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A novel free-standing flexible molecularly imprinted membrane for selective separation of synephrine in methanol–water media

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ABSTRACT

Flexibility was very important for molecularly imprinted membrane (MIM) to apply to practical use. A novel free-standing flexible MIM was prepared using methacrylic acid (MAA) and 2-hydroxyethyl acrylate (HEA) as co-functional monomer, and ionic liquid as porogen. HEA was able to effectively improve the flexibility of MIM. Ionic liquid, 1-butyl-3-methylimidazolium bromide, was able to accelerate the synthesis process and improve the selectivity and adsorption of the MIM. The properties of MIM were characterized by scanning electron microscopy (SEM), Fourier transform infrared (FT-IR), thermo gravimetric analysis (TGA), differential thermal analysis (DTA) and X-ray photoelectron spectroscopy (XPS). Two structurally similar compounds (octopamine and tyramine) were selected as competitors to examine the selective recognition of MIM to synephrine (SYN). The competitive adsorption and permeation selectivity experiments showed that the MIM could selectively recognize SYN, and was able to be used to selectively separate SYN from the standard mixtures or the extract of stir-baked *Aurantii Fructus Immaturus* in methanol/water (4:1, *v*/*v*) media.

1. Introduction

Molecularly imprinted polymers (MIPs), which have been called "antibody mimics" because they attempt to mimic the interactions of their natural counterparts, have been receiving much attention, and rapid developments have been achieved already in separation due to their stability, preparation with ease and feasibility in different kinds of conditions [1–4]. Especially, molecularly imprinted membranes (MIMs) can combine the advantages of membranes and MIPs, such as the high selectivity of MIPs, the less energy consumption and continuously separating mixtures of membrane separation. These characteristics are helpful for a large-scale continuous separation operation, especially in industrial applications [5]. Therefore MIMs are believed to be one of the most potential materials in the new century and are attracting considerable interest in separation and purification fields [6–8].

The main strategies for preparation of MIMs include preparation of membranes from previously synthesized "conventional" MIPs, i.e. particles, simultaneous formation of MIP structure and membrane morphology, and preparation of MIPs *on* or *in* support membranes with suited morphology [9]. in situ crosslinking polymerization, belonging to the strategy "simultaneous formation of MIP structure and membrane morphology", was often used to prepare MIM, but had some limitations that the MIMs were fragile and brittle due to its high degree of crosslinking. It is well known that MIMs should possess some flexibility for their handling [5,9,10], otherwise, the MIMs will be too fragile for practical application. Many methods were considered to improve flexibility and mechanical stability of the membranes, such as by adding the plasticizer, oligourethane acrylate [11,12], polyurethane [13,14], polybutyl acrylate [7], or by using mixed crosslinker [10], or by lowing the proportions of crosslinker [13], but maybe these means will decrease the MIM performance [13,15]. Therefore, a novel preparation of flexible MIM should be developed.

Moreover, recently ionic liquids have been used as solvent or porogen in the preparation of MIPs, which can accelerate the synthesis process and improve the selectivity and adsorption of MIPs [16–19]. Especially, during the process of thermo-polymerization avoiding the solvent or porogen to escape from the system is very important to form the pore structure of MIPs. The low vapor pressure of ionic liquids makes them act as a good pore template in polymerization reactions, accelerating the synthesis process and improving the performance of MIPs [17].

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Therefore, as a continuation of our earlier study [20,21], in this work, a novel method was presented to prepare a free-standing flexible MIM of synephrine (SYN) by using methacrylic acid (MAA) and 2-hydroxyethyl acrylate (HEA) as co-functional monomers, and using ionic liquid as porogen during MIM synthesis. SYN is one of the major alkaloids in *Aurantii Fructus Immaturus* (Chinese name: *Zhishi*) which is the immature dried fruit of *Citrus aurantium* L. (bitter oranges) or *Citrus sinensis* Osbeck (sweet oranges) and is widely used in herbal medicine, herbal weight loss products, or dietary supplements [22]. Octopamine (OCT) and tyramine (TYR) possess similar structures to SYN as shown in Fig. 1B, and they often coexist in this medicine.

2. Materials and Methods

2.1. Materials and reagents

The stir-baked *Aurantii Fructus Immaturus* with bran was purchased from Zhangshu Tianqitang Traditional Chinese Medicine Yinpian Co., LTD, Zhangshu, China. SYN hydrochloride (≥ 98% purity) and OCT hydrochloride (≥ 98% purity) were purchased from the Shaanxi Sciphar Biotechnology Co. Ltd., Xi'an, China, and Shaanxi Dongke Medicine Science and Technology Incorporated Company, Yanglin, China, respectively. TYR (≥ 98% purity), HEA, ethylene glycol dimethacrylate (EGDMA) and Amberlite® IR-120 (Na^+ form) cation exchange resin were purchased from Shanghai Aladdin Reagent Company, Shanghai, China. MAA and 2,2′-azoisobutyronitrile (AIBN) were purchased from the Damao Chemical Reagents Co., Tianjin, China. HPLC grade methanol was purchased from Tianjin Shield Company, Tianjin, China. Ionic liquids, 1-butyl-3-methylimidazolium bromide ([Bmim]Br), was synthesized according to our previous work [23]. All the other chemicals were analytical grade reagents; all solutions were prepared with deionized water.

SYN hydrochloride and OCT hydrochloride were converted to the free base by passing their aqueous solution into an ethanol/water prewashed column of Amberlite® IR-120 (H^+ form), and then elution with an ammonium hydroxide/ethanol (65:35) solution. The eluate was concentrated to dryness to obtain the free base as a white powder.

2.2. HPLC conditions

The HPLC analysis was performed on an Agilent Technologies 1100 LC system with a Hypersil BDS-C18 column (4.6 × 200 mm, 5 μm particle size, Sepax Technologies, Inc) at 20 °C, and with a mobile phase composed of methanol and an aqueous solution (containing 0.02% phosphoric acid, 0.02% triethylamine and 0.1% sodium dodecyl sulfate) in a volume ratio of 55/45 (*v*/*v*) at a flow rate of 1.0 mL min^{-1}. All analytes were detected at 224 nm and identified by retention time and comparison with the UV–visible spectrum of the standard.

2.3. Preparation of Aurantii Fructus Immaturus extract

One gram of pulverized stir-baked *Aurantii Fructus Immaturus* with bran was extracted by ultrasound assistance with an ultrasonic power of 420 W for 16 min in 12 mL methanol/water solution (4:1, *v*/*v*), and after that the extract was centrifuged for 30 min at 5000 rpm. An aliquot (1 mL) of the supernatant was diluted to 10 mL with methanol/water (4:1, *v*/*v*).

2.4. MIM preparation

A series of MIMs, labeled as MIM_1, MIM_2, …… MIM_{15}, were prepared and the preparation conditions were evaluated by varying the type or amount of functional monomer, porogen, and crosslinker according to Table 1. In a typical synthetic procedure, an amount of 0.2 mmol SYN (template), 0.46 g MAA/0.54 g HEA mixture (co-functional monomer) and 4.8 g [Bmin]Br (porogen) was mixed. The resulting mixtures were sonicated for 10 min and then stood overnight. Then 4 mmol EGDMA (crosslinker) and 0.02 mmol AIBN (initiator) were added to the solution. The pre-polymerization solution was shaken and sonicated for 10 min. The mixture was sealed and deoxygenated with a stream of nitrogen. The pre-polymerization solution was infiltrated between two glass plates by capillary force. A spacer between two glass plates was used to control the thickness and uniformity of the MIM (the scheme is shown in Fig. 1A). Prior to use, the glass plates were washed with potassium dichromate/H_2SO_4 solution

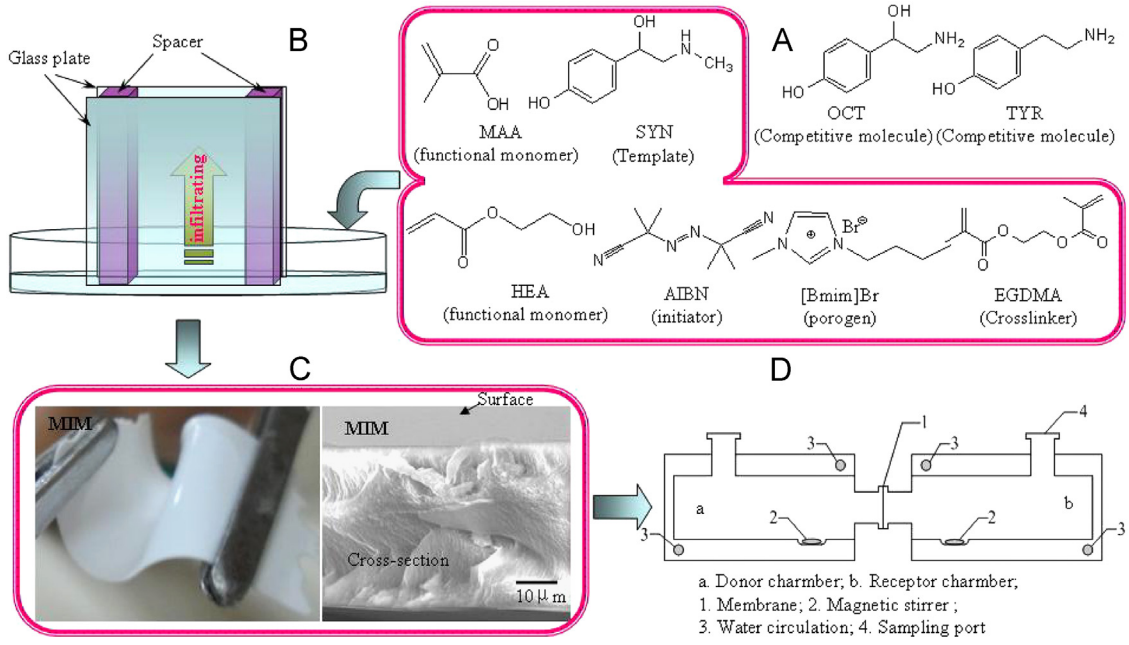

Fig. 1. Chemical structures of the relative compounds in this work (A); schematic illustration of the infiltration of prepolymerization solution between two glass plates (B); the digital photograph and SEM micrograph of MIM (C); schematic illustration of Valia–Chien permeation cells (D).