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Selective Transport of Alkali and Alkaline Earth Metallic Ions through a Supported Liquid Membrane Containing Tripentyl Phosphate as a Carrier

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ABSTRACT

A selective transport system for alkali and alkaline earth metallic ions with a perchlorate ion as a pairing ion species through a supported liquid membrane (SLM) containing tripentyl phosphate (TPP) as a carrier is described. The SLM used is a porous polypropylene membrane impregnated with TPP solution in *o*-nitrophenyloctylether. The effects of the pairing ion species, the initial perchlorate concentration, and the TPP concentration on metallic ion transportability are examined under various experimental conditions. The permeation velocities of the metallic ions in the transport system followed the sequence $Li^+ \gg Na^+ > K^+ > Mg^{2+}$; that is, a highly selective transport for Li^+ ion was observed. Compared with the transport rates of alkali metallic ions, those of transition metallic ions such as Cu^{2+} and Fe^{3+} ions are very low. The permeation velocities of alkali and alkaline earth metallic ions through an SLM are dependent on the concentrations of perchlorate and TPP. Equations for the permeation velocities of Li^+, Na^+, K^+, and Mg^{2+} ions through an SLM, based on two concentrations of perchlorate and TPP, are proposed.

Key Words. Alkali and alkaline earth metallic ions; Supported liquid membrane; Tripentyl phosphate; Equation for permeation velocity

INTRODUCTION

Many transport systems for metallic ions through a supported liquid membrane (SLM) containing a chelating agent as a carrier have recently been studied. Reports on the transport of alkali and/or alkaline earth metallic ions using an SLM have rarely appeared because the abilities for complex formation of their ions are very low. For example, transport systems for alkali and alkaline earth metallic ions through an organic liquid membrane, including monensin (1, 2) or crown ether compounds (3–11), such as 12-crown-6, dibenzo-12-crown-6, and dicyclohexyl-18-crown-6, have been investigated. However, the cost of using their ligands on an industrial scale is high because the crown ether compounds mentioned above are generally expensive.

In recent years the transport systems for some amino acids through an SLM containing a trialkyl phosphate ester, such as tributyl phosphate or tripentyl phosphate (TPP) as a carrier, and using a driving force supplied by the concentration gradient of hexafluoro phosphate ion or perchlorate ion, were reported (12, 13). We describe how some alkali metallic ions are cotransported with amino acids such as leucine, phenylalanine, and valine in our study of the transport system. It is suggested that trialkyl phosphate ester acts as a carrier of the alkali metallic ion. We were interested in the cotransport phenomenon of metallic ions. We have studied a transport system for alkali and alkaline metallic ions through an SLM including TPP and investigated the selectivity for metallic ions in the transport system. It was found that high permeation velocity and selectivity for Li^+ ion were obtained by the use of SLMs containing TPP.

EXPERIMENTAL

Reagents

The TPP used as a carrier for metallic ions was of analytical pure grade from Tokyo Kasei Co., and *o*-NPOE (*o*-nitrophenyloctylether) as a solvent for the membrane was purchased from Dojindo Laboratory Co. Lithium perchlorate trihydrates, sodium perchlorate, potassium perchlorate, magnesium perchlorate, and other compounds were of analytical pure grade and were supplied by Wako Pure Chemical Industries Co.

SLM

A microporous polypropylene membrane, Celgard 2500 (Daicel Chemical Industries Co.), with a pore size of 0.04–0.4 μm, a thickness of 25 μm, and a porosity of 45%, was used as a supporting medium to hold *o*-NPOE solution containing TPP. The membrane was cut into circular pieces of 8 cm diameter which were each impregnated with 50 μL TPP solution in *o*-NPOE in a concentration ranging from 0.324 to 1.62 mol/L by using a microsyringe at their center to give a circle of 6 cm diameter. The TPP concentrations in these SLMs were estimated to be in the range from 5×10^{-3} to 2.5×10^{-2} g/cm^2.

Apparatus and Measurement

The apparatus used for the transport experiment was the same as that used in an earlier paper (14). An SLM containing TPP was placed between two cylindrical glass cells of 150 cm^3 each. Equal volumes (150 mL) of the solution of the metallic ion (1×10^{-2} to 0.1 mol/L) and perchlorate ion (1×10^{-2} to 0.1 mol/L) as the normal extraction side and of deionized water as the back-extraction side were placed concurrently into the two compartments. The solutions in both cells were stirred with waterproof magnetic stirrers at a rate of 500 rpm in a water bath of 25°C during the metallic ion transport. Aliquots (1 mL) of the solutions in both phases were taken at definite time intervals. The concentrations of the metallic ions in the solution were then measured by atomic absorption spectrophotometry (AA-680 instrument, Shimadzu Co.).

Fundamental Equation for Permeation Velocity of Metallic Ion

A metallic ion, M^{n+}, in the normal extraction side solution is caught by the TPP at the SLM interface and forms a positive-charged complex ion $[M{\cdot}TPP]^{n+}$ with a positive charge, which then forms an ion pair with perchlorate ions, $nClO_4^-$ ions, to produce a neutral complex $[M{\cdot}TPP{\cdot}(ClO_4)_n]$ which dissolves and diffuses in the liquid membrane. The complex is transported from the normal extraction side to the back-extraction side in the SLM by the concentration gradient of the metallic and perchlorate ions and dissociates there, freeing the M^{n+} and $nClO_4^-$ ions into the aqueous solution. The freed TPP remains in the SLM and again acts as a carrier for the metallic ion. As a result, continuous transport of metallic ions occurs from the normal extraction side to the back-extraction side. The complex formation of alkali or alkaline earth metallic ions can be represented by

$$M^{n+} + nClO_4^- + TPP \rightleftarrows [M{\cdot}TPP{\cdot}(ClO_4)_n] \qquad (1)$$

For the transport system, the following equations for the permeation velocities of alkali and alkaline earth metallic ions are introduced at a constant temperature. The equation is based on the concentrations of two parameters, perchlorate and TPP, which have an effect on the permeation velocity.

$$N_A = K_A{\cdot}[M_AClO_4]^a{\cdot}[TPP]^b \qquad (mol/cm^2{\cdot}s) \qquad (2)$$

$$N_{AE} = K_{AE}{\cdot}[M_{AE}(ClO_4)_2]^c{\cdot}[TPP]^d \qquad (mol/cm^2{\cdot}s) \qquad (3)$$

where N_A and N_{AE} are the permeation velocities of alkali and alkaline earth metallic ions, respectively; K_A and K_{AE} are the permeation velocity constants of alkali and alkaline earth metallic ions, respectively; $[M_AClO_4]$, $[M_{AE}(ClO_4)_2]$, and [TPP] are the concentrations of the respective compounds (mol/L); and a, b, c, and d are the exponents of the respective parameters.

RESULTS AND DISCUSSION

Effect of Anion Species

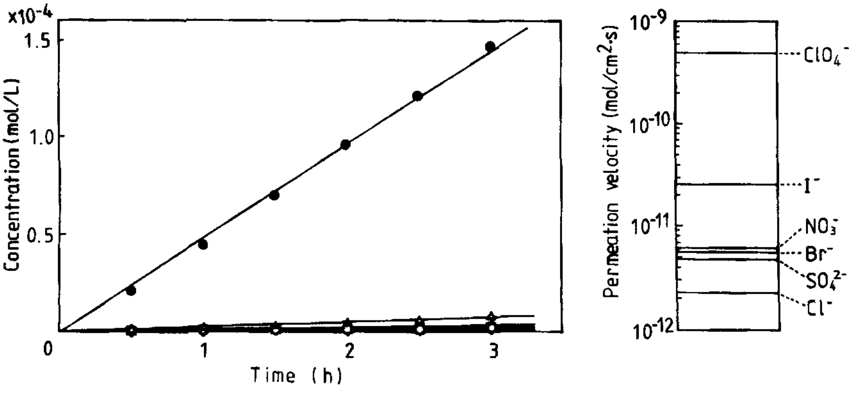
The effect of anion species as a pairing ion on the transport of Na^+ ion through an SLM containing TPP was investigated under the experimental conditions of 1.62 mol/L TPP and 0.1 mol/L Na^+ ion. The anion species used were Cl^-, Br^-, I^-, NO_3^-, ClO_4^-, and SO_4^{2-} ions.

The time courses of Na^+ ion concentrations in the back-extraction side solutions on some pairing ion species and the permeation velocities of Na^+ ion are shown in Fig. 1. The initial permeation velocity (N) of metallic ion, M^{n+}, through an SLM was calculated as follows:

$$N = (\Delta[M^{n+}]/\Delta t)/A \qquad (\text{mol/cm}^2\text{·s}) \tag{4}$$

where t is time (in seconds) and A is the effective area of an SLM (28.3 cm^2).

As a result, the driving force vis-à-vis the anion species, which is co-transported with Na^+ ion, followed the sequence $ClO_4^- \gg I^- > NO_3^- > Br^+ > SO_4^{2-} > Cl^+$. Compared with the permeation velocity of Na^+ ion



(A) (B)

FIG. 1 Concentrations of Na^+ ion as a function of time for solutions of the back-extraction side of some pairing ion species (A) and the permeation velocities of Na^+ ion (B). (●) ClO_4^- ion, (△) I^- ion, (□) NO_3^- ion, (▽) Br^- ion, (◇) SO_4^{2-} ion, (○)Cl^- ion.

using ClO_4^- ion as a pairing ion, the ratios of the permeation velocities of Na^+ ion using the other anion species were found to be $ClO_4^- : I^- : NO_3^- : Br^- : SO_4^{2-} : Cl^- = 1:0.068:0.017:0.016:0.013:0.006$, which means that a higher hydrophobic anion species gave a higher permeation velocity of Na^+ ion. The cause is assumed to be as follows. The hydrophobic anion species destroy the structure of the water molecules surrounding them. Hence ions with a higher hydrophobicity are supposed to be more strongly destructive and less likely to hydrate. It can therefore be assumed that the ClO_4^- ion easily forms an ion pair with a positive-charged complex ion ($[Na \cdot TPP]^+$) which is more readily extractable into an organic solvent at the SLM interface.

The reproducibility of the value (4.94×10^{-10} mol/cm^2·s) for the permeation velocity obtained by a permeation experiment with Na^+ ion using ClO_4^- ion as a pairing ion was such that the relative standard deviation calculated in experiments repeated seven times under the conditions in Fig. 1 was 4.4%.

Transports of Monovalent and Polyvalent Metallic Ions

Changes with time in the concentrations of metallic ions in the aqueous phase on the back-extraction side and the permeation velocities of their ions are shown in Fig. 2. The experimental conditions were as follows: initial concentrations of the metallic and ClO_4^- ions in the aqueous phase

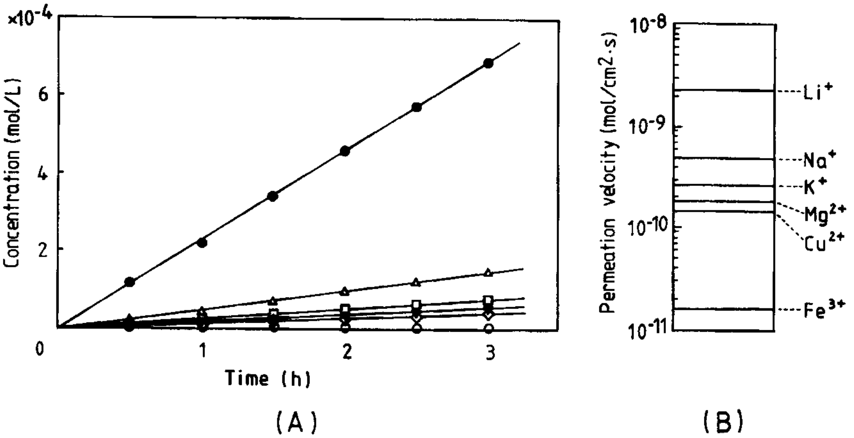


FIG. 2 Concentrations of metallic ions as a function of time for solutions of the back-extraction side on some metallic ion species (A) and the permeation velocities of their metallic ions (B). (●) Li^+ ion, (△) Na^+ ion, (□) K^+ ion, (▽) Mg^{2+} ion, (◇) Cu^{2+} ion, (○) Fe^{3+} ion.

on the normal extraction side, 0.1 and 0.1 mol/L, respectively; concentration of TPP, 1.62 mol/L.

The magnitude of the permeation velocity in the transport of metallic ions by SLMs using TPP as a carrier was in the order of monovalent > divalent > trivalent metallic ions, and the ratios of the permeation velocities for their cations against that of Li^+ ion were $Li^+:Na^+:K^+:Mg^{2+}:Cu^{2+}:Fe^{3+} = 1:0.184:0.106:0.0890:0.0721:0.00803$. Accordingly, it is obvious that TPP as a carrier possesses higher selectivities for alkali metallic ions than alkaline earth metallic ions and other metallic ions.

When a complex is formed at an SLM interface, the metallic–TPP complex ion ($[M \cdot TPP]^{n+}$), which has a positive charge consisting of *n*-valent, reacts with *n* mol of ClO_4^- ion to produce a neutral complex. It is therefore considered that the size of the molecule of the neutral complex consisting of a polyvalent metallic ion is larger than that consisting of a monovalent metallic ion. Accordingly, when their complexes diffuse from the normal extraction side to the back-extraction side in an SLM, the larger complexes (Fe–TPP and Cu–TPP complexes) show a larger resistance to diffusion by steric hindrance, resulting in a low rate of permeability for their metallic ions.

Relation between the Perchlorate Concentration and the Permeation Velocity

The effect of the initial concentration of metallic ion on the permeation velocity of the metallic ion was studied. The experimental conditions were as follows: concentration of TPP in the SLM, 1.62 mol/L; initial concentrations of metallic ion in the solution on the normal extraction side, 5×10^{-3} to 0.15 mol/L.

In Fig. 3 the relation between the initial concentration of perchlorate and the permeation velocity of the metallic ion is shown. In the range of the perchlorate concentrations mentioned above, linear relations were established between both parameters for the aforesaid metallic ions. The slopes of their lines for Li^+, Na^+, K^+, and Mg^{2+} ions were 1.40, 1.40, 1.59, and 1.96, respectively.

The ratios of the permeation velocities for the respective metallic ions against that of Li^+ ion are shown in Fig. 4. The metallic ion selectivities for the transport of alkali and alkaline earth metallic ions by an SLM containing TPP as a carrier follow the sequence $Li^+ \gg Na^+ > K^+ > Mg^{2+}$. It is considered that the main cause of the selectivities for these metallic ions is as follows. The electronegativities of Li^+, Na^+, K^+, and Mg^{2+} ions by the Pauling rule are 1.0, 0.9, 0.8, and 1.2 (0.6 per one positive charge), respectively. Accordingly, it is found that metallic ions which

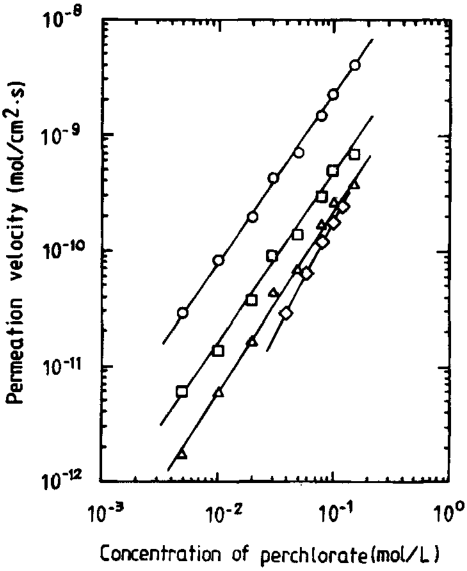


FIG. 3 Relation between the perchlorate concentration and the permeation velocity of metallic ions through an SLM. (○) Li^+ ion, (□) Na^+ ion, (△) K^+ ion, (◇) Mg^{2+} ion.

possess a smaller difference of electronegativity against an anion, ClO_4^- ion, i.e., metallic ions with a lower ionic bond ability, have a higher permeability from the normal extraction side to the back-extraction side. For this reason it is assumed that the formation of a coordination bond between a metallic ion with a high ionic bond ability and the oxygen atoms in a TPP molecule within an SLM is hindered at an SLM surface because the perchlorate with a more strongly ionic bond has a more strongly electrostatic attraction for the bond of cation and anion in the aqueous solution on the normal extraction side.

The metallic ion selectivities for the separation of metallic ions by the proposed transport system using an SLM containing TPP differ extremely from that ($Na^+ \gg K^+ > Li^+$) for monensin (1, 2) and that ($K^+ > Na^+ \gg Li^+$) for crown ethers such as dibenzo-18-crown-6 (3, 4, 7, 8, 10, 11) and dibenzo-24-crown-8 (4) as a carrier in a liquid membrane. In addition, although some crown ethers, 12-crown-4 (15) and dibenzo-14-crown-4 (16), which have four oxygen atoms in a molecule, possess a selectivity for Li^+ ion when their ligands are used as carrier of cations for an ion selective electrode, there are few reports on the transport of alkali metallic ions except for a transport system using an SLM containing 14-crown-4-nitrophenol derivatives (17).

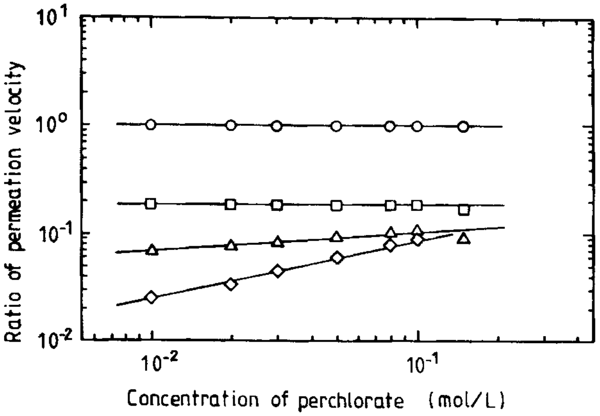


FIG. 4 Relation between the perchlorate concentration and the ratio of the permeation velocity of metallic ions against that of the Li^+ ion. (○) Li^+ ion, (□) Na^+ ion, (△) K^+ ion, (◇) Mg^{2+} ion.

For the conventional transport systems of metallic ion mentioned above, the permeability of Li^+ ion is low, and the cost of ligands which are commercially obtained is very expensive. By usage of the proposed transport system of metallic ion using an SLM containing TPP as a carrier, however, the selective extraction and concentration of Li^+ ion could be cheaply done.

Relation between the TPP Concentration and the Permeation Velocity

The dependence of the permeation velocity of alkali and alkaline earth metallic ions on the TPP concentration was examined. The experimental conditions were as follows: concentration of ligand, varied from 0.324 to 1.62 mol/L; perchlorate, 5×10^{-2} mol/L.

Figure 5 gives the value for the permeation velocity of the metallic ion as a function of the TPP concentration. In the range of the concentration of the TPP tested, the permeation velocity for any metallic ions was observed to increase linearly in proportion to the TPP concentration in the SLM. The slopes of the respective lines for Li^+, Na^+, K^+, and Mg^{2+} ions were determined to be 2.37, 2.38, 2.44, and 4.87, respectively.

The ratios for the permeation velocities of K^+, Na^+, and Mg^{2+} ions against that of Li^+ ion are shown in Fig. 6. None of the ratios for the Na^+ and K^+ ions were dependent on the ligand concentration, but that of a divalent cation, Mg^{2+} ion, was dependent on them. No transport of metallic ion was observed in the case of an SLM when no TPP was used.

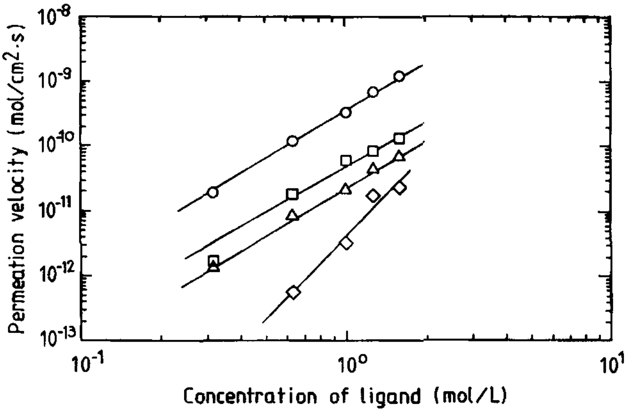


FIG. 5 Relation between the ligand concentration and the permeation velocity of metallic ions through an SLM. (○) Li^+ ion, (□) Na^+ ion, (△) K^+ ion, (◇) Mg^{2+} ion.

Equations for Permeation Velocity of Metallic Ions

For our system on the transport of metallic ions through an SLM containing TPP, the equations for the permeation velocities of the metallic ions were proposed as a function of two parameters: concentrations of alkali and alkaline earth metallic ions, and ligand. For Li^+ ion, the value of exponent a in Eq. (2) can be obtained by determining the slope value of a log-log diagram between the permeation velocity of Li^+ ion and the

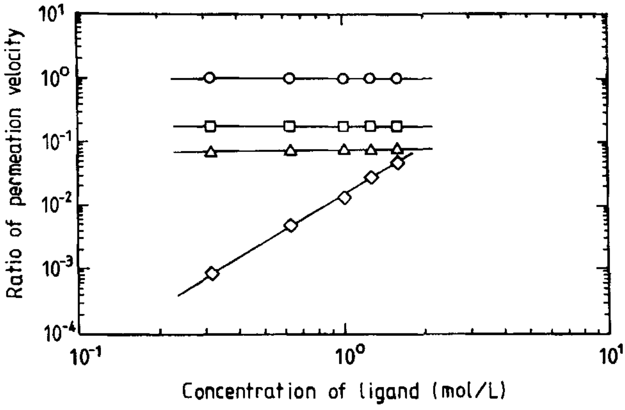


FIG. 6 Relation between the ligand concentration and the ratio of the permeation velocity of metallic ions against that of the Li^+ ion. (○) Li^+ ion, (□) Na^+ ion, (△) K^+ ion, (◇) Mg^{2+} ion.

concentration of lithium perchlorate. In the same way, exponent *b* is obtained from the relation between the permeation velocity of Li^+ ion and the TPP concentration. As a result, the values for exponents *a* and *b* for Li^+ ion were determined to be 1.40 and 2.37 from Figs. 3 and 5, respectively. By substituting these values into Eq. (2), the following equation was obtained:

$$N_{Li} = K_{Li} \cdot [LiClO_4]^{1.40} \cdot [TPP]^{2.37} \quad (mol/cm^2 \cdot s) \qquad (5)$$

To estimate the permeation velocity constant K_{Li}, the two parameters ($[LiClO_4]^{1.40}$ and $[TPP]^{2.37}$) and the permeation velocity of Li^+ ion were correlated by plotting their values in a log-log diagram as shown in Fig. 7. A nearly linear correlation was obtained in which the slope and the intercept of the line were 0.976 and −7.79, respectively. Hence the value for K_{Li} was determined to be 1.62×10^{-8}, which led to the equation mentioned above as the final expression:

$$N_{Li} = 1.62 \times 10^{-8} \cdot [LiClO_4]^{1.40} \cdot [TPP]^{2.37} \quad (mol/cm^2 \cdot s) \qquad (6)$$

Similarly, the values of the respective exponents *a* and *b* in equations for the permeation velocities of Na^+, K^+, and Mg^{2+} ions were determined.

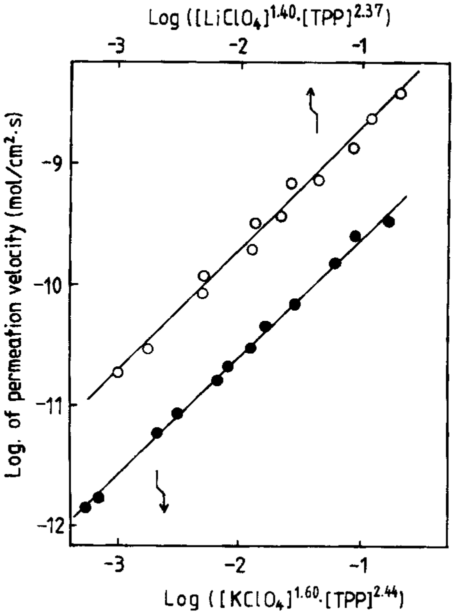


FIG. 7 Relation between the values of $[LiClO_4]^{1.40} \cdot [TPP]^{2.37}$ and $[KClO_4]^{1.60} \cdot [TPP]^{2.44}$ and the permeation velocities of Li^+ and K^+ ions.

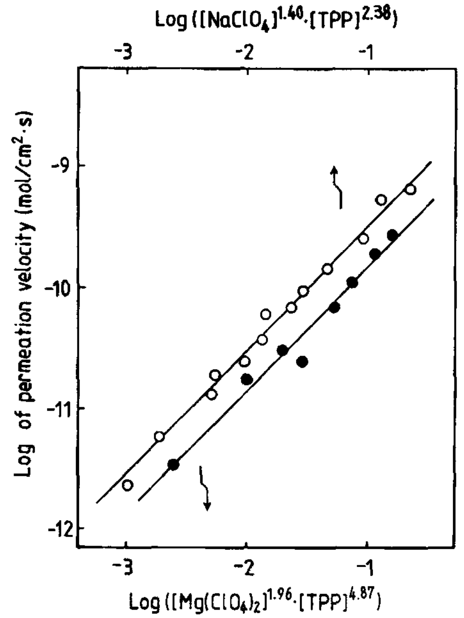


FIG. 8 Relation between the values of $[NaClO_4]^{1.40}\cdot[TPP]^{2.38}$ and $[Mg(ClO_4)_2]^{1.96}\cdot[TPP]^{4.87}$ and the permeation velocities of Na^+ and Mg^{2+} ions.

Further, the permeation velocity constants, K_{Na}, K_K, and K_{Mg}, were calculated using the values of the intercepts of the lines from the relation between $[M_AClO_4]^a\cdot[TPP]^b$ or $[M_{AE}(ClO_4)_2]^c\cdot[TPP]^d$ in Eqs. (2) and (3) and the permeation velocities of metallic ions, which are shown in Figs. 7 and 8. For Na^+, K^+, and Mg^{2+} ions, the following equations were introduced:

$$N_{Na} = 3.19 \times 10^{-9}\cdot[NaClO_4]^{1.40}\cdot[TPP]^{2.38} \quad (mol/cm^2\cdot s) \qquad (7)$$

$$N_K = 2.57 \times 10^{-9}\cdot[KClO_4]^{1.60}\cdot[TPP]^{2.44} \quad (mol/cm^2\cdot s) \qquad (8)$$

$$N_{Mg} = 1.35 \times 10^{-9}\cdot[Mg(ClO_4)_2]^{1.96}\cdot[TPP]^{4.87} \quad (mol/cm^2\cdot s) \qquad (9)$$

CONCLUSIONS

A transport system for alkali and alkaline earth metallic ions through an SLM containing TPP as a carrier was studied in connection with two important parameters: concentrations of alkali and alkaline earth metallic ions, and ligand.

As a result, in our transport system the ratios of the permeation velocities for Li^+, Na^+, K^+, and Mg^{2+} ions against that of Li^+ ion were

1:0.184:0.106:0.0890, respectively, which can transport Li^+ ions with high permeation velocity and highly selective permeability. The proposed transport system might be applicable to the separation, recovery, and concentration of Li^+ ion from aqueous solution samples such as wastewater, groundwater, and so forth.

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