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Takashi Saito[a]
[a] DEPARTMENT OF CHEMICAL TECHNOLOGY, KANAGAWA INSTITUTE OF TECHNOLOGY, ATSUGI, KANAGAWA, JAPAN

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Selective Transport of Copper(I, II), Cadmium(II), and Zinc(II) Ions through a Supported Liquid Membrane Containing Bathocuproine, Neocuproine, or Bathophenanthroline

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TAKASHI SAITO
DEPARTMENT OF CHEMICAL TECHNOLOGY
KANAGAWA INSTITUTE OF TECHNOLOGY
1030, SHIMOOGINO, ATSUGI, KANAGAWA, 243-02, JAPAN

ABSTRACT

Some selective transport systems for heavy metallic ions through a supported liquid membrane (SLM) containing a 2,2′-dipyridyl derivative ligand, 4,7-diphenyl-2,9-dimethyl-1,10-phenanthroline (bathocuproine), 2,9-dimethyl-1,10-phenanthroline (neocuproine), or 4,7-diphenyl-1,10-phenanthroline (bathophenanthroline), were investigated. The transport of copper(I, II), cadmium(II), zinc(II), lead(II), and cobalt(II) ions was accomplished with a halogen ion such as chloride, bromide, or iodide ion as a pairing ion species for any SLM. The ranking of the permeability of the metallic ions was $Cu^{+,2+}$, Zn^{2+}, $Cd^{2+} \gg Pb^{2+}$, Co^{2+}. When the oxidation-reduction potential gradient was used as a driving force for metallic ions, the transport of Cu^{+} ion was higher than those of Cd^{2+} and Zn^{2+} ions for any SLM containing bathocuproine, neocuproine, or bathophenanthroline. On the other hand, in the transport system which used the concentration gradient of pairing ion species, the permeability of the Cu^{2+} ion decreased whereas that of the Cd^{2+} ion increased. Moreover, it was found that the different selectivity for the transport of metallic ions is produced by using various pairing ion species.

Key Words. Heavy metallic ion; Dipyridyl derivative ligand; Supported liquid membrane; Permeation velocity; Permeation selectivity

INTRODUCTION

Since a 2,2′-dipyridyl compound, which is a bidentate ligand, was synthesized in 1888 (1), various dipyridyl derivatives have been designed and synthesized. These ligands have been used as coloring agents for $Fe^{2+,3+}$, $Cu^{+,2+}$, and other ions. A transport system of heavy metallic ions through a supported liquid membrane (SLM) containing a dipyridyl ligand as a carrier of metallic ions has been studied recently. In particular, the transport method of metallic ions through an SLM or a liquid membrane as a carrier has been investigated for either 4,7-diphenyl-2,9-dimethyl-1,10-phenanthroline (bathocuproine) or 4,7-diphenyl-1,10-phenanthroline (bathophenanthroline). A transport system for Cu^+ for the former ligand (2, 3) and a system for Cu^+ and Zn^{2+} (4, 5) have been reported. The author reported the transport of Zn^{2+} and Cd^{2+} ions (6–8) with high efficiency using an SLM containing bathocuproine as a carrier. However, there are few reports on the selectivity of the transport of heavy metallic ions through an SLM containing a dipyridyl derivative ligand.

Using three types of 1,10-phenanthroline-based ligands, neocuproine (2,9-dimethyl-1,10-phenanthroline), bathophenanthroline, and bathocuproine, the transport selectivity of major heavy metallic ions by SLMs containing these ligands as a carrier was investigated. At the same time, the effect of pairing ion species, which form an ion pair with a positive charged metallic complex ion, was also examined. As a result, it became clear that the pairing ion species contributes considerably to the transport selectivity of the metallic ion. This is an important factor for obtaining high transport using an SLM. The characteristics for the transport of metallic ions were ascertained by comparing the SLMs including the three ligands as carriers.

EXPERIMENTAL

Reagents

Copper sulfate, cadmium nitrate, zinc nitrate, and other metallic salts were analytical pure grade from Wako Pure Chemical Industries Co. Potassium chloride, iodide, nitrate, and perchlorate, used as pairing ion species, were analytical pure grade and were supplied by Wako Pure Chemical Industries Co.

Bathocuproine, bathophenanthroline, and neocuproine used as carriers were obtained from Dojindo Lab. Co.

SLM

A microporous polypropylene membrane, Celgard 2500 (Daicel Chemical Industries Co.), with a pore size of 0.04–0.4 μm, a porosity of 45%, a thickness of 25 μm, and a density of 0.49 g/cm^3, was used as a supporting membrane of SLM. The membrane was cut into circular pieces of 8 cm diameter. They were impregnated with 50 μL ligand solution (1×10^{-2} mol/L) in dibenzyl ether at the center to give a circle of 6 cm diameter. The ligand concentration in the SLM was estimated to be 1.77×10^{-8} mol/cm^2.

Apparatus and Measurements

The apparatus used for the transport experiment was the same as that used in our earlier paper (6). A prepared SLM was placed between two cylindrical glass compartments (150 cm^3 each). A solution (150 mL) consisting of metallic ion (1×10^{-4} mol/L), pairing ion (0.1 mol/L), ammonium acetate buffer solution (pH 7), and/or hydroxylammonium sulfate (5×10^{-2} mol/L) was placed in the cylinder to be used as the normal extraction side. Only ammonium acetate buffer solution (pH 7) was placed in the cylinder to be used as the backextraction side. The solutions in both compartments were stirred with magnetic stirrers at 500 rpm in a water bath at 25°C during the metallic ion transport. Aliquots (1 mL) of the solutions in both compartments were taken at definite time intervals, and the metallic ion concentrations in the solution were then measured by atomic absorption spectrophotometry (AA-680 instrument, Shimadzu Co.).

Permeation Mechanism

Three types of dipyridyl-based ligands, neocuproine (which has two methyl groups at the 2,9-position of 1,10-phenanthroline), bathocuproine (which has two phenyl groups at the 4,7-position of the above neocuproine), and bathophenanthroline (which has two phenyl groups at the 4,7-position of 1,10-phenanthroline), were compared for transport of metallic ions. Bathocuproine and neocuproine are coloring chelating agents with a high reactivity toward Cu^+ ion, whereas bathophenanthroline has a high reactivity toward Fe^{2+} ion. In this study the driving forces for the transport of metallic ions by either a transport system based on an oxidation-reduction potential gradient (PG) or a concentration gradient (CG) of the pairing ion were compared. Both transport models of metallic ions are shown in Fig. 1. In the PG system the metallic ion is transferred from the normal extraction side to the backextraction side according to the potential gradient between a reducing atmosphere (by a reducing agent) in the normal extraction side and an oxidizing atmosphere (dissolved oxygen in solution was used as an oxidizing agent) in the backextraction side. Additionally, the PG system may also include a driving force from a concentration gradient of pairing ion species.

On the other hand, in a CG system the metallic ions are transported in accordance with the concentration gradient of the anion and the pairing ion species between both extraction sides. The effect of the concentration gradient on the metallic ion will be negligible because the concentration of the metallic ion in comparison with that of the pairing ion is very low (several orders of magnitude lower, one-thousandth). It is expected that the molar ratio of the metallic ion and ligand of the cuproine type for the complex which is formed in an SLM is 1:2 for $Cu^{+,2+}$ (2, 3, 9–12), Cd^{2+} (8), and Zn^{2+} (5) ions, whereas the ratio for Co^{2+} (12) and $Fe^{2+,3+}$ (12–16) ions is 1:3. It is thought that the complex formation for $Cu^{+,2+}$, Cd^{2+},

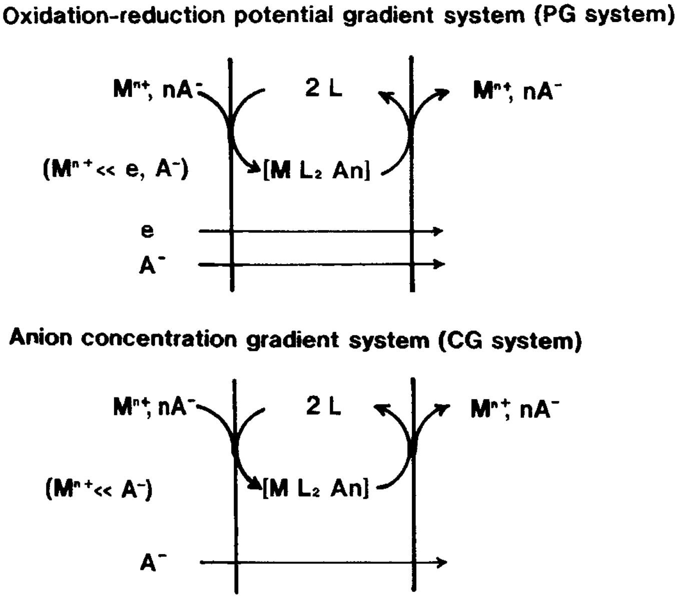

FIG. 1 Mechanism for the transport of M^{n+} ion through an SLM in an oxidation–reduction potential gradient transport system (PG system) and a pairing ion concentration gradient transport system (CG system). M^{n+}: metallic ion; A^-: pairing ion species; L: ligand.

and Zn^{2+} ions can be represented by

$$M^{n+} + nA^- + 2L \rightleftarrows [M \cdot L_2 \cdot A_n]$$

and for Co^{2+} and $Fe^{2+,3+}$ ions by

$$M^{n+} + nA^- + 3L \rightleftarrows [M \cdot L_3 \cdot A_n]$$

where M^{n+} is the metallic ion, A^- is the pairing ion, and L is the ligand.

RESULTS AND DISCUSSION

Transport of Metallic Ions through an SLM Containing Bathocuproine

Transport of various heavy metallic ions through an SLM containing bathocuproine was examined under the experimental conditions of 1×10^{-4} mol/L metallic ion, 0.1 mol/L potassium bromide, 0.5 mol/L ammonium acetate buffer solution (pH 7), and 5×10^{-2} mol/L hydroxylammonium sulfate.

By using bathocuproine as a carrier in the PG transport system, Cu^+, Cd^{2+}, and Zn^{2+} ions were transported from the normal extraction side to the backextraction side. In addition, small amounts of Pb^{2+} and Co^{2+} ions were also transported. These are shown in Figs. 2 and 3. However,

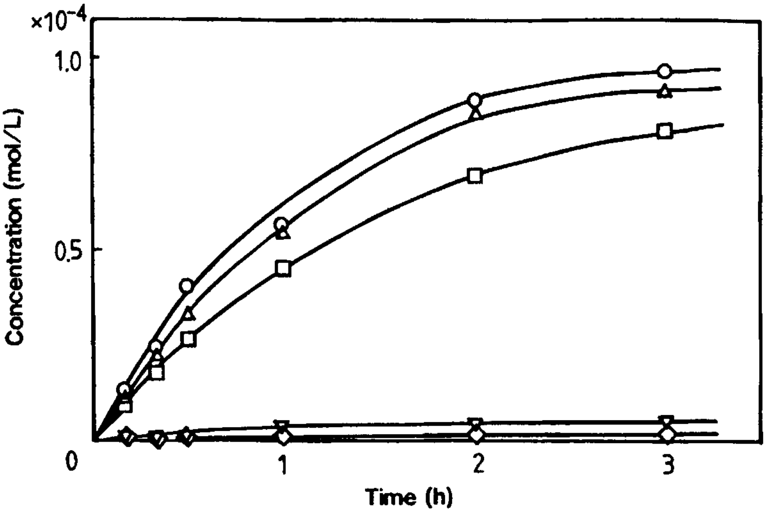

FIG. 2 Concentrations of the metallic ions as a function of time for solutions in the backextraction side of the PG transport system using a bathocuproine-SLM. (○) Cu^+ ion, (△) Cd^{2+} ion, (□) Zn^{2+} ion, (▽) Pb^{2+} ion, (◇) Co^{2+} ion.

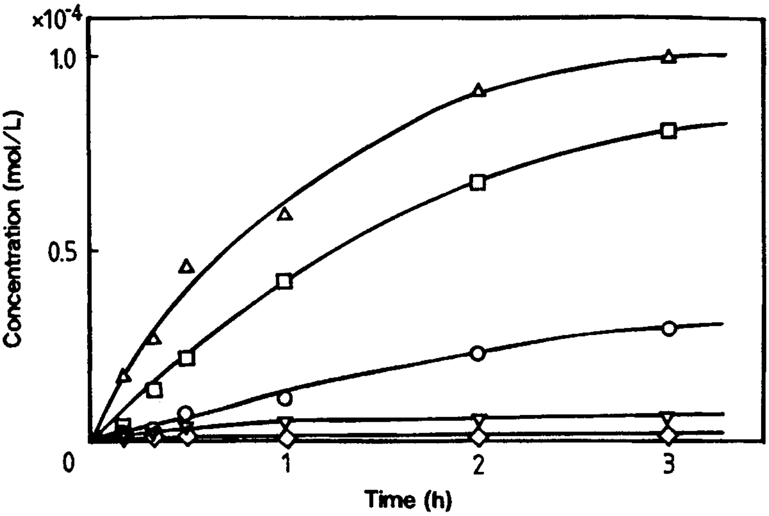

FIG. 3 Concentrations of the metallic ions as a function of time for solutions in the back-extraction side of the CG transport system using a bathocuproine-SLM. (○) Cu^{2+} ion, (△) Cd^{2+} ion, (□) Zn^{2+} ion, (▽) Pb^{2+} ion, (◇) Co^{2+} ion.

no Fe^{2+} ions were transported even though bathophenanthroline preferentially reacts with Fe^{2+} ion to form a chelate complex (12–16). Furthermore, no transport phenomenon of Fe^{2+} ion was observed, similar to the case of bathocuproine when bathophenanthroline was used as a carrier in the SLM. For this reason, it is thought that the Fe–bathophenanthroline complex can not dissociate at the backextraction side interface of the SLM because the Fe–bathophenanthroline complex, $[Fe{\cdot}L_3{\cdot}Br_2]$, which was formed in the SLM is very stable. Accordingly, it is clear that the complexes of a tetrahedral geometry type with four coordinates (Cu^+–, Cd^{2+}–, and Zn^{2+}–L_2 complexes) have a higher permeability than those of an octahedral geometry type with six coordinates (Fe^{2+}– and Co^{2+}–L_3 complexes). Based on this, the molecular sizes of the complexes of the octahedral geometry type are larger than those of the tetrahedral geometry type, resulting in less permeability due to the higher degree of diffusion resistance in an SLM by steric hindrance.

In the PG system (Fig. 2), the permeability of metallic ions was in the order $Cu^+ > Cd^{2+} > Zn^{2+} \gg Pb^{2+} > Co^{2+}$, but in the CG system (Fig. 3) it was in the order $Cd^{2+} > Zn^{2+} > Cu^{2+} \gg Pb^{2+} > Co^{2+}$. Essentially, because bathocuproine specifically forms a chelate complex with a monovalent copper ion (9–12), Cu^+ ion was found to have a high permeability on the transport system based on an oxidation-reduction potential gradient as a driving force. However, for the pairing ion concentration gradient system, the permeability of the divalent copper ion was considerably lower. On the other hand, Cd^{2+} and Zn^{2+} ions yielded a high permeability in any transport system. The value of the slope in a straight region of the curve (e.g., Figs. 2 and 3), which illustrates the relationship between the concentration of the metallic ion and time, is used to calculate the quantity of M^{n+} ion transported in 30 minutes from the beginning of the experiment through an SLM. The initial permeation velocity (N) of the metallic ion, M^{n+}, was calculated as follows:

$$N = (\Delta[M^{n+}]/\Delta t)/A \qquad (\text{mol/cm}^2\cdot\text{s})$$

where $\Delta[M^{n+}]$ is the metallic ion concentration in the backextraction side (mol/L), Δt is the time (seconds), and A is the effective area of the SLM (28.3 cm^2).

Selectivity of Metallic Ions through an SLM

The effect of the pairing ion species on a transport system using SLMs containing dipyridyl ligands as a carrier was examined for $Cu^{+,2+}$, Cd^{2+}, and Zn^{2+} ions which have a high permeability. The permeation velocities of the respective metallic ions for the PG and CG transport systems using SLMs containing bathocuproine are shown in Figs. 4 and 5, respectively. Similarly, the results for the transport system of an SLM containing batho-

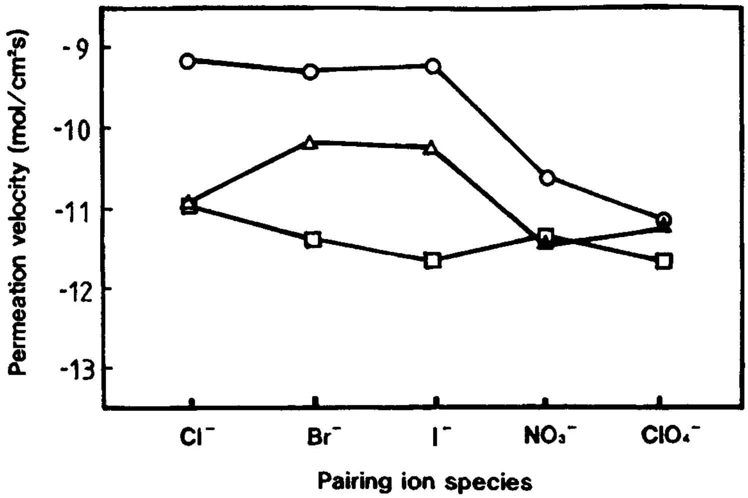

FIG. 4 Selectivity of metallic ions for pairing ion species in the PG transport system using a bathocuproine-SLM. (○) Cu^+ ion, (△) Cd^{2+} ion, (□) Zn^{2+} ion.

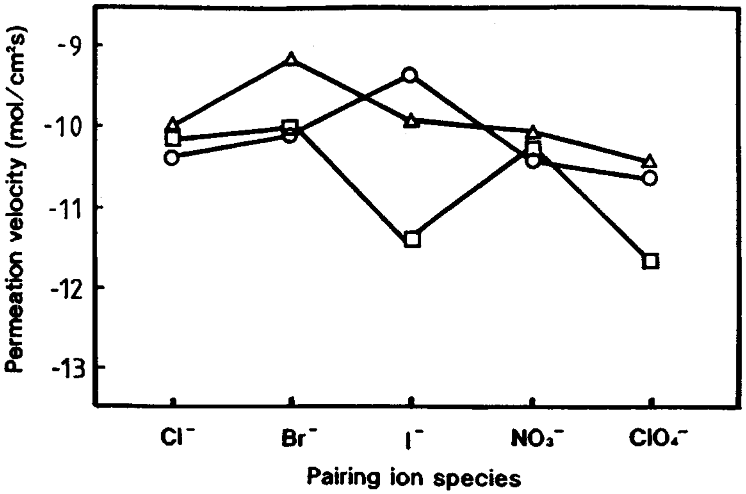

FIG. 5 Selectivity of metallic ions for pairing ion species in the CG transport system using a bathocuproine-SLM. (○) Cu^+ ion, (△) Cd^{2+} ion, (□) Zn^{2+} ion.

phenanthroline are shown in Figs. 6 and 7, and those of an SLM containing neocuproine are shown in Figs. 8 and 9. In addition, any transport experiences which mixed three metallic ions, $Cu^{+,2+}$, Cd^{2+}, and Zn^{2+} ions, i.e., a cotransport system, were also investigated.

In the PG transport system it was found that the permeability of Cu^+ ion was higher for any dipyridyl ligands and any pairing ion species. In particular, a very high selectivity for Cu^+ ion was obtained in the bathocuproine–SLM system with Cl^- ion and in the neocuproine–SLM system with Cl^- or Br^- ion as a pairing ion species. The permeation velocity of the Cu^+ ion against that of the Cd^{2+} ion was 60.4 times for the former bathocuproine–SLM system, and those for the latter neocuproine–SLM system were 114 times for use of Cl^- ion and 156 times for Br^- ion, respectively, depending on the pairing ion species. However, when anion species such as NO_3^- and ClO_4^- ions, which have a large ion size, were used as the pairing ion species, the permeability and the selectivity of Cu^+ ion decreased. Based on this, it is concluded that the magnitude of the neutral chelate complexes of $[Cu{\cdot}L_2{\cdot}NO_3]$ and $[Cu{\cdot}L_2{\cdot}ClO_4]$ is larger than that of the complexes of $[Cu{\cdot}L_2{\cdot}Cl]$ and $[Cu{\cdot}L_2{\cdot}Br]$, which results in a reduction of the diffusion velocity of the chelate complex in the SLM. Furthermore, for the CG system, i.e., for the transport of copper ion as a divalent ion, the selectivity of that ion through an SLM disappeared. Accordingly, in order to accomplish the transport of copper ion with high

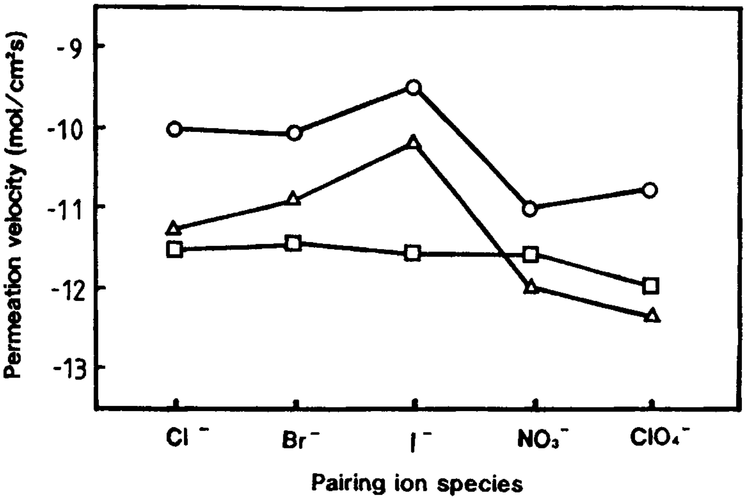

FIG. 6 Selectivity of metallic ions for pairing ion species in the PG transport system using a bathophenanthroline-SLM. (○) Cu^+ ion, (△) Cd^{2+} ion, (□) Zn^{2+} ion.

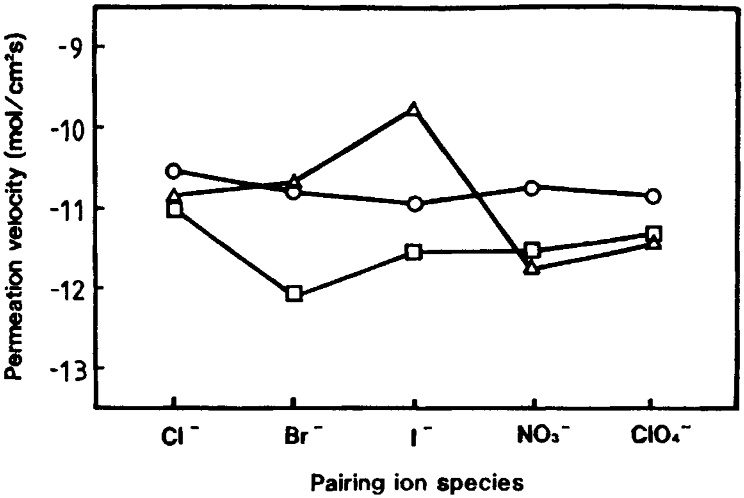

FIG. 7 Selectivity of metallic ions for pairing ion species in the CG transport system using a bathophenanthroline-SLM. (○) Cu^+ ion, (△) Cd^{2+} ion, (□) Zn^{2+} ion.

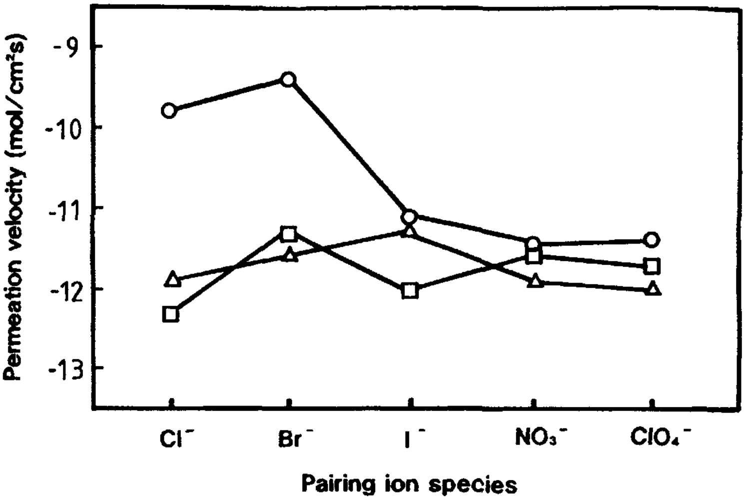

FIG. 8 Selectivity of metallic ions for pairing ion species in the PG transport system using a neocuproine-SLM. (○) Cu^+ ion, (△) Cd^{2+} ion, (□) Zn^{2+} ion.

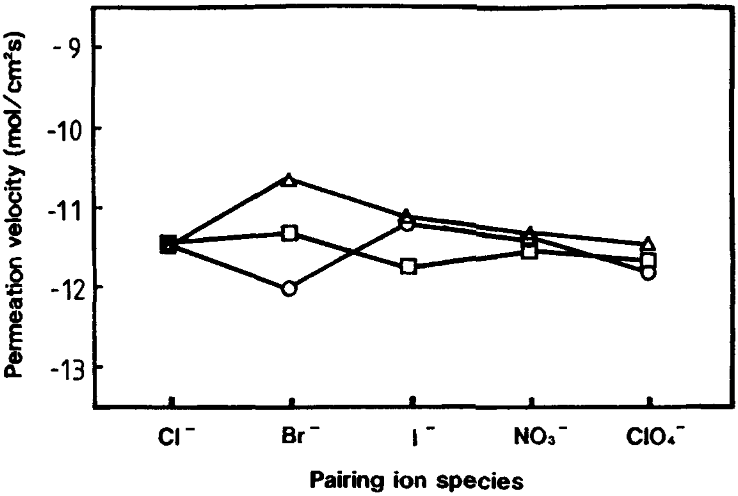

FIG. 9 Selectivity of metallic ions for pairing ion species in the CG transport system using a neocuproine-SLM. (○) Cu^+ ion, (△) Cd^{2+} ion, (□) Zn^{2+} ion.

efficiency, it should be used with the bathocuproine–SLM transport system or the neocuproine–SLM transport system using either a Cl^- or Br^- ion as a pairing ion with the PG system. For neocuproine, however, the transport rate of a metallic ion showed a tendency to slow down gradually with time during a transport experiment. No such phenomenon was observed for the bathocuproine–SLM and bathophenanthroline–SLM systems. The difference in behavior is thought to be caused by the differences in the solubilities of their ligands in water. Therefore, when using the neocuproine–SLM transport system for the purpose of inhibiting exfoliation of the liquid membrane solvent and ligand from the SLM, it should be utilized as a composite membrane sandwiched between two dialysis membranes (7, 17, 18).

On the other hand, the transport system of Cu^{2+}, Cd^{2+}, and Zn^{2+} ions in the CG system showed a tendency to increase the selectivity of Cd^{2+} ion in contrast to the transport of Cu^+ ion mentioned above. For the transport of Zn^{2+} ion, the effect relative to the type of pairing ion species was not observed for any of the transport systems. The permeability of the three metallic ions was in the order bathocuproine > bathophenanthroline > neocuproine. For Cd^{2+} transport using Br^- ion as a pairing ion species in the bathocuproine–SLM transport system, the selectivity of Cd^{2+} ion was higher by one order compared with the selectivity of the transport of Zn^{2+} or Cd^{2+} ions. Similarly, for the neocuproine–SLM transport system using Br^- ion, the Cd^{2+} ion could be transported with a high efficiency as well as in the bathocuproine–SLM system. One of the reasons for similar results for these SLM systems is that both ligands have a similar molecular structure. On the other hand, different behavior was observed for the bathophenanthroline–SLM transport system. When I^- ion was used as a pairing ion species, the permeation velocity of the Cd^{2+} ion was 51.6 times that of Zn^{2+} ion, and 15.2 times that of the Cu^{2+} ion. In conclusion, based on the bathophenanthroline–SLM transport system using I^- ion as a pairing ion, a transport system which has a high selectivity for Cd^{2+} ion can be constructed.

CONCLUSION

Permeation selectivity for the transport of heavy metallic ions through SLMs containing bathocuproine, bathophenanthroline, or neocuproine as a carrier was studied. In the PG system, the ranking of the permeability of metallic ions was $Cu^+ > Cd^{2+} > Zn^{2+} \gg Pb^{2+} > Co^{2+}$, and in the CG system, the selectivity of the Cu^{2+} ion disappeared. For the former system the selectivity of metallic ions was in the order bathocuproine > bathophenanthroline > neocuproine, and for the latter system the difference between the ligand species was not observed. It became clear that the anion species as a pairing ion contribute considerably to the permeation velocity of the metallic ion. It was found that selective transport of Cu^+ ion in the PG transport system and selective transport of Cd^{2+} ion in the CG transport system could be accomplished.

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