

Metal ion-selective membrane prepared by surface molecular imprinting

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Abstract

Surface molecular imprinting was applied to the preparation of an ion-selective polymeric membrane for the first time. The use of acrylonitrile-butadiene rubber and a porous solid support in the polymer matrix resulted in improved flexibility and mechanical strength of the imprinted membrane. The asymmetric porous structure of the membrane was observed by scanning electron microscopy. The selectivity of the zinc(II)-imprinted membrane was evaluated by competitive adsorption and permeation studies. The imprinted membrane showed higher adsorption affinity and permeation selectivity towards the imprinted zinc ion than the non-imprinted counterpart. On the basis of the results obtained, the permeation mechanism of the metal ions was considered to be hopping of metal ions on the binding sites in the membranes.

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1. Introduction

Membrane-mediated separation of metal ions has attracted much attention due to promising properties such as easy and low energy of operation and high selectivity, and the resulting low cost of operation. The selectivity of membranes for a targeted molecule is a key factor determining the success of a membrane separation process. Many efforts have been made to prepare membranes having a specific selectivity [1–3]. One of the strategies to enhance the selectivity of the membrane is incorporation of highly selective binding sites into the membrane.

Molecular imprinting is a convenient and powerful technique for preparing polymeric materials with artificial receptor-like binding sites for various substances [4,5]. Use of the imprinting technique has provided membrane specific selectivity for the separation of several organic compounds [6–10]. Recently, Kimaro et al. reported a uranyl ion (UO_2^{2+})-selective membrane prepared by imprinting techniques [11]. In their study, free-standing membranes imprinted against

uranyl ions were prepared by bulk polymerization of uranyl vinylbenzoate and styrene/divinylbenzene. To our knowledge, this is the only report on the application of the molecular imprinting technique to the preparation of metal ion-permselective membranes.

In the present study, a different approach for creating a metal ion-imprinted polymeric membrane is proposed. The surface imprinting technique utilizing water-in-oil (W/O) emulsions [12,13] was applied for the first time to the preparation of a metal ion-imprinted membrane. A zinc(II) ion-imprinted membrane was prepared by emulsion polymerization with 1,12-dodecanediol-*O,O'*-diphenylphosphonic acid (DDDPA, functional host molecule), L-glutamic acid dioleylester ribitol ($2\text{C}_{18}\Delta^9\text{GE}$, emulsion stabilizer), and divinylbenzene (DVB, polymer matrix-forming monomer) [14]. To obtain flexible and mechanically stable membranes for practical applications, the polymerization was conducted in the presence of acrylonitrile-butadiene rubber (NBR) and hydrophilized poly(tetrafluoroethylene) (PTFE) membranes. The morphology of the imprinted membrane was characterized by scanning electron microscopy. To evaluate selectivity and an imprinting effect for the Zn(II)-imprinted membrane, competitive adsorption and permeation experiments

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were carried out. Finally, the origin of selective permeation and the mechanism of ion transport through the membrane are discussed.

2. Experimental section

2.1. Materials

The functional molecule, DDDPA and the emulsion stabilizer, $2C_{18}\Delta^9GE$ were synthesized according to procedures reported in previous works [15,16]. Fig. 1 shows the molecular structures of DDDPA and $2C_{18}\Delta^9GE$. NBR (19–22 wt.% acrylonitrile) was purchased from Aldrich (Milwaukee, WI, USA). PTFE membranes (10 μm pore size and 100 μm thick) were from Millipore (Tokyo, Japan). DVB from Wako Pure Chemical Industries (Osaka, Japan) was used after treatment with silica gel to remove the inhibitor. Other reagents were of commercially available analytical grades.

2.2. Preparation of the Zn(II)-imprinted membrane

The Zn(II)-imprinted membrane was prepared by the surface template polymerization technique utilizing W/O emulsions [14]. Five milliliters of DVB, containing DDDPA (0.22 g), $2C_{18}\Delta^9GE$ (0.12 g), NBR (0.12 g) and 2,2'-azobis(2,4-dimethylvaleronitrile) (0.045 g), was mixed with 2.5 mL of toluene containing 15% (v/v) 2-ethyl-1-hexanol. An aqueous buffer solution (3.75 mL, pH 3.5) of 0.1 M acetic acid–sodium acetate and 0.01 M zinc nitrate was added to the DVB solution. In order to obtain a W/O emulsion, the mixture was treated with a homogenizer (PT-2100, KINEMATICA, Switzerland) at 24,000 rpm for 4 min. The emulsion obtained was degassed in a sonicating water bath and coated on the sup-

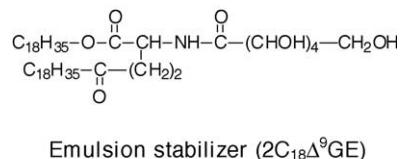
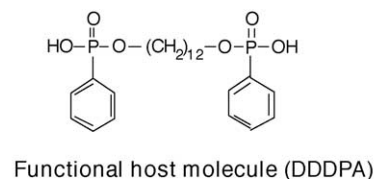


Fig. 1. Structures of the functional host molecule and the emulsion stabilizer used in this study.

port material (hydrophilized PTFE membrane). The substrate was then placed between two glass plates with a fixed distance of 240–340 μm . Radical polymerization was carried out for 5 h at 50 $^\circ\text{C}$ under a nitrogen flow. The schematic illustration of the membrane preparation is shown in Fig. 2. Thereafter, the polymeric membrane was dried in vacuo and washed with 1 M hydrochloric acid to remove the template. The amount of DDDPA in the washing solutions was determined by measuring the phosphorus atom with an inductively-coupled plasma optical emission spectrometer (OPTIMA 3100RL, Perkin-Elmer). Finally, the imprinted membrane was dried under vacuum for a few days. A non-imprinted membrane was prepared under the same conditions, but in the absence of the zinc ion. Similarly, a control membrane was also prepared in the absence of DDDPA, but in the presence of zinc ion.

The morphology of the Zn(II)-imprinted membrane was observed by a scanning electron micrograph (SEM), SS-550

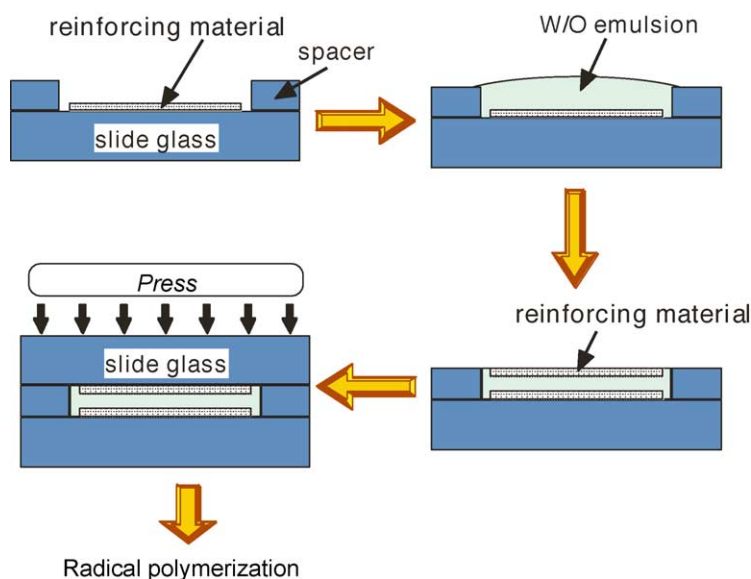


Fig. 2. Schematic illustration of preparation of metal-ion imprinted membrane.

(Shimadzu, Japan), after gold sputtering using an ion coater (IB-3, Eiko, Japan).

2.3. Adsorption experiments

A typical procedure for the competitive adsorption tests was as follows: a dry membrane (0.03 g) was incubated with 1.5 mL of an aqueous buffer solution containing zinc and copper nitrate (0.1 mM each) for 4 days at 20 °C. The pH in the aqueous solution was adjusted with 0.1 M acetic acid–sodium acetate. After filtration with a syringe-driven filter unit (Millex-LG, Millipore, Japan), the concentrations of free metal ions in the filtrate were determined by an atomic absorption spectrophotometer (AA-6700, Shimadzu, Japan).

2.4. Permeation experiments

The membrane, with an exposed cross-sectional area of 0.6 cm², was mounted in a two-compartment glass cell (each compartment 5 mL in volume). The feed phase consisted of zinc and copper nitrate (10 mM each) and 0.1 M acetic acid–sodium acetate (pH 5.9). An aqueous solution containing 0.1 M acetic acid–sodium acetate (pH 5.9) was used as the receiving phase. Both compartments were stirred using a magnetic stirrer at a constant rate. The amounts of the metal ions that permeated through the membrane were determined by analyzing an aliquot of the solution from the receiving phase with the atomic absorption spectrophotometer. To maintain a constant volume, the volume of the solution removed for analysis was replaced with the pure receiving solution. All permeation experiments were carried out at room temperature.

3. Results and discussion

3.1. Characteristics of the Zn(II)-imprinted membrane

To prepare an effective molecularly imprinted polymer by the surface template polymerization technique, it is necessary to immobilize the functional host molecules (specific binding sites) on a rigid polymer matrix. In previous studies, highly cross-linked polymers (e.g. poly(DVB)) providing rigidity were used as the matrix of the surface imprinted polymer particles [14,17]. However, such a polymer tended to yield a brittle membrane. To improve the mechanical strength of the membrane, it was prepared by emulsion polymerization of DVB in the presence of NBR and hydrophilized PTFE membrane, which resulted in a flat sheet membrane with flexibility and mechanical stability. The NBR content of the membrane is relatively low (ca. 2 wt.%), and therefore the resulting polymer would have a two-phase nature with poly(DVB) as a continuous phase and NBR as a dispersed phase [18]. Then, most of the functional host molecules are expected to be sufficiently fixed on the rigid poly(DVB) matrix by the π – π stacking interaction [14]. In support of this opinion, the

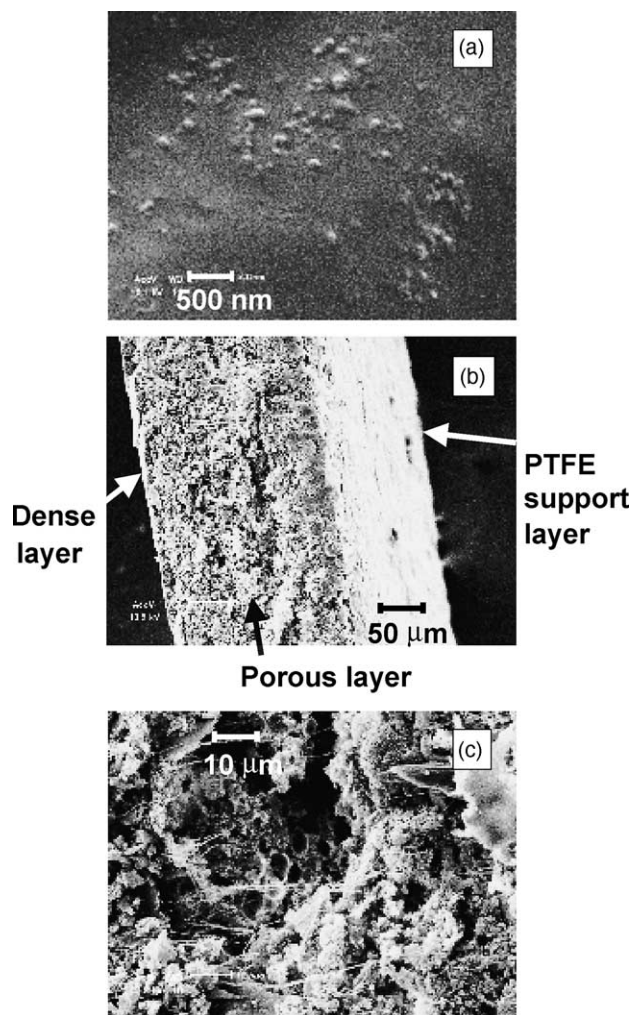


Fig. 3. Typical SEM photographs of the surface (a) and the cross section (b) of the Zn(II)-imprinted membrane, and the porous layer with micron-scale pores in the imprinted membrane (c).

amount of DDDPA eluted from the membranes in the washing step was negligible (<1%).

Fig. 3 shows SEM photographs of the surface and the cross section of the Zn(II)-imprinted membrane. These photographs indicate that the surface of the membrane is mostly smooth and the thickness of the membrane is about 300 μ m. It is also evident from the cross-sectional image (Fig. 3b) that the imprinted membrane has an asymmetric structure, which consists of a thin and dense layer, a large porous layer having pores in the micron range, and a PTFE support layer whose pores were filled with the polymer matrix. In the porous layer (Fig. 3c), a number of cavities corresponding to traces of the aqueous phases in the W/O emulsions are present, which is consistent with the morphology of Zn(II)-imprinted polymer particles similarly prepared with W/O emulsions [14]. It can be deduced that hydrophilic functional groups, such as phosphonic acid groups of DDDPA forming Zn²⁺-selective binding sites, distribute densely on the surface of these cavities, whereas the other part of the membrane consists of

hydrophobic polymer matrix. The cavities function as a specific ion channel when the imprinted membrane is applied to the permeation experiments.

3.2. Adsorption behavior of metal ions on the Zn(II)-imprinted membrane

The effect of pH on the adsorption of Zn²⁺ and Cu²⁺ to the Zn(II)-imprinted membrane was investigated along with that of the non-imprinted and the control membranes. Adsorption abilities of the Zn(II)-imprinted and non-imprinted membranes were influenced by the pH of the incubation buffers. With an increasing pH, the percent adsorption was enhanced for both Zn²⁺ and Cu²⁺ (Fig. 4). This behavior suggests that complexation between the metal ions and phosphonic acid groups immobilized on the polymer matrix plays a substantial role in the adsorption of the metal ions. This idea is supported by the result that the control membrane prepared without DDDPA hardly adsorbed Zn²⁺ and Cu²⁺ under the same buffer conditions (data not shown). The Zn(II)-imprinted membrane exhibited higher adsorption affinity and selectivity towards Zn ions than the non-imprinted membrane at pH 4.5 and 6. This result can be attributed to the imprinting effect: by the surface template polymerization technique, Zn²⁺-selective binding sites would be effectively created on the accessible internal surfaces of the Zn(II)-imprinted membrane.

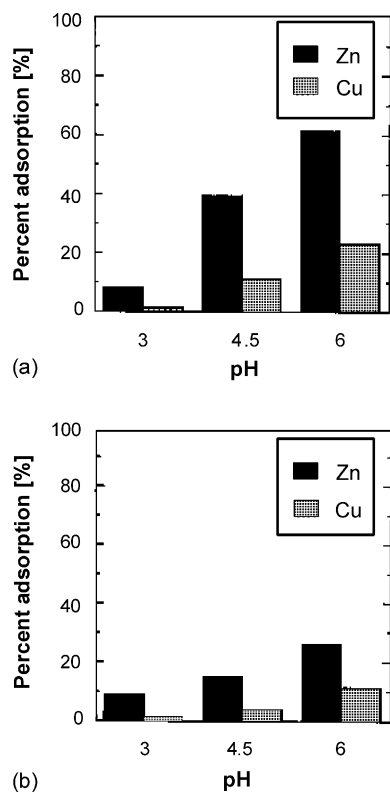


Fig. 4. Adsorption characteristics of the Zn(II)-imprinted membrane (a) and the non-imprinted membrane (b) as a function of pH. Each experiment was performed in duplicate. The average values are plotted.

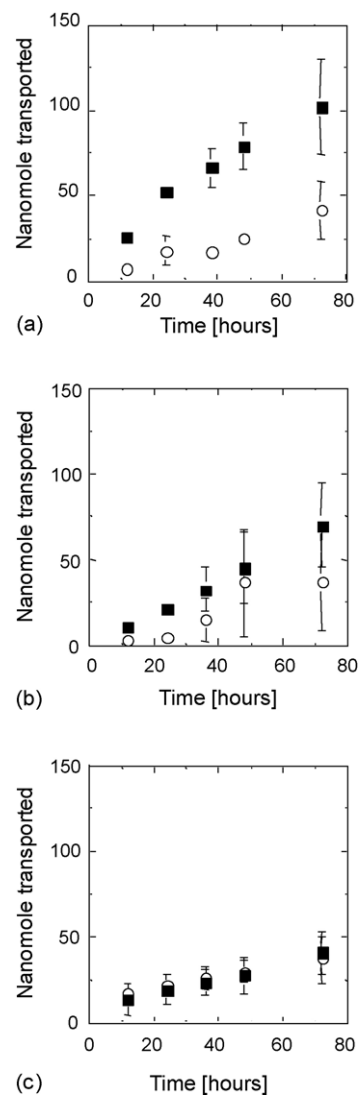


Fig. 5. Plots of nanomoles of zinc(II) (■) and copper(II) (○) ions permeated through the Zn(II)-imprinted membrane (a), the non-imprinted membrane (b) and the control membrane (c) vs. time. The points represent the mean values of three measurements. The error bars displayed on the graphs show the standard deviation and in some cases they are smaller than the size of the point marker.

In contrast, at pH 3, the adsorption of Zn ions by the non-imprinted membrane was comparable to that by the Zn(II)-imprinted membrane. It would be because non-specific interaction between Zn²⁺ and DDDPA randomly immobilized on the polymer matrix is dominant in the ion-adsorption mechanism. Selective adsorption of Zn²⁺ on the non-imprinted membrane can be explained by the intrinsic selectivity in the complexation of DDDPA [14].

3.3. Ion permeability of the Zn(II)-imprinted membrane

To assess the permselectivity of the Zn(II)-imprinted membrane, competitive ion permeation experiments using Zn²⁺ and Cu²⁺ were conducted. In this system, the concentration difference between ions in the feed and receiving phases

Table 1
Flux, separation factor (α) and relative selectivity coefficient (α') values for the membranes prepared in this study

Membrane	Flux (nmol/cm ² h)		α [–] ^a	α' [–] ^b
	Zn ²⁺	Cu ²⁺		
Zn(II)-imprinted	2.3	0.95	2.4	1.3
Non-imprinted	1.6	0.86	1.9	
Control	0.95	0.86	1.1	–

^a $\alpha = \text{flux}_{\text{Zn}}/\text{flux}_{\text{Cu}}$.

^b $\alpha' = \alpha_{\text{imprinted}}/\alpha_{\text{non-imprinted}}$.

was adopted as a driving force for the membrane permeation. Fig. 5 shows time courses of the permeation of metal ions through the Zn(II)-imprinted, non-imprinted, and control membranes. The fluxes of Zn²⁺ and Cu²⁺ were calculated from the amounts of the metal ions permeated across the membranes in 72 h (Table 1). A separation factor α was defined as the ratio of the flux between Zn²⁺ and Cu²⁺. In order to evaluate an imprinting effect, a relative selectivity coefficient α' was defined as follows: $\alpha' = \alpha_{\text{imprinted}}/\alpha_{\text{non-imprinted}}$. The fluxes through these membranes were comparable with those measured for the ion transport through the uranyl ion-imprinted membranes reported by Kimaro et al. [11]. When the Zn(II)-imprinted or non-imprinted membrane was used in these tests, selective permeation of Zn²⁺ over Cu²⁺ was observed ($\alpha > 1$). The value of α' (1.3) exceeded unity, indicating that the surface imprinting process enhanced the permselectivity of the membrane. Since the control membrane did not exhibit any selectivity, these data suggest that the presence of the functional host molecule (DDPPA) is essential in ensuring permselectivity of the imprinted membrane.

As seen in Fig. 5, Zn²⁺ was preferentially permeated through the Zn(II)-imprinted and non-imprinted membranes, and these membranes showed higher adsorption affinity towards Zn²⁺ than Cu²⁺ (Fig. 4). This implies that ion distribution from the feed phase into the membrane phase is a rate-limiting step in the permeation system. This distribution process must involve the complexation reaction between the metal ions and ion-binding sites composed of phosphonic acid groups, and this leads to Zn²⁺ selectivity. In this case, the Zn(II)-imprinted membrane has specific binding sites for Zn²⁺, therefore, one can imagine that highly selective sorption of Zn²⁺ over Cu²⁺ into the imprinted membrane was achieved. This results in selective permeation of Zn²⁺ through the imprinted membrane over the non-imprinted one. After the sorption step, it is assumed that the metal ions are transported through the membrane by hopping of the ions from one binding site to another [7,19–21]: fast exchange reactions between the metal ions and the binding sites could occur in the region enriched with immobilized DDPPA molecules, i.e., the internal surface of the membrane. On the other hand, the permeation of the metal ions through the control membrane would take place by non-specific diffusion following a concentration gradient. In order to gain further insight into the permeation mechanisms, a detailed investigation of the system is now underway.

4. Conclusions

This work demonstrated the potential of the surface template polymerization technique for the preparation of a polymeric membrane that shows specific permselectivity towards targeted water-soluble substrates. A Zn(II)-imprinted membrane was successfully prepared by the surface template polymerization technique utilizing W/O emulsions. Emulsion polymerization was carried out in the presence of NBR and a porous solid support (hydrophilized PTFE membrane), and flat sheet membranes with a good flexibility and mechanical strength were obtained. The resulting membrane exhibited a high adsorption ability towards the template, namely Zn²⁺. In permeation studies using the Zn(II)-imprinted membrane, selective permeation of Zn²⁺ over Cu²⁺ was observed, which suggests that the sorption of metal ions in the initial step is the rate-determining step in the membrane permeation. However, there remain several issues to be solved, such as low permeate flux and long-time performance. We are currently studying the imprinted polymeric membrane capable of separation of valuable metal ions.

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