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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.

Keywords: Metal ion; Membrane; Surface template polymerization; Separation; Ion exchange

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 ($2C_{18}\Delta^9$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, $2C_{18}\Delta^9$GE were synthesized according to procedures reported in previous works [15,16]. Fig. 1 shows the molecular structures of DDDPA and $2C_{18}\Delta^9$GE. 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), $2C_{18}\Delta^9$GE (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 support 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 °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.

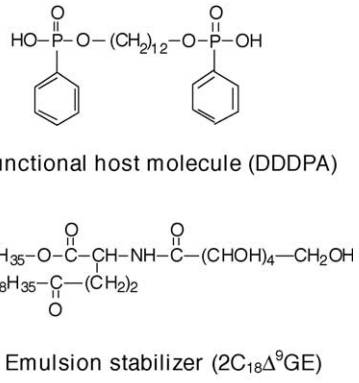

Fig. 1. Structures of the functional host molecule and the emulsion stabilizer used in this study.

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

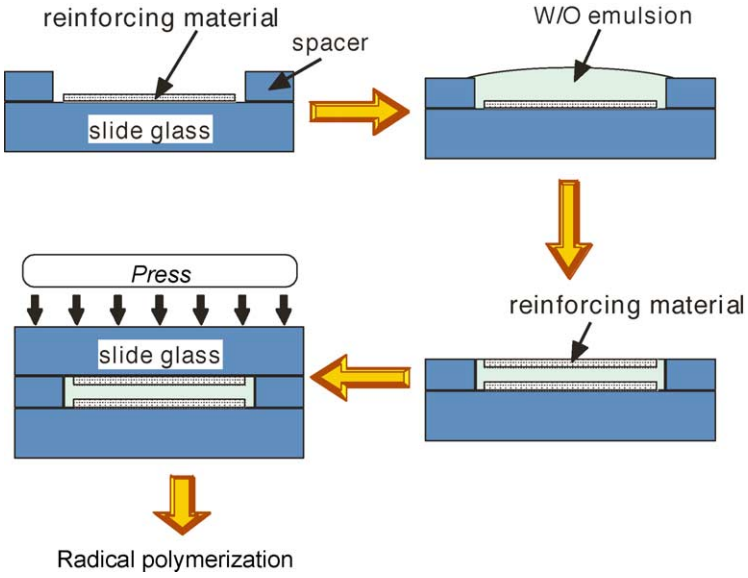

Fig. 2. Schematic illustration of preparation of metal-ion imprinted membrane.