

Transport of Cesium and Potassium Ions across Bilayer Lipid Membranes
-Cesium Accumulation in Biological Cells According to the Membrane Potential-

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Abstract

The transport of Cs^+ across a bilayer lipid membrane between two aqueous phases containing chloride and perchlorate salts was readily observed when compared to using K^+ , because Cs^+ is more hydrophobic than K^+ . After the Cs^+ was distributed from the aqueous to the BLM with a counter anion, such as Cl^- and ClO_4^- , the antiport of Cs^+ and the counter anion across the bilayer lipid membrane was caused by applying the potential difference between the two aqueous phases. By comparing the permeability in the presence of chloride salts with that in the presence of perchlorate salts, it can be appreciated that the standard potential for the transport of Cs^+ from the aqueous phase to the bilayer lipid membrane is about 60 mV more negative than that of K^+ . According to the ion transport mechanism, the accumulation of Cs^+ within living cells is assumed to be caused by the membrane potential, which is mainly generated by the transport of K^+ across the cell membrane between the outside and inside. By use of a liquid membrane cell, it was verified that the membrane potential generated by the concentration ratio of K^+ between two aqueous phases caused the accumulation of Cs^+ .

1.Introduction

Large amounts of radioactive isotopes, such as ^{131}I , ^{134}Cs , ^{137}Cs and ^{90}Sr , were leaked from the Fukushima Dai-ichi nuclear power plant on 11 March 2011 [1-3]. Nowadays, ^{131}I hardly exists around the nuclear power plant, because the half-life of ^{131}I is about 8 d [4]. On the other hand, since the half-lives of ^{134}Cs and ^{137}Cs are about 4 and 30 a, respectively [4], most of the ^{134}Cs and ^{137}Cs remains on the ground surface (soil), in the waste water produced from the nuclear power plant and in the environmental water contaminated by the fallout [5-7].

It is empirically known that the cesium ion (Cs^+) is frequently accumulated within living bodies, particularly muscle cells, where the concentration of potassium ion (K^+) is higher than those in the other organs, because the chemical properties of Cs^+ are very similar to those of K^+ [8-10]. While parts of various potassium channels seem to serve as transporters of Cs^+ in biocells [11], it has been reported that Cs^+ acts as a typical inhibitor of a number of potassium channels [12-14]. Thus, the mechanism of the uptake of Cs^+ into living bodies or living cells from the outer solution has not been elucidated at all.

Since a bilayer lipid membrane (BLM), which forms the framework of a cell membrane, behaves as a permeation barrier for hydrophilic ions, such as the K^+ , sodium ion (Na^+) and chloride ion (Cl^-), the ionic composition of the inner cell is usually different from that in the outer cell [15-17]. In the presence of any ion transporters, such as ion pumps/channels, carrier compounds and hydrophobic ions within the cell membrane, it is generally accepted that ions can be transported across the cell membrane [16,18,19]. The more hydrophobic ions contain in the aqueous phases, the higher the ion permeability within the BLM becomes [19-23]. When slightly hydrophobic electrolyte ions, such as the Cs^+ , bromide ion (Br^-), iodide ion (I^-), perchlorate ion (ClO_4^-), *etc.*, are used as an hydrophobic ion of which the concentration is more than 10^{-2} M ($\text{M} = \text{mol dm}^{-3}$), the current due to the ion transport across the BLM can be clearly

observed [24]. The author's group has already reported that the current observed at the applied membrane potential is caused by the antiport of both the cation and the anion across the BLM [19,20,25]. In addition, it has been reported that the transports of several ions across the cell membrane are coupled to hold the electroneutrality of each phase in the closed system such as biocells and liposomes [26]. The accumulation of Cs^+ in the biocell seems to be caused by coupling the transport of Cs^+ with that of K^+ . However, further details have not yet been elucidated.

In the present study, the permeability of Cs^+ across the BLM was evaluated by comparison to that of K^+ based on their electrochemical properties. The mechanism for the accumulation of Cs^+ from the outside to inside the cell system was elucidated by considering the physicochemical and electrochemical properties. By using liquid membrane systems containing lipids, the authors substantiated that Cs^+ was accumulated from the outside to the inside by the constant membrane potential determined by the concentration ratio of K^+ inside and outside the liposome.

2. Experimental

2.1 Chemicals

Lithium chloride, sodium chloride, rubidium chloride, lithium perchlorate, sodium perchlorate, cholesterol, tetrahydrofuran (THF), polyvinyl chloride (PVC) and *n*-decane were purchased from Wako Pure Chemical Ind., Ltd. Potassium chloride, cesium chloride, potassium perchlorate, rubidium perchlorate, cesium perchlorate, tetrahexylammonium chloride (THACl) and phosphatidylcholine were obtained from the Sigma-Aldrich Co. LLC. 2-Nitrophenyl octyl ether (NPOE) was available from Dojindo Chemicals. 1,3-Alternate thiacalix[4]biscrown-6,6 (cesium ionophore III) was obtained from the Fluka Chemical Co. All chemicals were of

reagent grade and used without further purification.

Sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (NaTFPB) was previously prepared [27]. The TFPB⁻ salts of potassium (KTFPB), cesium (CsTFPB) and tetrahexylammonium (THATFPB) were formed by mixing a methanol solution of NaTFPB with an aqueous solution of KCl, CsCl and THACl, respectively. The precipitates of KTFPB, CsTFPB and TEATFPB were purified by recrystallization based on the temperature dependence of the solubility of the salt in acetone.

High purity water ($\rho = 18.2 \text{ M}\Omega \text{ cm}$) was used to prepare all the aqueous solutions.

2.2 Electrochemical measurements

2.2.1 Electrochemical measurements for the ion transport across the pBLM

The electrochemical cell is shown in Fig. 1(A). Two compartments, which were filled with 15 mL of aqueous solutions (W1 and W2), were separated by a 0.1-mm thick polytetrafluoroethylene sheet (PTFE, Yodogawa Hu-tech Co.). An *n*-decane solution containing phosphatidylcholine (10 mg mL⁻¹) and cholesterol (2.5 mg mL⁻¹) was prepared as the BLM-forming solution. Planar bilayer lipid membranes (pBLM) were obtained as black lipid membranes by smearing the BLM-forming solution on two apertures (1.0-mm diameter) drilled in the sheet. The formation of the pBLM was confirmed by microscopic observation of light reflection from the surface of the pBLM and capacitance measurements. The area of the pBLM was also estimated from the microscopic observations.

Fig. 1

Voltammetry for the ion transport across the pBLMs was performed using a potentiostat/galvanostat (Hokuto Denko, HA1010mM1A), a function generator (Hokuto Denko, HB-305) and an A/D converter (Graphtec Corp., Midi Logger GL 900). The electrochemical cell was placed in a Faraday cage in order to reduce the external electric noise. Two Ag|AgCl

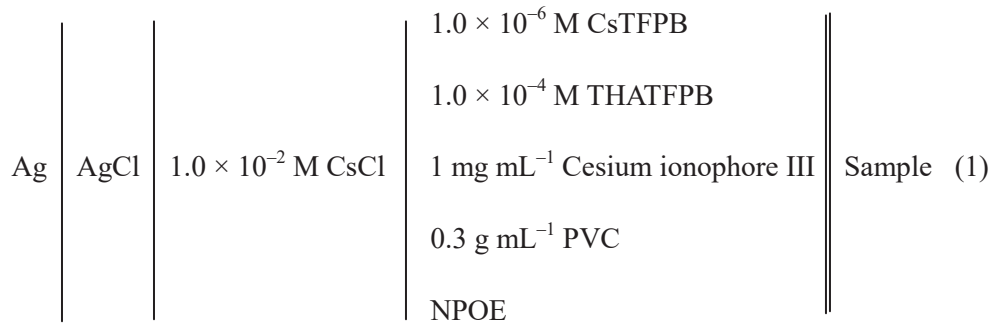
electrodes (Ag | AgCl | 0.1 M KCl aq., RE1 and RE2) were used as the reference electrodes in W1 and W2, respectively, and two Pt wires (CE1 and CE2) were used as the counter electrodes in W1 and W2, respectively. The voltammograms were recorded by scanning the potential difference between RE1 and RE2, E_{W1-W2} , and measuring the current between W1 and W2 across the pBLM, i . The current density, I , was evaluated by dividing i by the area of the pBLM.

The membrane potential at zero current, $E_{W1-W2, i=0}$, was measured by a handmade electrometer. After changing the electrolyte concentration in W2, the potential difference between W1 and W2 was recorded. All measurements were performed at 25 ± 1 °C.

2.2.2 Cesium accumulation according to the membrane potential formed by the ratio of the potassium concentration in one aqueous phase to that in another

The electrochemical cell used for this investigation is shown in Fig. 1(B). An *n*-decane solution containing phosphatidylcholine (10 mg mL^{-1}), cholesterol (2.5 mg mL^{-1}) and KTFPB (saturated) was impregnated in a porous PTFE sheet (with a pore size of $1.0 \text{ }\mu\text{m}$, a diameter of 25 mm and a thickness of $50 \text{ }\mu\text{m}$). The PTFE sheet was sandwiched by two glass tubes (an inner diameter of 8 mm). The two aqueous phases (W1 and W2) of which the volumes were 150 mL and $150 \text{ }\mu\text{L}$, respectively, were then separated by this PTFE sheet, which was used as a liquid membrane (LM). W1 contained $4.5 \times 10^{-2} \text{ M MgCl}_2$ and 10 mM KCl , and W2 contained 0.1 M KCl . To mimic a biocell system, W1, LM and W2 were regarded as an extracellular aqueous solution, a cell membrane and an intracellular aqueous solution, respectively. A reference electrode (RE1: Ag|AgCl| $4.5 \times 10^{-2} \text{ M MgCl}_2$ and 10 mM KCl aq.) was inserted into W1 and a reference electrode (RE2: Ag|AgCl| 0.1 M KCl aq.) and a cesium ion selective electrode (Cs^+ -ISE) were inserted into W2. This was made in a manner similar to that reported by Choi, et

al. [27]. After an aqueous solution containing CsCl was added to W1 to become 1.0×10^{-4} M, the response of Cs^+ -ISE and the membrane potential were recorded as the potential difference of Cs^+ -ISE to RE2 and that of RE2 to RE1, respectively. The change in the concentration of Cs^+ in W2 was then evaluated by using the Cs^+ -ISE. The Cs^+ -ISE was prepared according to a previous study [27]. The cell composition is represented by Eq. (1)

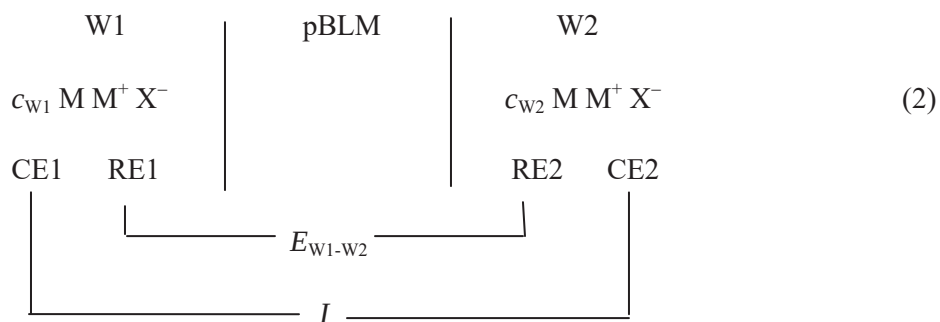


As the control experiment, the concentration of K^+ in W1 was measured using K^+ -ISE in the absence of Cs^+ in the cell. system The K^+ -ISE was prepared using K^+ and valinomycin instead of Cs^+ and cesium ionophore III, respectively, in a manner similar to that described by Eq. (1).

Two potentiometers (Model R8240 Digital Electrometer, Advantest) and an A/D converter (Midi Logger GL 900, Graphtec Co.) were used in this experiment.

3. Theoretical

The cell system employed in this study in described by Eq. (2).



Here, c represents the concentration of the electrolyte ($\text{M}^{z+}\text{X}^{z-}$). The subscripts, W1 and W2,

indicate the phases in which the electrolyte exists. The potential difference, E_{W1-W2} , between RE1 and RE2 is the sum of the potential difference, $E_{W1|M1}$, at the W1|M1 interface, the diffusion potential, E_{BLM} , in the BLM phase and the potential difference, $E_{M2|W2}$, at the W2|M2 interface. Here, M1 and M2 represent the surface regions of the BLM phase adjacent to W1 and W2, respectively. The ohmic drop in W1 and W2 is negligible as indicated by Eq. (3) because a sufficient amount of electrolyte exists in the aqueous phases.

$$E_{W1-W2} = E_{W1|M1} + E_{BLM} + E_{M2|W2} \quad (3)$$

The potential difference at the W|BLM interface can be regarded as the ion transfer energy between the aqueous and the BLM phases. In general, the electrochemical potential $\tilde{\mu}_{i^{z_i},P}$ of a given ion, i^{z_i} , in phase P is expressed by Eq. (4).

$$\tilde{\mu}_{i^{z_i},P} = \mu_{i^{z_i},P}^{\circ} + RT \ln a_{i^{z_i},P} + z_i F E_P, \quad (4)$$

where $\mu_{i^{z_i},P}^{\circ}$, $a_{i^{z_i},P}$, z_i , E_P , F , R , T are the standard chemical potential of i^{z_i} in the phase P, the activity of the ion in phase P, the charge of the ion, the Galvani potential in phase P, the Faraday constant, the gas constant and the absolute temperature, respectively. Hereinafter, $a_{i^{z_i},P}$ of Eq. (4) is replaced by $c_{i^{z_i},P}$. By assuming that the distribution of the electrolyte at the W|BLM phase interface (W1|M1 or W2|M2) attains equilibrium fairly rapidly, Eqs. (5) and (6) hold.

$$\tilde{\mu}_{i^{z_i},W1} = \tilde{\mu}_{i^{z_i},M1} \quad (5)$$

$$\tilde{\mu}_{i^{z_i},W2} = \tilde{\mu}_{i^{z_i},M2} \quad (6)$$

The potential differences at the interfaces of W1|M1 and W2|M2, $E_{W1|M1}$ and $E_{W2|M2}$, are expressed by Eqs. (7) and (8), respectively.

$$E_{W1|M1} = E_{i^{z_i},W|BLM}^{\circ} - \frac{RT}{z_i F} \ln \frac{c_{i^{z_i},W1}}{c_{i^{z_i},M1}} \quad (7)$$

$$E_{W2|M1} = E_{i^{z_i}, W|BLM}^\circ - \frac{RT}{z_i F} \ln \frac{c_{i^{z_i}, W2}}{c_{i^{z_i}, M2}} \quad (8)$$

Here, $E_{i^{z_i}, W|BLM}^\circ$ is the standard potential for the transport of i^{z_i} at the W|BLM interface.

To simplify the relation, we consider the ion transport in the presence of a 1-1 electrolyte (MX). When the concentration of MX in W1 is equivalent to that in W2, it is predicted that $E_{W1|M1}$ is very close to $E_{W2|M2}$. Therefore, Eq. (3) can be regarded as Eq. (9).

$$E_{W1-W2} \approx E_{BLM} \quad (9)$$

In this case, the rate-determining step seems to be the diffusion of ions within the BLM phase.

Based on the Henderson assumption ($\frac{dc_{i^{z_i}}}{dx} = \text{const.}$), the relation between current density, I , and E_{BLM} is described by Eq. (10) [26].

$$I = \frac{F^2}{RTd} \left\{ E_{BLM} \sum_i \frac{z_i D_i (c_{i^{z_i}, M2} - c_{i^{z_i}, M1})}{\ln \frac{c_{i^{z_i}, M2}}{c_{i^{z_i}, M1}}} + \frac{RT}{F} \sum_i z_i D_i (c_{i^{z_i}, M2} - c_{i^{z_i}, M1}) \right\} \quad (10)$$

Here, d and D_i are the thickness of the pBLM and the diffusion coefficient of i^{z_i} , respectively.

The membrane potential, $E_{BLM(i=0)}$, at $i = 0$ can be expressed by Eq. (11).

$$E_{BLM(i=0)} = -\frac{RT}{F} \cdot \frac{\sum_i z_i D_i (c_{i^{z_i}, M2} - c_{i^{z_i}, M1})}{\sum_i \frac{z_i^2 D_i (c_{i^{z_i}, M2} - c_{i^{z_i}, M1})}{\ln \frac{c_{i^{z_i}, M2}}{c_{i^{z_i}, M1}}}} \quad (11)$$

When the concentration of MX in W2 is r times higher than that in W1, Eqs. (10) and (11) are rewritten by Eqs. (12) and (13).

$$I = \frac{F^2 (r-1)}{RTd} \beta_{MX} c_0 \left\{ \frac{E_{BLM}}{\ln r} (z_+^2 |z_-| D_{M^{z_+}} + z_+ z_-^2 D_{X^{z_-}}) + \frac{RT}{F} (z_+ |z_-| D_{M^{z_+}} + z_+ z_- D_{X^{z_-}}) \right\} \quad (12)$$

$$E_{\text{BLM}(i=0)} = \frac{z_+ |z_-| D_{\text{M}^{z+}} + z_+ z_- D_{\text{X}^{z-}}}{z_+^2 |z_-| D_{\text{M}^{z+}} + z_+ z_-^2 D_{\text{X}^{z-}}} \cdot \frac{RT}{F} \ln r, \quad (13)$$

where β_{MX} and c_0 are the distribution coefficient at the W|BLM interface and the initial concentration of the electrolyte in W1, respectively, and r , β_{MX} and c_0 are represented by Eqs. (14), (15) and (16), respectively.

$$r \equiv \frac{c_{\text{M}^{z+}, \text{W2}}}{c_{\text{M}^{z+}, \text{W1}}} = \frac{c_{\text{X}^{z-}, \text{W2}}}{c_{\text{X}^{z-}, \text{W1}}} \quad (14)$$

$$\beta_{\text{MX}} \equiv \frac{c_{\text{M}^{z+}, \text{M1}}}{c_{\text{M}^{z+}, \text{W1}}} = \frac{c_{\text{M}^{z+}, \text{M2}}}{c_{\text{M}^{z+}, \text{W2}}} = \frac{c_{\text{X}^{z-}, \text{M1}}}{c_{\text{X}^{z-}, \text{W1}}} = \frac{c_{\text{X}^{z-}, \text{M2}}}{c_{\text{X}^{z-}, \text{W2}}} \quad (15)$$

$$c_0 \equiv \frac{c_{\text{M}^{z+}, \text{W1}}}{|z_-|} = \frac{c_{\text{X}^{z-}, \text{W1}}}{z_+} \quad (16)$$

When the electrolyte used is a 1-1 electrolyte, Eqs. (12) and (13) can be simplified as Eqs. (17) and (18), respectively.

$$I = \frac{F^2}{RT} P_{\text{MX}} c_0 E_{\text{W2-W1}} \quad (\text{at } r = 1) \quad (17)$$

$$E_{\text{W1-W2}(i=0)} = \frac{1 - \alpha_{\text{MX}}}{1 + \alpha_{\text{MX}}} \cdot \frac{RT}{F} \ln r \quad (18)$$

Here, P_{MX} and α_{MX} are the sum of the permeation coefficients of M^+ and X^- across the pBLM, and the ratio of D_{M^+} to D_{X^-} , respectively.

$$P_{\text{MX}} = P_{\text{M}^+} + P_{\text{X}^-} = \frac{\beta_{\text{MX}} \cdot (1 + \alpha_{\text{MX}}) D_{\text{X}^-}}{d} \quad (19)$$

$$\alpha_{\text{MX}} \equiv \frac{D_{\text{M}^+}}{D_{\text{X}^-}} \quad (20)$$

The relation of $E_{i^{z_i}, \text{W|BLM}}^\circ$ and β_{MX} is represented by Eq. (21).

$$E_{\text{W|BLM}, i^{z_i}} = E_{\text{W|BLM}, i^{z_i}}^\circ + \frac{RT}{z_i F} \ln \beta_{\text{MX}} \quad (21)$$

Since the potential difference due to the transport of the cation is equivalent to that due to the transport of the anion, Eq. (22) is derived.

$$E_{\text{W|BLM}, \text{M}^{z+}}^{\circ} - E_{\text{W|BLM}, \text{X}^{z-}}^{\circ} = -\left(\frac{1}{z_{+}} - \frac{1}{z_{-}}\right) \frac{RT}{F} \ln \beta_{\text{MX}} \quad (22)$$

As for the 1-1 electrolyte (MX), Eq. (22) is transformed into Eq. (23).

$$E_{\text{W|BLM}, \text{M}^{+}}^{\circ} - E_{\text{W|BLM}, \text{X}^{-}}^{\circ} = -\frac{2RT}{F} \ln \beta_{\text{MX}} \quad (23)$$

When M_1X and M_2X are used as the electrolyte, the difference between the standard potential for the ion transport at aqueous|BLM interface of M_1^{+} and that of M_2^{+} is expressed by the following equation.

$$E_{\text{W|BLM}, \text{M}_1^{+}}^{\circ} - E_{\text{W|BLM}, \text{M}_2^{+}}^{\circ} = -\frac{2RT}{F} \ln \frac{\beta_{\text{M}_1\text{X}}}{\beta_{\text{M}_2\text{X}}} \quad (24)$$

4. Results and discussion

4.1 Ion transport across the planar bilayer lipid membrane between two aqueous phases in the presence of a chloride salt

When W1 and W2 contain 0.1 M of MCl (M: Li, Na, K, Rb, Cs), ion transport voltammograms were obtained as shown in Fig. 2(A). The conductivity for the ion transport across the pBLM increased in order ($\text{Li}^{+} < \text{Na}^{+} < \text{K}^{+} < \text{Rb}^{+} < \text{Cs}^{+}$), as described in Table 1. The value in the case of CsCl was about 2.8 times higher than that of KCl. The ion transport current was observed even when LiCl was used as the electrolyte. Thus, the ion transport across the BLM occurs even if the electrolyte in W1 and/or W2 contains a hydrophilic salt such as LiCl.

Fig. 2(B) shows the ion transport voltammograms when ClO_4^{-} was used as a counter ion. The ion transport current increased with an increase in the hydrophobicity of the alkali metal cation analogous to the ion transport current in the presence of the chloride salts. When the

Fig. 2

Table 1

cation of the electrolyte was common, the conductivity in the presence of the perchlorate salts was about 4 times higher than that in the presence of chloride salts, as noted in Table 1. This seems to be attributed to the difference in the hydrophobicity of the anions. It is generally accepted that the conductivity is in proportion to the permeability coefficient, P_{MX} , of M^+ within the pBLM in a steady state [29]. Since d is almost constant, the conductivity is proportional to β_{MX} and the ratio of D_{M^+} to D_{X^-} according to Eq. (19). When the concentration of the electrolyte in W1 is different from that in W2, the membrane potential is represented by Eq. (18). Therefore, the membrane potential does not depend on β_{MX} , but it depends on α_{MX} . The $E_{BLM(i=0)}$ values are indicated in Fig. 3 when Cl^- and ClO_4^- were used as the anions 3A and 3B, respectively. It is clear that D_{M^+} increases with an increase in the atomic number. Table 2 shows D_{M^+} / D_{K^+} of the alkali metal cations to that of K^+ , which was evaluated by use of the data in the presence of the chloride salt or the perchlorate salt. The D'_{M^+} / D'_{K^+} value was then calculated using the hydration ion radii or the crystal ion radii of the alkali metal cation [30]. By comparison of the calculated values with the experimental values, the experimental values are close to those estimated using the crystal ion radii. This trend indicates that the alkali metal cation might exist as non-hydrated ion within the BLM.

Fig. 3

Table 2

According to Eqs. (19)-(24), the ratio of the distribution coefficient of M_1X to that of M_2X can be evaluated from both the ratio of P_{M^+} of each cation to that of K^+ and the ratio of D_{M^+} of each cation to D_{X^-} . D_{M^+} / D_{K^+} corresponds to the difference between $E_{i^{zi}, W|BLM}^\circ$ of M_1^+ and that M_2^+ from the aqueous phase to the BLM. Figure 4 shows the differences between $E_{M^+, W|BLM}^\circ$ of the alkali metal cation (Li^+ , Na^+ , K^+ , Rb^+ and Cs^+) from the aqueous

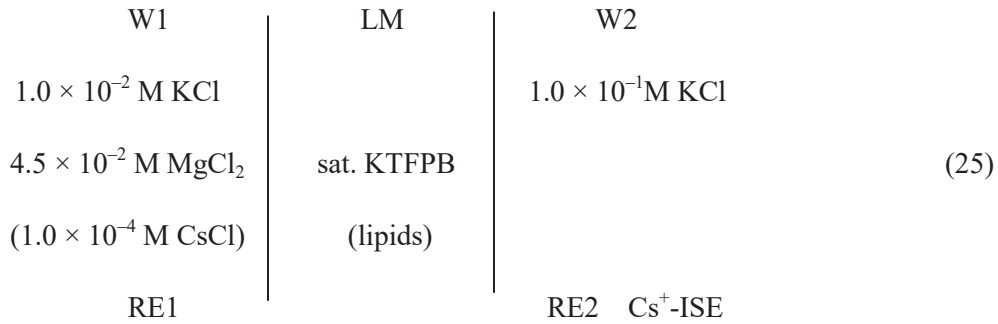
Fig. 4

phase to the BLM and that of K^+ . The higher the atomic number, the more negative $E_{M^+, W|BLM}^\circ$.

$E_{M^+, W|BLM}^\circ$ of Cs^+ from the aqueous phase to the BLM interface is about 60 mV more negative than that of K^+ . That is to say, the distribution coefficient of Cs^+ between the aqueous phase and the BLM is about 10 times higher than that of K^+ .

4.2 The accumulation of Cs^+ according to the membrane potential determined by the ratio of the potassium concentration in one aqueous phase to that in another aqueous phase

In order to mimic the biocell system, E_{W1-W2} across the PTFE sheet (LM) impregnated with the *n*-decane solution containing lipids was formed by the ratio of the K^+ concentration in one aqueous phase (W1) to that in another aqueous phase (W2), as shown by Eq. (25).



Before the addition of CsCl to W1, the potential differences at the W1|LM and W2|LM interfaces were depolarized by the transport of K^+ at the interfaces and the iR drop of the cell system was negligible because of the presence of sufficient electrolytes in each phase. At the initial condition, the potential difference between W1 and W2 was nearly -59 mV, as indicated in Fig. 5. Thus, E_{W1-W2} was determined by the ratio of the concentration of K^+ in W1 to that in W2. Assuming that TFPB $^-$ and Cl $^-$ have not moved to the other phases, K^+ and Mg $^{2+}$ seem to transport across the LM under this condition.

Fig. 5

After the addition of CsCl of which the final concentration became to 1.0×10^{-4} M, Cs^+ began to distribute from W1 to the LM and started to penetrate to W2, as shown in Fig. 5. Since Cs^+ is still more hydrophobic than Mg^{2+} [28], it is considered that the antiport of K^+ and Cs^+ across the LM occurred according to the membrane potential. Thus, the electroneutrality in each phase should be maintained by the antiport of Cs^+ and K^+ .

By considering $\Delta\tilde{\mu}_{\text{Cs}^+, \text{W1-W2}} (\equiv \Delta\tilde{\mu}_{\text{Cs}^+, \text{W1}} - \Delta\tilde{\mu}_{\text{Cs}^+, \text{W2}})$, Eq. (26) is valid.

$$\Delta\tilde{\mu}_{\text{Cs}^+, \text{W1-W2}} = RT \ln \frac{c_{\text{Cs}^+, \text{W1}}}{c_{\text{Cs}^+, \text{W2}}} + z_i F (E_{\text{W1}} - E_{\text{W2}}) \quad (26)$$

Here, $E_{\text{W1}} - E_{\text{W2}}$ denotes the membrane potential, which is generated by r between the intracellular and extracellular conditions. Therefore, Eq. (26) is rewritten as Eq. (27).

$$\Delta\tilde{\mu}_{\text{Cs}^+, \text{W1-W2}} = RT \ln \frac{c_{\text{Cs}^+, \text{W1}}}{c_{\text{Cs}^+, \text{W2}}} - z_i RT \ln \frac{c_{\text{K}^+, \text{W1}}}{c_{\text{K}^+, \text{W2}}} \quad (27)$$

Since the difference in the electrochemical potentials is zero under the equilibrium condition, Eq. (28) is formed.

$$\frac{c_{\text{Cs}^+, \text{W1}}}{c_{\text{Cs}^+, \text{W2}}} - \frac{c_{\text{K}^+, \text{W1}}}{c_{\text{K}^+, \text{W2}}} = 0 \quad (28)$$

It was confirmed that the concentration of Cs^+ in W2 increased to more than 4×10^{-3} M. Although the concentration of Cs^+ in W2 is expected to become about 10^{-3} M, it requires more than three days. Since *n*-decane was pulled from the PTFE sheet, the experiment was continued for three days in the present experiments. In the absence of Cs^+ in the cell system, the concentration of K^+ in W1 slightly increased. This indicated that K^+ was transported from W2 to W1 according to the difference in the K^+ concentration. Accordingly, Cs^+ was accumulated from W1 to W2 by the antiport of Cs^+ and K^+ at a constant membrane potential.

5. Conclusion

The standard potentials of alkali metal cations for ion transport from an aqueous solution to the BLM were compared. They are proportional to the hydration energies, and it is predicted that the alkali metal cations exist as non-hydrated ions within the BLM based on the ratio of the diffusion coefficient of the cation to that of the counter anion. In particular, the standard potential of Cs^+ for the transport from the aqueous to the BLM is about 60 mV more negative than that of K^+ . The diffusion coefficient of Cs^+ is lower than that of K^+ . If the membrane potential is formed by the concentration ratio of K^+ inside and outside as in biocells, it is predictable that Cs^+ easily transports to the cell membrane and that Cs^+ is accumulated inside the cell according to the membrane potential.

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Figure captions

Fig. 1 Electrochemical cells for (A) the pBLM system and (B) the liquid membrane cell.

Fig. 2 Voltammograms for the ion transport across pBLMs in the presence of (A) alkali chlorides and (B) alkali perchlorate in W1 and W2. Cation species of the electrolytes: Li^+ (1), Na^+ (2), K^+ (3), Rb^+ (4) and Cs^+ (5). Potential scanning rate: 10 mV s^{-1} .

Fig. 3 Relation between the zero current potentials in the case of (A) chloride salts and (B) perchlorate salts and the concentration ratio of the electrolyte between W1 and W2.

Fig. 4 Relation between the standard potentials of the transport of the alkali metal cation (Li^+ , Na^+ , K^+ , Rb^+ and Cs^+) from the aqueous phase to the BLM and the hydration energies.

Fig. 5 Time-courses of the concentration of Cs^+ in W2 (curve 1), that of K^+ in W1 (curve 2) and the potential difference between W1 and W2 (curve 3).

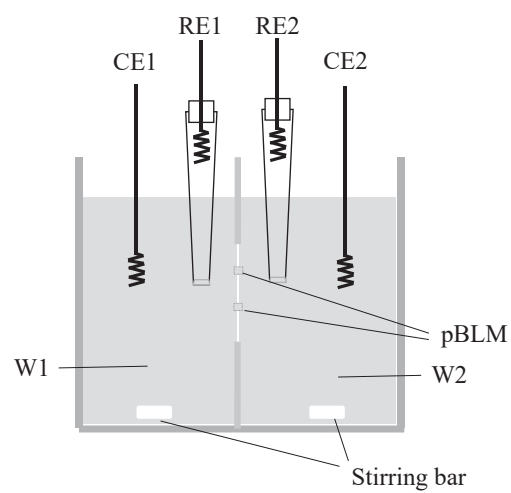
Table 1 Membrane conductance for the ion transport (IE_{w2-w1}^{-1} / mA V⁻¹ cm⁻²)

	Li ⁺	Na ⁺	K ⁺	Rb ⁺	Cs ⁺
Cl ⁻	6.1	10	19	26	52
ClO ₄ ⁻	20	46	69	93	180

Table 2 Ratio of the diffusion coefficient of the alkali metal cation within the BLM to that of potassium ion and its calculated value evaluated from the hydration ion radii or the crystal ion radii.

cation	D_{M^+} / D_{K^+}	D_{M^+} / D_{K^+}	D'_{M^+} / D'_{K^+}	D'_{M^+} / D'_{K^+}
	(Cl ⁻)	(ClO ₄ ⁻)	(hydration)	(crystal)
Li ⁺	2.0	3.0	0.88	2.0
Na ⁺	1.3	1.8	0.97	1.4
K ⁺	1.0	1.0	1.0	1.0
Rb ⁺	0.78	0.82	1.0	0.93
Cs ⁺	0.67	0.63	1.0	0.81

(A)



(B)

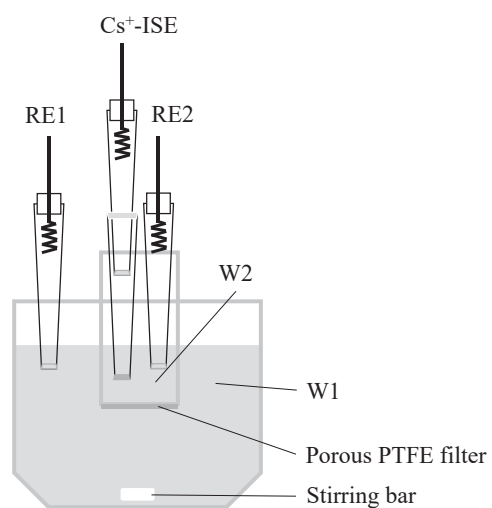
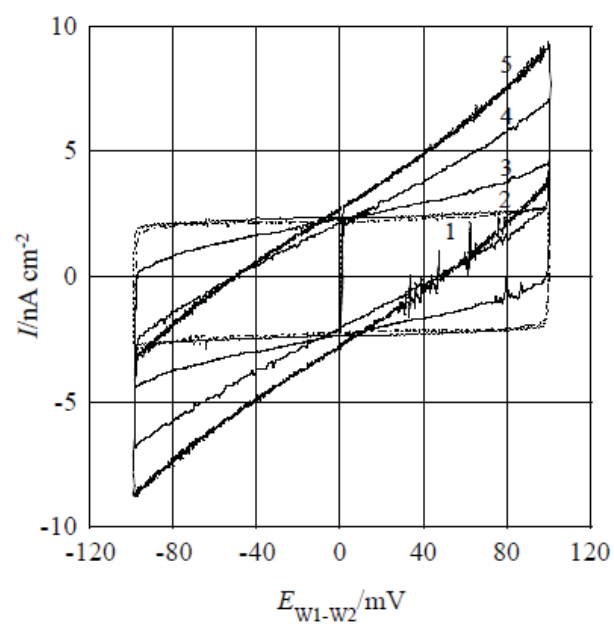


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(A)



(B)

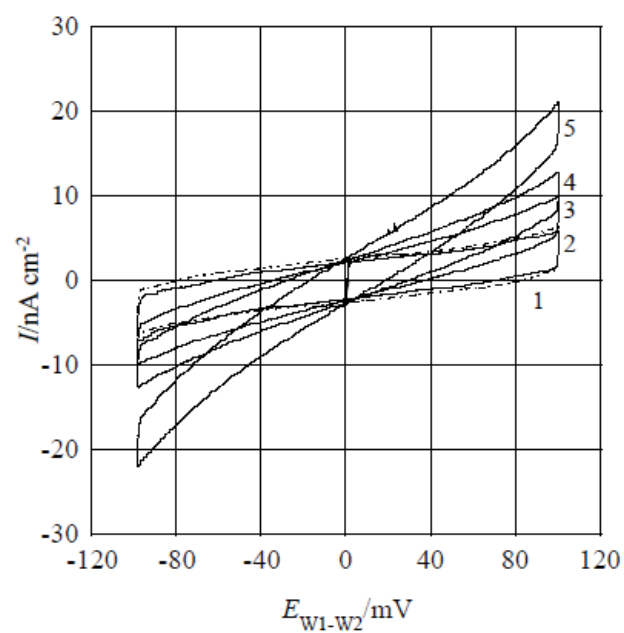
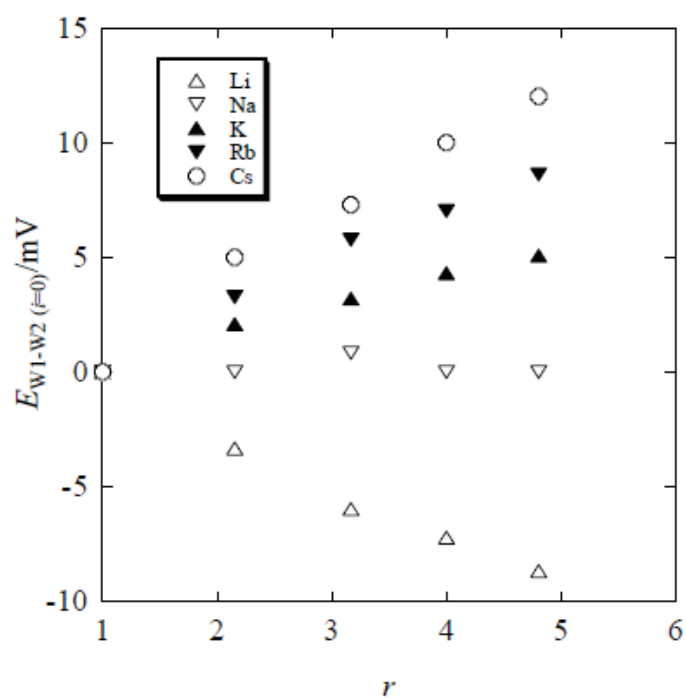


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(A)



(B)

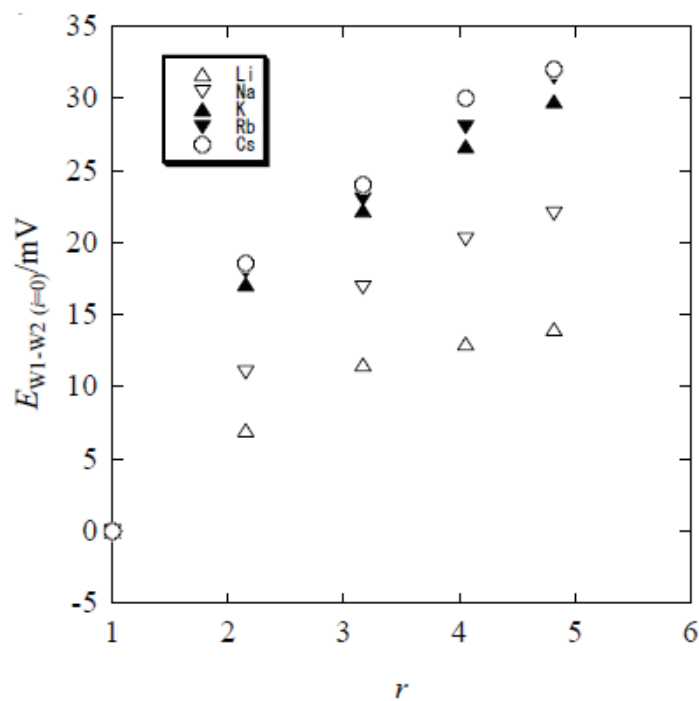


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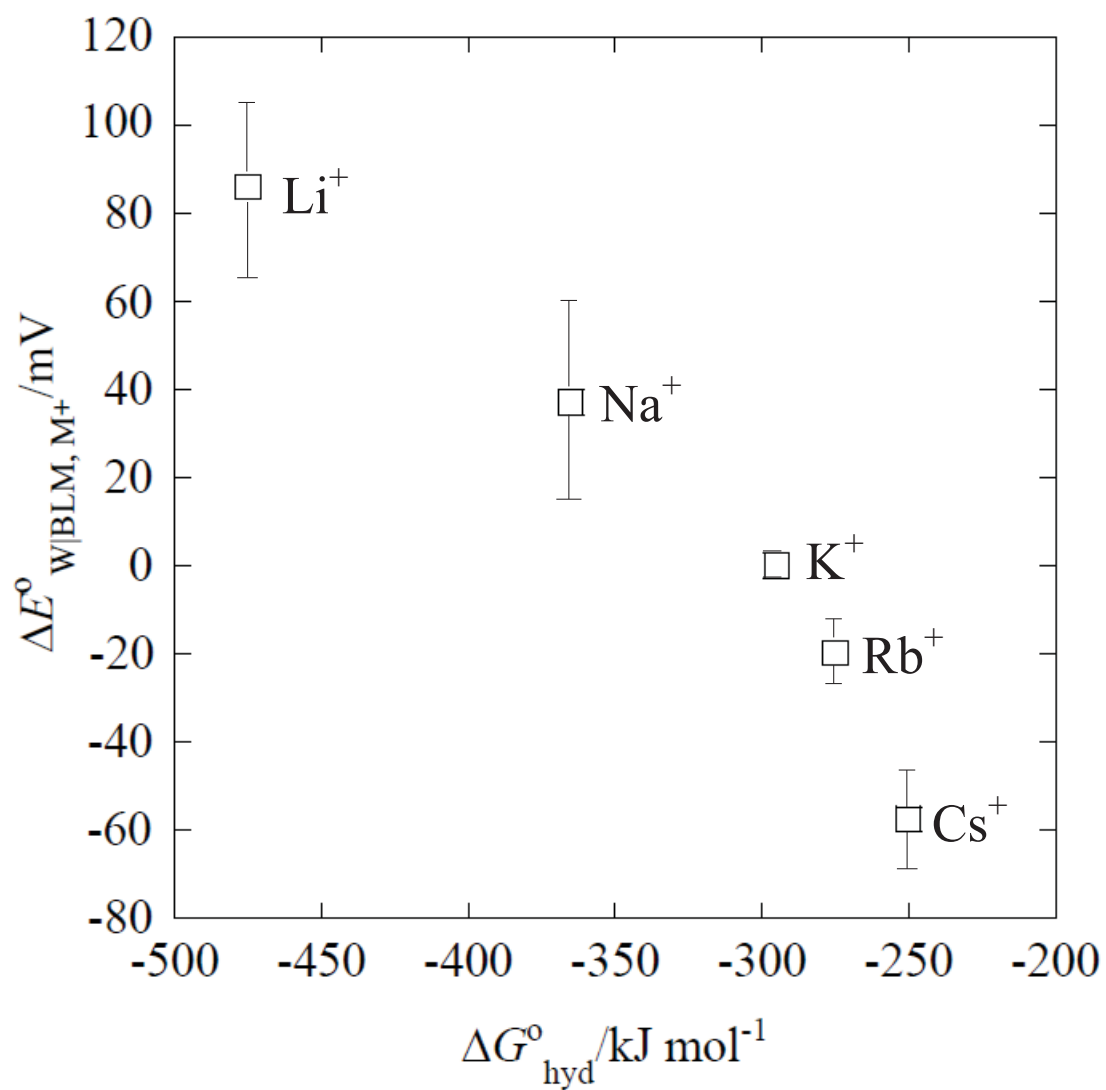


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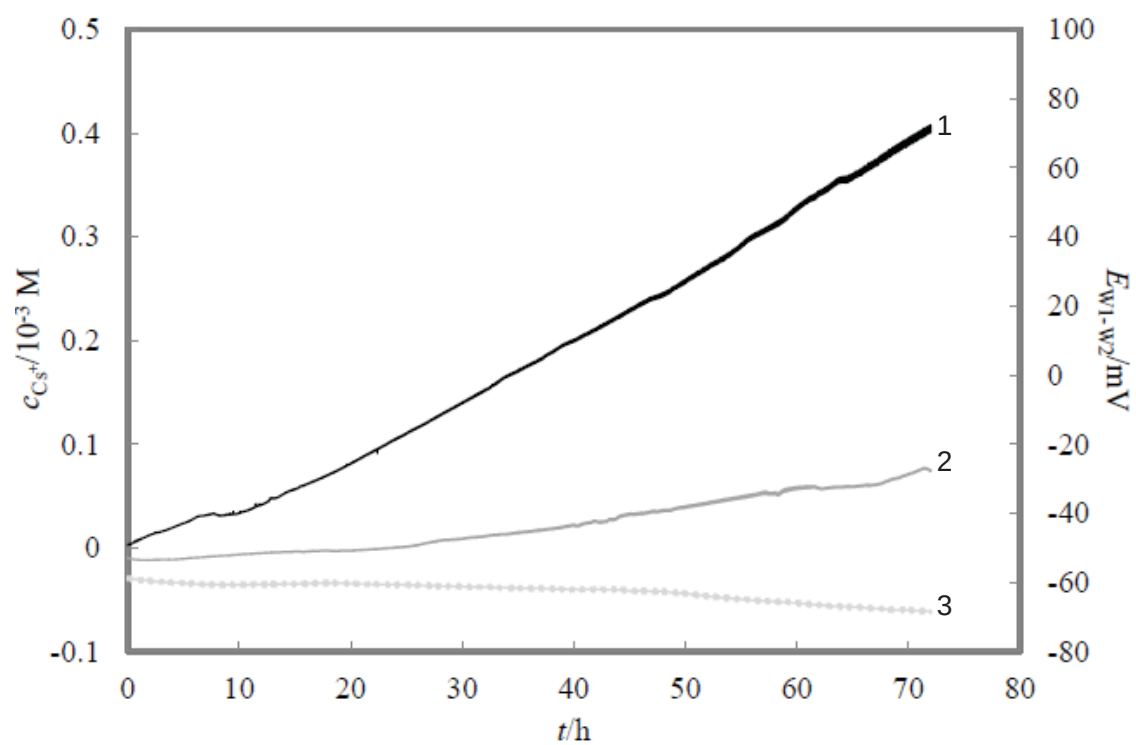


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