Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Saito, Takashi(1991) 'Transport of Cadmium(II) Ion through a Supported Liquid Membrane Containing a Bathocuproine', Separation Science and Technology, 26: 12, 1495 — 1506
To link to this Article: DOI: 10.1080/01496399108050546
URL: http://dx.doi.org/10.1080/01496399108050546

SEPARATION SCIENCE AND TECHNOLOGY, 26(12), pp. 1495–1506, 1991

Transport of Cadmium(II) Ion through a Supported Liquid Membrane Containing a Bathocuproine

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Abstract

The active transport of cadmium ions across a supported liquid membrane (SLM) containing a ligand based on a driving force supplied by the concentration gradient of the chloride ion is described. The SLM used is a microporous polypropylene membrane impregnated with a bathocuproine (4,7-diphenyl-2,9-dimethyl-1,10-phenanthroline) solution in dibenzyl ether as a carrier. The characteristics of the cadmium ion transport system are examined under various experimental conditions. The active transport of cadmium ions through an SLM is dependent on the concentrations of the cadmium ion, ligand, and chloride ion. An equation for the permeation velocity of cadmium ions, consisting of three important factors for this transport system, is proposed.

INTRODUCTION

The transport of metallic ions through a supported liquid membrane (SLM) containing a suitable carrier can be effectively used for selective and continuous extraction and for the concentration of the targeted metallic ions. In addition, it is economical in terms of extracting solvent and chelating agent compared with conventional liquid–liquid extraction. There has been some work on transport systems for metallic ions using SLMs containing dipyridyl derivative ligands as the carrier (*1–3*). We have also worked on transport system using such SLMs for the transport of cuprous copper and zinc ions (*4–9*), and it was recently found that cadmium ion can be effectively transported by the use of the system (*10*). It is well known that cadmium ion can cause environmental pollution. In some regions in Japan, for example, cadmium compounds contained in the industrial wastewater discharged to rivers from some mining and metal-plating works have caused diseases such as osteomalacia and diabetes mellitus among people who live on the rice produced by using such polluted river water: the cases are the well-known, so-called "Itai-Itai disease." As a result, there are now strict environmental quality standards for water (below 0.01 ppm). At present there are few reports of work on the transport of cadmium ion through an SLM. For these reasons, a transport system with good selectivity and efficiency for the recovery and purification of metallic ions from complex mixtures such as industrial wastewater is needed. In the present work a transport system for cadmium ion using SLMs containing bathocuproine as the carrier is studied with regard to the effects of the concentrations of bathocuproine, anion, and cadmium ion on the permeation velocity of cadmium ion in order to investigate the characteristics of the system and introduce an equation for the permeation velocity of cadmium ion. At the same time, pH, ligand species, and temperature are also examined for their effects on cadmium ion transport.

EXPERIMENTAL

Reagents

Cadmium nitrate, lithium chloride, and dibenzyl ether were obtained from Wako Pure Chemical Industries Co. Bathocuproine, bathophenanthroline (4,7-diphenyl-1,10-phenanthroline), and neocuproine (2,9-dimethyl-1,10-phenanthroline), used as carriers of cadmium ion, were supplied by Dojindo Lab. Co. and were used without purification.

SLM

A microporous polypropylene membrane 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 the supporting membrane to hold an organic solvent containing a ligand. The membrane, Celgard 2500, was supplied by Daicel Chemical Industry Co. The membrane was cut into circular pieces of 8 cm diameter which were each impregnated with 50 μL bathocuproine solution in dibenzyl ether of a concentration ranging from 5×10^{-3} to 2×10^{-2} mol/L at their center to give a circle of 6 cm diameter. The bathocuproine concentrations in these SLMs were estimated to be in the range from 3.19×10^{-6} to 1.28×10^{-5} g/cm^2.

Apparatus and Measurements

The apparatus used for the transport experiment of cadmium ion was the same as used in an earlier paper (*9*). An SLM was placed between two cylindrical glass cells of 150 mL. One filled with a solution of cadmium nitrate (1×10^{-4} to 1.2×10^{-3} mol/L) and lithium chloride (0 to 0.8 mol/

L) as the normal extraction side, and the other was filled with 150 mL purified water as the back-extraction side. The contents of both cells were stirred with magnetic stirrers at 500 rpm in a water bath of constant temperature. Solutions of 1 mL each were taken from each of the cells at definite time intervals. The concentration of cadmium ions was determined by atomic absorption spectrophotometry by using a Shimadzu AA-680 instrument.

Permeation Mechanism

Bathocuproine forms a complex selectivity with cuprous ion and has been used in colorimetry and extraction. The ability for complex formation of bathocuproine with cupric ion, however, is lower than that with cuprous ion, resulting in a lower selectivity to the cupric ion than to the cuprous ion. Because zinc and cadmium ions have an electronic configuration similar to that of cuprous ion, bathocuproine can also form complexes with them. The molar ratio of the cadmium ion (Cd^{2+}), the bathocuproine (L), and the chloride ion (Cl^-) for the cadmium complex formation is 1:2:2, and the complex formation is expressed by

$$Cd^{2+} + 2L + 2Cl^- = [Cd{\cdot}L_2{\cdot}Cl_2] \qquad (1)$$

Figure 1 shows the permeation mechanism of the Cd^{2+} ion in the present system. On the normal extraction side, the Cd^{2+} ion in solution produces coordinate bonds with the nitrogen atoms of bathocuproine at the SLM interface to form a positive-charged complex ion ($[Cd{\cdot}L_2]^{2+}$) which, in turn, forms an ion pair with two Cl^- ions; that is, a neutral complex ($[Cd{\cdot}L_2{\cdot}Cl_2]$). The neutral complex then diffuses through the SLM from

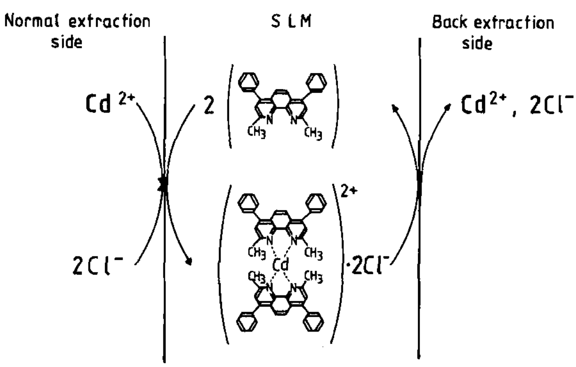

FIG. 1. Mechanism for transport of Cd^{2+} ion through an SLM-containing bathocuproine.

the normal extraction side to the back-extraction side due to the concentration gradient of the Cl^- ion as a driving force, and it dissociates at the SLM interface of the back-extraction side to release the Cd^{2+} and Cl^- ions into the aqueous solution there. The freed bathocuproine, which is hydrophobic, remains within the SLM, and again forms the complex with the Cd^{2+} and Cl^- ions at the SLM interface on the normal extraction side where it acts as a carrier of the Cd^{2+} ion, thus resulting in the continuous transport of the Cd^{2+} ion.

For this transport system of the Cd^{2+} ion, the following equation for the permeation velocity of the Cd^{2+} ion is introduced. It is based on the concentrations of three parameters, Cd^{2+} ion, ligand, and Cl^- ion, which have an effect on the permeation velocity.

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

where N is the permeation velocity; K is the permeation velocity constant; $[Cd^{2+}]$, $[L]$, and $[Cl^-]$ are the molar concentrations of the Cd^{2+} ion, bathocuproine, and the Cl^- ion, respectively; and a, b, and c are the exponents of the respective parameters. The value for exponent a can be obtained by determining the correlation between the permeation velocity and the Cd^{2+} ion concentration. Similarly, the values for exponents b and c can be obtained from the correlations between the permeation velocity and the ligand concentration, and between the permeation velocity and the Cl^- ion concentration, respectively. The value for constant K can be obtained by use of the values for three parameters mentioned above, and finally the equation for the permeation velocity of Cd^{2+} ion for the system can be obtained.

RESULTS AND DISCUSSION

Transport of Cd^{2+} Ion through an SLM

Figure 2 shows the concentration of Cd^{2+} ion against time for solutions on the normal and back-extraction sides where the experimental conditions were as follows: initial concentrations of Cd^{2+} and Cl^- ions in the solution on the normal extraction side, 5×10^{-4} and 0.1 mol/L, respectively; concentration of bathocuproine, 2×10^{-2} mol/L; temperature, 25°C. It can be seen from Fig. 2 that the concentrations of Cd^{2+} ion became equal in the solutions on the normal and back-extraction sides a little less than 2 h after the beginning of the experiment. Even after that point, Cd^{2+} ion transport continued steadily against the concentration gradient of the Cd^{2+} ion, resulting in the Cd^{2+} ion becoming concentrated in the solution on

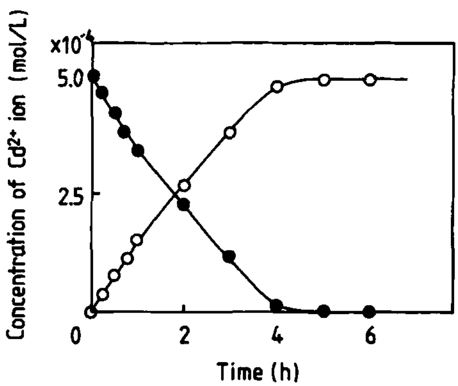

FIG. 2. Concentration of Cd^{2+} ion as a function of time for solutions of both the normal and back-extraction sides at 25°C. (●) Normal extraction side contained 5×10^{-4} mol/L $Cd(NO_3)_2$ and 0.1 mol/L LiCl. (○) Back-extraction side did not contain $Cd(NO_3)_2$ and LiCl.

the back-extraction side. For this experiment, the initial permeation velocity of the Cd^{2+} ion was calculated by

$$N = (\Delta[Cd^{2+}]/\Delta t)/A \quad (3)$$

where t is the time (s) and A is the effective area of the SLM (28.3 cm^2). To obtain the value for the initial permeation velocity, the quantity of Cd^{2+} ion transported in 30 min from the beginning of the experiment was used: the value of N was determined to be 1.81×10^{-9} mol/cm^2·s. The experimental reproducibility of the value for the permeation velocity of the Cd^{2+} ion was confirmed to be 4.8% in relative standard deviation by repeating the experiment three times under the same experimental conditions.

Effect of Ligand Species

Different SLMs containing three different dipyridyl derivative ligands, bathocuproine, bathophenanthroline, and neocuproine, were prepared and used in our transport experiments on the Cd^{2+} ion. These ligands are all derivatives of 1,10-phenanthroline, and they belong to the group of bidentate ligands which has two nitrogen atoms in the molecular structure. We have not found any detailed reports of the complex formation of these ligands with Cd^{2+} ions. They form complexes with a Cd^{2+} ion that has a coordination number of 4 in a molar ratio of 2:1, the complexes having a tetrahedral structure as in the case of copper ion. The Cd^{2+} ion can, however, have a coordination number of 6, similar to the Fe^{2+} ion, and will form ligand complexes with an octahedral structure in a molar ratio of 3:1. This complex, however, has a larger molecular diameter, resulting in slower diffusion in SLM. In addition, the formation constant of the complex must be higher than that of a Cd^{2+} ion having a coordination number of 4. For these reasons, and considering the fact that Fe^{2+} ion was not transported by our present system, complex formation with a Cd^{2+} ion having a coordination number of 6 is unlikely to occur in the SLM.

The three ligands mentioned above were compared for their carrier performance for Cd^{2+} ion transport under the following experimental conditions: Cd^{2+} ion, 5×10^{-4} mol/L; Cl^- ion, 0.1 mol/L; ligand, 1×10^{-2} mol/L; temperature, 25°C. The experimental results are shown in Fig. 3 where the Cd^{2+} ion concentration in the solution on the back-extraction side is plotted against time. As seen in Fig. 3, bathocuproine and bathophenanthroline give efficient transport of the Cd^{2+} ion and show approximately the same behavior: the permeation velocity of Cd^{2+} ion was found to be 1.09×10^{-9} for the former and 1.06×10^{-9} mol/cm²·s for the latter. For bathophenanthroline, however, Cd^{2+} ion transport showed a tendency to slow down gradually with time. This difference in behavior is thought to be caused by the differences in their solubilities in water.

Neocuproine did not show any Cd^{2+} ion transport, and it is concluded that it cannot function as a carrier. No transport of Cd^{2+} ion was observed in the case of SLM when no ligand was used.

Effect of pH

When a metallic ion and a ligand form a complex with coordination bonding, the pH value has a strong effect on the rate of complex formation.

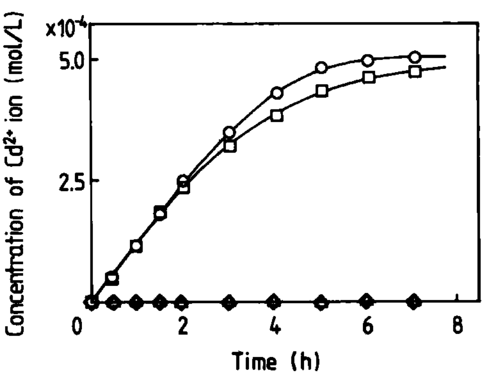

FIG. 3. Concentration of Cd^{2+} ion as a function of time for solutions of the back-extraction side against the ligand species. (○) Bathocuproine, (□) bathophenanthroline, (◇) neocuproine, and (△) without ligand.

For this reason, the pH value effect on the permeation velocity of Cd^{2+} ion was investigated by varying the pH value in the solutions on both the normal and back-extraction sides. The experimental conditions were as follows: Cd^{2+} ion, 5×10^{-4} mol/L; ligand, 1×10^{-2} mol/L; Cl^- ion, 0.1 mol/L; pH, varied from 3.2 to 9.0; temperature, 25°C. An acetic acid–sodium acetate buffer solution was used for pH lower than 5.6, and a boric acid–sodium borate buffer solution was used for pH higher than 6. Figure 4 shows the permeation velocity of Cd^{2+} ion as a function of pH value. In the pH range from 4 to 8, the permeation velocity was constant. In the pH ranges lower than 4 and higher than 8, the permeation velocity decreased rapidly. Without buffer solution (pH 5.7), the permeation velocity was steady. The transport experiments were therefore carried out without use of buffer solution. It is known that bathocuproine forms a complex with Cu^+ ion in general in the pH range from 4 to 10, and it was found to form a complex with Cd^{2+} ion in the pH range from 4 to 8.

Relation between the Initial Concentration of Cd^{2+} Ion and the Permeation Velocity

The dependence of the permeation velocity on the initial concentration of Cd^{2+} ion was examined as described below. The experimental conditions were as follows: initial concentration of Cd^{2+} ion, varied from 1×10^{-4} to 1.2×10^{-3} mol/L; Cl^- ion, 0.1 mol/L; bathocuproine, 1×10^{-2} mol/L; temperature, 25°C. Figure 5 shows the value for the permeation velocity (log N) as a function of the Cd^{2+} ion concentration (log $[Cd^{2+}]$). In the range of initial concentration of Cd^{2+} ion tested, the permeation velocity of Cd^{2+} ion increased linearly from 1.75×10^{-10} up to 2.91×10^{-9} mol/cm^2·s in proportion to the initial concentration of Cd^{2+} ion. This suggests that the diffusion of Cd^{2+} ion in the water phase to the SLM surface played

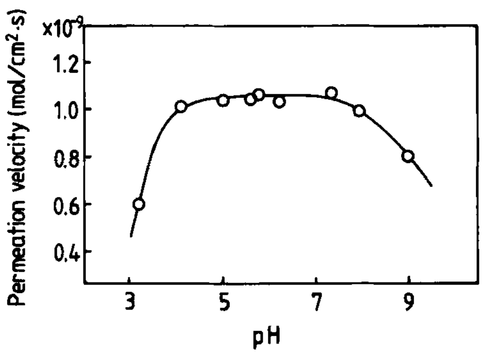

FIG. 4. Relation between the pH and the permeation velocity of Cd^{2+} ion.

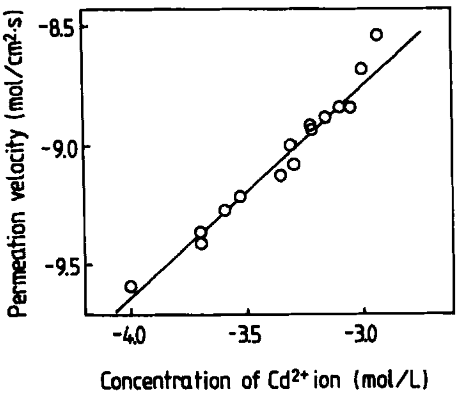

FIG. 5. Log–log diagram between the Cd^{2+} ion concentration and the permeation velocity of Cd^{2+} ion through an SLM.

an important role as a rate-determining step of Cd^{2+} ion transport because the motive force for the diffusion of Cd^{2+} ion must decrease with a decrease in the initial concentration of Cd^{2+} ion. Based on the slope of the line in Fig. 5, the permeation velocity of Cd^{2+} ion depended on the initial concentration of Cd^{2+} ion with an exponent of 0.91. Accordingly, the value for exponent a in Eq. (2) should be 0.91.

Relation between the Ligand Concentration and the Permeation Velocity

The effect of bathocuproine concentration on the permeation velocity of Cd^{2+} ion was investigated. The experimental conditions were as follows: Cd^{2+} ion, 5×10^{-4} mol/L; Cl^- ion, 1×10^{-2} mol/L; bathocuproine, varied from 5×10^{-3} to 2×10^{-2} mol/L; temperature, 25°C. The experimental results are shown in Fig. 6 where the permeation velocity (log N) is plotted against the bathocuproine concentration (log [L]). The permeation velocity of Cd^{2+} ion is observed to increase linearly in proportion to the concentration of the ligand in the SLM with a slope of 0.83. The value for exponent b in Eq. (2) should therefore be 0.83. The permeation velocity of Cd^{2+} ion would probably show an upper limit (constant permeation velocity) at a certain higher concentration of the ligand and would no longer depend on the ligand concentration due to the rate-determining diffusion of cadmium complex in the SLM, but such an upper limit was not observed in the range of ligand concentrations tested here. It was impossible to use bathocuproine at so high a concentration level because it has limited solubility in dibenzyl ether.

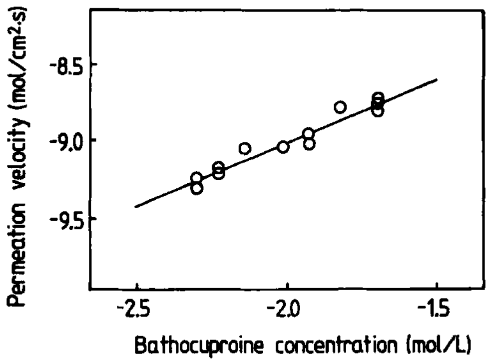

FIG. 6. Log–log diagram between the bathocuproine concentration and the permeation velocity of Cd^{2+} ion through an SLM.

Relation between the Cl^- Ion Concentration and the Permeation Velocity

In our system, Cl^- ion plays an important role in producing the driving force for Cd^{2+} ion transport, and its concentration must be directly reflected in the permeation velocity of the Cd^{2+} ion. For this reason, the effect of Cl^- ion concentration on the permeation velocity of Cd^{2+} ion was examined under the following experimental conditions: Cd^{2+} ion, 5×10^{-4} mol/L; ligand, 1×10^{-2} mol/L; Cl^- ion, varied from 5×10^{-4} to 0.3 mol/L; temperature, 25°C. The results are given in Fig. 7 where the permeation velocity (log N) is plotted against the initial concentration of Cl^- ion (log $[Cl^-]$).

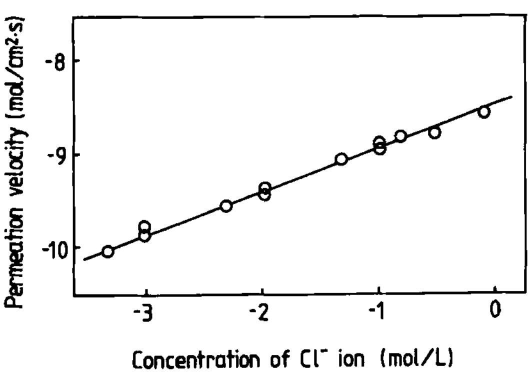

FIG. 7. Log–log diagram between the Cl^- ion concentration and the permeation velocity of Cd^{2+} ion through an SLM.

It is seen that the permeation velocity of Cd^{2+} ion increases linearly in proportion to the Cl^- ion concentration over a wide range. Cd^{2+} ion transport continues as long as the Cl^- ion concentration is sufficiently higher on the normal extraction side than on the back-extraction side even after the Cd^{2+} ion concentration becomes higher in the latter than in the former. The permeation velocity of Cd^{2+} ion depended on the Cl^- ion concentration with an exponent of 0.45. In the range of Cl^- ion concentrations tested here, diffusion of Cl^- ion in the solution on the normal extraction side to the SLM interface would be rate-determining. From the fact that no Cd^{2+} ion transport was observed in a system which did not contain Cl^- ions, it is concluded that any NO_3^- ion coexisting on the normal extraction side solution did not play a role in the driving force.

Effect of Temperature

Figure 8 shows the Arrhenius plot of the permeation velocity of Cd^{2+} ion against temperature under the following experimental conditions: Cd^{2+} ion, 5×10^{-4} mol/L; Cl^- ion, 0.1 mol/L; bathocuproine, 1×10^{-2} mol/L. In the temperature range from 20 to 50°C, the permeation velocity of Cd^{2+} ion increased gradually in proportion to the temperature at a rate of 6.73×10^{-12} mol/cm^2·s per 1°C. From this, it is suggested that the use of a higher temperature is a favorable means to increase the permeation velocity of Cd^{2+} ion in terms of activation of diffusion of Cd^{2+} and Cl^- ions in aqueous solution and, at the same time, to increase the diffusion

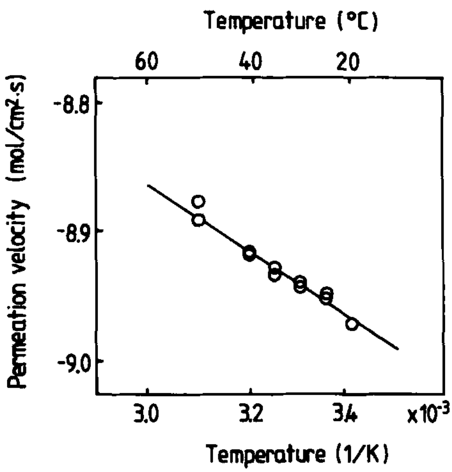

FIG. 8. Arrhenius plot of the permeation velocity of Cd^{2+} ion through an SLM against the temperature.

velocity of cadmium complex in the SLM. However, use of a higher temperature leads to the problem of SLM deterioration. The values in Fig. 8 for the permeation velocity of Cd^{2+} ion are those from the beginning of experiment and cannot involve the effect of SLM deterioration. When the temperature was higher than 50°C, however, the SLM was observed to deteriorate with the loss of dibenzyl ether and bathocuproine, resulting in a decrease in the permeation velocity of Cd^{2+} ion after several hours (6–7 h). In order to make use of the system at a higher operating temperature, the SLM would have to be prevented from deterioration by sandwiching it with some other types of hydrophilic membranes (*5*, *8*), fixing it by using polyvinyl chloride material (*6*), or continuously supplying an organic solvent to the SLM (*11*, *12*), for example.

Equation for the Permeation Velocity of Cd^{2+} Ion

For our system of Cd^{2+} ion transport through an SLM, an equation for the permeation velocity of Cd^{2+} ion was proposed as a function of three parameters: concentrations of Cd^{2+} ion, ligand, and Cl^- ion. As mentioned above, the values for the three exponents *a*, *b*, and *c* in Eq. (2) were determined to be 0.91, 0.83, and 0.45, respectively. By substituting these values into Eq. (2), the following equation was obtained:

$$N = K \cdot [Cd^{2+}]^{0.91} \cdot [L]^{0.83} \cdot [Cl^-]^{0.45} \quad (mol/cm^2 \cdot s) \tag{4}$$

To determine the permeation velocity constant *K*, the three parameters and the permeation velocity of Cd^{2+} ion were correlated by plotting their values at 25°C in a log–log diagram as shown in Fig. 9. A nearly linear

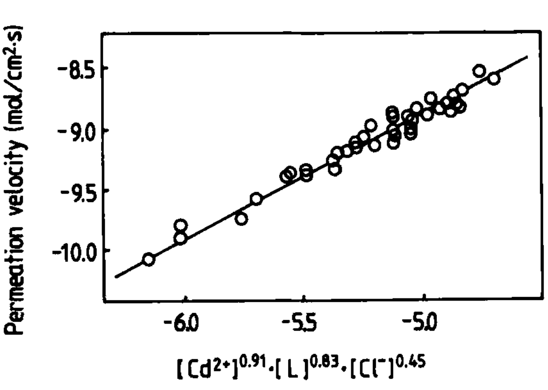

FIG. 9. Relation between the value of $[Cd^{2+}]^{0.91} \cdot [L]^{0.83} \cdot [Cl^-]^{0.45}$ and the permeation velocity of Cd^{2+} ion.

correlation was obtained in which the slope and the intercept of the line were 0.999 and −3.89, respectively. This value for the intercept must correspond to that for log K in Eq. (4), and hence the value for K was determined to be 1.29×10^{-4}. In conclusion, the permeation velocity of Cd^{2+} ion for our system at 25°C is expressed by

$$N = 1.29 \times 10^{-4} \cdot [Cd^{2+}]^{0.91} \cdot [L]^{0.83} \cdot [Cl^{-}]^{0.45} \quad (mol/cm^2 \cdot s) \quad (5)$$

CONCLUSION

With regard to Cd^{2+} ion, which is now under strict effluent control regulations as a toxic substance, we have developed a system of Cd^{2+} ion transport through an SLM containing bathocuproine as carrier. An equation for the permeation velocity of Cd^{2+} ion is proposed for our transport system at 25°C:

$$N = 1.29 \times 10^{-4} \cdot [Cd^{2+}]^{0.91} \cdot [L]^{0.83} \cdot [Cl^{-}]^{0.45} \quad (mol/cm^2 \cdot s)$$

It is expected that the transport system will be widely used in such fields as separation, concentration, and recovery of Cd^{2+} ions contained in a variety of aqueous solution samples, industrial wastewater, and so forth.

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Received by editor September 17, 1990