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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 days [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 (M = 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

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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 able 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 ($\rho = 18.2\ M\Omega\ cm$) 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.

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 (1CE and 2CE) were used as the counter electrodes in W1 and W2, respectively. The voltammograms were recorded by scanning the potential difference between RE1 and RE2, $E_{W1\text{-}W2}$, 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.

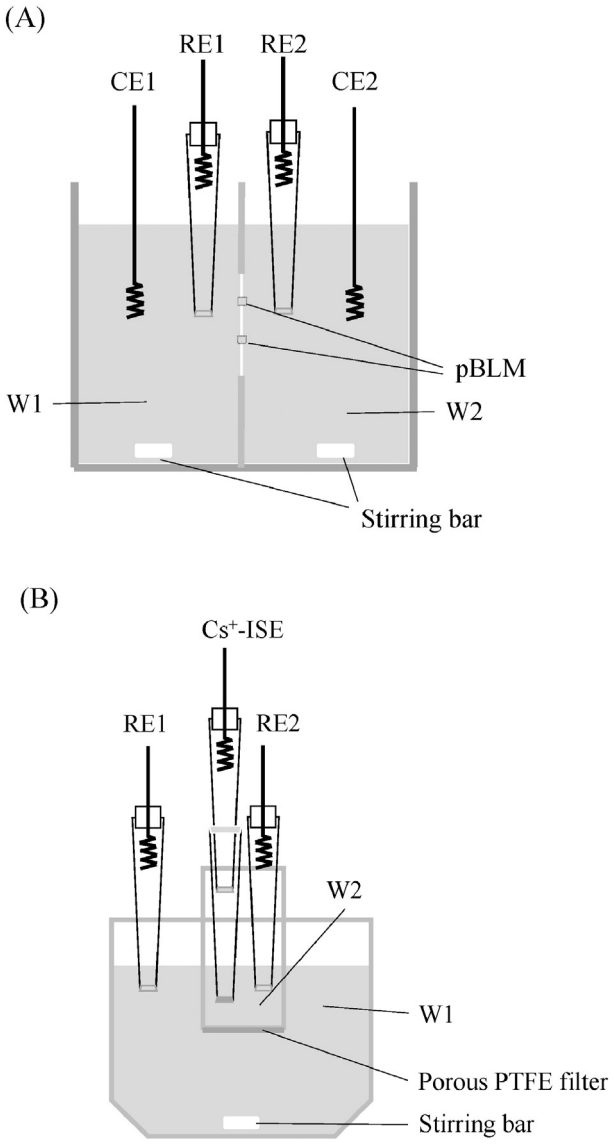

Fig. 1. Electrochemical cells for (A) the pBLM system and (B) the liquid membrane cell.

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 μm, a diameter of 25 mm and a thickness of 50 μm). 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 μL, respectively, were then separated by this PTFE sheet, which was used as a liquid membrane (LM). W1 contained 4.5×10^{-2} 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|4.5×10^{-2} 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

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