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Investigation of imprinting parameters and their recognition nature for quinine-molecularly imprinted polymers

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Abstract

A series of molecularly imprinted polymers (MIPs) was prepared using quinine as the template molecules by bulk polymerization. The presence of monomer–template solution complexes in non-covalent MIPs systems has been verified by both fluorescence and UV–vis spectrometric detection. The influence of different synthetic conditions (porogen, functional monomer, cross-linkers, initiation methods, monomer–template ratio, etc.) on recognition properties of the polymers was investigated. Scatchard analysis revealed that two classes of binding sites were formed in the imprinted polymer. The corresponding dissociation constants were estimated to be 45.00 μmol l^{-1} and 1.42 mmol l^{-1}, respectively, by utilizing a multi-site recognition model. The binding characteristics of the imprinted polymers were explored in various solvents using equilibrium binding experiments. In the organic media, results suggested that polar interactions (hydrogen bonding, ionic interactions, etc.) between acidic monomer/polymer and template molecules were mainly responsible for the recognition, whereas in aqueous media, hydrophobic interactions had a remarkable non-specific contribution to the overall binding. The specificity of MIP was evaluated by rebinding the other structurally similar compounds. The results indicated that the imprinted polymers exhibited an excellent stereo-selectivity toward quinine.

Keywords: Molecularly imprinted polymers; Quinine; Spectrometric detection; Synthetic conditions; Binding characteristics

1. Introduction

A high selective molecular recognition system has a vital important significance in living organism, such as the interactions between antigen–antibody, substrate–enzyme and protein–DNA and so on. The challenge of synthesizing artificial acceptor capable of molecular recognition has attracted much attention over recent decades. Molecular imprinting technology provides a promising alternative way to design artificial recognition sites within a synthetic polymer network via the template polymerization process. In this process, polymerizable functional monomers are pre-arranged around a template molecule in porogenic solvent. The resulting pre-polymer complexes are copolymerized with an excess of cross-linking monomer in the presence of a free radical initiator under thermal or photochemical conditions. After the removal of the template by extraction, binding sites complementary to the template molecule both in shape and chemical functionality are left within the polymer matrices that allow rebinding of the template with high specificity. To date, molecularly imprinted polymers (MIPs) have been exploited extensively in many different applications including their use as separation materials [1,2], chemical sensors [3], reaction catalysts [4], enzyme mimics [5] and in particular, as solid-phase extraction (SPE) adsorbents [6,7].

Depending upon the nature of chemical bonds involved, MIPs synthesis techniques can be classified into two common approaches (covalent imprinting and non-covalent imprinting). Of the two strategies, the latter has been most widely adopted in many laboratories due to the merits of being more flexible in terms of the choice of functional monomers and possible template molecules. In theory, non-covalent imprinting may synthesize a receptor for any target chemical species. However, it does have some limitations. The non-covalent bonds (e.g., hydrogen bonds or other electrostatic interactions) formed during pre-arrangement are relatively weak. Therefore, imprinting parameters must be carefully chosen to shift the equilibrium

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toward complexes formation. Inspite of the great need for such work, various attempts have been made in recent years to obtain highly specific recognition materials for different particular template, which include using different functional monomers, cross-linkers, solvents, polymerization temperature, etc. [8,9].

Quinine, as a cinchona alkaloid, derives from certain cinchona barks and is usually used to treat malaria in medicine. Our recent studies reported the design and the preparation of molecularly imprinted polymer receptors for the quinine by utilizing two-step seed swelling and surface imprinting methods, and then evaluated the imprinting effect of MIPs to rebinding the template [10,11]. In parallel to above work, in this paper, we have prepared a series of MIPs by bulk polymerization using quinine as template. By examining binding characteristics of MIPs prepared under varying polymerization conditions (different functional monomers, cross-linkers, solvents, initiation methods, template/monomer ratios, etc.), we expected not only to understand their underlying origin of recognition properties, but also to be able to evaluate these parameters which were important in determining the ability of MIPs to recognize template molecules. Meanwhile, the quantity of binding sites of the MIP was examined by using Scatchard analysis and a multisite binding model in the molecular imprinting technique. In addition, the binding selectivity of MIPs and their subsequent recognition mechanism in organic and aqueous media were also explored in detail.

2. Experimental

2.1. Materials

Quinine, quinidine, cinchonidine and quinoline were purchased from Acros. Ethylene glycol dimethacrylate (EDMA), divinylbenzene (DVB) and 2-vinylpyridine (2-VP) were Sigma products. Acryl-amide (AA) and methacrylic acid (MAA) were obtained from Shanghai Chemical Reagent Co. Ltd. 2,2′-Azo-bis-isobutyronitrile (AIBN) was obtained from the Fourth Chemical Plant of Shanghai. 1,6-Hexanediol diacrylate (HDDA), trimethylolpropane triacrylate (TMPTA) and tripropylene glycol diacrylate (TPGDA) were donated by the Goldrising Technology Co. Ltd. EDMA, TMPTA, TPGDA, DVB, 2-VP, MAA and AIBN were all purified before use. Other reagents were all of analytical grade. Fig. 1 shows the chemical structures of all substrates and cross-linkers available for this study.

2.2. Measurements

All binding experiments and UV–vis spectra were performed using a CARY-100 Ultraviolet-visible spectrophotometer. The emission spectra were recorded on an F-4500 luminescence spectrometer at 25 °C. The surface morphology of imprinted polymer was observed by a ZSM-6300 field emission scanning electron microscope (SEM) on gold-sputtered sample. Porosimetry analysis was performed on a Micromeritics ASAP 2010 using a 100-point pressure table and 10 s equilibration times after polymer particles were degassed at 150 °C for 3 h.

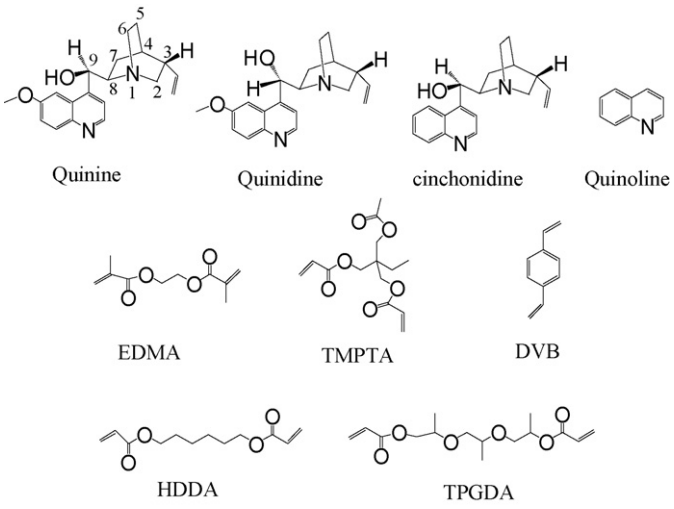

Fig. 1. The chemical structure of the substrates and cross-linkers.

2.3. Polymer preparation

The chemical composition and initiation method for making MIPs are shown in Table 1. The synthetic procedure for the preparation of the standard polymer P_1 was as follows: 0.3240 g (1 mmol) of quinine and 0.2583 g (3 mmol) of functional monomers (MAA) were dissolved in chloroform (6 ml) in 50 ml glass ampoule. After oscillating for 30 min, 4.4600 g (22.5 mmol) of cross-linker and AIBN (0.03 g) were added. The solution was degassed in a sonicating bath, and deoxygenated with a stream of nitrogen for 10 min. Then, the ampoule was placed into an ice bath apparatus and sealed under vacuum. The polymerization was allowed to carry out in a constant water bath at 55 °C or under ultraviolet lamp (365 nm) at 15 °C for 24 h. The resultant rigid polymers were ground to pass through a 77 μm sieve. Fine particles were removed by decantation in acetone. The resulting particles were placed in a Soxhlet apparatus and washed with 10% acetic acid methanolic solution until the template could no longer be detected at 278 nm in the elution. Then, the particles were washed with pure methanol to remove residual acetic acid and dried to constant weight under vacuum at 80 °C. As a control, the non-imprinted polymers (NIPs) in the absence of the template were prepared and treated by using the same method.

2.4. Spectroscopic analysis

The changes in fluorescence emission spectra of quinine were recorded using spectroscopic titration by adding MAA into a constant concentration of quinine solution (20 $\mu mol\,l^{-1}$) in $CHCl_3$. The excitation and emission wavelength were chosen at 271 and 406 nm, respectively. The changes in absorption spectra of quinine were also recorded by adding MAA into a constant concentration of quinine solution (0.1 $mmol\,l^{-1}$) in $CHCl_3$ with corresponding pure MAA solution as blank.