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Takashi Saito

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Transport of Silver(I) Ion through a Supported Liquid Membrane Using Bathocuproine as a Carrier

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

ABSTRACT

The active transport of silver ions through a supported liquid membrane (SLM) containing bathocuproine (4,7-diphenyl-2,9-dimethyl-1,10-phenanthroline) as a carrier was investigated under various experimental conditions. The magnitude of the permeation velocity of metallic ions through the SLM was in the order $Ag^+ > Cd^{2+} \gg Zn^{2+} > Cu^{2+}$ when nitrite ion was used as the pairing ion species that is cotransported with metallic ion. The permeation velocity of silver(I) ions through an SLM was dependent on the concentrations of the silver ion, bathocuproine, and nitrite ion. An equation for the transport of silver ions, consisting of three important factors, i.e., the concentrations of metallic ion, carrier, and pairing ion species, was derived.

Key Words. Silver ion; Bathocuproine; Supported liquid membrane; Permeation velocity; Permeation velocity equation

INTRODUCTION

Silver has been widely used in many commercial fields including the manufacture of photographic film and silver products and the plating treatment of metallic parts. Silver(I) ions that are included in wastewater have to be recovered because the metal is very expensive and it causes environment pollution. Therefore, the development of an effective recovery method for the metallic ions in aqueous samples is desired.

Some new transport methods of metallic ions through a supported liquid membrane (SLM) containing a carrier have recently been studied. The transport system of the targeted metallic ion using an SLM has some advantages. For example, the metallic ions can be recovered from aqueous samples using a relatively simple extraction operation, and it is easy to reuse the obtained component because it is obtained in the form of ions. The author reported some transport systems of metallic ions such as copper, cadmium, and zinc ions through an SLM containing 2,2′-dipyridyl derivative ligands such as 4,7-diphenyl-2,9-dimethyl-1,10-phenanthroline (bathocuproine) (1–6), 2,9-dimethyl-1,10-phenanthroline (neocuproine) (6), or 4,7-diphenyl-1,10-phenanthroline (bathophenanthroline) (6–8).

In this study the selective transport systems of metallic ions with many pairing ion species under various operating conditions were investigated. As a result, it was found that the transport of silver ion selectively occurred using an SLM containing bathocuproine as the carrier and nitrite ion as the pairing ion species, although the chelating agent is efficient as a carrier for Cu^+ ion (9). So the characteristics of the transport of silver ion through the SLM was examined in detail, and an equation for the permeation velocity of silver ion was determined.

EXPERIMENTAL

Reagents

Silver nitrate, sodium nitrite, and dibenzyl ether were of analytical pure grade and were obtained from Wako Pure Chemical Ind. Co. Bathocuproine, used as the carrier of silver ion, was supplied by Dojindo Lab. Co. The other reagents were purchased from Wako Pure Chemical Ind. Co.

SLM

The supporting membrane, Celgard 2500, that holds the organic solvent containing a ligand, was the same as that used in earlier papers (3–6). It was supplied by Daicel Chemical Ind. Co. The membrane had 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. The membrane was cut into circular pieces of 8 cm diameter which were impregnated with 50 μL bathocuproine solution (7.5×10^{-4} to 2×10^{-2} mol/L) in dibenzyl ether at their center that produced a 6-cm diameter circle.

Apparatus and Measurements

The apparatus used for the transport experiment of Ag^+ ion was the same as that used in our earlier papers (3–6). An SLM was sandwiched between two cylindrical glass compartments (150 cm^3 each). A solution (150 mL) consisting of Ag^+ ions (5×10^{-6} to 1×10^{-4} mol/L) and NO_2^- ions (2.5

$\times 10^{-5}$ to 0.1 mol/L) was placed in the cell to be used as the normal extraction side. Another cylinder was filled with 150 mL purified water as the backextraction side. The contents in both cells were stirred (500 rpm) at 25°C. Solutions of 1 mL each were taken from each of the cells at specific time intervals, and the Ag^+ ion concentrations in the solutions were then measured using an atomic absorption spectrophotometer (AA-680 instrument, Shimadzu Co.).

Permeation Mechanism

Bathocuproine is known to selectively form a complex with Cu^+ ion. Cu^+ ion is selectively transported using an SLM containing a bathocuproine based on the oxidation-reduction potential gradient, but in an oxidizing atmosphere system, the permeation velocity of Cu^{2+} ion is lower than that of Cu^+ ion (6). However, it is not known if bathocuproine reacts with Ag^+ ion to form a complex. Accordingly, the permeation mechanism of Ag^+ ion through an SLM was assumed to be based on that of Cu^+ ion (2, 6); it is shown in Fig. 1. On the normal extraction side, the Ag^+ ion in the solution produces coordinate bonds with the nitrogen atoms of bathocuproine at the SLM interface to form a positively charged complex ion, $[Ag{\cdot}L]^+$, which, in turn, forms an ion pair with a NO_2^- ion, i.e., $[Ag{\cdot}L{\cdot}NO_2]$. The silver complex formed in the SLM is transported to the backextraction side from the normal extraction side based on the concentration gradient of NO_2^- ion as the driving force, and after the complex is dissociated at the SLM interface of the back-extraction

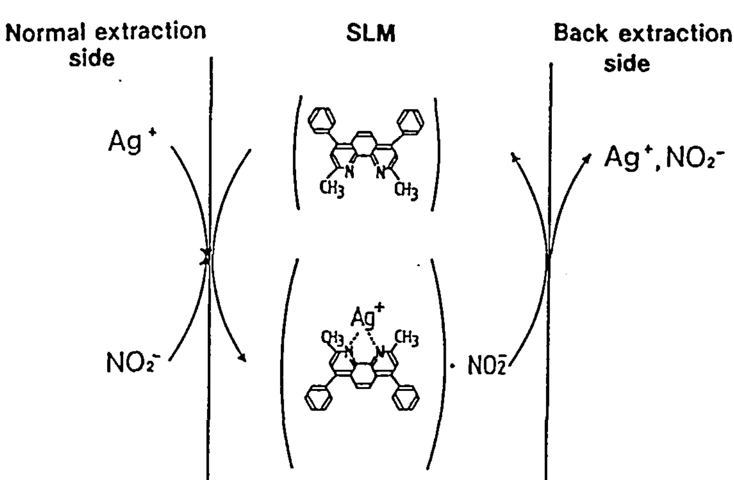

FIG. 1 Mechanism for transport of Ag^+ ion through an SLM containing bathocuproine.

side, the Ag^+ ion is released into the backextraction side solution. The complex formation of Ag^+ ion can be represented by

$$Ag^+ + NO_2^- + L \rightleftarrows [Ag \cdot L \cdot NO_2] \qquad (1)$$

The following equation is for the permeation velocity of Ag^+ ion introduced at a constant temperature. It is based on the concentrations of three parameters: Ag^+ and NO_2^- ions and bathocuproine.

$$N = K \cdot [Ag^+]^a \cdot [\text{Bathocuproine}]^b \cdot [NO_2^-]^c \qquad (\text{mol/cm}^2 \cdot \text{s}) \qquad (2)$$

where N is the permeation velocity ($\text{mol/cm}^2 \cdot \text{s}$), K is the permeation velocity constant, and $[Ag^+]$, [bathocuproine] (L), and $[NO_2^-]$ are the initial molar concentrations of each component in the solution which was prepared, and a, b, and c are the exponents of the respective parameters.

RESULTS AND DISCUSSION

Effect of Pairing Ion Species on Transport of Ag^+ Ion through an SLM

The effect of pairing ion species on the permeation transport of Ag^+ ion through an SLM containing bathocuproine was investigated under the conditions of 1×10^{-4} mol/L Ag^+ ion, 1×10^{-2} mol/L bathocuproine, and 0.1 mol/L pairing ion. The changes in Ag^+ ion concentrations versus time in the backextraction side solution for various pairing ion species and the permeation velocities of Ag^+ ion are shown in Fig. 2. The permeation velocity, N, of Ag^+ ion through an SLM was calculated as follows:

$$N = (\Delta [Ag^+]/\Delta t)/A \qquad (\text{mol/cm}^2 \cdot \text{s}) \qquad (3)$$

where $[Ag^+]$ is the molar amount (mol) of permeated Ag^+ ion per 1 L of solution on the backextraction side, t is the permeation time (s), and A is the effective area (28.3 cm^2) of an SLM.

It was found that the effect of pairing ion species as a driving force for the permeation transport of Ag^+ ion increases in the order $NO_2^- \gg NO_3^- > CH_3COO^- > HSO_3^- \gg ClO_4^- > SO_4^{2-} > S_2O_3^-$. The ratios of the permeation velocity of Ag^+ ion on various pairing ion species was $NO_2^- : NO_3^- : CH_3COO^- : HSO_3^- : ClO_4^- : SO_4^{2-} : S_2O_3^- = 1.0 : 0.50 : 0.31 : 0.19 : 0.13 : 0.054 : 0$. The permeation velocity of Ag^+ ion in the permeation transport system using a pairing ion, including a nitrogen atom as the coordination element in the molecule, was higher than that by a pairing ion that included a sulfur atom, probably because the reaction of Ag^+ ion and bathocuproine in an SLM leads to a strained complex ion of Ag^+ ion while the pairing ion containing sulfur has high stability. Additionally, when Cl^- and Br^- ions are used as a pairing ion species, Cu^+ and Cd^{2+} ions are transported with a high

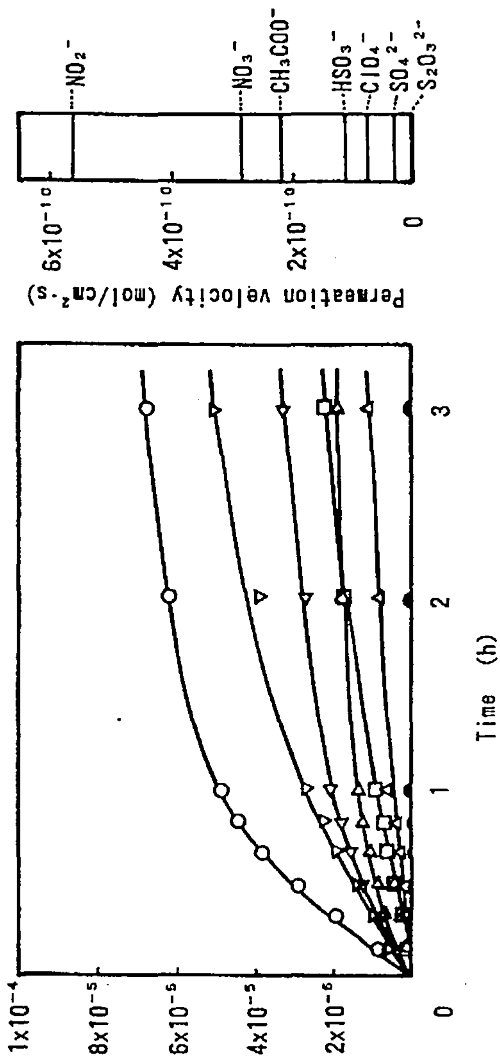

FIG. 2 Concentrations of Ag^+ ion as a function of time for solutions of the backextraction side against the anion species. (○) NO_2^-, (▽) NO_3^-, (◁) CH_3COO^-, (▷) HSO_3^-, (□) ClO_4^-, (△) SO_4^{2-}, and (●) $S_2O_3^-$.

selectivity, respectively (4). However, no transport of Ag^+ ion through the SLM was found that would produce the AgCl or AgBr precipitate.

Transport of Metallic Ions

The 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, 1×10^{-3} mol/L $NaNO_2$, and 1×10^{-2} mol/L bathocuproine. They are shown in Fig. 3.

The magnitude of the permeation velocity of metallic ions increased in the order $Ag^+ > Cd^{2+} > Zn^{2+} > Cu^{2+}$, and the ratios of the permeation velocities for their metallic ions versus that of Ag^+ ion was $Ag^+:Cd^{2+}:Zn^{2+}:Cu^{2+}$ = 1.0:0.61:0.12:0.083. Based on these results, a high transport for Ag^+ ion took place, and the permeation velocity of Ag^+ ion was 5.63×10^{-10} mol/cm^2·s. In addition, no transport of other metallic ions such as Pb^{2+}, Co^{2+}, and Fe^{3+} was found.

Effect of Ligand Species

Using SLMs containing different dipyridyl derivatives which are derivatives of 1,10-phenanthroline, the permeation velocity of Ag^+ ion was measured under the conditions of 1×10^{-2} mol/L ligand, 1×10^{-4} mol/L Ag^+

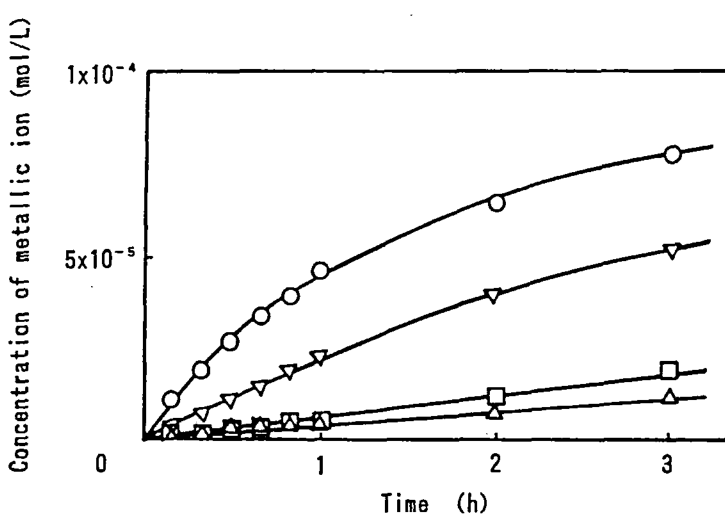

FIG. 3 Concentrations of the metallic ions as a function of time for solutions of the backextraction side against the metallic ion species. (○) Ag^+, (▽) Cd^{2+}, (□) Zn^{2+}, and (△) Cu^{2+}.

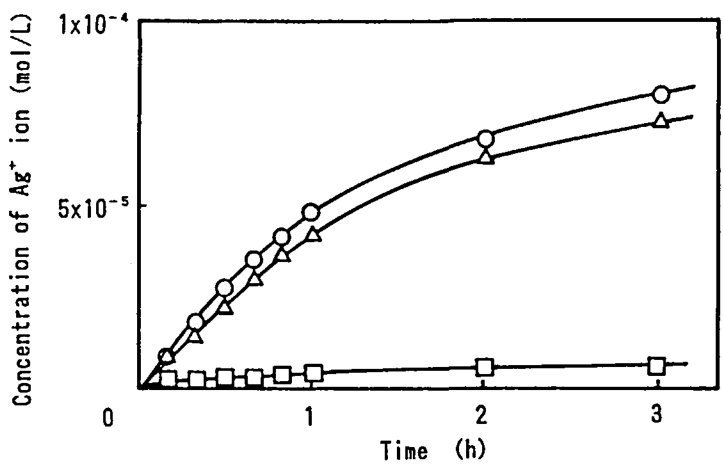

FIG. 4 Concentrations of Ag^+ ion as a function of time for solutions of the backextraction side against the carriers. (○) Bathocuproine, (△) bathophenanthroline, and (□) neocuproine.

ion, and 1×10^{-3} mol/L NO_2^- ion. Those ligands belong to the bidentate ligand groups which have two nitrogen atoms in their molecular structure. It is assumed that they form complexes at a molar ratio of 1:1 with a Ag^+ ion that has a coordination number of 2.

As carriers to transport Ag^+ ion across an SLM, bathocuproine and bathophenanthroline were superior, but neocuproine was did not work very well (Fig. 4). No transport of Ag^+ ion was observed in the case of the SLM without a ligand, i.e., for an SLM impregnated with only dibenzyl ether.

Relation between Initial Concentration of Ag^+ Ion and Permeation Velocity

The relation between the initial concentration of Ag^+ ion and the permeation velocity was examined under the experimental conditions of 5×10^{-6} to 1×10^{-4} mol/L Ag^+ ion, 1×10^{-2} bathocuproine, and 1×10^{-3} mol/L NO_2^-.

In the range of Ag^+ ion concentration tested, the permeation velocity of Ag^+ ion increased linearly from 1.79×10^{-11} to 3.08×10^{-10} mol/cm^2·s in proportion to the concentration of Ag^+ ion (Fig. 5). It is considered that the diffusion velocity of Ag^+ ion in the normal extraction side solution to the SLM surface is rate-determining in the concentration range of Ag^+ ion. The permeation velocity of Ag^+ ion through an SLM depended on the concentration of Ag^+ ion with an exponent of 1.30, based on the slope of the line in

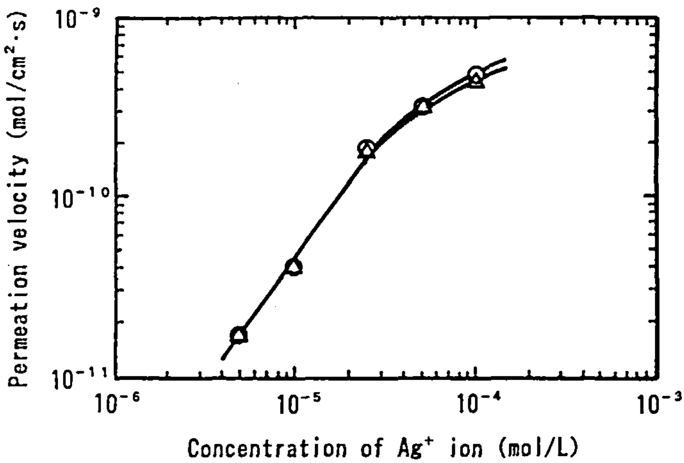

FIG. 5 Relation between the concentration of Ag^+ ion and the permeation velocity of Ag^+ ion through an SLM.

the linear range of Fig. 5. Therefore, the value for exponent *a* in Eq. (2) should be 1.30.

Relation between NO_2^- Concentration and Permeation Velocity

The effect of the concentration of NO_2^- as a pairing ion species on the permeation transport of Ag^+ ion was investigated. The concentrations of Ag^+ ion, ligand, and NO_2^- ion were 1×10^{-4}, 1×10^{-2}, and 2.5×10^{-5} to 0.1 mol/L, respectively.

Figure 6 shows the relation between the concentration of NO_2^- ion and the permeation velocity of Ag^+ ion through an SLM. A linear relation between the both parameters (NO_2^- ion concentration vs permeation velocity) was obtained in the range from 2.5×10^{-5} to ca. 1×10^{-3} mol/L NO_2^- ion, and the slope of the line was 0.330, i.e., the value for exponent *b* in Eq. (2) is 0.330.

The permeation velocity of Ag^+ ion depends on the concentration of NO_2^- ion in the range of concentration below 1×10^{-3} mol/L. On the other hand, that of the Ag^+ ion remained constant when the concentration of NO_2^- ion exceeded 1×10^{-3} mol/L. This suggests that the diffusion velocity of the Ag^+ complex in an SLM is the rate-determining step for the transport of Ag^+ ion.

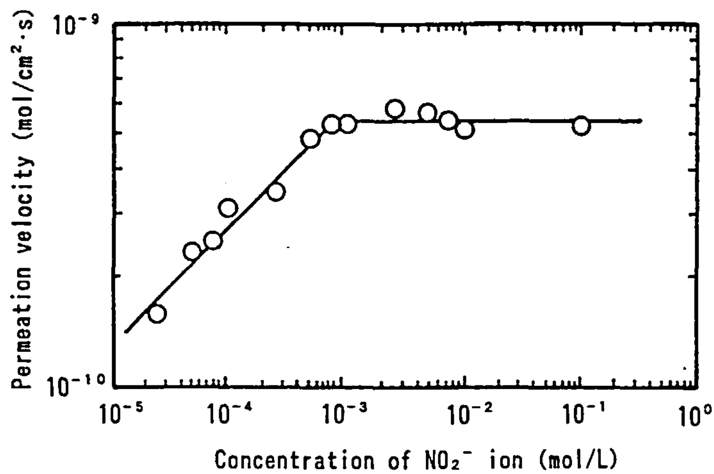

FIG. 6 Relation between the concentration of NO_2^- ion and the permeation velocity of Ag^+ ion through an SLM.

Relation between Ligand Concentration and Permeation Velocity

The permeation velocity of Ag^+ ion for various concentrations of bathocuproine in an SLM was measured under the conditions of 2.5×10^{-5}, 4.25×10^{-5}, and 1.0×10^{-4} mol/L Ag^+ ion, 1×10^{-3} mol/L NO_2^-, and 7.5×10^{-4} to 2.0×10^{-2} mol/L bathocuproine. These results are shown in Fig. 6.

The permeation velocity of Ag^+ ion increased with increasing concentration of bathocuproine for the experimental conditions below 4.0×10^{-3} mol/L ligand, and the slope of the line was 1.20. Accordingly, the value of exponent c in Eq. (2) should be 1.20. However, when the concentration of Ag^+ ion exceeded 4.25×10^{-5} mol/L, the permeation velocity of Ag^+ ion had an upper limit (3.0×10^{-10} mol/cm^2·s) over 4.0×10^{-3} mol/L ligand and no longer depended on the ligand concentration. Similarly, that of Ag^+ ion for 2.5×10^{-5} mol/L Ag^+ ion became constant (1.37×10^{-10} mol/cm^2·s) over 2.0×10^{-3} mol/L ligand. Since a constant permeation velocity was produced, it is believed that the diffusion rate of Ag^+ ion from the solution on the normal extraction side to the surface of an SLM is the rate-determining step.

Equation for the Permeation Velocity of Ag^+ Ion

For our proposed system concerning the transport of Ag^+ ion through an SLM containing bathocuproine, an equation for the permeation velocity of

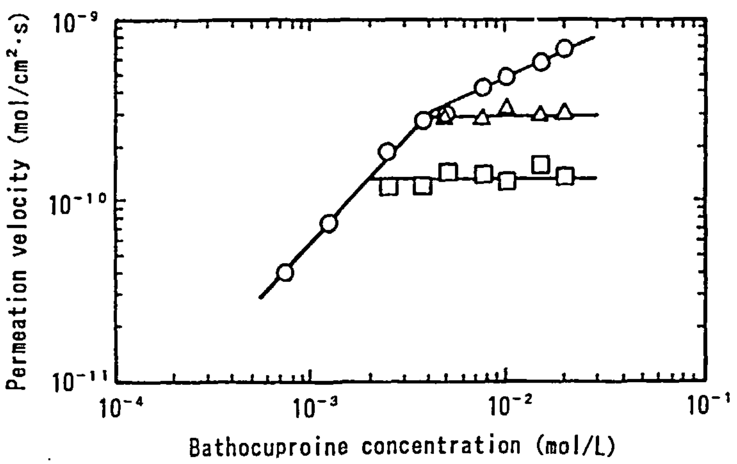

FIG. 7 Relation between the concentration of bathocuproine and the permeation velocity of Ag^+ ion through an SLM. Concentration of Ag^+ ion; (○) 1.0×10^{-4} mol/L, (△) 4.25×10^{-5} mol/L, and (□) 2.5×10^{-5} mol/L.

Ag^+ ion was determined as a function of three parameters: the concentration of Ag^+ and NO_2^- ions and the ligand. Substituting the values of the parameters into Eq. (2), the values for the three exponents a, b, and c in the equation were 1.30, 0.330, and 1.20, respectively, and the following equation was obtained:

$$N = K \cdot [Ag^+]^{1.30} \cdot [\text{bathocuproine}]^{0.330} \cdot [NO_2^-]^{1.20} \quad (4)$$

The three parameters and the permeation velocity of Ag^+ ion were correlated by plotting their values on a logarithmic graph (Fig. 7) in order to determine the permeation velocity constant, K. A nearly linear correlation between the three parameters and the permeation velocity of Ag^+ ion was obtained, and the slope and the intercept of the line were 0.998 and -0.510, respectively. The latter value must then correspond to that for log K in Eq. (4), and the value of K was estimated to be 0.309. In conclusion, the permeation velocity of Ag^+ ion for this transport system is expressed by

$$N = 0.309 \cdot [Ag^+]^{1.30} \cdot [\text{bathocuproine}]^{0.330} \cdot [NO_2^-]^{1.20} \quad (5)$$

By using the above equation for the permeation velocity of Ag^+ ion, the permeation velocity for the transport of Ag^+ ion can be estimated from each parameter of Ag^+ ion, bathocuproine, and NO_2^- ion at 25°C (Fig. 8).

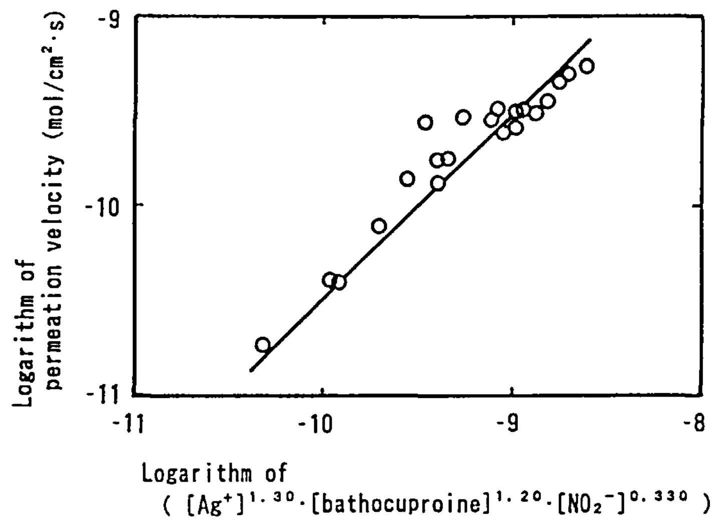

FIG. 8 Relation between the value of $[Ag^+]^{1.30}\cdot[\text{bathocuproine}]^{1.20}\cdot[NO_2^-]^{0.330}$ and the permeation velocity of Ag^+ ion through an SLM.

CONCLUSIONS

A new transport system for Ag^+ ion through an SLM containing a carrier for metallic ion was investigated in connection with three important parameters: concentrations of Ag^+ and NO_2^- ions and the carrier. As a result it became clear that the pairing ion species significantly contributes to the selective permeability of a metallic ion. The selective transport of Ag^+ ion through an SLM was achieved using NO_2^- ion as the pairing ion species with bathocuproine as the carrier. Fundamental data obtained for the proposed transport system could be used for the construction of a recovery or separation system of Ag^+ ion from industrial wastwater, environmental samples, etc.

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