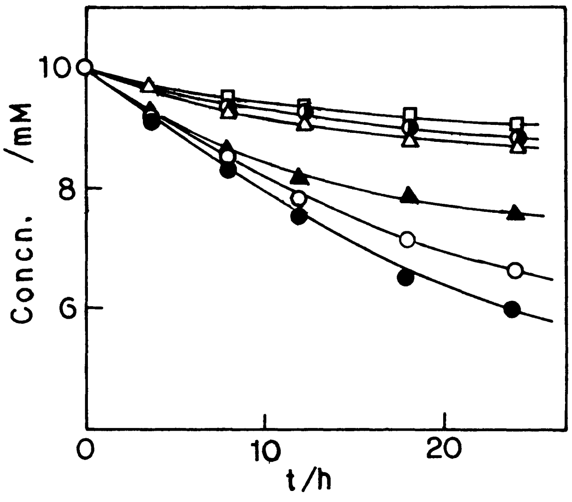

Fig. 3. Transport of various anions. The anion (10 mM) was added only in W_{ox} phase, other conditions being the same to the text. ●, sodium perchlorate; ○, sodium thiocyanate; ▲, sodium picrate; △, sodium nitrate; ◑, sodium bromide; □, sodium chloride or none.

transported through the membrane from W_{red} to W_{ox}, and the resulting accumulation of the negative charge in W_{ox} phase was compensated by the flow of thiocyanate anions in the opposite direction, i.e., from W_{ox} to W_{red}. In the control experiments, sodium dithionite in W_{red} phase or Aliquat 336S in the membrane phase was eliminated. Neither the decrease in hexacyanoferrate(III) concentration nor the change in thiocyanate concentration was observed, indicating that the presence of the co-carrier Aliquat 336S in the membrane phase and the difference of redox potential across the membrane is essential to this anion transport system.5)

The dependence of the transport rate on the nature of anion was investigated. Figure 3 shows the change of hexacyanoferrate(III) concentration in W_{ox} phase against time for various anions to be transported. In the case of picrate, the decrease in the picrate concentration was determined by measuring the absorbance at 357 nm7) because the visible absorption of hexacyanoferrate(III) was hidden by the strong absorption of picrate.

The rate of transport of anions decreased in the order, $ClO_4^- > SCN^- >$ picrate $> NO_3^- > Br^- > Cl^-$. As expected, the so-called lipophilic anions are more capable of being transported.6,8) However, picrate, in spite of its high lipophilicity, was found to have rather low permeation ability. This result may be ascribable to the fact that the anion underwent the reduction to an aminophenol at the W_{red}-liquid membrane interface.9)

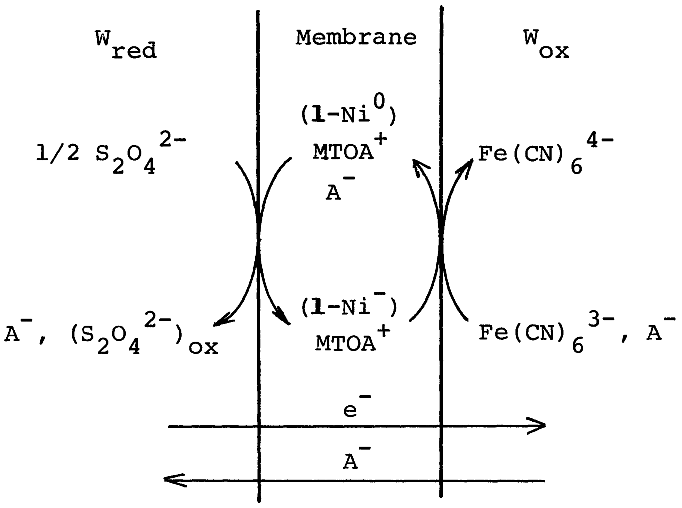

Fig. 4. Mechanism of anion transport in the multi-component carrier system.

The mechanism of the anion transport can be understood by considering the following elementary steps (Fig. 4): (i) $\mathbf{1}$-Ni^0 is reduced to $\mathbf{1}$-Ni^- by $S_2O_4^{2-}$ at the W_{red}-membrane interface, and the anion $\mathbf{1}$-Ni^- forms an ion-pair association complex with methyltrioctylammonium in the membrane phase ($MTOA^+ \cdot \mathbf{1}$-Ni^-); (ii) the ion-pair diffuses across the membrane; (iii) $\mathbf{1}$-Ni^- in the ion-pair is reoxidized to $\mathbf{1}$-Ni^0 at the W_{ox}-membrane interface. The free $MTOA^+$ forms an ion-pair with the anion to be transported (denoted as A^-); (iv) the ion-pair $MTOA^+ \cdot A^-$ and $\mathbf{1}$-Ni^0 diffuse back across the membrane; (v) at the W_{red}-membrane interface, $\mathbf{1}$-Ni^0 is reduced to $\mathbf{1}$-Ni^-; the latter releases A^- into W_{red} phase from the ion-pair $MTOA^+ \cdot A^-$. The cycle is repeated. As a result, electrons flow from W_{red} to W_{ox} phase, and the anions are simultaneously transported, against its concentration gradient, from W_{ox} to W_{red} phase in a continuous manner.

The present observation suggests that the TMPD-based anion transport system2) could be made to transport cations instead of anions. It has, however, not yet been successful. The major problem was in the unavailability of suitable co-carrier anions, which are required to be highly lipophilic and stable under ordinary redox conditions.8a)

In summary, the combined use of an electron carrier with an ordinary ion carrier provides a new possibility in modeling redox potential-driven ion transport phenomena in biomembranes, and widens the future application of redox potential to ion separations and related processes.

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References and Notes

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5) In the absence of thiocyanate ion in W_{ox} phase, i.e., in the absence of the anion to compensate the flow of electrons, the redox reaction itself should not take place if the system is working ideally. However, the reaction did occur (as indicated by the decrease of hexacyanoferrate(III) concentration in W_{ox} phase), though the rate decreased to 20 - 25 % of the normal system. It is possible that anions other than thiocyanate replaced the role of thiocyanate, though less effectively. The oxidizing anion, hexacyanoferrate(III), itself can be one of the candidates, because it is known to be extracted with $MTOA^+$ into an organic solution (Ref. 6). In fact, an appreciable amount of iron was detected in W_{red} phase during the transport experiment in the absence of thiocyanate salt (atomic absorption photometry).

6) J. Itoh, H. Kobayashi, and K. Ueno, Anal. Chim. Acta, **105**, 383 (1979).

7) The molar absorption coefficient of picrate at this wave length is *ca.* 16 times larger than that of hexacyanoferrate(III) at 420 nm, and the latter did not disturb the determination of the former.

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9) Picrate ion was reduced by dithionite in W_{red} phase to a reddish-colored aminophenol of yet unknown structure, the compound which was also obtainable from the reduction of picramic acid. The reaction was quantitative when the amount of dithionite was in a large excess, but as the concentration of the permeating picrate increased, the reaction at the membrane interface became complicated, giving rise to various side products. In transport experiments at a reduced anion concentration (1 mM, one tenth of that in the text), the reversed (and probably reasonable) permeability order, picrate $>$ SCN^-, was in fact observed.

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