

Ion Transport across Bilayer Lipid Membranes in the Presence of Tetrphenylborate

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Abstract

A pair of symmetrical cathodic and anodic peaks is observed in cyclic voltammograms for the ion transport across a bilayer lipid membrane (BLM) between two aqueous phases in the presence of tetraphenylborate (TPhB^-). Although TPhB^- serves as a carrier of a hydrophilic counter ion (Na^+) under the steady-state condition, the reason for the appearance of symmetrical peaks has not been clearly explained until now. From the chronoamperometric analysis, it is turned out that the symmetrical peaks are attributed to the translocation of TPhB^- between two adsorbed layers on the surface of the BLM.

Introduction

Since a bilayer lipid membrane (BLM), which forms the structural frame of biomembranes, serves as a permeation barrier for hydrophilic ions such as K^+ , Na^+ and Cl^- , the difference of ionic composition between the cell inside and outside is kept at constant in usual.¹⁻³ In the presence of any ion transporters such as ion pumps, ion channels, carrier compounds, and hydrophobic ions, it is generally regarded that hydrophilic ions can transport across the cell membrane.⁴⁻⁸ Since there are various objects including transporters and redox compounds within actual cells, it is difficult to examine physicochemical properties of the objective transporter by use of the actual cell membrane as it is. Therefore, the objective transporter is extracted and reconstituted on the artificial BLM to evaluate the physicochemical properties.^{9,10} Thus, planar BLMs have been used to elucidate their functions. Cyclic voltammetry is one of useful methods to evaluate electrochemical properties.¹¹ Several research groups have already reported the electrochemical properties on the ion transport across the BLMs in the presence of hydrophobic ions.¹²⁻¹⁶ When only 10^{-7} - 10^{-5} mol dm⁻³ (M) of hydrophobic ions such as tetraphenylborate (TPhB⁻), dipicrylamine (DPA⁻), etc. were added into the cell system containing 0.1 M of hydrophilic electrolytes such as KCl, NaCl, etc., a pair of anodic and cathodic peaks symmetrical to 0 V appeared in cyclic voltammograms.¹⁷⁻¹⁹ Most of research groups decided that the ion transport current is attributed to the translocation of hydrophobic ions adsorbed on two surfaces of the BLM.²⁰⁻²² In the case of hydrophobic weak acids, it has been reported that H^+ can permeate across the BLM because hydrophobic weak acids serve as carrier compounds.²³⁻²⁵ However, the author's group proved that the transport current observed in the presence of DPA⁻ under the steady-state was mainly caused by the transport of the counterion (Na^+) of DPA⁻ using the radioisotope

(^{22}Na).²⁶ In addition, the author's group has already reported that the steady-state current observed at the applied membrane potential is caused by the antiport of both the cation and the anion across the BLM.²⁷⁻³¹ From the waveform of cyclic voltammograms, Kutnik and Tien suggested that the symmetrical peak was caused by the adsorption and desorption of the hydrophobic dye ions.¹⁸ Then, Bender and Tien proposed the transport of the hydrophobic ions distributed in the BLM comparing the ion transfer between two immiscible electrolyte solutions.¹⁹ Based on these mechanisms, it is difficult to explain the steady-state current observed at a constant membrane potential. On the other hand, Murakami, et al. and Omatsu, et al. pointed out that not only the transport of a coexisting counterion across the BLM but also the adsorption and desorption of rhodamine 6G on the surface of the BLM.³²⁻³⁴ Nevertheless, the waveform of cyclic voltammograms in the presence of hydrophobic ions has not accurately been analyzed yet.

In the present study, the waveform of cyclic voltammograms in the presence of TPhB^- , which is a typical hydrophobic ion, was analyzed taking into account both the transfer of TPhB^- adsorbed on the surface of the BLM and the permeation of both TPhB^- and the counter cation (Na^+) across the BLM. In particular, it is important that the transport of Na^+ and TPhB^- within the BLM varies according to the ionic composition because the ratio of the transport of Na^+ within the BLM to that of TPhB^- depends on the concentration ratio of Na^+ to TPhB^- in aqueous phases.

Experimental

Chemicals

Sodium chloride, sodium tetraphenylborate (NaTPhB), cholesterol, and *n*-decane were purchased from Wako Pure Chemical Ind., Ltd. Phosphatidylcholine was obtained

from the Sigma-Aldrich Co. LLC. All chemicals were of reagent grade and used without further purification.

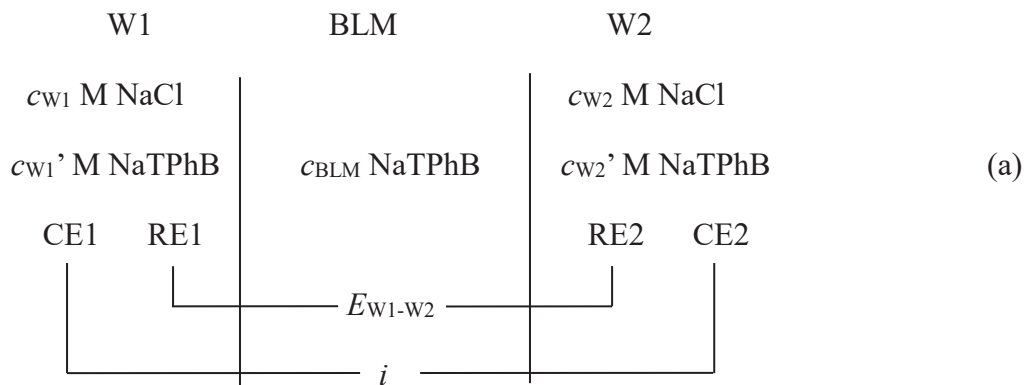
High purity water ($\rho = 18.2 \text{ M}\Omega \text{ cm}$) was used to prepare all aqueous solutions.

Electrochemical measurements

The electrochemical cell is shown in Fig. 1. Two compartments, which were filled with 20 mL of aqueous solutions (W1 and W2), were separated by a 0.2-mm thick polytetrafluoroethylene sheet (PTFE, Yodogawa Hu-tech Co.). As a BLM-forming solution, phosphatidylcholine (10 mg mL^{-1}) and cholesterol (5 mg mL^{-1}) were dissolved in *n*-decane. Planar bilayer lipid membranes (BLMs) were obtained as black lipid membranes by brushing the BLM-forming solution on the aperture (1.0-mm diameter) drilled in the PTFE sheet. The formation of the BLM was confirmed by microscopic observation of total reflection light from the BLM and capacitance measurements. The area of the BLM was also estimated from the microscopic observations.

Fig. 1

The cell configuration employed in the present study was described by scheme (a).



Here, c represents the concentration of sodium salt (NaCl or NaTPhB). The subscripts, W1, BLM, 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 at the W1|BLM1 interface, the diffusion potential within the BLM phase, and the potential

difference at the W2|BLM2 interface. Here, BLM1 and BLM2 represent the surface regions of the BLM phase adjacent to W1 and W2, respectively. The membrane current between W1 and W2, i , is the sum of the charging current on the surface and the current due to the transport of Na^+ and TPhB^- between W1 and W2.

Cyclic voltammograms for the ion transport across BLMs were recorded using a potentiostat/galvanostat (Hokuto Denko, HA1010mM1A), a function generator (Hokuto Denko, HB-105), and a data acquisition board (National Instruments Co., Ltd, NI PCI-6281) with LabVIEW software (National Instruments Co., Ltd). The electrochemical cell was placed in a Faraday cage in order to reduce the external electric noise. Two Ag|AgCl electrodes ($\text{Ag}|\text{AgCl}|0.1 \text{ M KCl}$, RE1 and RE2) were used as the reference electrodes in W1 and W2, respectively. Similarly, two Pt wires (CE1 and CE2) were used as the counter electrodes in W1 and W2, respectively. RE2 was served as the reference electrode in the standard side. Cyclic voltammograms were obtained by scanning the potential difference, $E_{\text{W1-W2}}$, between RE1 and RE2 and measuring the current, i , between CE1 and CE2. The current density, I , was evaluated by dividing i by the area of the BLM. Similarly, time courses of the current density were conducted by applying $E_{\text{W1-W2}}$ and recording time-courses of I . Normal pulse voltammetry was used to evaluate I values under the steady-state. In each step, $E_{\text{W1-W2}}$ was maintained at 0 V for 100 s by use of a potentiostat, and then the rectangular pulse voltage (20, 40, 60, 80, 100, -20, -40, -60, -80, and -100 mV) was applied for 30 s.

All electrochemical measurements were obtained at $25 \pm 1 \text{ }^\circ\text{C}$.

Results and Discussion

When W1 and W2 contained 0.1 M of NaCl only, cyclic voltammograms were obtained as shown in Fig. 2. In these voltammograms, charging currents were mainly observed and

Fig. 2

faradaic currents due to the ion transport were not obtained clearly.

Blue and red solid lines in Fig. 2 shows the ion transport voltammograms when TPhB⁻ was added in W1 and W2 to be 10⁻⁶ M. Anodic and cathodic current peaks symmetrical about the origin (0 V, 0 A) were clearly observed. The current height (0.61 $\mu\text{A cm}^{-2}$) observed at 100 mV s^{-1} was about 4.1 times larger than that (0.15 $\mu\text{A cm}^{-2}$) observed at 10 mV s^{-1} . When TPhB⁻ was added to W1 only, the waveform of CV was identical to that observed in the presence of TPhB⁻ in both W1 and W2. The peak height and the current height under the steady-state in the presence of TPhB⁻ in only W1 were about 70 % of those observed in the presence of TPhB⁻ in both W1 and W2. Regardless of the supply of TPhB⁻ from the aqueous phase to the BLM, the waveforms were symmetrical with the origin (0 V, 0 A). Therefore, it is estimated that the anodic and cathodic current peaks were attributed to not only the ion transport of both Na⁺ and TPhB⁻ between W1 and W2 but also the translocation of TPhB⁻ between the adsorbed layers on the surface of the BLM on the basis of the dependence of the potential-scanning rate ($\sqrt{10} < 4.1 < 10$), as shown in scheme 1. Since there are three phases and two interfaces in the membrane system, the contribution of the potential scanning to the translocation of TPhB⁻ is always varied.²⁷ On the other hand, Bender and Tien reported that a linear relationship between the peak height and the square root of the potential scanning rate between 10 and 50 mV s^{-1} and that the wave form indicated a thin-layer electrode process.¹⁹ Since the wave form was symmetrical about the origin (0 V, 0 A) in the presence of TPhB⁻ in only one aqueous phase and the peak height depended on the species of the counterion and its concentration, the authors' group concluded that not only TPhB⁻ but also the counterion transported at the same time.^{27,29}

Scheme 1

Figure 3 indicates time-courses of I values at $E_{\text{W1-W2}} = 100 \text{ mV}$ in the presence and absence of 10⁻⁶ M TPhB⁻ in W1 and W2 containing 0.1 M NaCl. In the absence of TPhB⁻

Fig. 3

in W1 and W2, $0.14 \mu\text{A cm}^{-2}$ flowed just after applying 100 mV. The I value rapidly decreased and settled at $0.006 \mu\text{A cm}^{-2}$ 5 s later. It is thought that the initial current flow is caused by the charging current at both W1|BLM and BLM|W2 interfaces. The capacitance is evaluated at $0.26 \mu\text{F cm}^{-2}$ from the coulomb number $0.026 \mu\text{C cm}^{-2}$. This approximately agrees with reported values ($0.316 \pm 0.011 \mu\text{F cm}^{-2}$).³⁵ When 10^{-6} M TPhB⁻ was existed in W1 and W2, the coulomb number for 30 s was evaluated at $0.99 \mu\text{C cm}^{-2}$. The coulomb number ($0.99 \mu\text{C cm}^{-2}$) seems to be caused by transition of TPhB⁻ adsorbed on the surface of the BLM from the BLM|W2 interface to the W1|BLM interface. Since the cross-sectional area of phosphatidylcholine was estimated at about $5 \times 10^{-19} \text{ m}^2$, the molecular ratio of PC to TPhB⁻ was found to be about 32 : 1 in the adsorption layer.³ It is thought that the adsorption layer exists on two BLM surfaces, as shown in scheme 1.

Figure 4 illustrates the relation between the applied $E_{\text{W1-W2}}$ and the I values recorded under the steady-state by normal pulse voltammetry. In the absence of TPhB⁻ in W1 and W2, the current slightly increased with an increase in the absolute value of the applied $E_{\text{W1-W2}}$, as shown in Fig. 2. The current seems to be caused by the counter transport of Na⁺ and Cl⁻ based on the previous study.³¹ Since faradaic currents due to the counter transport of electrolyte ions indicated the steady-state flows, it is predictable that the facilitated transport of Na⁺ by TPhB⁻ served as a carrier behaves the steady-state flow. Since the concentrations of Na⁺ and TPhB⁻ seemed to be constant, Na⁺ of which concentration in W1 and W2 was 10^5 times higher than that of TPhB⁻ in the BLM should move mainly. The dotted line indicates the fitting curve of the relationship between the applied $E_{\text{W1-W2}}$ and the I values, which has a sigmoidal shape. In this case, the BLM containing TPhB⁻ was served as a cation-exchange membrane and the membrane current under the steady-state was controlled by the concentration of Na⁺ within the BLM. The similar steady-state curve on the relation between the applied $E_{\text{W1-W2}}$ and the I values

Fig. 4

obtained by Le Blanc, Jr., and he concluded that TPhB⁻ was the only species possible to transport across the BLM.¹³ However, the authors' group decided that both Na⁺ and TPhB⁻ could transport across the BLM and that TPhB⁻ was served as a carrier of Na⁺ because the relation between the applied E_{W1-W2} and the I values symmetrical about the origin (0 V, 0 A) was observed in the presence of TPhB⁻ in only one aqueous phase.²⁹ In addition, the authors' group confirmed the transport of Na⁺ in the presence of dipicrylamine, which is frequently used as a hydrophobic anion similarly to TPhB⁻, using radioisotope ²²Na.²⁶ Omatsu et al. reported a similar sigmoidal I - E_{W1-W2} curve in the presence of rhodamine 6G.³⁴

The translocation of TPhB⁻ adsorbed on the surfaces is discussed hereafter. Now, $\Gamma_{t,W1}$ and $\Gamma_{t,W2}$ are defined as the numbers of all sites where TPhB⁻ can be adsorbed at W1|BLM and W2|BLM interfaces, respectively. Then, $\Gamma_{ad,W1}$ and $\Gamma_{ad,W2}$ are regarded as the numbers of adsorbed TPhB⁻ at W1|BLM and W2|BLM interfaces, respectively. $\Gamma_{f,W1}$ and $\Gamma_{f,W2}$ are the numbers of empty sites at W1|BLM and W2|BLM interfaces ($\Gamma_t = \Gamma_{ad} + \Gamma_f$). In this case, the potential difference, E , for the translocation of TPhB⁻ is representable by eq. (1) based on the thin-layer theory.¹¹

$$E = E^{\circ'} + \frac{RT}{F} \ln \left(\frac{\Gamma_{ad,W2}}{\Gamma_{ad,W1}} \right) \quad (1)$$

Here, $E^{\circ'}$ is the equilibrium potential for the translocation of TPhB⁻ when $\Gamma_{ad,W1}$ is equivalent to $\Gamma_{ad,W2}$. Assuming that the translocation of adsorbed TPhB⁻ to another interface is reversible, the current due to the translocation is expressed by eq. (2).

$$I = \pm \frac{F^2 A v \Gamma_{ad} \exp \left[\frac{F}{RT} (E - E^{\circ'}) \right]}{RT \left\{ 1 + \exp \left[\frac{F}{RT} (E - E^{\circ'}) \right] \right\}^2} \quad (2)$$

Since the coulomb number due to the transition of TPhB⁻ between two surfaces was estimated at 0.99 $\mu\text{C cm}^{-2}$, the initial value of $\Gamma_{ad,W1}$ ($= \Gamma_{ad,W2}$) corresponds to 1.0×10^{-12} mol cm^{-2} . Cyclic voltammograms on the translocation at 10 and 100 mV s⁻¹ are simulated

as shown in Fig. S11. Considering the usual charging current of Na^+ and Cl^- on two surfaces of the BLM, transition of the absorbed TPhB^- between two surfaces of the BLM, and the steady-state transport of Na^+ between W1 and W2 across the BLM, the relations between the applied $E_{\text{W1-W2}}$ and the I values are estimated by combination of those relation as indicated in Fig. 5. In this time scale, the contribution of the direct transport of TPhB^- between two aqueous phases is assumed to be negligible. Since the charge densities of cyclic voltammograms observed at 10 and 100 mV s^{-1} are 1.1 and 0.63 $\mu\text{C cm}^{-2}$, respectively, the translocation of the adsorbed TPhB^- is predictable to be quasi-reversible. The peak separation increased with an increase in the potential scanning rate [data not shown]. The difference in shape between the simulated and actual voltammograms seems to be caused by the irreversibility of the translocation of adsorbed TPhB^- .

Conclusions

The ion transport across the BLM between two aqueous phases containing 0.1 M NaCl in the presence of TPhB^- was investigated. The current would be caused by the charging current on the surface of the BLM, the translocation of TPhB^- absorbed on the surface of the BLM, and the steady-state transport of Na^+ between W1 and W2 across the BLM. Accordingly, the current flow is mainly caused by the transport of Na^+ across the BLM under the steady-state. To the contrary, the current peak observed in the cyclic voltammogram at the potential-scanning rate faster than 10 mV s^{-1} is mainly produced by the translocation of TPhB^- absorbed on the surface of the BLM.

Acknowledgements

The authors thank Prof. Kenji Kano for his encouragement and useful comments.

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Figure Captions

Fig. 1 Schematic illustration of electrochemical cell.

Fig. 2 Cyclic voltammograms for the ion transport across the BLM in the absence and presence of TPhB⁻.

Concentration of NaCl in W1 and W2: 0.1 mol dm⁻³. Concentration of TPhB⁻ in W1 and W2, 0 mol dm⁻³; blue and red broken lines, 10⁻⁶ mol dm⁻³; blue and red solid lines. Potential region: -0.1 – 0.1 V. Potential scanning rate: 10 mV s⁻¹; blue lines, 100 mV s⁻¹; red lines.

Fig. 3 Time courses of the current based on normal pulse voltammograms for the ion transport across the BLM in the presence (solid line) and absence of TPhB⁻ (dotted line). Concentration of NaCl in W1 and W2: 0.1 mol dm⁻³. Concentration of TPhB⁻ in W1 and W2, 0 mol dm⁻³; broken line, 10⁻⁶ mol dm⁻³; bold line. Initial Potential: 0 V. Applied Potential: 100 mV.

Fig. 4 The relation between the potential and current on the steady-state ion transport across the BLM in the presence of TPhB⁻.

Concentration of NaCl in W1 and W2: 0.1 mol dm⁻³. Concentration of TPhB⁻ in W1 and W2: 10⁻⁶ mol dm⁻³. Potential region: -0.1 – 0.1 V. Data sampling: 30 s after the potential change (NPV). Dotted line: fitting curve.

Fig. 5 Combination $I-E_{W1-W2}$ curves of the steady-state $I-E_{W1-W2}$ curve and the $I-E_{W1-W2}$ curves due to reversible translocation of adsorbed TPhB⁻.

Concentration of TPhB⁻, 10⁻⁶ mol dm⁻³. Potential region: -0.1 – 0.1 V. Potential scanning

rate: 10 mV s^{-1} ; broken lines, 100 mV s^{-1} ; bold lines.

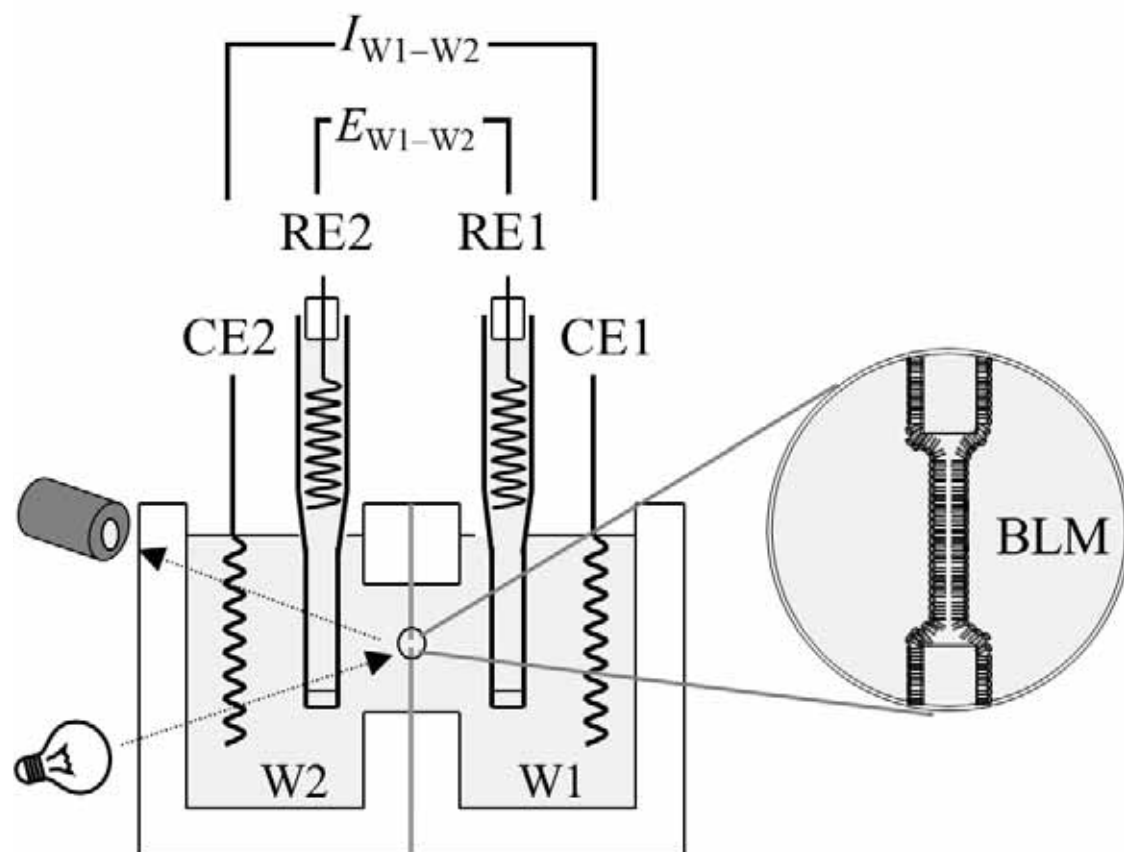


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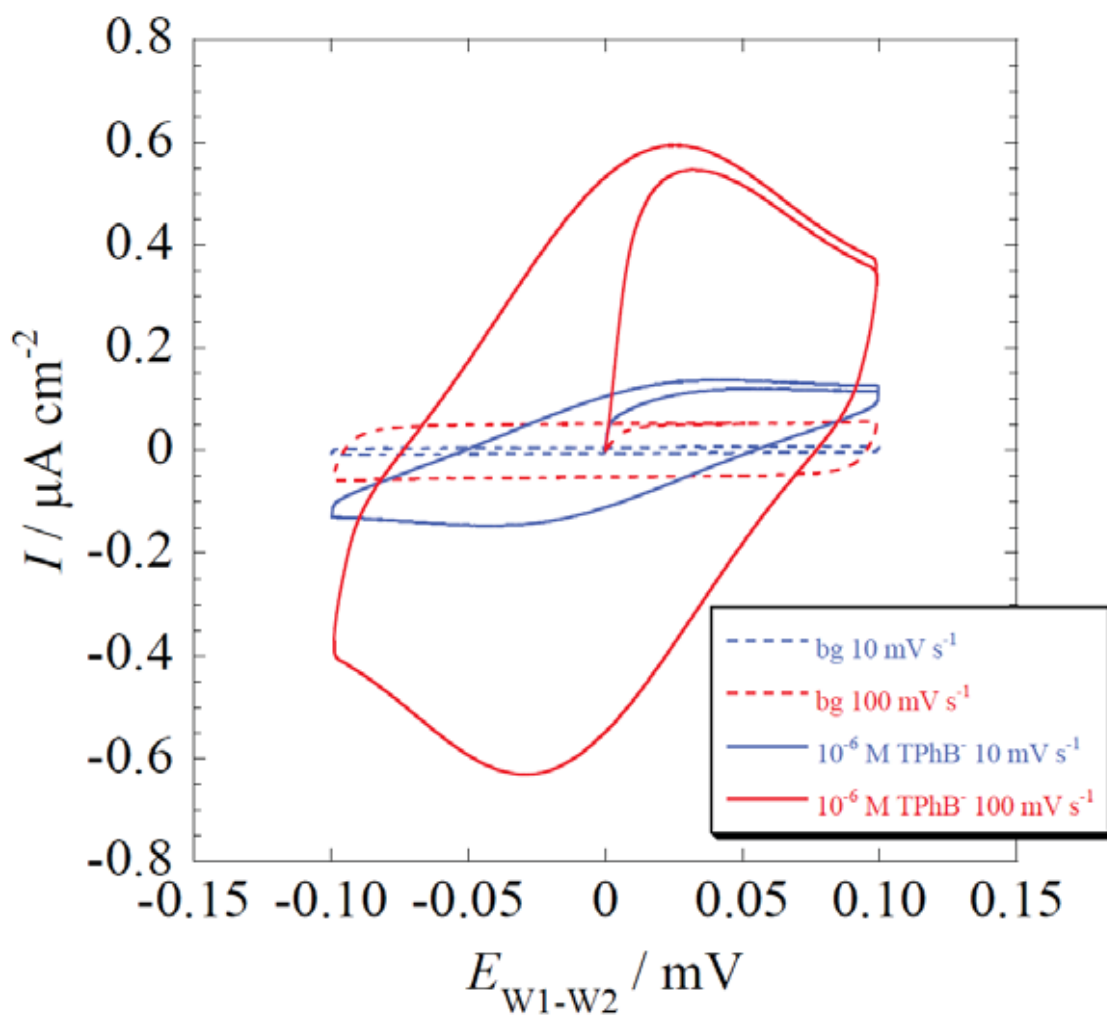


Fig. 2 Cyclic voltammograms for the ion transport across the BLM in the absence and presence of TPhB⁻.

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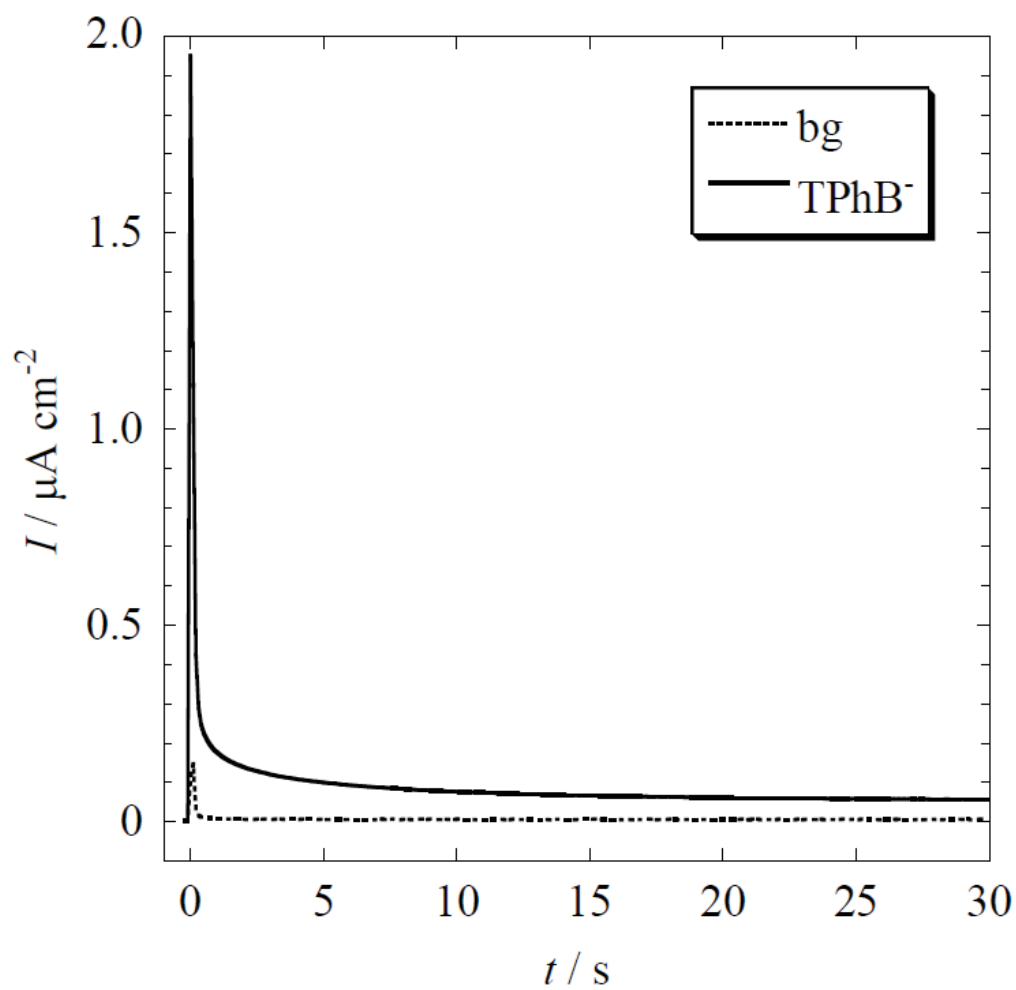


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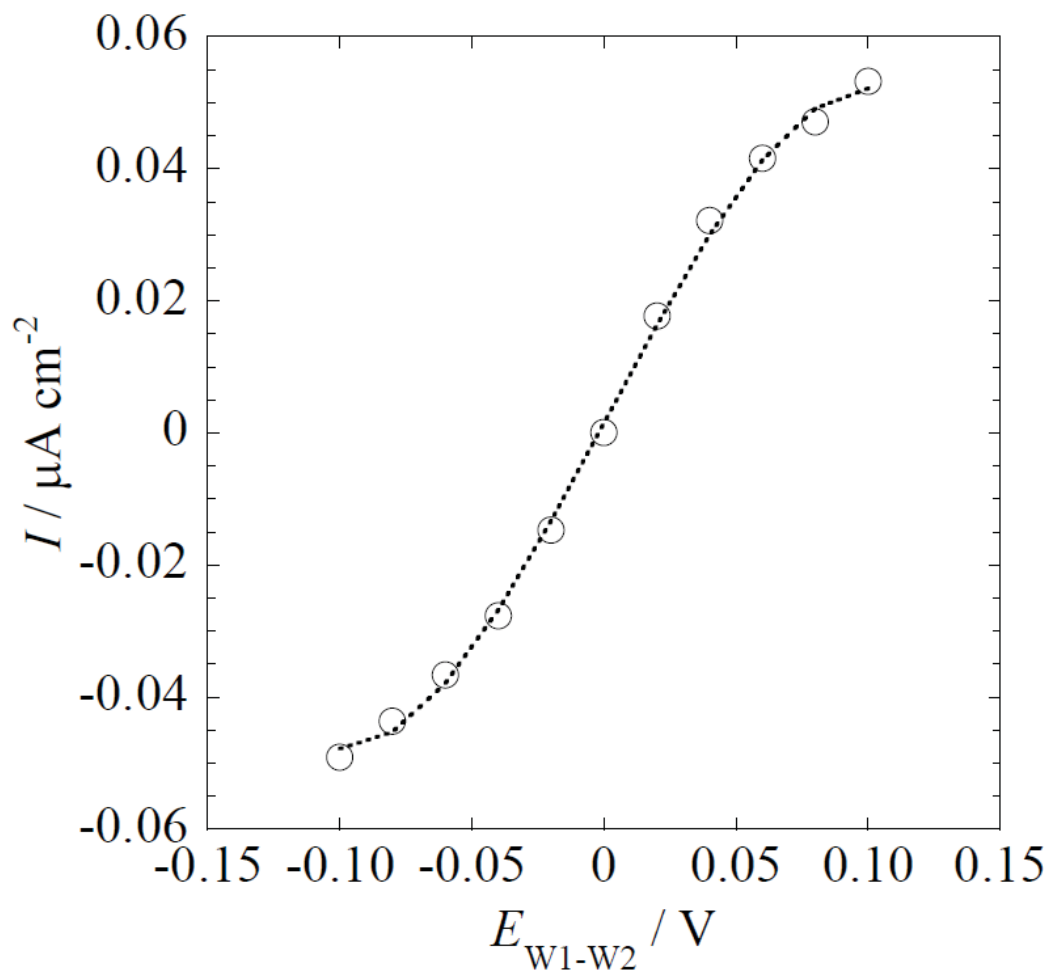


Fig. 4 The relation between the potential and current on the steady-state ion transport across the BLM in the presence of TPhB^- .

Concentration of NaCl in W1 and W2: 0.1 mol dm^{-3} . Concentration of TPhB^- in W1 and W2: $10^{-6} \text{ mol dm}^{-3}$. Potential region: $-0.1 - 0.1 \text{ V}$. Data sampling: 30 s after the potential change (NPV). Dotted line: fitting curve.

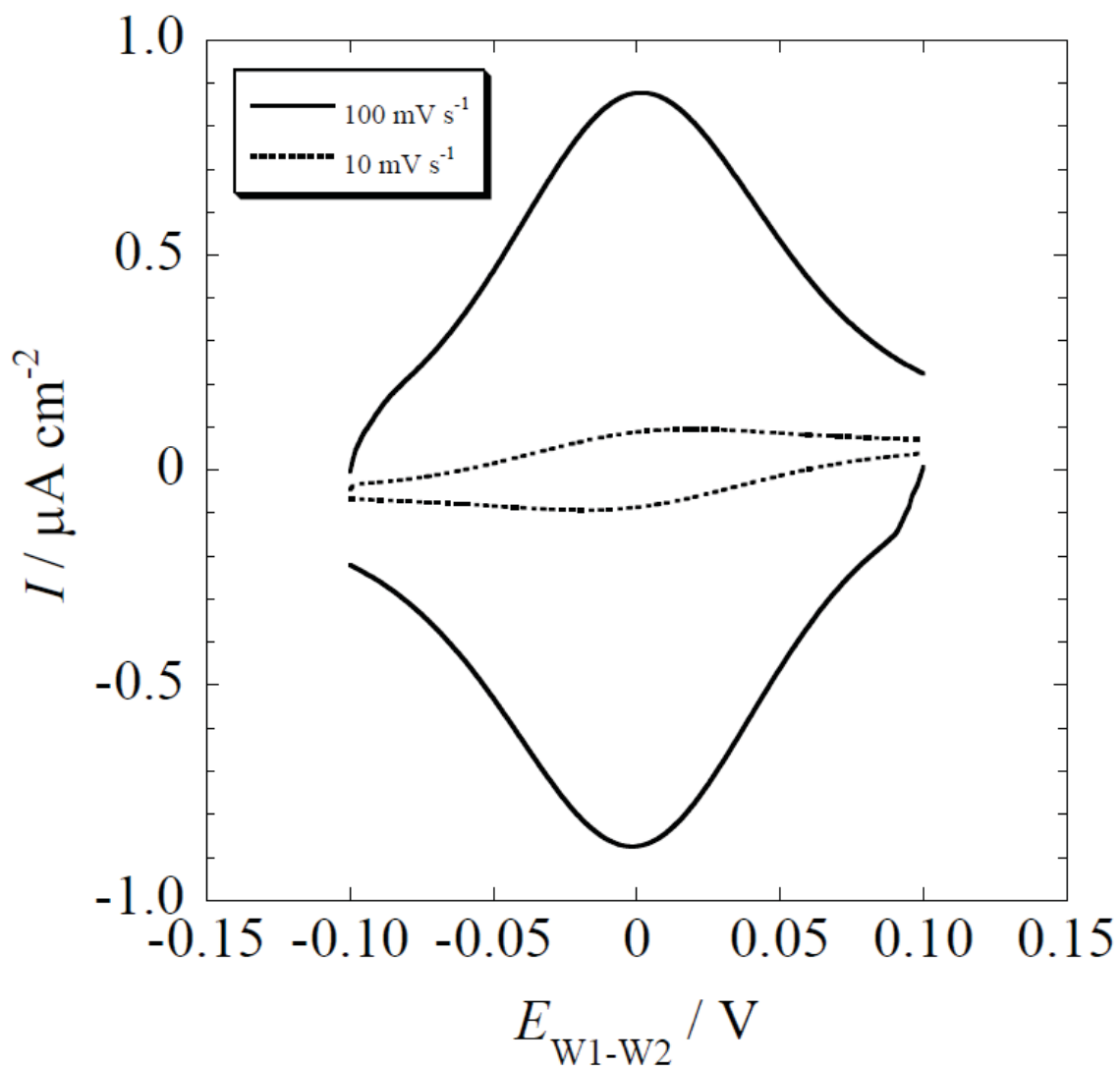
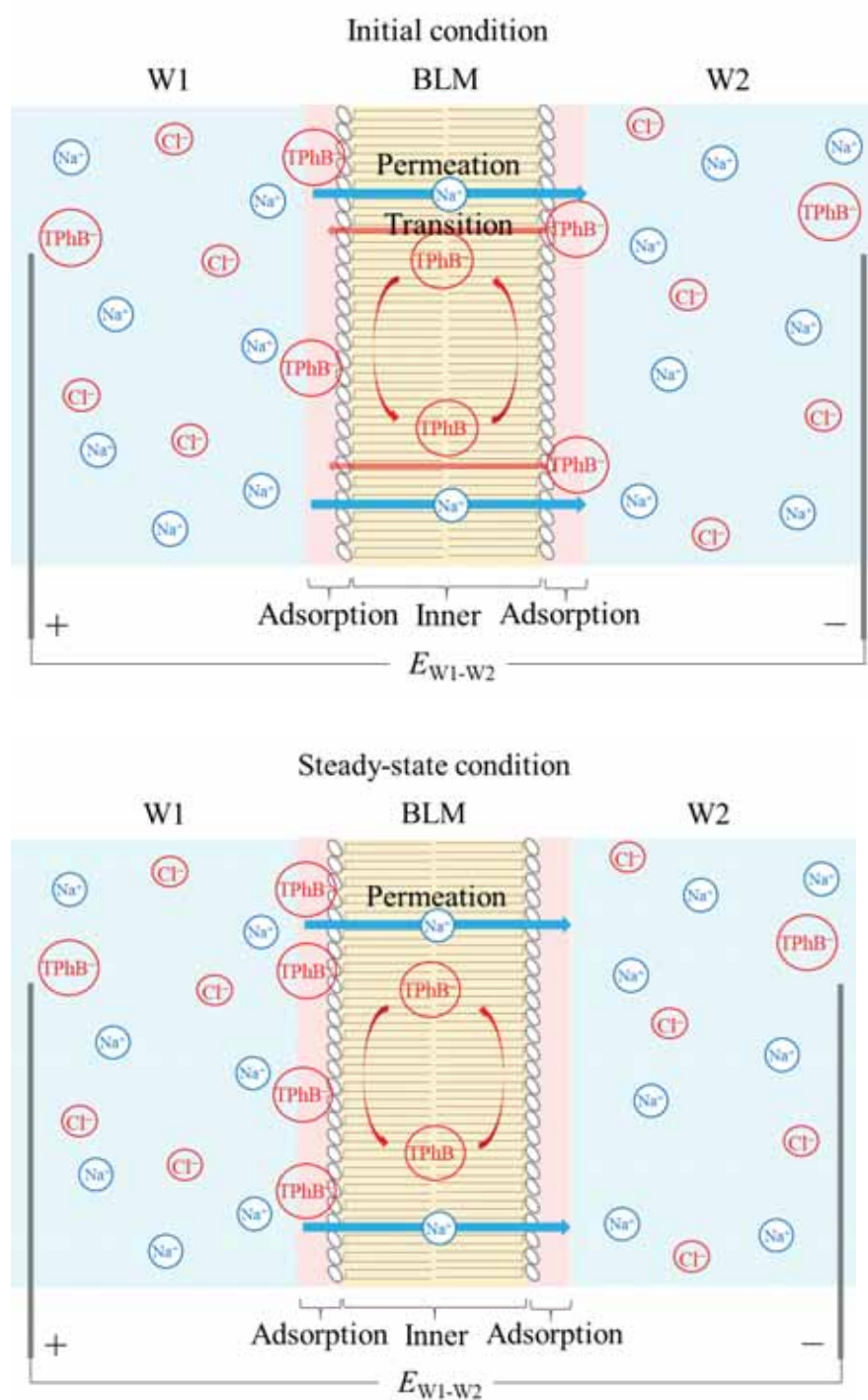


Fig. 5 Combination I - $E_{\text{W1-W2}}$ curves of the steady-state I - $E_{\text{W1-W2}}$ curve and the I - $E_{\text{W1-W2}}$ curves due to reversible translocation of adsorbed TPhB^- .

Concentration of TPhB^- , $10^{-6} \text{ mol dm}^{-3}$. Potential region: $-0.1 - 0.1 \text{ V}$. Potential scanning rate: 10 mV s^{-1} ; dotted lines, 100 mV s^{-1} ; bold lines.

Scheme 1



Scheme 1 Proposed schemes on the ion transport across the BLM

Graphical Index

