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Selective and Active Transport of In^{3+} through *N*-Nitroso-*N*-*p*-octadecylphenylhydroxylamine Ammonium Salt Impregnated Membrane

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Selective and active transport of In^{3+} was studied through a polypropylene membrane impregnated with *N*-nitroso-*N*-*p*-octadecylphenylhydroxylamine ammonium salt (**3**). In^{3+} is selectively concentrated from In^{3+}–Zn^{2+}, In^{3+}–Al^{3+} and In^{3+}–Zn^{2+}–Al^{3+} mixtures by an antiport mechanism as a counter flow of H^+, respectively. The selective transport of In^{3+} was found to be attributed to the chelating affinity between **3** and In^{3+}. As a model experiment of the practical use, the separation of In^{3+} from the solution of containing 10—100 folds of Zn^{2+} was investigated. The present membrane selectively separates In^{3+}, the separation factor is 200—250. It is suggested that the present membrane system is useful for separation of indium from the ore containing indium such as the zincblende.

In connection with an increasing need for resources and energy-savings, selective separation of rare metal on aqueous phase becomes an important problem. For the separation, various technics which consume much heat and electronic energy such as adsorption, electrolysis, carbonation, sedimentation, and solvent extraction have been industrially used. On the other hand, membrane separation is one of the most promising methods of energy-saving technic. Two constitutions of liquid membrane have been reported for the membrane separation of multivalent metal ions from aqueous phase. One is liquid surfactant membrane, and the other is impregnated membrane using hydrophobic microporous membrane such as polypropylene, polyethylene, and poly(tetrafluoroethylene) as a support of the carrier. The latter is more practical and useful method, because of its stability and simplicity. In recent year, transport through impregnated membrane using chelating agents, ion-pair extractant as carriers have been investigated for the selective separation of divalent metal ion in aqueous phase. For example, transport of Cu^{2+} with LIX65N (2-hydroxy-5-nonylbenzophenone oxime), SME529 (2-hydroxy-5-nonylacetophenone oxime), bathocuproine, and thioether as a carrier,[1–5] transport of UO_2^{2+} with LIX65N and tributyl phosphate as a carrier,[6,7] transport of Zn^{2+} and Eu^{3+} with bis(2-ethylhexyl)hydrogenphosphate as a carrier[8,9] were reported. However, the carrier mediated selective transport of trivalentrare metal ions such as Ga^{3+} and In^{3+} with membrane have been scarcely studied.

In the previous paper, the authors reported the selective and active transport of Ga^{3+} from a Ga^{3+}–Al^{3+} binary solution through long-chain alkylated cupferron impregnated membrane.[10] The authors described that Ga^{3+} was selectively transported and concentrated from a Ga^{3+}–Al^{3+} binary solution by an antiport mechanism, in which long-chain alkylated cupferron played a role as carrier of Ga^{3+}, and H^+ transport was used as a driving force. Also, the authors found that long-chain alkylated cupferron selectively adsorbed Ga^{3+} with a separation factor greater than 1000, even in the presence of a large amount of Al^{3+} (Ga^{3+}:Al^{3+}, 1:200 w/w) in the acidic solution (pH=1).[11]

It is well known that indium is an important source for new semiconductor materials such as InP, InAs and InSb, and its demand is rapidly increasing. A main source of indium is leaching solution by hydrochloric acid of zincblende,[13,14] which is containing large amount of zinc and aluminum. Many informations about enrichment of indium appear in patent, they are concerned with solvent extraction, sedimentation and adsorption with chelate resin. There is no publication about the selective separation of indium with membrane. *N*-Nitrosophenylhydroxylamine ammonium salt (cupferron) is one of the most common chelating agents for multivalent metal ions. Many metal ions form cupferron chelate in acidic condition above a certain pH values characterized by every metals. In^{3+} forms cupferron-chelate in higher concentrated acid solution than Zn^{2+} and Al^{3+}.[14]

The present paper describes the selective and active transport of In^{3+} from In^{3+}–Zn^{2+}, In^{3+}–Al^{3+}, and In^{3+}–Zn^{2+}–Al^{3+} mixture through impregnated membrane with *N*-nitroso-*N*-*p*-octadecylphenylhydroxylamine ammonium salt as a carrier.

Experimental

Synthesis of *N*-Nitroso-*N*-*p*-octadecylphenylhydroxylamine Ammonium salt (3). Nitrooctadecylbenzene was synthesized as described previously.[10] The nitrooctadecylbenzene was dissolved in hexane–chloroform (90—10, v/v), and then the solution was subjected to silica-gel column (Merck, Kieselgel 60, 3.4 cmϕ×35.0 cm) to isolated *p*-nitrooctadecylbenzene (**1**); mp 42 °C. The *N*-nitroso-*N*-*p*-octadecylphenylhydroxlamine ammonium salt (**3**) was synthesized from **1** according to Fig. 1; mp 78 °C.

^{1}H NMR spectra were recorded at 270 MHz on a JEOL JNM-GX270 FTNMR spectrometer. The spectra were measured at 25 °C, using 30 g dm^{-3} $CDCl_3$ (for **1**) or 2 g dm^{-3} DMSO-d_6 (for **3**) with tetramethylsilane (TMS) as an internal

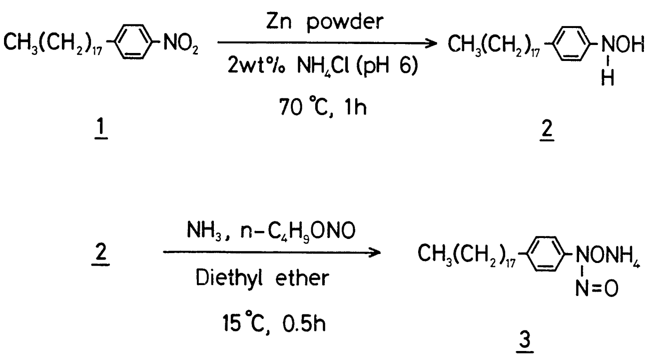

Fig. 1. Synthetic scheme of *N*-nitroso-*N*-*p*-octadecylphenylhydroxylamine ammonium salt (**3**).

standard. The ^{1}H NMR spectrum of **1** shows peaks at δ 8.13 and 7.32 for phenyl protons; 2.72, 1.65, 1.26, and 0.88 for alkyl-chain protons. The ^{1}H NMR spectrum of **3** shows peaks at δ 8.18 and 7.51 for phenyl protons; 2.73, 1.58, 1.24, and 0.86 for alkyl-chain protons. The area of peak correspond exactly with the number of protons. The raio of the peak areas for phenyl protons (8.13/7.32 for **1** and 8.18/7.51 for **3**) are around one, respectively.

IR spectra were taken on Parkin-Elmer 1750 FTIR spectrometer. The IR spectrum of **1** shows the following specific absorption bands; 1517 cm^{-1} (asymmetric stretching vibration of $-NO_2$); 1353 cm^{-1} (symmetric stretching vibration of $-NO_2$); 860 cm^{-1} (stretching vibration of –C–N=); 719 cm^{-1} (rocking bending vibration of the zigzag methylene). The IR spectrum of **3** contains the following specific absorption bands; 1430 cm^{-1} (stretching vibration of –N–N=O); 3148 cm^{-1} (stretching vibration of NH_4^+); 1411 cm^{-1} (bending vibration of NH_4^+); 719 cm^{-1} (rocking bending vibration of zigzag methylene).

Elemental analysis of **1** shows the following. Found: C, 76.90; H, 11.11; N, 3.78%. Calcd for $C_{24}H_{41}NO_2$: C, 76.80; H, 10.93; N, 3.73%. Elemental analysis of **3**: Found: C, 70.45%; H, 10.97; N, 9.92%. Calcd for $C_{24}H_{45}N_3O_2$: C, 70.76; H, 11.06; N, 10.32%.

Preparation of Membrane Containing 3. A microporous polypropylene (PP) membrane (Ube Indurstrials Ltd., 5 cm×5 cm, 30 μm thickness, 73% porosity, 0.27 μm average pore size), was used as a support of the impregnated membrane. The membrane was impregnated with **3** as follows: the microporous PP membrane was immersed in 4.91×10^{-4}—2.46×10^{-3} mol dm^{-3} kerosene solution of **3** for 30 min under ultrasonication.

Transport through the Membrane. The cell of transport through the membrane was used as described previously.[10,11] The metal ions solution were prepared by dissolving commercial indium chloride, zinc chloride, and alminum chloride in buffer solution (potassium chloride/hydrochloric acid, pH 1.0 and 2.0; potassium hydrogen phthalate/hydrochloric acid, pH 3.0; potassium hydrogen phthalate/sodium hydroxide, pH 4.0 and 4.8). The solution of metal ions (In^{3+}, Zn^{2+}, Al^{3+}, In^{3+}-Zn^{2+}, In^{3+}-Al^{3+}, and In^{3+}-Zn^{2+}-Al^{3+}) were placed on one side or both side of the membrane. The PP membrane impregnated with **3** was placed between the two chambers of the transport cell, each of which was equipped with a magnetic stirrer. The transport experiments were carried out at ambient temperature. Concentration of metal ions were mesured with a Shimadzu AA-670 atomic absorption spectrometer.

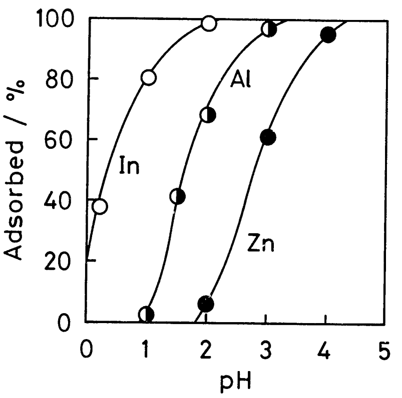

Fig. 2. Effect of pH on the adsorption of In^{3+}, Zn^{2+}, and Al^{3+} by **3**. $[In^{3+}]=[Zn^{2+}]=[Al^{3+}]=5\times10^{-3}$ mol dm^{-3}; molar ratio of In^{3+} or Al^{3+} to **3**=1:3; molar ratio of Zn^{2+} to **3**=1:2; adsorption time 8 h. Adsorbed/% is defined as $([M]_0-[M]_r)/[M]_0\times100$, where $[M]_0$ and $[M]_r$ are the concentration of metal ions in the initial and residual solutions, respectively.

The flux is defined from the concentration of metal ions in the chamber as

$$J=\frac{M}{A\ t} \qquad (1)$$

where, J is flux (mol cm^{-2} s^{-1}) of metal ions; M is transported metal ions (mol); A is membrane area (cm^2); t is transporting time (s).

Results and discussion

Interaction of 3 and Metal Ions. The interaction of carrier and substrate is one of the essential factors which governs the selectivity of the transport through membrane. In present paper, the interaction of **3** and metal ions were investigated by means of the adsorption of metal ions by **3**. **3** was added to aqueous solutions of metal ions at certain pH, and vigorous stirring at an ambient temperature. Adsorbed metal ions were estimated by measuring the concentration of metal ions in the residual aqueous solution. In Fig. 2, the adsorpbed of metal ions on **3** are plotted against the pH of the initial aqueous solution. The adsobed metal increased with pH. Every metal ions has a characteristic pH-adsorption profiles. The amount of In^{3+} adsorbed on **3** at lower pH values is more than Zn^{2+} and Al^{3+}. It is suggested that the hydrophobic membrane containing **3** can selectively transport In^{3+} other than Zn^{2+} and Al^{3+}.

The Effect of pH and Carrier Concentration on Transport of Metal Ion. Taking into account the above characteristics of **3**, the transport of In^{3+}, Zn^{2+}, and Al^{3+} through the membrane cansisting of **3** in kerosene/PP microporous membrane (**3**/PP membrane) was studied. The effect of pH on the flux of metal ions through the **3**/PP membrane is shown in Fig. 3. The initial concentration of metal ions of the feed side (L side) and the pH of the permeate side (R side) were maintained 5×10^{-3} mol dm^{-3} and about 0.5, respectively. Of every metal ion, the flux increased with increasing pH (pH of the L side −pH of the R side), as was expected from the fact that the adsorption of metal ions on **3** increased with pH. Also, the flux of In^{3+} exceeds that of Zn^{2+} or Al^{3+}. For example, in the case of the pH 3 (the initial pH of L side), the In^{3+} flux is about 35 folds of Al^{3+} flux and about 190 folds of Zn^{2+} flux, respectively. It is considered that the **3**/PP membrane function as selective and active transport membrane of In^{3+} from In^{3+}–Zn^{2+} and/or In^{3+}–Al^{3+} mixture. Figure 4 shows the effect of concentration of **3** in the membrane on In^{3+} flux. In this concentration range, In^{3+} flux was proportional to the concentration of **3**. The membrane without **3** did not show observable tranport of In^{3+}. It is suggested that **3** play a role as carrier of metal ions, the driving force of transport is a counter flow of H^+.

Selective and Active Transport of In^{3+} through 3/PP Membrane. The typical time–transport curves of In^{3+} are shown in Figs. 5, 6, and 7. The concentration of In^{3+} on the R side increased, while that on the L side inversely decreased. No transfer of chloride anion from the L side to the R side was observed during the transport experiment. At the initial stage of transport, change of pH of L side was negligible. However, pH of L side was slightly decreased with time. As a control experiment, In^{3+} solution without buffer was placed on the L side of the membrane, and then transport experiment was carried out. Adjusting the pH of the L side being ca. 5, the pH of the L side was extremely decreased with the transfer

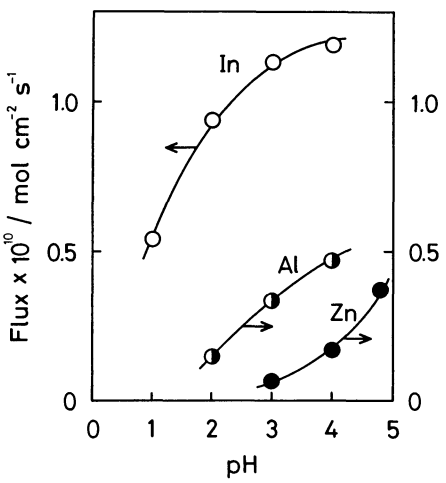

Fig. 3. Effect of pH of the feed side on the fluxes of In^{3+}, Zn^{2+}, and Al^{3+} through the **3**/PP membrane. Initial conditions. R side, pH 0.5; L side, [M]= 5×10^{-3} mol dm^{-3}, [**3**]=2.46×10^{-3} mol dm^{-3}.

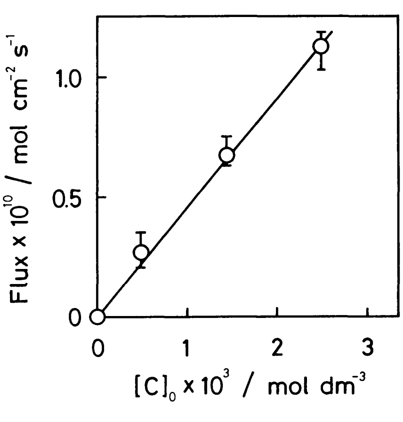

Fig. 4. Effect of carrier concentration on the flux of In^{3+} through the **3**/PP membrane. $[In^{3+}]_R=[In^{3+}]_L=3\times10^{-3}$ mol dm^{-3}; R side, pH 0.5; L side, pH 3.0.

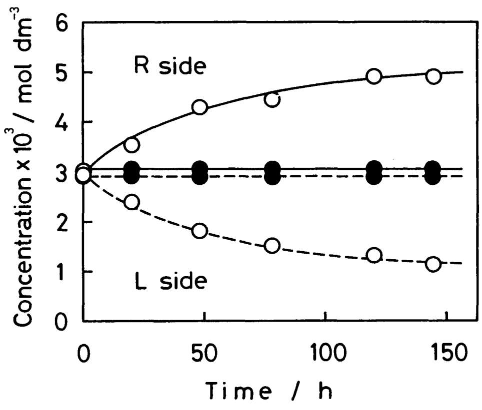

Fig. 5. Time-transport curve of the In^{3+}–Zn^{2+} binary solution through **3**/PP membrane. Initial conditions. $[In^{3+}]=[Zn^{2+}]=3\times10^{-3}$ mol dm^{-3}; L side, pH 0.5; L side, pH 3.0; ○, In^{3+}; ●, Zn^{2+}; —, R side; ----, L side.

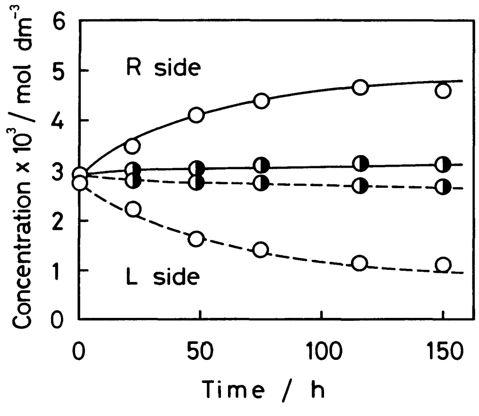

Fig. 6. Time-transport curve of the In^{3+}–Al^{3+} binary solution through **3**/PP membrane. Initial conditions. $[In^{3+}]=[Al^{3+}]=3\times10^{-3}$ mol dm^{-3}; R side, pH 0.5; L side, pH 3.0; ○, In^{3+}; ◑, Al^{3+}; —, R side; ----, L side.

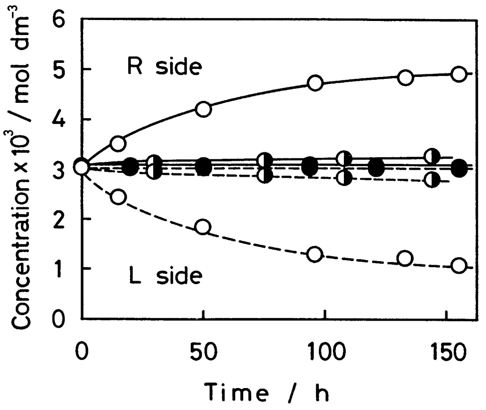

Fig. 7. Time-transport curve of the In^{3+}–Zn^{2+}–Al^{3+} ternary solution through **3**/PP membrane. Initial conditions. $[In^{3+}]=[Zn^{2+}]=[Al^{3+}]=3\times10^{-3}$ mol dm^{-3}; R side, pH 0.5; L side, pH 3.0; ○, In^{3+}; ●, Zn^{2+}; ◑, Al^{3+}; —, R side; ----, L side.

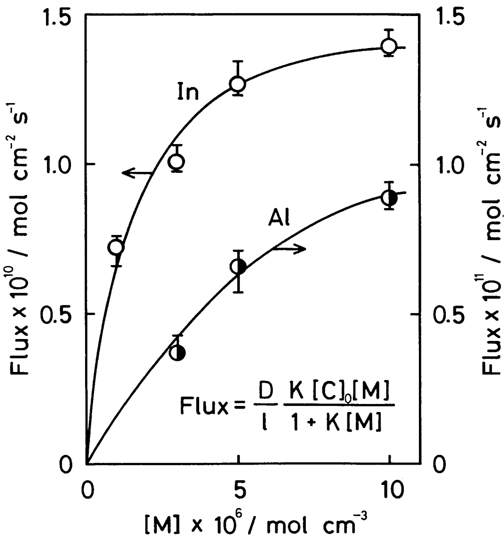

Fig. 8. Effect of initial concentration of metal ion on the fluxes of In^{3+} and Al^{3+} in the In^{3+}–Al^{3+} binary solution through **3**/PP membrane. $[C]_0=2.46\times10^{-3}$ mol dm^{-3}; $[In^{3+}]/[Al^{3+}]=1.0$; R side, pH 0.5; L side, pH 3.0.

of In^{3+}. These results support that the driving force of the In^{3+} transport is counter-flow of the H^+ from the R side to the L side. On the other hand, the concentration change of Zn^{2+} and Al^{3+} was hardly observed during the transport experiment. The order of the concentration change of metal ion is the following: $In^{3+} \gg Al^{3+} > Zn^{2+}$. This order coincides with that of the flux in the single component system as shown in Fig. 3. Namely, it is concluded that the present membrane selectively and actively transports In^{3+} from In^{3+}–Zn^{2+}, In^{3+}–Al^{3+}, and In^{3+}–Zn^{2+}–Al^{3+} mixtures by an antiport mechanism.

Figure 8 shows the dependance of the initial flux on the concentration of metal ion on L side in In^{3+}–Al^{3+} binary system. The pH of L side and that of R side are 0.5 and 3.0, and the concentration of **3** in the membrane is 2.46×10^{-3} mol dm^{-3}. The relationship of the initial flux and the concentration of metal ion on L side indicates a Michaelies–Menten type profile. This result supports a carrier-mediated transport for In^{3+} and Al^{3+} through **3**/PP membrane. The flux is presented by the following equation:

$$J = \frac{D}{l}\frac{K[C]_0[M]}{1+K[M]} \tag{2}$$

In this equation, J is the flux of metal ions; K is the complex formation constant between **3** and metal ions; D is diffusion coefficient of the complex in the membrane; $[C]_0$ denotes the concentration of **3** in the membrane; [M] is concentration of metal ion. In these concentration region, In^{3+} flux is larger than Al^{3+} flux, that is, In^{3+} is selectively transported by **3**/PP membrane. Also, the ratio of In^{3+} flux and Al^{3+} flux in the present system is nearly equal to that in the single component system (Fig. 3). The selectivity is one of most important function of membrane. In the present membrane, the selectivity can represent by the ratio of the flux of each metal ion in the mixture transport system. In the case of carrier-mediated transport, the selectivity is governed by the complex formation constant between the carrier and the transport species and/or the diffusion coefficient of the complex in the membrane. In order to evaluate the high selectivity of the present membrane for In^{3+} transport in In^{3+}–Al^{3+} binary system, a Lineweaver–Burk plot (Fig. 9) was obtained by using data shown in Fig. 8. The slope and the intercept of the line in Fig. 9 gave value of K and D. The results are shown in Table 1. The difference of the diffusion coefficient, D, is small, because of the ionic radii of In^{3+} and Al^{3+} are 0.81×10^{-8} cm and 0.55×10^{-8} cm, respectively. While, the complex formation constant, K, of In^{3+} is approximetely 50 fold of K for Al^{3+}. These results show that selective transport of In^{3+} through the present membrane is largely attributed to the chelate interaction between In^{3+} and **3**.

The interactions between In^{3+}, Zn^{3+}, or Al^{3+} and **3** were also investigated by FTIR spectrometry. The band shift of stretching vibration of *N*-nitroso moiety (–N–N=O) in the infrared spectra of treated **3** with In^{3+}, Al^{3+}, and Zn^{2+} are summarized in Table 2, which shows that interaction towared **3** decreases in the following order: $In^{3+} \gg Al^{3+} > Zn^{2+}$. This order is in accord with that of the flux in Fig. 4. This result suggested that *N*-nitrosohydroxyamino group in **3** may interact with In^{3+} more preferential than Al^{3+} and Zn^{2+}. As a result, the selective transport of In^{3+} is achieved by PP membrane containing **3**. These FTIR data support the carrier-mediated selective transport of In^{3+} through the present membrane.

Selective Separation of In^{3+} in the Presence of Large Amount of Zn^{2+}. As described above, indium is found mainly in zincblende with large amount of zinc. A leaching residue of zincblende with hydrochloric acid is one of a raw material of indium. Accordingly, the present study was investigated with selective separation of In^{3+} in the presence of large amount of Zn^{2+}. The metal ion solution containing from 10 to 100 folds of Zn^{2+} to In^{3+} was placed on the L side chamber. The pH's of R side and L side is 0.5 and 3.0, respectively. Selectivity was evaluated by separation factor as follows:

$$\text{Separation factor} = \frac{[In^{3+}]_R/[Zn^{2+}]_R}{[In^{3+}]_L/[Zn^{2+}]_L} \tag{3}$$

where a denominater and a numerator express initial concentration of metal ions on the L Side and concentration of metal ions on the R side after 24 hours, respectively. Obtained results are shown in Table 3. In these ratio of initial concentration, **3**/PP membrane has been achieved selective separation of In^{3+}. These separation factors indicate the close value to the ratio of flux of In^{3+} and Zn^{2+} (In^{3+}flux/Zn^{2+}-flux=about 190) in the single component transport experiment as shown in Fig. 3. The high selective separation of In^{3+} is caused by complex formation between In^{3+} and **3**. It is found that the present membrane can selectively separate In^{3+} even in the presence of large amount of Zn^{2+} in the above conditions. This result suggests that indium is selectively separated from acidic residue of indium containing ore such as zincblende by the present membrane system.

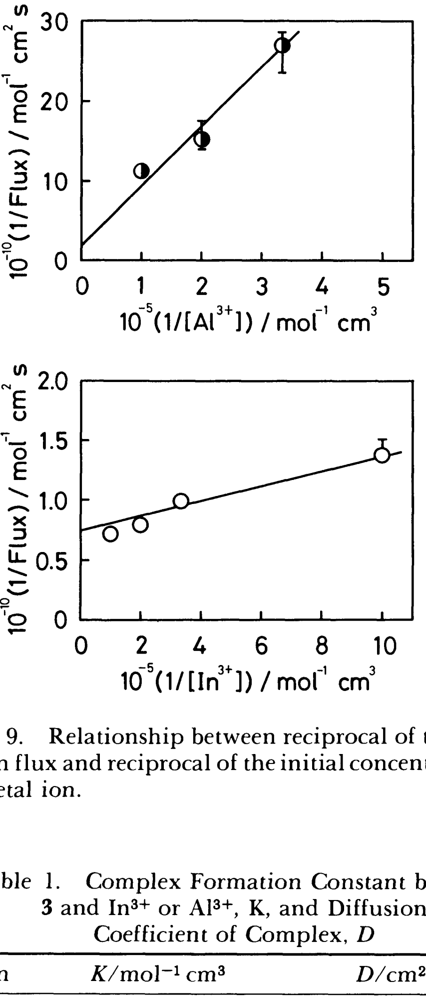

Fig. 9. Relationship between reciprocal of the metal ion flux and reciprocal of the initial concentration of metal ion.

Table 1. Complex Formation Constant between **3** and In^{3+} or Al^{3+}, K, and Diffusion Coefficient of Complex, *D*

Ion	K/mol^{-1} cm^3	D/cm^2 s^{-1}
In^{3+}	$(1.20\pm0.33)\times10^6$	$(1.63\pm0.10)\times10^{-7}$
Al^{3+}	$(2.66\pm0.98)\times10^4$	$(0.62\pm0.21)\times10^{-7}$

In conclusion, the membrane impregnated with **3** has been achieved selective and active transport of In^{3+} from In^{3+}-Zn^{2+}, In^{3+}-Al^{3+}, and In^{3+}-Zn^{2+}-Al^{3+} mixture. The transport of metal ions through the present membrane shows a Michaelies-Menten type profile. It is found that the chelate interaction between **3** and In^{3+} is cause of the selectivity for In^{3+} by the present

Table 2. Results of Spectroscopic Measurement of **3** Treated with Various Metal Ion by FTIR

Metal ion	$\nu_{\text{-N-N=O}}$/cm^{-1}
Non	1430
In^{3+}	1362
Al^{3+}	1407
Zn^{2+}	1421

3, 1.8×10^{-4} mol; $[In^{3+}]=[Al^{3+}]=[Zn^{2+}]=10^{-2}$ mol dm^{-3}, 100 cm^3; **3** was added to aqueous solution of metal ions at pH 3, and vigorous stirring at ambient temperature for 6 h with N_2 gas bubbling. The resulting product was dried under vacuum at ambient temperature for 48 h.

Table 3. Selective Separation of In^{3+} in the Presence of Large Amount of Zn^{2+} through the **3**/PP Membrane

$[M]_L\times10^3$/mol dm^{-3} a)		$[M]_R\times10^4$/mol dm^{-3} b)		Separation factor
In^{3+}	Zn^{3+}	In^{3+}	Zn^{3+}	
1.00	10	5.18	0.23	225
1.00	20	5.14	0.41	251
1.00	50	4.65	0.98	237
1.00	100	3.76	1.73	217

Concentration of **3**, 2.46×10^{-3} mol dm^{-3} kerosene solution; ambient temperature. a) Initial concentration of metal ion in L chamber. b) Concentration of metal ion in R chamber after 24 h.

membrane. Furthermore, the present membrane functions as selective separation membrane of In^{3+} in the presence of large amount of Zn^{2+}.

References

1) R. W. Baker, M. E. Tuttle, D. J. Kelly, and H. K. Lonsdale, *J. Memb. Sci.,* **2**, 213 (1977).

2) T. Largman and S. Sifniades, *Hydrometallurgy,* **3**, 153 (1978).

3) T. Imato, H. Ogawa, S. Morooka, and Y. Kato, *J. Chem. Eng. Jpn.,* **14**, 289 (1981).

4) S. Matsuno, A. Ohki, M. Takagi, and K. Ueno, *Chem. Lett.,* **1981**, 1543.

5) A. Ohki, T. Takeda, M. Takagi, and K. Ueno, *J. Membr. Sci.,* **15**, 231 (1983).

6) K. Akiba and T. Kanno, *Sep. Sci. Tech.,* **18**, 831 (1983).

7) T.-C. Huang and C.-T. Huang, *J. Membr. Sci.,* **29**, 295 (1986).

8) T.-C. Huang and R.-S. Juang, *J. Membr. Sci.,* **31**, 195 (1987).

9) P. R. Danesi, E. P. Horwitz, and P. Rickert, *Sep. Sci. Tech.,* **17**, 1183 (1982).

10) T. Shimidzu and H. Okushita, *J. Membr. Sci.,* **27**, 349 (1986).

11) T. Shimidzu and H. Okushita, *J. Chem. Soc., Chem. Commun.,* **1986**, 1173.

12) "Kagaku Binran, Oyokagakuhen I," Maruzen, Tokyo (1986) p. 347.

13) C. Reid, *Chem. Ind.,* **58**, 837 (1939).

14) N. H. Furman, W. B. Mason, and J. S. Pekola, *Anal. Chem.,* **21**, 1325 (1949).