CHEMISTRY LETTERS, pp. 1543-1546, 1981.

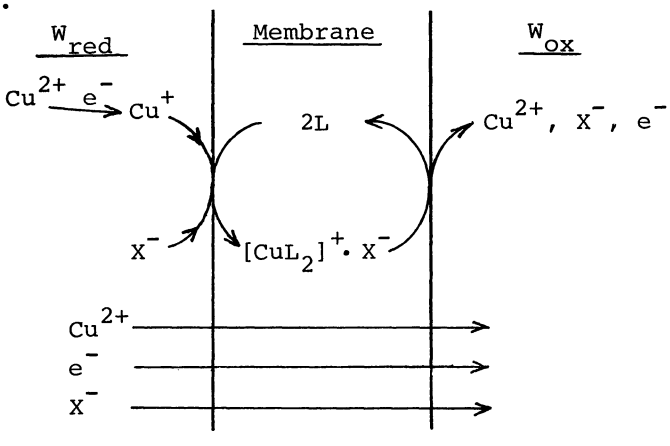
BATHOCUPROINE-MEDIATED COPPER TRANSPORT THROUGH LIQUID MEMBRANE DRIVEN BY REDOX POTENTIAL

Shugo MATSUNO, Akira OHKI*, Makoto TAKAGI, and Keihei UENO
Department of Organic Synthesis, Faculty of Engineering,
Kyushu University, Hakozaki, Higashi-ku, Fukuoka 812
* Center of Instrumental Analysis, Faculty of Engineering,
Kyushu University, Hakozaki, Higashi-ku, Fukuoka 812

A new device of metal separation system driven by redox potential is presented. Bathocuproine, which is known as an extraction agent specific to copper with the aid of reducing agent, could serve as a mediator in transporting copper through a polymer-supported liquid membrane.

Several groups have described the chemical devices for a selective ion transport through liquid membranes which are driven by redox potential.[1] Quite recently, Maruyama *et al.* reported an anion transport system in which a bathophenanthroline-metal complex served as both an electron carrier and an anion carrier.[2] In a previous paper, we described an anion transport system by the use of nickel bisdithiolene complex (electron carrier) and a lipophilic cation (anion carrier).[3] These systems are important in modeling some of the bioenergetic systems and in giving practical application in separation chemistry.

In all of the systems hitherto reported, the species transported do not undergo redox reaction themselves. They are simply transferred through the membrane in the form of ion-pairs solubilized in the membrane phase. Lipophilic electron carriers such as bathophenanthroline-metal, nickel bisdithiolene, ferrocenes, and ubiquinones are bound in the membrane phase and repeatedly serve as pairing ions. We would like to report here another type of ion transport system which occurs in a coupled manner to a redox reaction. The system concerns with the transport of a metal ion which itself can undergo a redox process between two valence states.



L : Bathocuproine

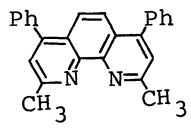


Fig. 1. Bathocuproine-mediated copper transport.

Bathocuproine (2,9-dimethyl-4,7-

diphenyl-1,10-phenanthroline, L) is well-known as a powerful extraction agent specific to copper. It stabilizes the lower valence state of copper, and copper(II) is reduced to copper(I) in the presence of a reducing agent. The resulting cationic complex CuL_2^+ is solubilized in organic solvent by forming a lipophilic ion-pair $[CuL_2]^+ \cdot X^-$ with an appropriate anion X^-. On contact with an oxidizing agent, the complex is decomposed to copper(II) species liberating L (Fig. 1).

The apparatus used was the same as that described in the previous paper.[3] Two compartments, W_{red} and W_{ox} (each 150 ml capacity), were separated by a plastic film-supported liquid membrane of effective area 28 cm^2. A micro-porous polypropylene film, Duragard 2500 was used as a support, on which a diphenyl ether solution (ca. 0.04 ml) containing a carrier was applied.

In a typical run, W_{red} phase was initially filled with a buffered aqueous solution (0.5 M ammonium acetate, 1 M = 1 mol/dm^3) of 0.1 mM copper(II) nitrate, 5 mM hydroxylamine sulfate, and 10 mM potassium chloride, while W_{ox} phase was filled with a buffered aqueous solution (0.5 M ammonium acetate), not containing a specific oxidizing agent. Oxygen dissolved in W_{ox} phase acted as an oxidizing agent. The membrane phase (diphenyl ether solution) contained 10 mM bathocuproine. The aqueous

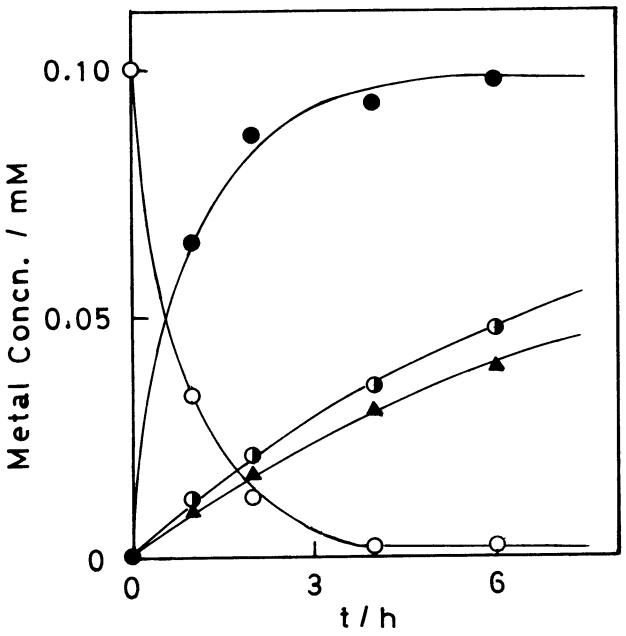


Fig. 2. Change in copper concentration against time under three conditions: the complete system (● , in W_{ox}; ○ , in W_{red}), without hydroxylamine (▲ , in W_{ox}), without potassium chloride (◑ , in W_{ox}).

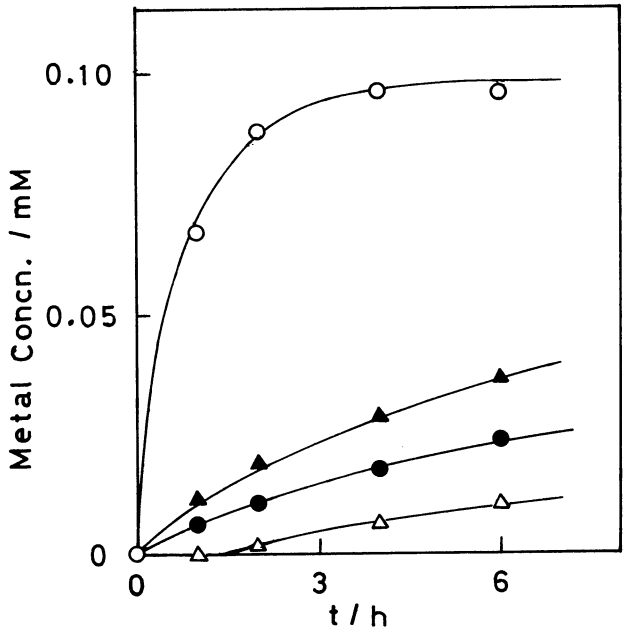


Fig. 3. The competitive transport of copper and zinc. The change in concentration of metal ions in W_{ox} phase against time under two conditions: the complete system (○ , copper; △ , zinc), without hydroxylamine (● , copper; ▲ , zinc).

solutions were stirred at 30°C, and the aliquots of the solutions were taken with time intervals and analyzed. The copper concentration was determined by atomic absorption photometry.

Figure 2 shows the change in the concentration of copper ion in W_{red} phase and in W_{ox} phase against time under various conditions. In the complete system, the copper concentration in W_{red} phase decreased with an elapse of time and finally reached almost zero; the process was accompanied by the increase in the copper concentration in W_{ox} phase in the same amount. It is evident that the copper transport from W_{red} to W_{ox} phase occurred and the concentration of copper against its concentration gradient was achieved (active transport). In the absence of reducing agent, hydroxylamine, the transport of copper proceeded until the concentration in W_{red} phase became equal to that in W_{ox} phase. This was due to the passive transport of divalent copper, in which the copper was extracted as $Cu^{II}LX_2$ type complex at the W_{red}-membrane interface and stripped at the other side of the membrane.

When potassium chloride in W_{red} phase was eliminated, the copper transport against its concentration gradient was still observed but the rate was considerably decreased in comparison with that of the complete system. This fact suggests that chloride ion is preferable to the other anions in W_{red} phase (*e.g.*, acetate and sulfate) as a counter anion (X^-) to be transported along with copper.[4] When the so-called lipophilic anion such as picrate and perchlorate was added to W_{red} phase instead of chloride ion, the rate of copper transport was greatly retarded. The ion-pair between CuL_2^+ and this kind of anion seems to be too lipophilic to release the anion and copper at the W_{ox}-membrane interface.[5]

Figure 3 shows the change of metal concentration in W_{ox} phase against time in the competitive transport of copper and zinc.[6] When the reducing agent was absent, *i.e.*, the transport both in a divalent state was concerned, zinc was transported in preference to copper. However, in the presence of reducing agent, the transport of copper preceded that of zinc because the transport mechanism for copper shown in Fig. 1 took place. Bathocuproine is a common carrier for copper and zinc, but in the presence of reducing agent, the carrier is preferentially occupied by copper(I) species, and as a result, only a limited portion of the carrier is available for a zinc transport. Such a phenomenon is peculiar to the carrier-mediated membrane transport system.[7] The use of cadmium in the place of zinc led to a similar result.

The mechanism of the copper transport system can be understood by considering the following elementary steps (Fig. 1): (i) copper(II) is reduced to copper(I) by hydroxylamine and the univalent species is extracted as $[CuL_2]^+ \cdot X^-$ complex at the W_{red}- membrane interface; (ii) the complex diffuses across the membrane; (iii) at the W_{ox}-membrane interface, copper is stripped to W_{ox} phase by oxidation back to copper (II) species; (iv) the free ligand, L, diffuses back across the membrane. The cycle is repeated. As a result of these processes, the active transport of copper against its concentration gradient from W_{red} to W_{ox} phase is achieved, accompanying the flow of both electrons and anions in the same direction, *i.e.*, from W_{red} to W_{ox} phase. Provided that the system shown in Fig. 1 is working ideally, the species which can permeate through the membrane are only copper(I) and the pairing anion X^-.

Accordingly, the copper transport proceeds until the chemical potential of $Cu^{I}X$ in both aqueous phases is equal. Even if the total concentration of copper as well as the X^- concentration in both aqueous phases is equal, the transport of copper ion occurs because the concentration of copper(I) in W_{red} phase is higher than that in W_{ox} phase.

Finally, it is added that the copper transport can be assisted by light if a photochemical device to produce reducing species is incorporated in W_{red} phase. However, a number of difficulties were encountered which made these systems less practical. Thus, the irradiation of a titanium oxide suspension[8] in W_{red} phase in the presence of a small amount of added methanol increased the rate of copper transport to the double of the control, but the rate dropped soon because the membrane surface became stuck with the photosensitizing semiconductor powder. The photosystem, acriflavine - triethanolamine - methyl viologen,[1c] assisted the copper transport, but triethanolamine itself acted as a reducing agent to some extent in the absence of light, and the effect of the light was not pronounced. Obviously, more sophisticated devices should be developed in order to drive the present system fully with light.

Acknowledgment. This research was supported by the Grant-in-Aid for Scientific Research from the Ministry of Education, Science, and Culture.

References

1) (a) S. S. Anderson, I. G. Lyle, and R. Paterson, Nature, **259**, 147 (1976).
(b) I. Tabushi and M. Funakura, J. Am. Chem. Soc., **98**, 4684 (1976).
(c) J. J. Grimaldi, S. Boileau, and J. M. Lehn, Nature, **265**, 229 (1977).
(d) T. Shinbo, K. Kurihara, Y. Kobatake, and N. Kamo, Nature, **270**, 277 (1977).
(e) J. J. Grimaldi and J. M. Lehn, J. Am. Chem. Soc., **101**, 1333 (1979).
2) K. Maruyama and H. Tsukube, Chem. Lett., **1981**, 1133.
3) A. Ohki, M. Takagi, and K. Ueno, Chem. Lett., **1980**, 1591.
4) The decrease of copper transport rate was observed with an decrease in the concentration of chloride ion in W_{red} phase, suggesting that in addition to the redox potential the chloride ion potential is also essential to this copper transport system.
5) Evidences are currently being collected that the complexes too stable in the membrane phase have a lower efficiency in the carrier-mediated transports: J. D. Lamb, J. J. Christensen, J. L. Oscarson, B. L. Nielsen, B. W. Asay, and R. M. Izatt, J. Am. Chem. Soc., **102**, 6820 (1980).
6) Zinc nitrate (0.1 mM) was added in W_{red} phase, other conditions being the same as the text.
7) M. Takagi and K. Ueno, Maku (Membrane), **4**, 348 (1979).
8) T. Kawai and T. Sakata, J. Chem. Soc., Chem. Commun., **1980**, 694.

(Received September 2, 1981)