



Preparation of metallic pivot-based imprinted monolith for polar template



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ABSTRACT

One of the main challenges in MIPs preparation is the proper MIP monolith design for water-soluble compounds due to the difficulty in satisfying the demands of both good column permeability and affinity to polar template. A new strategy of metallic pivot in a ternary porogenic system of dimethyl sulfoxide (DMSO)-dimethylformamide (DMF)-1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim]BF₄) was suggested to solve this problem. An imprinted monolithic column with high porosity and good permeability was synthesized using a mixture of methyl gallate (template), 4-vinylpyridine, ethylene glycol dimethacrylate, and cobalt acetate. Some polymerization factors, such as template-monomer molar ratio and the composition of the ionic liquid, on the imprinting effect of the resulting MIPs monoliths were systematically investigated. In a mobile phase of acetonitrile-buffer, the greatest imprinting factor of 10.9 was obtained on the MIPs monolith with the optimized polymerization parameters. Thermodynamic analysis for separation demonstrated that the separation between the template and its analogs on the ion-mediated MIPs monolith is an enthalpy-controlled process.

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1. Introduction

Molecular imprinting is a technique for the preparation of polymeric materials that can act as selective synthetic receptors for certain target molecules [1,2]. The principle of the molecular imprinting is that a target molecule (template) and functional monomers are polymerized with a crosslinking reagent. After removal of the template, the functional groups in the resulting binding sites should be arranged in positions suitable for interaction with the template molecule. Due to their favorable molecular recognition capability and stability, as well as low cost, applications of MIPs have been found in broad areas, such as catalysis [3], bio-mimetic sensors [4], drug delivery system [5], solid-phase extraction [6] and chromatography [7].

One of the main challenges in MIPs preparation is the proper MIP design for water-soluble compounds because of the necessity of hydrophobic porogenic solvents (i.e., toluene, chloroform) in classical approach to MIPs preparation. To date, several methods

have been developed for water-soluble compounds, including metal ion as pivot [8–10], metal complexes as binding interaction [11,12], ion-pair as template [13], the incorporation of polar or non-polar co-monomers in the MIP matrix [14], surface imprinting technique [15], and β -cyclodextrin as functional monomer [16,17]. Among these methods, creating a metallic pivot for molecular self-assembly has recently demonstrated to be an efficient and simple approach to highly specific imprinted materials. Using this strategy, the weak linkage between the monomer and template, such as hydrogen bond or Coulomb force, is placed by stronger coordination binding. However, the resulting MIPs mentioned above usually require considerable post-polymerization processing to afford useable MIPs. In a tedious and time-consuming process, MIPs have to be grounded and sieved to the desired particles to an appropriate size, which often results in some interaction sites to be destroyed, thus lower MIP loading capacity than expected values.

Monolithic column is macroporous material with structure of continuous bed prepared in situ [18]. In comparison to packed-bed columns, their merits include the lower back pressure, high versatility with controlled porosity, improved mass-transfer kinetics and the application to chromatography directly [19]. Thus, the combination of MIPs and monolithic column is regarded as one of the promising approach to overcoming the problems of the MIPs prepared in classical polymerization [20–22]. In the procedure of

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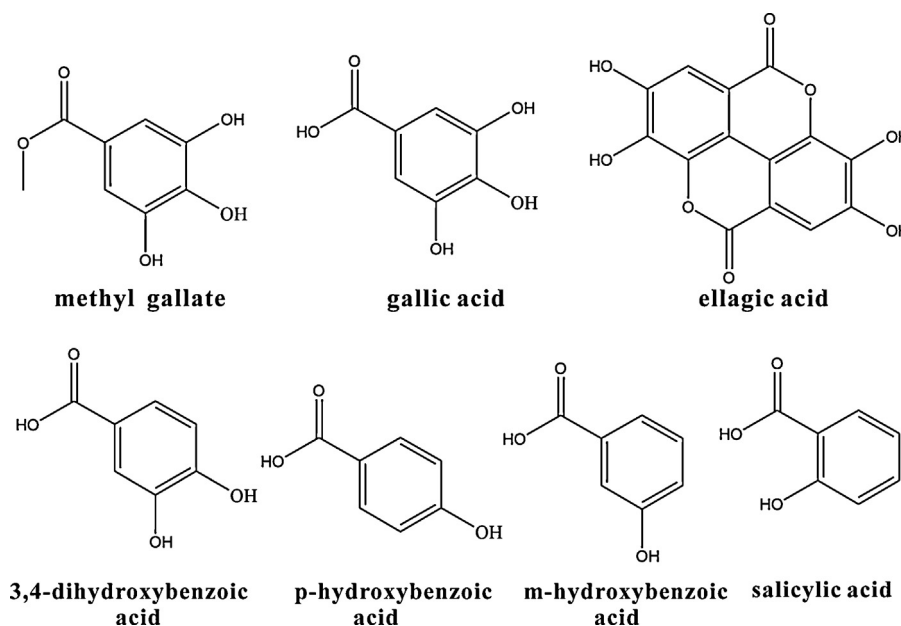


Fig. 1. Structures of methyl gallate and analogs tested.

the preparation of MIPs monolith, a porogen with similar solubility parameters to polymer has to be included to ensure the formation of porous structures with both pore size and pore volume, which is usually non-polar solvent, i.e., good solvent. For the preparation of MIP monolith applicable to polar template, however, the key work is how to overcome the immiscible of the good solvent and the polar solvent to solve the polar molecules.

Successful systems of porogen for preparing MIP monolith consisted of a mixture of solvents, e.g., toluene/1-dodecanol [12], dichloromethane/dodecanol [23], molecular crowding agents [24], tetrahydrofuran/isooctane (ISO) [25], acetonitrile/2-propanol [26], ISO/toluene [27] and ternary porogen [14]. However, polar template can not be dissolved in the porogen above.

Room temperature ionic liquid is a unique solvent of low vapor pressure with excellent solvation qualities and chemical/thermal stability. Recently, it has been used as solvent or porogen to prepare MIPs and shown to be able to accelerate the polymerization and improve effect of imprinting [28–32]. The latter might be attributed to low degree of polymer swelling [28], which is markedly different from MIPs prepared with traditional porogen. For example, MIPs prepared with [Bmim]BF₄ were 2 times more selective than the corresponding MIPs generated under classical porogen, acetonitrile [28]. However, up to date, the use of ionic liquid to prepare MIP is quite limited, probably due to decreased imprinting effect derived from its polar nature that may affect the formation of complexes in non-covalent imprinting method. Thus, to synthesize imprinted monolith with metal ion as pivot in the presence of ionic liquid is expected to take advantage of its merits above.

A strategy of metallic pivot in a ternary porogenic system of dimethyl sulfoxide (DMSO)-dimethylformamide (DMF)-1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim]BF₄) was suggested here to prepare MIP monolith for a water-soluble template (methyl gallate). [Bmim]BF₄ was chosen due to higher imprinting factor achieved on the MIPs prepared in the ionic liquid [29]. DMSO was used to solve metal ion, while the ratio of [Bmim]BF₄ to DMF was used to tune the retention of template on the resulting MIP monolith. Co²⁺ was used as metallic pivot in the present study. The effect of polymerization parameters such as template-monomer molar ratio, the composition of the ternary porogen and the degree of

crosslinking, and the amounts of Co²⁺ on the imprinting effect of this new MIP monolith was investigated.

2. Experimental

2.1. Reagents and chemicals

Methyl gallate (MG) was from Beijing Bailingwei Chemical Reagent (Beijing, China). Gallic acid (GA), ellagic acid (EA), salicylic acid (SA), *m*-hydroxybenzoic acid (MHA), *p*-hydroxybenzoic acid (PHA), 3,4-dihydroxy benzoic acid (DHA), as shown in Fig. 1, were obtained from Shanghai Guangtuo Chemical Reagent (Shanghai, China). 4-Vinylpyridine (4-VP) and ethylene glycol dimethacrylate (EDMA) were purchased from Sigma Company (St. Louis, MO, USA). Dimethyl sulfoxide (DMSO) and dimethylformamide (DMF) were obtained from Tianjin Jiangtian Chemical Industry Reagent (Tianjin, China). 1-Butyl-3-methylimidazolium tetrafluoroborate ([Bmim]BF₄) was purchased from Shanghai Chengjie Chemical Reagent (Shanghai, China). Cobalt acetate and 2,2-azobisisobutyronitrile (AIBN) were supplied by Kermel Chemical Reagent (Tianjin, China). HPLC-grade acetonitrile (ACN) was from Tianjin Biaoshiqi Chemical Reagent (Tianjin, China). Other analytical reagents were from Tianjin Chemical Reagent Ltd. Co. (Tianjin, China).

2.2. Preparation of imprinted monoliths

Methyl gallate imprinted monolith with metal ions was directly synthesized by in situ polymerization within the confines of a stainless-steel column tube (100 mm × 4.6 mm i.d.). Pre-polymerization mixture was prepared by mixing methyl gallate (template), 4-VP, DMF, DMSO, EDMA, [Bmim]BF₄, and cobalt acetate (Table 1). The amount of AIBN in all experiments was 20 mg.

The pre-polymerization mixture was sonicated for 15 min and filled into the steel column. The ends of the column were sealed and the column was kept at 60 °C for 16 h. After polymerization, the column was connected to an HPLC pump and flushed exhaustively with ACN and a mixture of methanol and acetic acid (9:1, v/v), respectively, until no residue of the template was found in the

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