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Transportation of Zinc(II) Ion through a Supported Liquid Membrane

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Transportation of Zinc(II) Ion through a Supported Liquid Membrane

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Abstract

The transportation system of the zinc ion using a driving force supplied by the concentration gradient of the anion is studied in terms of permeation through a supported liquid membrane (SLM) containing a carrier. The SLM was prepared by impregnating a porous polypropylene film with a 4,7-diphenyl-2,9-dimethyl-1,10-phenanthroline (bathocuproine) solution with dibenzyl ether as the carrier. The zinc ion permeation behavior through the film is studied under various experimental conditions. The effects of the zinc ion concentration, anion, and carrier are determined, and a permeation velocity equation for the zinc ion through the membrane is proposed. The effects of types of carrier as well as of anions are also investigated.

INTRODUCTION

Compared with liquid–liquid extraction based on the partition principle between two phases (aqueous and organic), extraction of metallic ions based on their transportation by means of permeation through an SLM placed between two different aqueous solutions is characterized by normal and back-extraction occurring in parallel, and it is possible to extract a metallic ion continuously from an aqueous solution to the other solution. In addition, it can be carried out with the use of only a small amount of an extracting agent that reacts specifically with the extracting solvents and the metallic ions. As the extracting agents of metallic ions, it is possible to use a variety of ligands that can form chelate complexes or ion pairs selectively with the targeted metallic ions.

The use of dipyridyl-based ligands (such as bathocuproine) and the use of a redox potential gradient for metallic ion transportation using SLMs were reported recently (*1*–*8*). Ohki et al. reported the permeation of cuprous ion under reductive conditions (*2*). The selectivity of bathocuproine for forming complex compounds with the copper ion is higher for the cuprous ion than for the cupric ion which exists predominantly under conditions where there is no reducing agent (*2*, *3*, *11*).

Our present work started from the fact that, similarly to the copper ion, the zinc ion forms a coordinate bond with bathocuproine to produce a complex compound (*9*, *10*). An SLM was prepared, and the permeation of zinc ion through it was studied under various experimental conditions to obtain the characteristics of this system. This paper proposes an equation for the permeation velocity of zinc ion and discusses the effects of types of counteranions and of ligands.

EXPERIMENTAL

Materials

Bathocuproine and the other ligands used as carriers of the zinc ion were of analytical purity grade from Dojindo Lab. Co. Ltd. Zinc sulfate, lithium chloride, lithium bromide, potassium iodide, dibenzyl ether, and other reagents of analytical purity grade were supplied by Wako Pure Reagents Co. and were used without purification.

Preparation of SLM

Porous polypropylene film (Duragard 2500, Polyplastics Co. Ltd.) with a density of 0.49 g/cm^3, a thickness of 25 μm and a pore size of 0.04 × 0.4 μm was used for the preparation of a supporting membrane to hold an extracting solvent containing carrier. The film was cut into circular pieces of 8 cm diameter which were each impregnated with 50 μL of bathocuproine solution in dibenzyl ether of a concentration ranging from 5×10^{-3} to 2×10^{-2} mol/L by the use of a microsyringe at their center to give a circle of 3 cm radius (effective area of membrane = 28.3 cm^2), and were used as the SLMs. The concentrations of bathocuproine in these SLMs were determined to be in the range 3.19×10^{-6} to 1.28×10^{-5} g/cm^2.

Apparatus and Procedure

Figure 1 shows the apparatus used. An SLM was placed between two cylindrical glass cells of 150 mL, one filled with a solution of zinc sulfate (5×10^{-5} to 2.5×10^{-4} mol/L) and lithium chloride (0 to 0.1 mol/L) as the normal extraction side and the other with 150 mL purified water as the back-extraction side. The contents of both cells were stirred with magnetic stirrers at 500 rpm, and the apparatus was in a constant temperature water bath at 25°C.

Samples of 1 mL each were taken from each of the cells by the use of a pipette at.definite time intervals. The concentration of zinc ions was determined by colorimetry using a Shimadzu UV/VIS-160 instrument according to the zincon method (*12*).

Permeation Mechanism

The permeation mechanism of the zinc ion in our system is proposed in Fig. 2. A Zn^{2+} ion in the normal extraction side solution is caught by the bathocuproine (L) at the SLM interface and forms a complex ion with a positive charge at a mol ratio of 1:2, which then forms an ion pair with the anion (Cl^-) to produce a neutral complex $[Zn^{2+} \cdot 2L \cdot 2Cl^-]$ which dis-

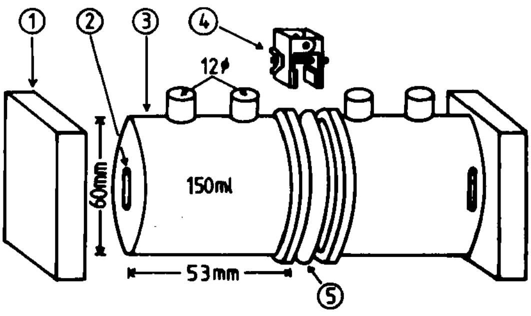

FIG. 1 Apparatus for transportation experiment. (1) Magnetic stirrer, (2) Teflon rotor, (3) glass cell, (4) clamp, (5) supported liquid membrane.

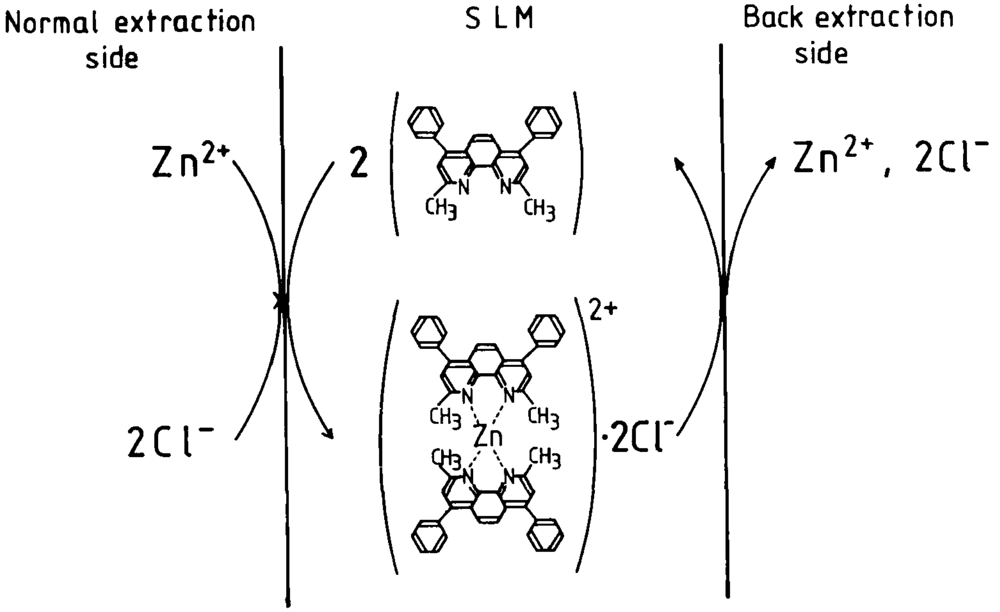

FIG. 2. Mechanism for transportation of Zn^{2+} ion.

solves in the liquid membrane. The formation of the zinc coordinate complex is expressed by

$$Zn^{2+} + 2L + 2Cl^- = [ZnL_2Cl_2]$$

As a result of the driving force produced by the Cl^- ion concentration gradient, the complex is transported to the opposite side of the SLM (i.e., the back-extraction side) and dissociate there, freeing the Zn^{2+} and Cl^- ions into the aqueous solution. The freed bathocuproine remains in the membrane and diffuses to the normal extraction side where it again acts as a carrier of the Zn^{2+} ion. In this manner, continuous transportation of zinc ion occurs from the normal extraction side to the back-extraction side.

RESULTS AND DISCUSSION

Active Transport of Zn^{2+} ion

Figure 3 shows the change in Zn^{2+} ion concentration as a function of time for solutions of both the normal and back-extraction sides, whereby the initial concentration of Zn^{2+} and Cl^- ions in the former solution were 2×10^{-4} and 0.1 mol/L, respectively. It is seen from Fig. 3 that the Zn^{2+} ion concentration became the same in both extraction sides after ~50 min, then reversed because of the concentration gradient, and that finally, after ~3 h, the Zn^{2+} ions initially present in the normal extraction side were transported to the back-extraction side through the SLM.

The permeation velocity of Zn^{2+} ion was calculated for the case of Fig. 3 according to

$$N = (\Delta[Zn^{2+}]/\Delta t)/A$$

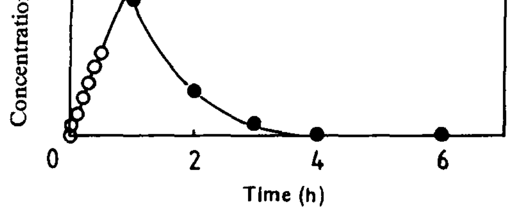

FIG. 3. Concentration of Zn^{2+} ion as a function of time for solutions of both the normal and back-extraction sides at 298 K. (●) Normal extraction side contained 2×10^{-4} mol/L $ZnSO_4$ and 0.1 mol/L LiCl. (○) Back-extraction side did not contain $ZnSO_4$ and LiCl.

where N is the permeation velocity (mol/cm$^2 \cdot$ s), [Zn^{2+}] is the zinc ion concentration (mol/L), t is the time (s), and A is the effective area of the membrane (cm^2). The zinc ion permeation velocity was obtained from the curve for the back-extraction side in Fig. 3 by using the increase in Zn^{2+} ion concentration against time (from the start of experiment to about 30 min). The slope of the line gave a value of 1.20×10^{-9} mol/cm$^2 \cdot$ s. The experimental reproducibility was confirmed by three experiments under the same conditions, and the relative standard deviation was 4.5%.

Effect of Ligand Species

Three types of dipyridyl-based ligand, neocuproine (2,9-dimethyl-1,10-phenanthroline), bathophenanthroline (4,7-diphenyl-1,10-phenanthroline), and bathocuproine, were compared under the experimental conditions mentioned above. These ligands are derivatives of 1,10-phenanthroline. They have two pyridine rings and can form coordinate bonds at their nitrogen atoms with metallic ions to produce positive-charged complex ions.

SLMs were prepared with the use of these three ligands and subjected to a comparison test of zinc ion permeation. The concentration of ligand and the initial concentrations of Zn^{2+} and Cl$^-$ ions were 1×10^{-2}, 2×10^{-4}, and 0.1 mol/L, respectively. The result of this comparison test is shown in Fig. 4, from which the value for the permeation velocity of Zn^{2+} ion was found to be 1.61×10^{-10} for neocuproine, 2.86×10^{-10} for bathophenanthroline, and 1.20×10^{-9} (mol/cm$^2 \cdot$ s) for bathocuproine; that is, neocuproine < bathophenanthroline < bathocuproine. These differences in permeation velocity values were due to the different reactivities of these ligands with zinc ion to form their complex ions; i.e., their increasing order is the same as that mentioned above and is caused by their different solubilities in water. The lipophilic substitutes are fewer in number and the molecular sizes are smaller in the order bathocuproine, bathophenanthroline, and neocuproine, resulting in less hydrophobic properties due to the higher degree of availability of the properties of the pyridine ring and eventually to a slightly higher solubility in water. For this reason, it is concluded that the SLMs deteriorated faster in the same order of ligands as mentioned above and showed a higher time-dependent exfoliation of ligand in water. The SLM prepared by dibenzyl ether impregnation without the addition of any ligand showed no permeation of Zn^{2+} ion, from which it is clear that the ligands used here played the role of a Zn^{2+} ion carrier.

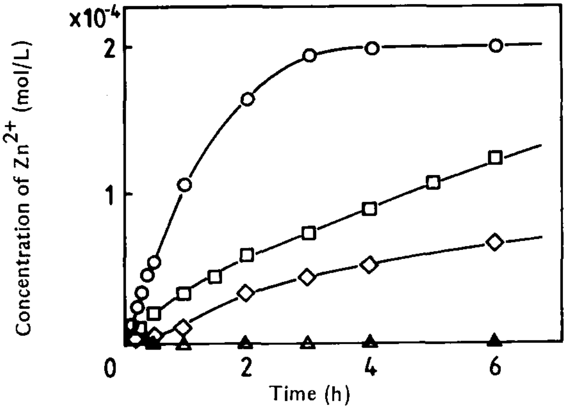

FIG. 4. Concentration of Zn^{2+} ion as a function of time for a solution of the back-extraction side against the ligand species. (○) Bathocuproine, (□) bathophenanthroline, (◇) neocuproine, and (△) without ligand.

Effect of Ligand Concentration

Figure 5 shows the value for the permeation velocity (log N) as a function of bathocuproine concentration (log [L]) under initial concentrations of Zn^{2+} and Cl^- ions of 5×10^{-4} and 1×10^{-2} mol/L, respectively. From Fig. 5 it is obvious that the value for the permeation velocity was depend-

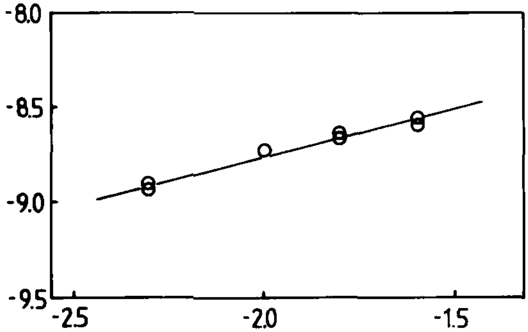

FIG. 5. Relationship between the concentration of the ligand and the permeation velocity of Zn^{2+} ion through an SLM.

ent on the concentration of ligand in the SLM. The slope of the line was 0.57, which indicates that the permeation velocity value is proportional to $[L]^{0.57}$

Effect of Cl^{-1} Ion Concentration

It was mentioned above that the gradient of Cl$^-$ ion concentration acts as the driving force for the transportation of Zn^{2+} ion in our system. To confirm this, the effect of Cl$^-$ion concentration in the solution on the normal extraction side on the permeation velocity of Zn^{2+} ion was tested, which is shown in Fig. 6 as the relation between the permeation velocity (log*N*) and Cl$^-$ ion concentration (log [Cl$^-$]). When the Cl$^-$ ion concentration was less than 2×10^{-2} mol/L, the slope of the line was 0.43, which indicates that the permeation velocity depends on $[Cl^-]^{0.43}$. However, the value for the permeation velocity was not found to increase when the Cl$^-$ ion concentration was higher than 2×10^{-2} mol/L, which indicates that the permeation velocity did not depend on the Cl$^-$ ion concentration in this range. This observation suggests that the transfer (diffusion) velocity of the zinc complex through the SLM was rate-determining. From the test result that a system which did not contain Cl$^-$ ions supplied no zinc ion transportation, it is concluded that any sulfate ion coexisting in the solution had no effect on the permeation velocity value.

In addition to Cl$^-$ ions, Br$^-$ and I$^-$ ions were tested as the anions to form ion pairs with the complex ions under the same conditions to those of Fig.

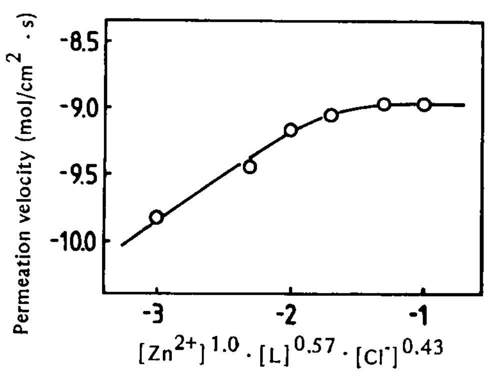

FIG. 6. Relationship between the initial concentration of Cl$^-$ ion and the permeation velocity of Zn^{2+} ion through an SLM.

3. Compared with the result for Cl^- ions, the permeation velocity value was found to increase by 13% (1.36×10^{-9} mol/cm$^2 \cdot$ s) for Br^- ions and by 18% (1.42×10^{-9} mol/cm$^2 \cdot$ s) for I^- ions, which means that a halogen with a larger ion radius and smaller electronegativity gave a slightly larger permeation velocity value. Cl^-, Br^-, and I^- ions are all structure-destructive to the water molecules surrounding them. Ions of larger radius are assumed to be more strongly structure-destructive and thus less likely to hydrate, resulting in their being more readily associated with cations and consequently more readily extractable by an organic solvent. The ion radius of the Cl^- ion is 1.81 Å, of the Br^- ion 1.96 Å, and of the I^- ion 2.20 Å, and it can therefore be assumed that these ions form ion pairs with $[Zn \cdot L_2]^{2+}$ which are more readily extractable at the interface of the SLM in the order Cl^-, Br^-, and I^-. The lipophilic picrate ion permeation velocity value was found to be almost the same as the Cl^- ion.

Effect of Zn^{2+} Ion Concentration

Figure 7 shows the value of the permeation velocity (log *N*) as a function of the initial concentration (log $[Zn^{2+}]$) of Zn^{2+} ion in a normal extraction side solution at 25°C. The concentration used was 0.1 for Cl^- ion and from 5×10^{-5} to 2.5×10^{-4} mol/L for Zn^{2+} ion. It is clear from Fig. 7 that the permeation value was proportional to the initial concentration of Zn^{2+} ion and depended on it with an order of 1.0. It is concluded that the formation

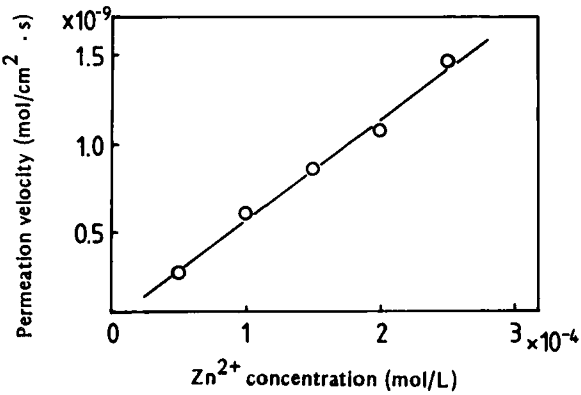

FIG. 7. Relationship between the initial concentration of Zn^{2+} ion and the permeation velocity of Zn^{2+} ion through an SLM.

of a complex among Zn^{2+} ion, ligand, and Cl^- ion was rate determining in this concentration range.

Equation of Permeation Velocity

We propose an equation for the permeation velocity of Zn^{2+} ion for our system of Zn^{2+} ion transportation through an SLM at 25°C:

$$N = K \cdot [Zn^{2+}]^a \cdot [L]^b \cdot [Cl^-]^c \quad (mol/cm^2 \cdot s)$$

where K is a permeation velocity constant, and the values for exponents a, b, and c were determined experimentally to be 1.0, 0.57 and 0.43, respectively, as mentioned above.

To obtain the value for permeation velocity constant K, $\log N$ is plotted against $\log ([Zn^{2+}]^{1.0} \cdot [L]^{0.57} \cdot [Cl^-]^{0.43})$ as shown in Fig. 8. The slope of the line is approximately 1 and the intercept point is 9.00×10^{-5}, which leads to the equation mentioned above as the final expression:

$$N = 9.00 \times 10^{-5} \cdot [Zn^{2+}]^{1.0} \cdot [L]^{0.57} \cdot [Cl^-]^{0.43} \quad (mol/cm^2 \cdot s).$$

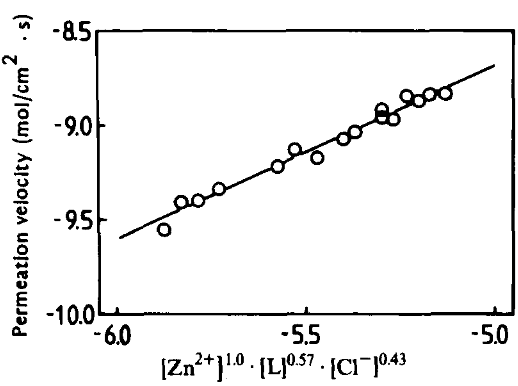

FIG. 8. Relationship between the value of $[Zn^{2+}]^{1.0} \cdot [L]^{0.57} \cdot [Cl^-]^{0.43}$ and the permeation velocity of Zn^{2+} ion.

CONCLUSION

Transportation of Zn^{2+} ion through an SLM containing bathocuproine as carrier was studied in connection with three important parameters. The permeation velocity of Zn^{2+} ion was observed to depend on the concentration of ligand of the order of 0.57, on the concentration of Cl^- ion (which caused the driving force of Zn^{2+} ion transportation) of the order of 0.43 when its range was less than 0.02 mol/L, and on the concentration of Zn^{2+} ion of the order of 1.0.

As a result, an equation for the permeation velocity of Zn^{2+} ion was proposed for our system at 25°C:

$$N = 9.00 \times 10^{-5} \cdot [Zn^{2+}]^{1.0} \cdot [L]^{0.57} \cdot [Cl^-]^{0.43} \quad (\text{mol/cm}^2 \cdot \text{s}).$$

Our system can be used for the extraction, concentration, and recovery of zinc ions from a variety of environmental samples. Further development is expected.

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