

Control of Uphill-transport Modes of Ions through Temperature-responsive Bipolar Membranes: Effect of the Charged Layer Structure on their Transport Properties

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We describe the design and preparation of a novel temperature-responsive bipolar membrane that can control the modes of *uphill* transport in response to temperature changes. In this study, *uphill* transport is defined as the transport of ions against their own concentration gradient. A temperature-responsive bipolar membrane was prepared by pasting a positively-charged layer and temperature-responsive negatively-charged layer together. In order to examine the effect of the charged layer structure on membrane transport properties, the permeation of Ca^{2+} ions and Li^+ ions in a dialysis system consisting of the membrane and mixed electrolyte solutions was measured at temperatures of 10°C and 50°C . The permeation experiments show that in response to the temperature changes, the membrane can control the modes of the *uphill* transport of both Ca^{2+} ions and Li^+ ions in two ways: *forward uphill transport* (the *uphill* transport in the direction of the concentration gradient of the driving electrolyte) and *backward uphill transport* (the *uphill* transport in the direction opposite to the concentration gradient).

Key words: Temperature-responsive, Bipolar membrane, Permeation, Uphill transport, Charge density

1. INTRODUCTION

A bipolar membrane has a sandwich-like structure of a positively charged layer, P, and a negatively charged layer, N, joined together in series. This membrane has many interesting transport phenomena such as rectification properties[1-3], permselectivity for univalent ion[4-6] and water splitting[7-18] and electrical oscillations[19,20]. These phenomena are very important clues for developing highly selective membranes as well as for making clear the mechanism of ionic transport in biological systems. Transport properties of a bipolar membrane depend on membrane constitution, which means the charge densities and the thickness of layers in the membrane, and the sequence (Pn or Np) of component layers in a system[21-25].

Let us consider a diffusion dialysis system where a bipolar membrane separates two cells. The two cells contain both the m species E_k electrolytes ($1 \leq k \leq m$) and the n species E_j electrolytes ($1 \leq j \leq n$). Initially, the concentration of E_k in the two cells is identical, and the concentrations of E_j have different values between the cells. Higa et al.[26] have simulated that in such a case, the cations or the anions of

E_k electrolytes are transported against their concentration gradients due to the diffusion of the driving electrolyte (E_j) under suitable conditions. This transport is referred to as *uphill* transport. There are two modes of *uphill* transport: *forward uphill transport* (the *uphill* transport in the direction of the concentration gradient of the driving electrolyte) and *backward uphill transport* (the *uphill* transport in the direction opposite to the concentration gradient). The simulations and the experiments by Higa et al.[27] show that the modes of *uphill* transport as well as the valence selectivity in the transport will be controlled by changing the membrane constitutions. Higa et al.[28] have reported that a negatively charged membrane made from poly(vinyl alcohol), *N*-isopropylacrylamide and a polyanion has a fast and reversible temperature response in the charge density. These results indicate that a bipolar membrane made from a temperature-responsive negatively charged layer and positively charged layer will control the modes of *uphill* transport in response to temperature changes.

This study aims to describe the design and preparation of a novel temperature-responsive bipolar (T-BIP) membrane. In order to examine the effect of the

charged layer structure on membrane transport properties, the permeation of Ca^{2+} ions and Li^+ ions in a dialysis system consisting of the membrane and mixed electrolyte solutions was measured at temperatures of 10°C and 50°C .

2. EXPERIMENTAL

2.1. Sample membranes.

Aqueous solutions of a mixture of PVA [poly(vinyl alcohol), Aldrich] and PAAm [poly(allylamine), Nittobo Industries Inc.] were cast for positively-charged membranes. The volume fraction of PVA to PAAm was changed to control the charge densities. A temperature-responsive negatively charged membrane was prepared as follows: the *in situ* polymerization of N-isopropylacrylamide on PVA was carried out using a potassium persulfate as an initiator. A membrane was prepared by casting a dimethyl sulfoxide solution of a mixture of the polymer obtained, PVA and AP-2. The AP-2 polymer contains sulfonic groups which provide negatively-charged sites. A temperature-responsive bipolar (T-BIP) membrane was made by pasting the negatively charged membranes and the positively charged ones together with a mixture of PVA and PAAm aqueous solution as binder.

2.2 Measurement of the membrane potential.

In order to obtain the charge density of the two charged layers, the total membrane potential was measured in two dialysis systems: Pn and Np. In system Pn, layer P contacted with the solution of the high-concentration side of the system; in system Np, the membrane was turned over so that layer P contacted with the low-concentration side. The membrane potential was measured by using Ag/AgCl electrodes [TOA, HS-205S] with salt bridges (3N KCl) using the same apparatus as shown elsewhere [28].

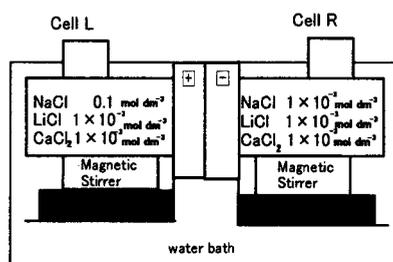


Fig. 1 Apparatus for permeation experiment of system Pn. In this system, layer P contacted with the solution of the high-concentration side of the system.

2.3 Permeation Experiments.

The permeation of Li^+ and Ca^{2+} ions in the dialysis systems shown in Fig. 1 was measured. In the dialysis

systems, two cells contain mixed salt solution of LiCl and CaCl_2 , and a driving electrolyte, NaCl. Initially, the concentration of LiCl and CaCl_2 in the two cells are identical, $0.001 \text{ mol dm}^{-3}$, and the concentration of the driving electrolyte, NaCl, in cells L and R are 0.1 mol dm^{-3} and $0.001 \text{ mol dm}^{-3}$, respectively. The membrane area was 7.07 cm^2 and the volume of the two cells was 100 cm^3 . The concentration change of the two cations in cell L was measured by an ion chromatograph [TOSOH, IC-8010] and an atomic absorption spectrometry [HITACHI, Z-5310].

3. RESULTS AND DISCUSSION

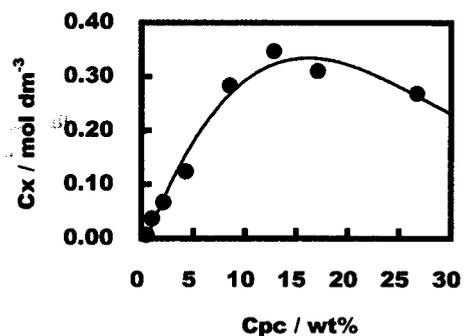


Fig. 2 The charge density of positively charged membranes as a function of the PAAm content, C_{pc} .

Figure 2 shows the charge density of the positively charged membranes as a function of the content of polycation PAAm, C_{pc} . The charge density is defined as the division of the number of the charged groups by the water content. The water content, whose results are not described here, increased with increasing C_{pc} . Hence, the charge density increased at initial stage as C_{pc} increased; however, decreased after it has a maximum value at $C_{pc}=12.5\text{wt}\%$.

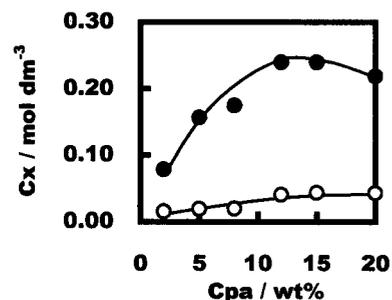


Fig.3 The charge density of temperature-responsive negatively charged membranes as a function of the AP-2 content, C_{pa} . (●):the data at 50°C , (○): at 10°C .

Figure 3 shows the charge density of the temperature-responsive negatively charged membranes at 50°C and 10°C as a function of the content of polyanion AP-2, C_{pa} . The charge densities at 50°C were higher than those at 10°C. The temperature changes in the charge density are due to phase separation in the membrane: Aqueous solutions of poly(NIPAAm) exhibit a lower critical solution temperature (LCST) at around 32°C. Hence, the poly(NIPAAm) in the membrane are soluble in the water phase in the membrane at temperatures below the LCST. At temperatures above the LCST, phase separation occurs; poly(NIPAAm) forms insoluble aggregates, and the charged groups in the membrane concentrates in the water phases. Therefore, increases in the charge density occur at temperatures above the LCST. The values of the charge density both at 50°C and 10°C increased with C_{pa} because the number of the charged groups in the membrane increased with C_{pa} . The charge density at 50°C had a maximum value at $C_{pa}=12.5\text{wt}\%$ because the water content increased with the AP-2 content. The data in Figs. 2 and 3 show that $C_{pc}=7\text{wt}\%$ for the positively charged layer and $C_{pa}=12.5\text{wt}\%$ for the temperature-responsive negatively charged layer are the best polyelectrolyte contents for making a T-BIP membrane.

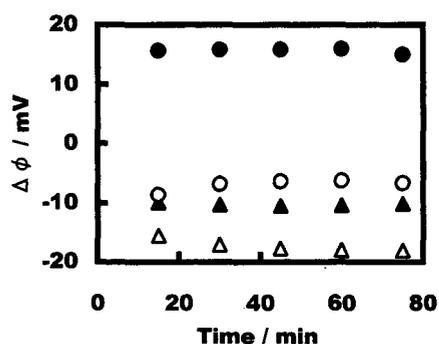


Fig. 4 Membrane potential across T-BIP membrane. (●) and (○) are the data at 50°C and at 10°C, respectively, in system Pn; (▲) and (△) are the data at 50°C and at 10°C, respectively, in system Np.

Figure 4 shows membrane potential across T-BIP membranes as a function of time. The potentials had a constant value after 60 min. In system Np, the potentials have negative values both at 50°C and at 10°C. However, in system Pn, the potentials have positive values at 50°C and negative values at 10°C. These results show that the charge density in the negatively charged layer, C_x^N , of the T-BIP membrane was higher than that in the

positively charged layer, C_x^P , at 50°C, and *vice versa* at 10°C. Our simulations showed that *forward* uphill transport occurs when $C_x^N > C_x^P$, and *backward* uphill-transport occurs when $C_x^N < C_x^P$. Hence, the potential data indicates that the modes of the uphill transport: *forward* and *backward* across a T-BIP membrane will be controlled by changing the temperature.

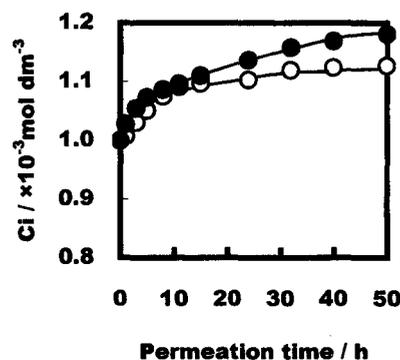
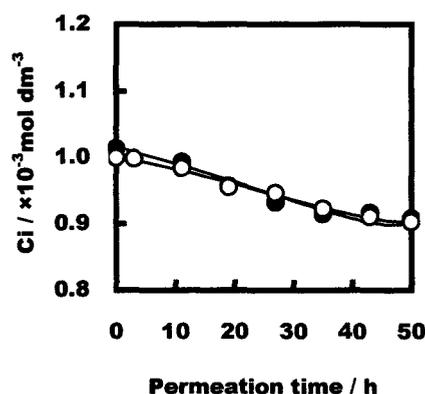


Fig. 5 Time-concentration curves in cell L at 50°C in the system shown in Figure 1.



(●):the data for Li^+ ions, (○): for Ca^{2+} ions.
Fig. 6 Time-concentration curves in cell L at 10°C in the system shown in Figure 1.
(●):the data for Li^+ ions, (○): for Ca^{2+} ions.

Figure 5 shows time-concentration curve in cell L at 50°C in the system shown in Figure 1. The increase of the concentration of both Li^+ ions and Ca^{2+} ions indicates that the two ions were transported against their concentration gradients from cell R to cell L. This means that *backward* uphill-transport occurred at 50°C.

Figure 6 shows time-concentration curve in cell L at 10°C in system Pn. The decrease of the concentration of both Li^+ ions and Ca^{2+} ions indicates that the two ions

were transported against their concentration gradients from cell L to cell R. This means that *forward* uphill-transport occurred at 10°C. These results show that the modes of the uphill transport across T-BIP membrane can be controlled by changing the temperature. The permeation data in system Np, whose results are not described here, revealed that in the system, *forward* uphill-transport occurred both at 50°C and 10 °C.

Our simulations predicted that T-BIP membrane has permeselectivity for bivalent ions in system Pn. In our experiments, system Pn did not show the permeselectivity because the mobility of Ca²⁺ ion in the membrane is much smaller than that of Li⁺ ion.

4. CONCLUSION

We prepared a temperature-responsive bipolar membrane by pasting a positively-charged membrane and temperature-responsive negatively-charged membrane. In a dialysis system consisting of the T-BIP membrane and mixed NaCl, LiCl and CaCl₂ solutions when layer P contacted with the solution of the high-concentration side of the system, *backward* uphill-transport occurred at 50°C, and *forward* uphill-transport occurred at 10°C. The modes of the uphill transport across T-BIP membrane can be controlled by changing the temperature.

5. ACKNOWLEDGMENT

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