The Transport of Metal Ions against Their Concentration Gradients through a 1,2-Dichloroethane Membrane

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The uphill transport of metal ions such as copper, zinc, cobalt, and iron(II) ions through a bulk 1,2-dichloroethane membrane in the presence of various chelating agents has been studied. The membrane separated two aqueous phases, one containing the metal ion and potassium or lithium sulfate, and the other containing the metal ion and lithium nitrate or chloride. The chelating agents used were derivatives of 1,10-phenanthroline and acetylacetone. The accumulation of the metal ions in the aqueous phase containing the potassium or lithium sulfate was observed for only the following chelating agents: copper: 4,7-diphenyl-2,9-dimethyl- and 4,7-diphenyl-1,10-phenanthroline; zinc: 4,7-diphenyl-, 3,8-diphenyl-, 2,9-dimethyl-, and 4,7-diphenyl-2,9-dimethyl-1,10-phenanthroline; cobalt: 3,8-diphenyl- and 4,7-diphenyl-1,10-phenanthroline; and iron(II): 3,8-diphenyl-1,10-phenanthroline. In the system containing lithium sulfate in the aqueous phase, the rate of transport of the metal ions was slightly higher than that in the system containing potassium sulfate. The reduction of the nitrate ion in the aqueous phase brought about a lowering of the rate of transport of the metal ions. The transport of the metal ions was, however, unaffected by the electrostatic effect. The metal ion complexed by the chelating agent may be transferred in the 1,2-dichloroethane phase, thus forming an ion-pair with the nitrate or chloride ion.

In a previous paper,[1] the present authors studied the uphill transport of the picrate anion through a bulk 1,2-dichloroethane membrane. The picrate anion was transported against its concentration gradient by coupling to a diffusion of potassium ions *via* various potassium ionophores.

Using a membrane system similar to that used for the picrate transport and various chelating agents, we have now made an attempt to make metal ions move against their concentration gradient. This report will concern the uphill transport of some metal ions, such as copper, zinc, cobalt, and iron(II) ions.

Experimental

Apparatus. The apparatus used for measuring the transport of the metal ions was the same as that used in the previous paper.[1] In the transport cell (cylindrical glass vessel:[2] 7 cm i.d.,; height, 7 cm), the dichloroethane phase (100 ml), containing a 10^{-3} M chelating agent, separated two aqueous phases (50 ml each), one (Phase I) containing 5×10^{-4} M metal sulfate and 0.05 M potassium or lithium sulfate, and the other (Phase II) containing 5×10^{-4} M metal sulfate and 0.1 M lithium nitrate or chloride.

Materials. As lipophilic chelating agents, derivatives of 1,10-phenanthroline and acetylacetone were used: the 5-methyl-, 5-nitro-, 5-chloro-, 2,9-dimethyl-, 4,7-dimethyl-, and 3,8-diphenyl-1,10-phenanthroline, dibenzoylmethane, benzoyltrifluoroacetone, and benzoylacetone were commercial products from the Tokyo Kasei Kogyo Co., Ltd., while the 4,7-diphenyl- and 4,7-diphenyl-2,9-dimethyl-1,10-phenanthroline and 2-thenoyltrifluoroacetone were from the Dojindo Lab. The metallic salts, copper, zinc, cobalt, and iron(II) sulfate and the other chemicals were reagent-grade and were not subsequently purified.

Procedure. The technique used for measuring the rate of transport of the metal ions and the membrane potential was the same as that described in the previous paper.[1] The measurements were carried out at 25 °C. The dichloroethane used as the liquid membrane was pre-equilibrated with a 5×10^{-4} M metal sulfate solution containing a potassium or lithium sulfate and lithium nitrate or chloride, whose concentrations were equal to those in the two aqueous phases, I and II. After this treatment, the membrane system was constructed in the transport cell as has been described above. The determination of the metal-ion concentration in Phases I and II at regular time intervals was carried out by a colorimetric method, after a small volume of the aqueous solutions had been pipetted off (copper; 0.5 ml, zinc; 0.2 ml, cobalt; 0.5 ml, iron(II); 0.5 ml); the concentration of copper was determined by the neocuproine method,[3] the zinc, by the zincon method,[4] the cobalt, by the 2-nitroso-1-naphthol method,[5] and the iron(II), by the 1,10-phenanthroline method.[6]

Results

Uphill Transport of Various Metal Ions. The rates of transport of the metal ions across the dichloroethane membrane in the presence of various chelating agents were measured. The uphill transport was, however, observed for only the following chelating agents: copper: 4,7-diphenyl-2,9-dimethyl-, and 4,7-diphenyl-1,10-phenanthroline; zinc: 4,7-diphenyl-, 3,8-diphenyl-, 2,9-dimethyl-, and 4,7-diphenyl-2,9-dimethyl-1,10-phenanthroline; cobalt: 3,8-diphenyl- and 4,7-diphenyl-1,10-phenanthroline; iron(II): 3,8-diphenyl-1,10-phenanthroline. The curves of the concentrations of the metal ions in both aqueous phases and the membrane potential against the time for these chelating agents are shown in Figs. 1 to 3. The solid and dotted lines in each figure (a) represent the concentration curves in Phases I and II respectively. The polarity of the membrane potential was positive in Phase II with respect to Phase I. In these systems, Phase I contained 0.05 M potassium sulfate, and Phase II, 0.1 M lithium nitrate.

In the present experiment, 10^{-3} M was chosen as the concentration of the chelating agents in the dichloroethane phase. It was the most effective concentration for the transport of the metal ions. As an example of the effect of concentration of the chelating agents on the transport of the metal ions, the curves of the copper concentrations in both aqueous phases and the membrane potential against the time for various concentrations of 4,7-diphenyl-2,9-dimethyl-1,10-phenanthroline are shown in Fig. 4.

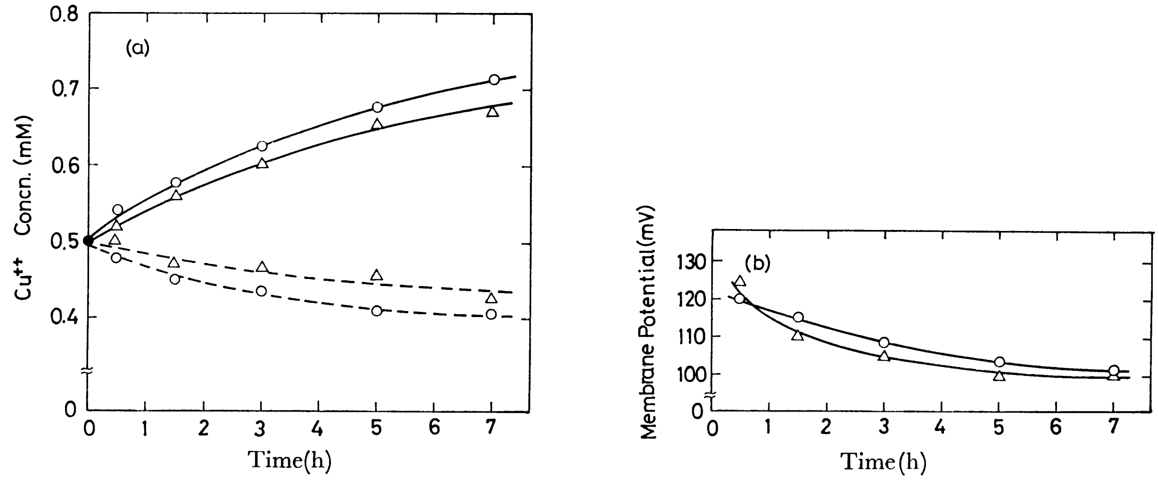

Fig. 1. (a) Copper concentrations in both aqueous phases against time curves. The solid and dotted lines represent the copper concentrations in Phases I and II respectively.
(b) Membrane potential against time curves for the copper.
Chelating agent;
○: 4,7-diphenyl-2,9-dimethyl-1,10-phenanthroline, △: 4,7-diphenyl-1,10-phenanthroline.
Phases I and II contained 0.05 M K_2SO_4 and 0.1 M $LiNO_3$ respectively.

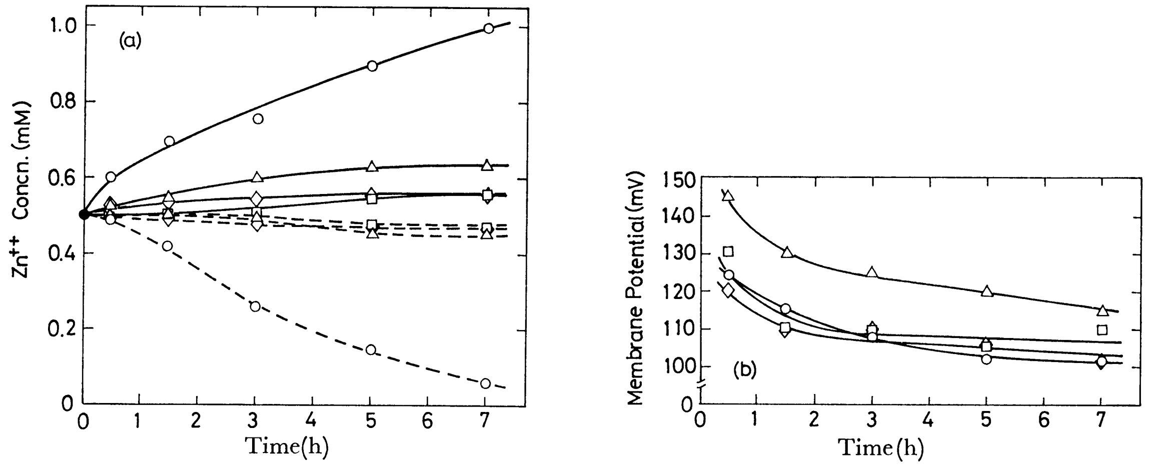

Fig. 2. (a) Zinc concentrations in both aqueous phases against time curves.
The curves have the same meanings as in Fig. 1.
(b) Membrane potential against time curves for the zinc.
Chelating agent;
○: 4,7-diphenyl-1,10-phenanthroline, △: 3,8-diphenyl-1,10-phenanthroline, ◇: 2,9-dimethyl-1,10-phenanthroline, □: 4,7-diphenyl-2,9-dimethyl-1,10-phenanthroline.
Phases I and II contained 0.05 M K_2SO_4 and 0.1 M $LiNO_3$ respectively.

In the case of the other phenanthroline and acetylacetone derivatives used, no transfer of the metal ions across the membrane was observed, though a membrane potential ranging from 100 to 200 mV was developed.

Effect of Potassium Ion and Lithium Counter-ions. When the lithium sulfate was added to Phase I in place of the potassium sulfate, the rate of transport of the metal ions increased slightly. The decrease in the concentration of the nitrate ion in Phase II brought about a lowering of the rate of transport of the metal ions. In the system containing the chloride in Phase II in place of the nitrate, a considerable high rate of transport of the metal ions was also observed. These results are illustrated in Fig. 5, which shows the data for the copper-4,7-diphenyl-2,9-dimethyl-1,10-phenanthroline system.

In the system containing the potassium and lithium sulfates in Phases I and II respectively, a membrane potential of approximately 60 mV was developed by the addition of a potassium ionophore such as dicyclohexyl-18-crown-6. No transfer of the metal ions across the membrane was, however, observed in this system.

Effect of Membrane Potential. In order to examine the role of the membrane potential, the potential difference between Phases I and II was clamped at 0 mV by means of a short-circuit method.[7] The results obtained are shown in Fig. 6. The data for the transport of the metal ions obtained with the voltage clamp

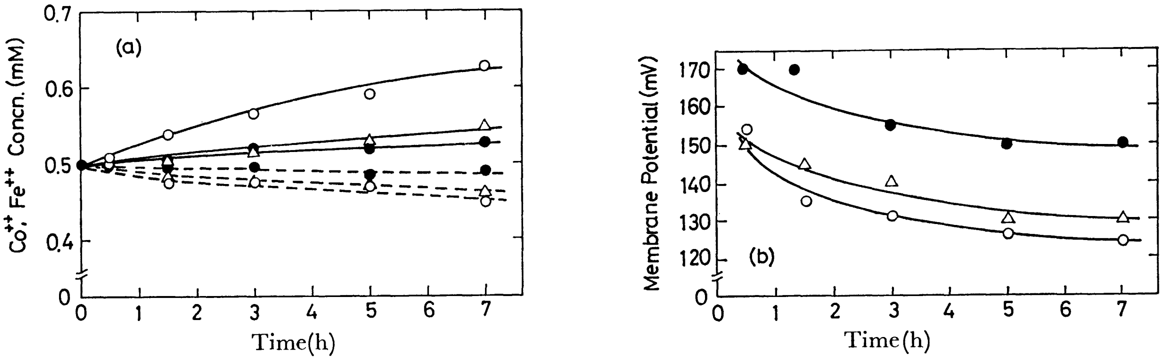

Fig. 3. (a) Cobalt and iron(II) concentrations in both aqueous phases against time.
The curves have the same meanings as in Fig. 1.
(b) Membrane potential against time for the cobalt and iron(II).
Chelating agent for cobalt; ○: 3,8-diphenyl-1,10-phenanthroline, △: 4,7-diphenyl-1,10-phenanthroline, for iron(II); ●: 3,8-diphenyl-1,10-phenanthroline.
Phases I and II contained 0.05 M K_2SO_4 and 0.1 M $LiNO_3$ respectively.

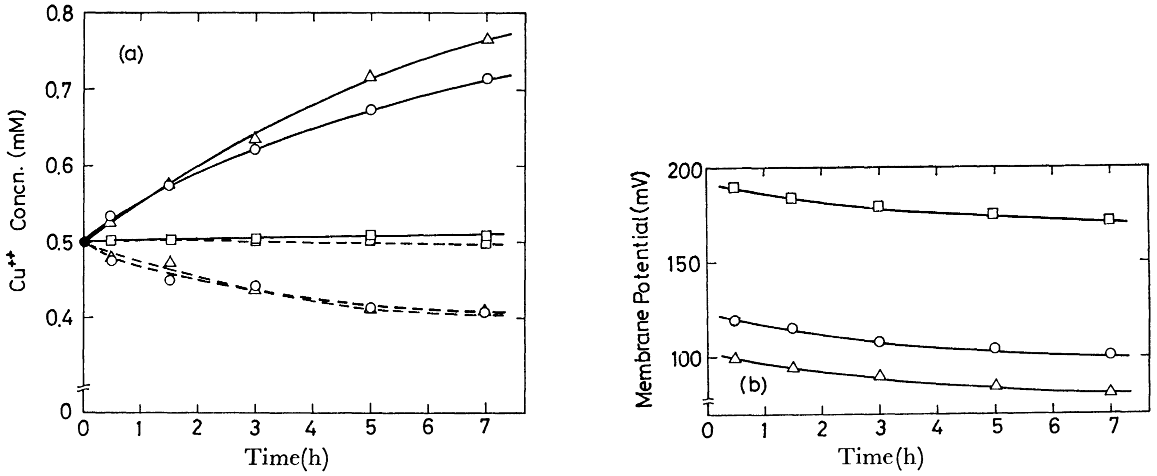

Fig. 4. Effect of concentration of chelating agent on the transport of copper.
(a) Copper concentrations in both aqueous phases against time for various concentrations of 4,7-diphenyl-2,9-dimethyl-1,10-phenanthroline.
The curves have the same meanings as in Fig. 1.
(b) Membrane potential against time for the chelating agent.
Concentration of chelating agent; □: 10^{-4} M, ○: 10^{-3} M, △: 10^{-2} M.
Phases I and II contained 0.05 M K_2SO_4 and 0.1 M $LiNO_3$ respectively.

agreed almost entirely with those obtained without the voltage clamp.

Discussion

In the previous paper,[1)] the highest rate of picrate transport was observed in the system containing potassium sulfate and lithium nitrate in Phases I and II respectively. The membrane potential in this system was higher than that in the other systems used. Using the membrane system and various chelating agents, the present authors first attempted to make the metal ions move against their concentration gradient. As may be seen in Figs. 1 to 3, however, the uphill transport of the metal ions occurred for only some phenanthroline derivatives. In addition, the rate of transport of the metal ions differed from one another in the combination of chelating agent and metal ion.

The phenanthroline derivatives which can move the metal ions form complexes with the metal ions. However, they do not necessarily have a high stability constant for the formation of the complexes. Although some of the phenanthroline derivatives used form a stable complex with the metal ion,[8)] they cannot move the metal ion. On the other hand, the metal ions which can be moved by the phenanthroline derivatives have almost constant ionic radii:[9)] copper, 0.72 Å; zinc, 0.74 Å; cobalt, 0.72 Å; iron(II), 0.74 Å. The nickel and iron(III) ions whose ionic radii were 0.69 and 0.64 Å respectively could not be moved in the system used in the present experiment. It is assumed that the chelating agents can move the metal ions only when they form complexes with a specific structure which facilitates the transfer of the metal ions at the aqueous phase-

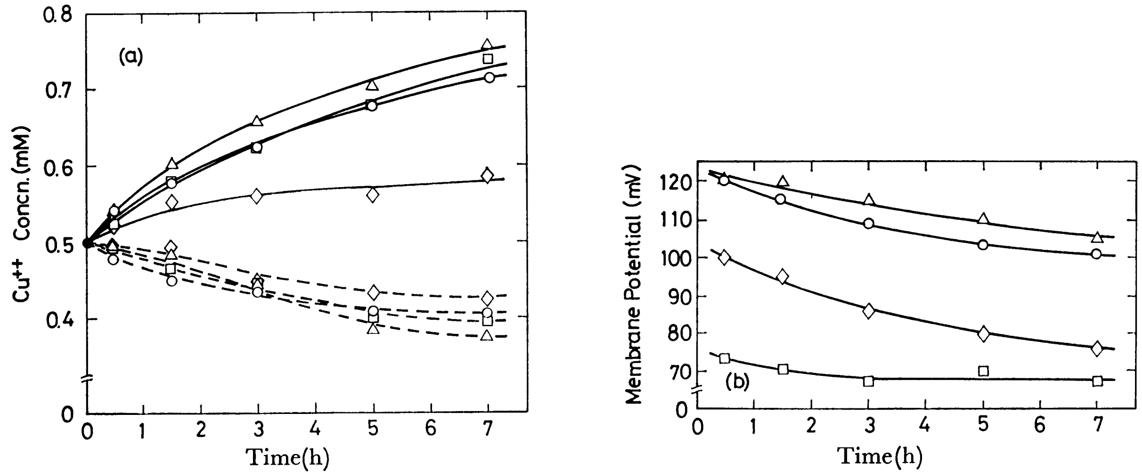

Fig. 5. Effect of potassium ion and lithium counter-ions on the transport of copper.

(a) Copper concentrations in both aqueous phases against time for various potassium and lithium salts systems. The curves have the same meanings as in Fig. 1.

(b) Membrane potential against time curves for the systems.

K and Li salts in Phases I and II; ○: 0.05 M K_2SO_4 (I)–0.1 M $LiNO_3$ (II), △: 0.05 M Li_2SO_4 (I)–0.1 M $LiNO_3$ (II), □: 0.05 M Li_2SO_4 (I)–0.1 M LiCl (II), ◇: 0.05 M Li_2SO_4 (I)–0.01 M $LiNO_3$, 0.045 M Li_2SO_4 (II).

Chelating agent; 4,7-diphenyl-2,9-dimethyl-1,10-phenanthroline.

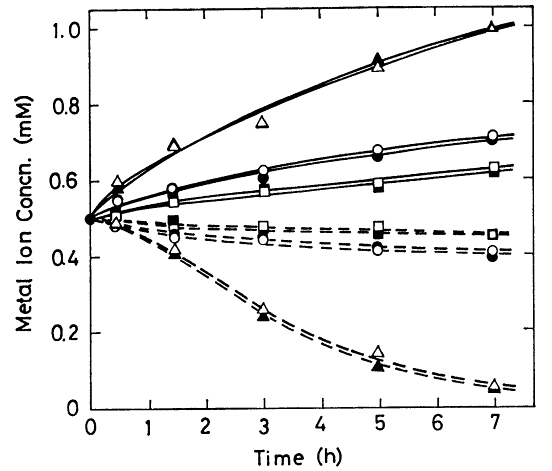

Fig. 6. Effect of membrane potential on the transport of metal ions.

Concentrations of metal ions in both aqueous phases against time.

The curves have the same meanings as in Fig. 1.

●,▲,■: Maintained at 0 mV with a voltage clamp, ○,△,□: without the voltage clamp.

Metal-chelating agent system; ○,●: copper–4,7-diphenyl-2,9-dimethyl-1,10-phenanthroline, △,▲: zinc–4,7-diphenyl-1,10-phenanthroline, □,■: cobalt-3,8-diphenyl-1,10-phenanthroline.

Phases I and II contained 0.05 M K_2SO_4 and 0.1 M $LiNO_3$ respectively.

membrane interfaces; the formation of a more stable metal-complex brings about a lowering of the rate of dissociation of the metal-complex.[10]

The phenanthroline derivatives which can move the metal ions are composed of lipophilic groups with a high solubility in the organic solvent. The partition coefficients of their metal-complexes between the aqueous and membrane phases must, therefore, be higher than that of the other phenanthroline derivatives. This high solubility in the membrane phase may also facilitate the transfer of the metal ions.

The acetylacetone derivatives could not move the metal ions. These compounds form fairly stable complexes with potassium and lithium ions as well as with the metal ions;[11,12] in this respect, they differ from the phenanthroline derivatives. The transfer of the metal ions in the membrane may be prevented by the formation of complexes with the potassium and lithium ions.

In the system containing lithium sulfate in Phase I, the rate of transport of the metal ions was slightly higher than that in the system containing potassium sulfate. In the case of the potassium sulfate, the transfer of the metal ions from Phase II to Phase I may be somewhat depressed by the diffusion of lithium ions from Phase II to Phase I, whereas in the case of the lithium sulfate the diffusion of the lithium ions does not occur.

The reduction of the nitrate ion in Phase II brought about a lowering of the rate of transport of the metal ions. In addition, in the potassium sulfate–lithium sulfate system containing a potassium ionophore, the transfer of the metal ions was not observed. The data for the transport of the metal ions with the voltage clamp agreed almost entirely with those for the ions without the voltage clamp. These facts show that the transfer of the metal ions occurs only in combination with the diffusion of nitrate ions (or chloride ions), which can penetrate the membrane.

In the previous paper,[1] the picrate anion in Phase I was dissolved in the dichloroethane phase, forming an ion-pair with a complexed cation consisting of an ionophore and the potassium ion, and then liberated into phase II by the dissociation of the ion-pair. The metal ions may also be transported by the same mechanism; the metal ion, complexed by the chelating agent in Phase II, was dissolved in the dichloroethane phase, thus forming an ion-pair with a nitrate ion (or a chloride ion), and then liberated into Phase I by the dissociations of the ion-pair and the complex.

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