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### Bathocuproine-Mediated Copper Transport through Liquid Membrane Driven by Redox Potential

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## Bathocuproine-Mediated Copper Transport through Liquid Membrane Driven by Redox Potential

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### Abstract

A new type of carrier-mediated copper transport system driven by redox potential was studied. The two aqueous solutions of different redox potentials were separated by a polymer-supported organic liquid membrane in which Bathocuproine (L) was dissolved as a "carrier". Copper(II) was reduced in the reducing phase to form  $[\text{Cu}^{\text{I}}\text{L}_2]^+\cdot\text{X}^-$  type complex at the membrane interface and extracted. The copper complex diffused to the other side of the membrane and decomposed to form the copper(II) species in the oxidizing phase, leaving the carrier in the membrane phase. The nature of the system under various operational conditions (pH, redox agents, pairing anions  $\text{X}^-$ , coexisting metals, etc.) was studied and compared with the metal transport system which can take place without the intervention of redox reaction. An extension of these transport reactions to water-in-oil-in-water type emulsion system was studied.

### INTRODUCTION

A selective ion transport through a liquid membrane is one of the current topics in separation chemistry (1-3). It introduces a new principle and a technique to separation and analytical chemistry. The energy for the ion

transport is usually supplied by a pH gradient or more generally an ion concentration gradient across the membrane. However, any chemical potential between two aqueous phases can, in principle, be applied to drive the transport system.

A redox potential-driven ion transport through a liquid membrane has been studied in the last few years from a bioenergetic point of view as well as for possible application in practical separations. The system concerns an electron flow through the membrane which is coupled with a cation flow (in the same direction) or an anion flow (in the counter direction). Several groups of investigators have described this type of transfer system using lipophilic electron carriers such as quinones (4, 5), ferrocenes (6), a metal-porphyrin complex (7), *N,N,N',N'*-tetramethylphenylenediamine (8), a nickel-bisdiethyleneglycol complex (9, 10), or a metal-Bathocuproine complex (11).

In all of the systems reported up to now which are driven by a redox potential, the species transported do not themselves undergo redox reaction. They are simply transferred through the membrane in the form of an ion-pair solubilized in the membrane phase. The lipophilic electron carriers

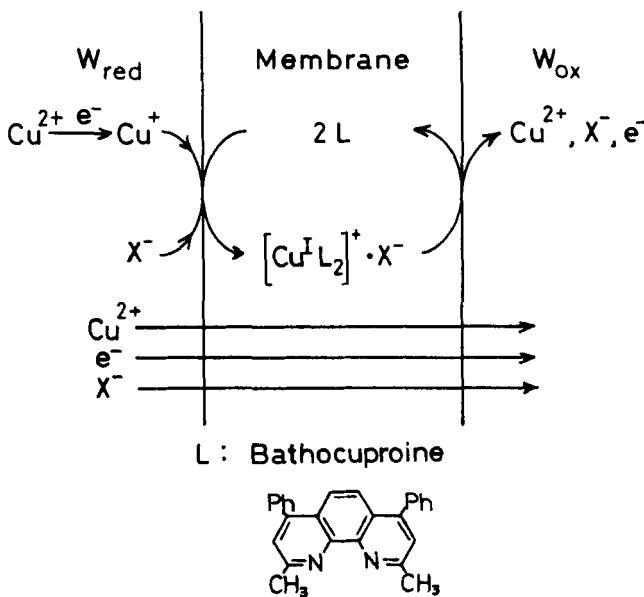


FIG. 1. Bathocuproine-mediated copper(I) transport driven by redox potential ( $Cu^{\text{I}}$  route).  $W_{\text{red}}$ , reducing aqueous phase;  $W_{\text{ox}}$ , oxidizing aqueous phase; membrane, diphenyl ether supported on a porous polypropylene film.

mentioned above are bound in the membrane phase and repeatedly serve as a pairing ion. Accordingly, the systems hitherto reported are not applicable to the transport of metal ions which themselves may undergo redox reactions between several valence states. These metal ions, however, may be transferred across the membrane in a principle somewhat different from that mentioned above by taking advantage of the variation in the valence state.

Bathocuproine (2,9-demethyl-4,7-diphenyl-1,10-phenanthroline, L) is a well-known extraction agent specific to copper with the aid of a reducing agent (12). Copper(II) is reduced to copper(I) in the presence of Bathocuproine and a reducing agent, and the resultant cationic complex  $[\text{Cu}^{\text{I}}\text{L}_2]^+$  is readily extractable to organic solvents forming a lipophilic ion-pair  $[\text{Cu}^{\text{I}}\text{L}_2]^+\cdot\text{X}^-$  with an appropriate anion  $\text{X}^-$ . On contact with an oxidizing agent, the complex in organic solution is decomposed to liberate copper(II) and a pairing anion in aqueous solution, leaving L in organic solution (Fig. 1) (13).

In the present report the Bathocuproine-mediated copper transport (13) and the related metal transport reactions are studied in detail in a polymer-supported liquid membrane system as well as in a liquid surfactant membrane system.

## EXPERIMENTAL

### Material

Bathocuproine was of analytical grade from Dojindo Lab. Ltd. Commercial diphenyl ether was purified by distillation. Other chemicals were of reagent grade and used as received.

### Supported Liquid Membrane

The apparatus used was the same as that described in the previous paper (10). The cell consisted of two compartments,  $W_{\text{red}}$  and  $W_{\text{ox}}$  (each of 150 mL capacity), which were separated by a liquid membrane supported by a microporous polypropylene film (Duragard 2500, Polyplastics Ltd.; thickness 25  $\mu\text{m}$ , porosity 45%, maximum pore size 0.4  $\times$  0.04  $\mu\text{m}$ ). The effective membrane area was 28  $\text{cm}^2$ . A diphenyl ether solution ( $\sim$ 0.04 mL) containing a carrier was applied to the film.

In a typical run the  $W_{\text{red}}$  compartment was initially filled with a buffered aqueous solution (0.5 M ammonium acetate, 1 M = 1 mol/dm<sup>3</sup>) of 0.1 mM copper(II) nitrate, 5 mM hydroxylamine sulfate, and 10 mM potassium

chloride, while the  $W_{\text{ox}}$  compartment was filled with a buffered aqueous solution (0.5 M ammonium acetate) not containing a specific oxidizing agent. Atmospheric oxygen dissolved in the  $W_{\text{ox}}$  phase acted as an oxidizing agent. The membrane phase (diphenyl ether solution) contained 10 mM Bathocuproine. The aqueous solutions were stirred at 30°, and aliquots of the solutions were taken periodically and analyzed. The copper and other metal concentrations were determined by atomic absorption photometry using a Nippon Jarrel-Ash AA-1 instrument.

### Liquid Surfactant Membrane

The membrane system is made up of water-in-oil-in-water (w/o/w) emulsion, i.e., oil-capsuled droplets of water are dispersed in water by means of surfactants (Fig. 2). The inner aqueous solution was named as the  $W_{\text{in}}$  phase while the outer aqueous solution was the  $W_{\text{out}}$  phase.

A typical run was performed as follows. The  $W_{\text{in}}$  phase consisted of a buffered aqueous solution [10 mM MES-sodium hydroxide, pH 5.5, MES: 2(N-morpholino)ethanesulfonic acid] containing 3 mM copper(II) sulfate, 10 mM potassium chloride, and 5 mM ammonia. The  $W_{\text{ox}}$  phase was simply a buffered aqueous solution (10 mM MES-sodium hydroxide, pH 5.5). The membrane phase (toluene solution) contained 2 wt-% of Span 80, a nonionic surfactant, and 0.5 mM Bathocuproine. In the first step the water-in-oil (w/o) emulsion was made from the aqueous solution ( $W_{\text{in}}$  phase, 25 mL) and the toluene solution (membrane phase, 50 mL) with the aid of a magnetic stirrer and an internal ultrasonic irradiation (2 min). Then, 50 mL of the w/o

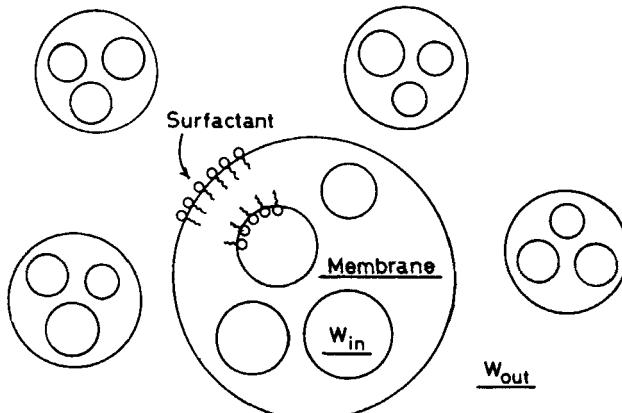


FIG. 2. Schematic representation of the liquid surfactant membrane.

emulsion was added to 200 mL of the  $W_{\text{ox}}$  phase in a reaction vessel (a flat-bottomed cylindrical glass cell; internal diameter 90 mm, depth 120 mm). The mixture was mechanically stirred at 25°C at a speed of 200 rpm giving the desired w/o/w emulsion. At this stage the transport reaction starts. Aliquots of the w/o/w emulsion were taken with time intervals. The  $W_{\text{out}}$  phase was then separated from the w/o emulsion (standing for 20–30 min) and analyzed for metal concentrations.

## RESULTS AND DISCUSSION

### Polymer-Supported Liquid Membrane

Figure 3 shows the change in the concentration of copper ion in the  $W_{\text{red}}$  phase and in the  $W_{\text{ox}}$  phase against time under various conditions. The figure illustrates some fundamental properties of the transport system. The copper transport takes place both in the presence and in the absence of redox potential. The former transport which proceeds via the Cu<sup>I</sup> species (Cu<sup>I</sup> route, Fig. 1) is greatly accelerated by the addition of chloride ion, while the latter via the Cu<sup>II</sup> species (Cu<sup>II</sup> route) is affected only slightly.

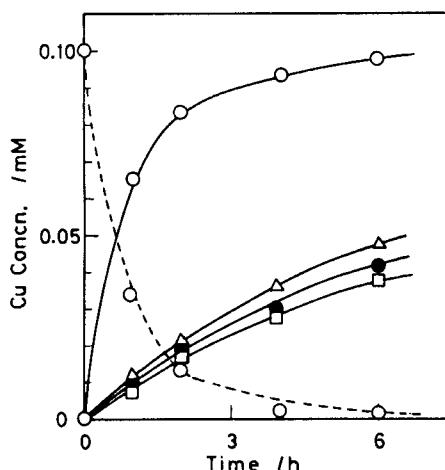


FIG. 3. Change in the copper concentration in  $W_{\text{ox}}$  phase (full line) and in  $W_{\text{red}}$  phase (dotted line) against time under various initial conditions. (○) The complete system, i.e.,  $W_{\text{red}}$  contained 0.1 mM Cu(NO<sub>3</sub>)<sub>2</sub>, 5 mM (NH<sub>3</sub>OH)<sub>2</sub>SO<sub>4</sub>, 10 mM KCl, and 0.5 M CH<sub>3</sub>COONH<sub>4</sub>, while  $W_{\text{ox}}$  contained 0.5 M CH<sub>3</sub>COONH<sub>4</sub>. (●) The salt (NH<sub>3</sub>OH)<sub>2</sub>SO<sub>4</sub> was excluded from the complete system. (△) KCl excluded. (□) (NH<sub>3</sub>OH)<sub>2</sub>SO<sub>4</sub> and KCl excluded.

The mechanism of the divalent copper transport ( $\text{Cu}^{\text{II}}$  route) is illustrated in Fig. 4. It can be shown that the complex of type  $\text{M}^{\text{II}}\text{LCl}_2$  is readily extracted into organic solvents for ( $\text{M} =$ ) copper, zinc, and cadmium. In fact, the latter two metal salts were found to be transported across the liquid membrane under their concentration gradient. Nickel(II) did not undergo this reaction since this metal cannot be extracted under the relevant reaction conditions. This type of metal transport has recently been described by Sugiura and Shinbo (14).

Thermodynamically, the  $\text{Cu}^{\text{II}}$  route can work until the chemical potential of the salt  $\text{M}^{\text{II}}\text{X}_2$  in the two aqueous phases becomes equal, i.e.,  $[\text{M}^{2+}]_{W_1}[\text{X}^-]_{W_1}^2 = [\text{M}^{2+}]_{W_2}[\text{X}^-]_{W_2}^2$  in a simplified expression in concentration terms. Thus the transport process is driven by the increase in concentration of the metal and the anion in the  $W_1$  phase. A result that the rate in the  $\text{Cu}^{\text{II}}$  route transport (Fig. 3) increased on addition of potassium chloride is consistent with this consideration, and in fact the copper(II) could be concentrated in the  $W_2$  phase against its concentration gradient when the concentration of potassium chloride is further raised in the  $W_1$  phase.

The equilibrium conditions for the  $\text{Cu}^{\text{I}}$  route transport is similarly given by  $[\text{Cu}^+]_{W_{\text{red}}}[\text{X}^-]_{W_{\text{red}}} = [\text{Cu}^+]_{W_{\text{ox}}}[\text{X}^-]_{W_{\text{ox}}}$ , and the transport process is driven by the concentration of copper(I) and the anion. The presence of reducing agent increases the concentration of the  $\text{Cu}^{\text{I}}$  species in the  $W_{\text{red}}$  phase, while the concentration of the low valent copper remains virtually zero in  $W_{\text{ox}}$ . Thus it is quite reasonable under such conditions that copper is concentrated in the  $W_{\text{ox}}$  phase as observed in Fig. 3.

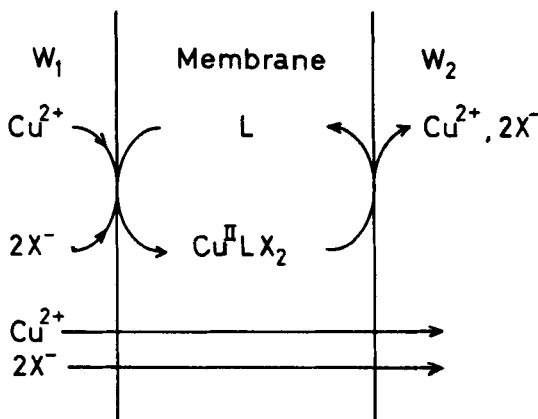


FIG. 4. Bathocuproine-mediated copper(II) transport ( $\text{Cu}^{\text{II}}$ -route).

A competitive transport of copper with other divalent metal ions was studied under conditions similar to those in Fig. 3. The transport of zinc and cadmium takes place only via the  $M^{II}$  route, and the process was not influenced by the presence of reducing agents. In the absence of reducing agents, these metals were transported 30–40% more efficiently than copper in a competitive experiment. However, on addition of reducing agents, the initial rate of zinc (or cadmium) transport was suppressed to about one-tenth of the previous rate. The transport of these metals took place only after ~90% of the copper was transferred from the  $W_{red}$  to the  $W_{ox}$  phase. This is explained in the following manner. Bathocuproine is a common carrier for copper and zinc (cadmium), but in the presence of reducing agents the carrier is preferentially occupied by the copper(I) species, and as a result only a limited amount of the carrier is available for a zinc (cadmium) transport. In this notion, the transport under reducing conditions is dominated by the  $Cu^I$  route.

The effect of pH on the rate of copper transport was investigated. As shown in Fig. 5, the most effective transport was observed at pH 7 in both aqueous phases. This fact is understood by considering the protonation of the carrier in the low pH region and the complexation of copper by ammonia in the  $W_{red}$  phase in the high pH region. Both factors tend to inhibit the

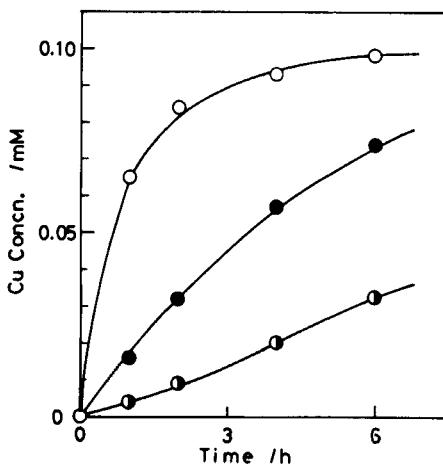


FIG. 5. Effect of pH on the rate of copper transport. Change in the copper concentration in  $W_{ox}$  phase against time under various initial conditions. (○)  $W_{red}$  contained 0.1 mM  $Cu(NO_3)_2$ , 5 mM  $(NH_3OH)_2SO_4$ , 10 mM KCl, and 0.5 M  $CH_3COONH_4$  (pH 7), while  $W_{ox}$  contained 0.5 M  $CH_3COONH_4$  (pH 7). (●, ◐) The pH was adjusted by 0.5 M  $CH_3COONH_4-NH_3$  (●, pH 9.2) and 0.5 M  $CH_3COOH-CH_3COONa$  (◐, pH 4.7).

extraction of copper into the membrane phase. As to the effect of carrier concentration, the tenfold decrease in Bathocuproine concentration in the membrane phase resulted in about a fivefold decrease in the initial rate of copper transport.

The effect of anionic species in the  $W_{\text{red}}$  phase on the  $\text{Cu}^{\text{I}}$  route transport rate is shown in Fig. 6. The rate decreased in the order chloride > nitrate > perchlorate > picrate. The determination of the picrate ion indicated that the anion was cotransported with copper in a 1:1 molar ratio as expected. The large accelerating effect of chloride ion is studied in more detail in Fig. 7.

The results in Figs. 6 and 7 indicate that in addition to the redox potential the chloride ion potential across the membrane is essential to effective copper transport. On the other hand, the addition of a so-called lipophilic anion, such as picrate and perchlorate, remarkably depressed the copper transport. The ion pair between  $\text{Cu}^{\text{I}}\text{L}_2^+$  and such an anion seems to be too lipophilic to be released at the  $W_{\text{ox}}$ -membrane interface. A possible assistance by the oxidizing agent to the metal releasing step was studied using various oxidizing agents such as ferricyanide, dichromate, permanganate, hypochlorite, or a  $\text{Fe}^{\text{II}}\text{-H}_2\text{O}_2$  reagent. However, any of these reagents could not increase the rate of copper transport, suggesting that the rate was controlled by the back-extraction or the stripping step of the complex  $[\text{Cu}^{\text{I}}\text{L}_2]^+\cdot\text{X}^-$  at

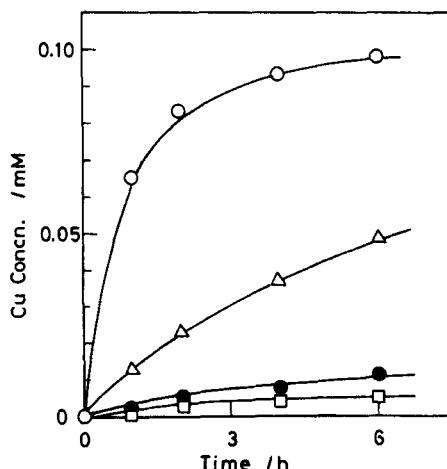


FIG. 6. Effect of anionic species in  $W_{\text{red}}$  phase on the rate of copper transport. Change in the copper concentration in  $W_{\text{ox}}$  phase against time under various initial conditions.  $W_{\text{red}}$  contained 0.1 mM  $\text{Cu}(\text{NO}_3)_2$ , 5 mM  $(\text{NH}_3\text{OH})_2\text{SO}_4$ , and 0.5 M  $\text{CH}_3\text{COONH}_4$ , while  $W_{\text{ox}}$  contained 0.5 M  $\text{CH}_3\text{COONH}_4$ ; 10 mM KCl (O), 10 mM  $\text{KNO}_3$  (Δ), 10 mM  $\text{NaClO}_4$  (●) or 1 mM sodium picrate (□) was added in  $W_{\text{red}}$  phase.

the membrane- $W_{\text{ox}}$  interface. Lamb et al. reported that the complexes too stable in the membrane phase had a lower efficiency in the carrier-mediated transport reactions (15). In this context it is possible that the ion-pair complex  $[\text{Cu}^{\text{I}}\text{L}_2]^+\cdot\text{Cl}^-$  had a suitable lipophilicity for the extraction and the stripping processes at the water-membrane interfaces. Moreover, the chloride anion provided an added advantage in that it stabilizes the copper(I) species in aqueous solution, resulting in the accumulation of the univalent copper in the  $W_{\text{red}}$  phase and thereby assisting the extraction and the subsequent processes to proceed smoothly.

The effect of anionic species on the  $\text{Cu}^{\text{II}}$  route is shown in Fig. 8. The rate of copper transport decreased in the order picrate > perchlorate > chloride > nitrate, indicating that the transfer of divalent copper is accelerated by the addition of lipophilic anions. Especially when the picrate was used, the copper concentration in the  $W_2$  phase exceeded that in the  $W_1$  phase within 4 h. Thus the effect of anion on the  $\text{Cu}^{\text{II}}$  route is approximately opposite to that on the  $\text{Cu}^{\text{I}}$  route. Sulfate, a divalent anion, did not work as a cotransport anion.

The scheme in Fig. 4 states that the molar ratio of copper to the anion cotransported is 1:2. The determination of picrate ion under conditions similar to those in Fig. 8 indicated that the ratio was actually 1:2.5–2.7.

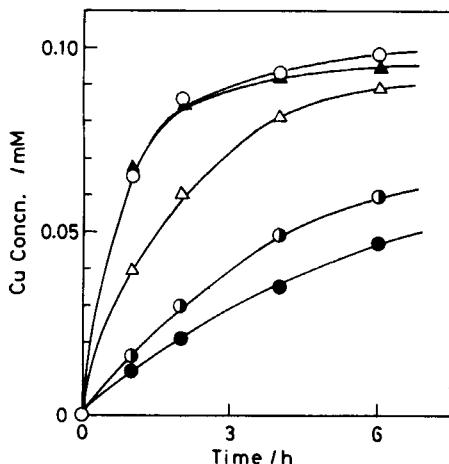


FIG. 7. Effect of chloride concentration in  $W_{\text{red}}$  phase on the rate of copper transport. Change in the copper concentration in  $W_{\text{ox}}$  phase against time under various initial conditions.  $W_{\text{red}}$  contained 0.1 mM  $\text{Cu}(\text{NO}_3)_2$ , 5 mM  $(\text{NH}_3\text{OH})_2\text{SO}_4$ , and 0.5 M  $\text{CH}_3\text{COONH}_4$ , while  $W_{\text{ox}}$  contained 0.5 M  $\text{CH}_3\text{COONH}_4$ ; 10 mM (○), 5 mM (▲), 0.6 mM (△), 0.1 mM (●), or no (●)  $\text{KCl}$  was added in  $W_{\text{red}}$  phase.

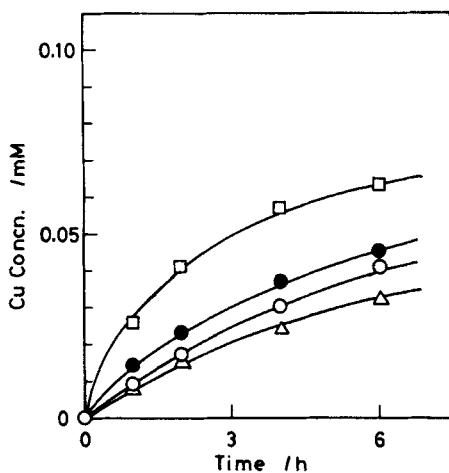


FIG. 8. Effect of anionic species in  $W_1$  phase on the rate of copper transport via  $\text{Cu}^{\text{II}}$  route. Change in the copper concentration in  $W_2$  phase against time under various initial conditions.  $W_1$  contained  $0.1 \text{ mM Cu}(\text{NO}_3)_2$  and  $0.5 \text{ M CH}_3\text{COONH}_4$ , while  $W_2$  contained  $0.5 \text{ M CH}_3\text{COONH}_4$ ;  $10 \text{ mM KCl}$  ( $\circ$ ),  $10 \text{ mM KNO}_3$  ( $\triangle$ ),  $10 \text{ mM NaClO}_4$  ( $\bullet$ ), or  $1 \text{ mM sodium picrate}$  ( $\square$ ) was added in  $W_1$  phase.

Picrate ion was extracted to some extent under these conditions by forming the ion-pair  $\text{HL}^+ \cdot \text{picrate}^-$ , and the transport of picrate according to this reaction overlapped the picrate transport by the  $\text{Cu}^{\text{II}}$  route.

### Application to Liquid Surfactant Membrane

The liquid surfactant membrane technique has been developed by Li (1-3, 16-18). With this technique a thin liquid membrane with a large interface area for the extraction and the stripping reactions is obtained. Many publications describe its application to the concentration of metals from dilute aqueous solutions (1-3), and it is one of the promising methods for industrial metal recovery processes.

We attempted to apply the Bathocuproine-mediated  $\text{Cu}^{\text{I}}$  route copper transport to the liquid surfactant membrane system. Since we failed to find suitable oxidizing agents to be introduced in the internal aqueous phase, our preliminary experiment was designed in such a way that the oxidizing agent (air) was applied to the external solution, i.e.,  $W_{\text{in}}$  and  $W_{\text{out}}$  phases were assigned to the reducing and the oxidizing phases, respectively. If the  $\text{Cu}^{\text{I}}$  route transport mechanism works ideally, copper ions are transported from the  $W_{\text{in}}$  to the  $W_{\text{out}}$  phase with a simultaneous flow of both electrons and anions in the same direction, i.e., from the  $W_{\text{in}}$  to the  $W_{\text{out}}$  phase.

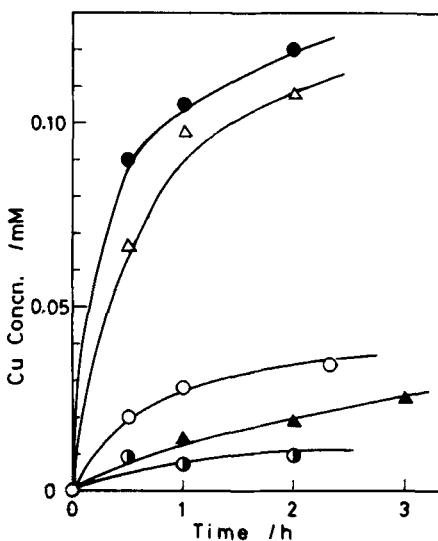


FIG. 9. Change in the copper concentration in  $W_{out}$  phase against time under various conditions. (○)  $W_{in}$  contained 3 mM CuSO<sub>4</sub>, 5 mM NH<sub>3</sub>, and 10 mM MES-NaOH, while  $W_{out}$  contained 10 mM MES-NaOH; 0.5 mM Bathocuproine was present in the membrane (reference conditions). The salts, 10 mM KCl (●), 10 mM KNO<sub>3</sub> (△), or 10 mM KCl and 5 mM (NH<sub>3</sub>OH)<sub>2</sub>SO<sub>4</sub> (●) were further added in  $W_{in}$  phase under the reference conditions. (▲) Bathocuproine was excluded from the membrane under the reference conditions.

Figure 9 shows the change in the concentration of copper ion in the  $W_{out}$  phase against time under various conditions. In the absence of Bathocuproine in the membrane phase, the copper concentration in the  $W_{out}$  phase reached  $1.7 \times 10^{-5} M$  after 2 h. This is due to the breakdown of the emulsion membrane and the resulting leakage of the internal copper to the external  $W_{out}$  phase during the stirring process. Taking account of the volume ratio of the  $W_{out}$  and  $W_{in}$  phases ( $\sim 12:1$ ), the degree of emulsion breakdown corresponded to about 7% loss of the  $W_{in}$  phase during 2 h of stirring.

On the introduction of Bathocuproine in the membrane phase, a higher rate of copper transport to the  $W_{out}$  phase was observed. When chloride ion was further added to the  $W_{in}$  phase, the rate of copper transport increased greatly, reaching  $1.2 \times 10^{-4} M$  copper in the  $W_{out}$  phase after 2 h. The amount of copper transported was about 40% of that initially added to the  $W_{in}$  phase. However, contrary to our expectation, the addition of the reducing agent hydroxylamine to the  $W_{in}$  phase brought about a great depression in the rate of copper transport, and the amount of copper detected in the  $W_{out}$  phase was less than that in the absence of the carrier (Fig. 9). Obviously, the reducing agent acted as an inhibitor rather than as a promoter. Similar results were obtained under some other experimental conditions.

One reason for the inhibitory effect of the reducing agent (Fig. 9) is obviously the leakage of the reducing agent from the  $W_{in}$  phase on the emulsion membrane breakdown. Since the  $W_{out}$  phase did not contain a strong oxidizing agent, hydroxylamine which leaked into the  $W_{out}$  phase remained undecomposed and hence eliminated the redox potential difference between the two phases. Another reason may be the strong affinity of the copper(I) complex to the membrane phase. The hydroxylamine in the  $W_{out}$  phase could be decomposed by the addition of sodium hypochlorite, but the copper transport rate was not enhanced. The situation seems to be similar to that observed in Fig. 6 for the perchlorate and picrate cotransport. Thus the copper transport is much more efficient in the absence than in the presence of a redox potential, and the transport process is obviously taking place via the  $Cu^{II}$  route.

[Univalent copper complex of Bathocuproine is brown-orange colored, and the presence of  $Cu^I$ -route is always indicated by this coloration. However, in the liquid surfactant membrane system, the emulsion assumed a brownish color even in the absence of reducing agent. Spectrophotometric study showed that the surfactant (or some ingredients of the surfactant) partially acted as a reducing agent. The extent of this reaction was minor, and the carrier could play a major role in the copper transport via the  $Cu^{II}$  route.]

Accordingly, the anion concentration gradient from the  $W_{out}$  to the  $W_{in}$  phase is expected to concentrate copper ions from the  $W_{out}$  into the  $W_{in}$  phase. As shown in Fig. 10, when 100 mM nitrate ion was initially added in the  $W_{out}$  phase, the copper concentration in the  $W_{out}$  phase decreased from 1 to 0.5 mM after 2 h, whereas in the absence of the added anion in the  $W_{out}$  phase the decrease in the copper concentration was only slight. The emulsion in the presence of 100 mM potassium nitrate was too viscous to disperse in the  $W_{out}$  phase under normal operational conditions, and hence an elevated stirring speed (270 rpm) was used in this experiment. After 2 h stirring the emulsion phase was separated from the  $W_{out}$  phase, dissolved in methanol containing acetylacetone to get a homogeneous solution, and analyzed for copper. The amount of copper present in this solution was comparable to the amount of copper decrease in the  $W_{out}$  phase. The reduction of nitrate concentration in the  $W_{out}$  phase caused a lowering of the rate of this copper transport.

Figure 11 shows the competitive transport of copper and zinc in the liquid surfactant membrane. The fairly high rate of copper transport in comparison with that in Fig. 9 is due to the larger concentration of univalent anion added in the  $W_{in}$  phase. As previously described, zinc was transported in preference to copper in the supported liquid membrane when the redox potential was not applied. However, in this liquid surfactant membrane system, the transport

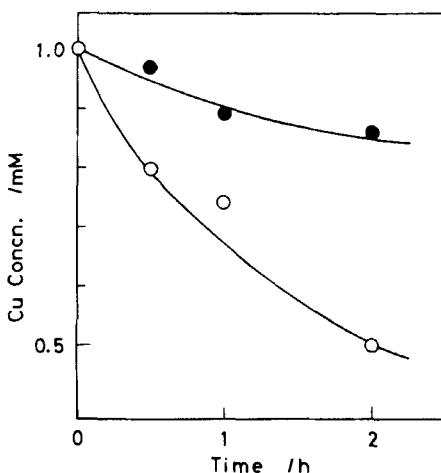


FIG. 10. Change in the copper concentration in  $W_{out}$  phase against time under two initial conditions. (○)  $W_{in}$  contained 50 mM  $K_2SO_4$ , 5 mM  $NH_3$ , and 10 mM MES-NaOH, while  $W_{out}$  contained 1 mM  $CuSO_4$ , 100 mM  $KNO_3$ , 5 mM  $NH_3$ , and 10 mM MES-NaOH; 0.5 mM Bathocuproine was present in the membrane. (●) The salts  $KNO_3$  and  $K_2SO_4$  were eliminated in the former conditions. Stirring, 270 rpm.

rate of copper was faster than that of zinc. Sugiura et al. reported that the rate of copper transport surpassed that of zinc in a bulk 1,2-dichloroethane membrane system using the same carrier (14). The toluene-surfactant membrane appears to be similar in the extraction and stripping behavior to a dichloroethane membrane rather than to a diphenyl ether membrane.

### Redox Reaction as a Driving Potential for Ion Separation

A proton concentration difference or a pH gradient has been the most widely studied as a driving potential for ion separation by liquid membrane techniques. The proton concentration difference is peculiar in that a free energy as much as  $RT \ln (1/10^{-14})$  is readily available using, e.g., 1  $M$  sodium hydroxide and 1  $M$  hydrochloric acid (energy released on the neutralization of acid and base). The free energy associated with a difference in concentration of ordinary salt solutions is much smaller, which may be around the order of  $RT \ln (1/10^{-4})$ , since the salt concentrations above 1  $M$  or below  $10^{-4} M$  are rather unrealistic in practice. In this respect it is quite understandable that the pH gradient has found wide application as a powerful and versatile driving potential in ion separation.

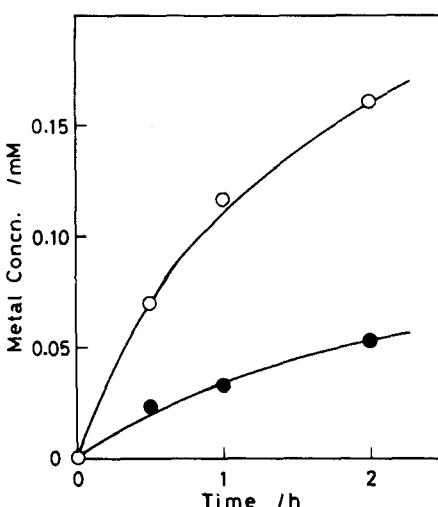


FIG. 11. Competitive transport of copper and zinc. Change in the concentration of metal ion ( $\text{Cu}$ ,  $\text{O}$ ;  $\text{Zn}$ ,  $\bullet$ ) in  $W_{\text{out}}$  phase against time.  $W_{\text{in}}$  contained 3 mM  $\text{Cu}(\text{NO}_3)_2$ , 3 mM  $\text{Zn}(\text{NO}_3)_2$ , 10 mM KCl, 10 mM  $\text{NH}_3$ , and 10 mM MES-NaOH, while  $W_{\text{out}}$  contained 10 mM MES-NaOH; 0.5 mM Bathocuproine was present in the membrane.

[It should be reminded that in Fig. 10 about 50% of copper in the  $W_{\text{out}}$  phase was concentrated in the  $W_{\text{in}}$  phase by using 100 mM potassium nitrate in the  $W_{\text{out}}$  phase. If 50 mM sulfuric acid is used in the  $W_{\text{in}}$  phase along with benzoylacetone as a carrier in the membrane phase, more than 80% of copper is readily concentrated in the  $W_{\text{in}}$  phase under similar reaction conditions. This exemplifies the effectiveness of the pH gradient-driven process (19).]

Redox reactions can give a free energy comparable in magnitude to the neutralization reaction, as one can easily conceive from tables of standard electrode potentials. However, the reactions are generally not simple, sometimes involving side reactions and quite often requiring catalysis for the reactions to proceed smoothly. This seems to limit seriously the practical usability of the redox energy to separation problems such as those treated in the present study. [The following exemplifies some of the difficulty in searching for a wider range of oxidizing agents for the  $\text{Cu}^{\text{I}}$  route transport. The use of ferricyanide as an oxidizing agent produced precipitates of ferricyanide complexes of copper or zinc, which were avoided only by the addition of excess ammonia. Permanganate gave precipitates of manganese dioxide. Hypobromite produced, under neutral pH conditions, a considerable amount of free bromine which is quite soluble in organic liquid membranes.

Cerium(IV) could be used only at such low pH regions that Bathocuproine could not work as a carrier.] In this respect, the use of redox potential cannot be as versatile as pH gradient. The redox potential, however, can be generated through photochemical processes, to which much research effort is currently devoted (20). The coupling of a photochemical redox reaction and the ion separation process is worth further studying (5, 13).

## CONCLUSION

Using Bathocuproine as a carrier, the uphill transport of copper ion through a liquid membrane driven by redox potential was realized. The process involved the extraction of the univalent copper complex into the organic membrane phase ( $Cu^I$  route), and, in general, was in competition with another copper transport mechanism which took place without the intervention of a redox reaction ( $Cu^{II}$  route). The  $Cu^I$  route is driven by a redox potential as well as by an anion concentration potential, while the  $Cu^{II}$  route is driven only by the latter potential. Both routes can be operated using a polymer-supported, simple liquid membrane, but the  $Cu^I$  route could not be realized in a liquid surfactant emulsion membrane system. Breakage of the emulsion membrane and failure in finding the proper combination of redox reagents are the causes for failure of the emulsion system. Finding the proper redox couples is the key to giving practical value to the redox potential-driven ion separation processes in a liquid surfactant membrane system.

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