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Preparation and Cyclic Voltammetry Characterization Of Cu-dipyridyl Imprinted Polymer

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Abstract: Polymer capable of specific binding to Cu-dipyridyl complex was prepared by molecular imprinting technology. The binding specificity of the polymer to the template (Cu-dipyridyl complex) was investigated by cyclic voltametric scanning using the carbon paste electrode modified by polymer particles in phosphate buffer solution. Factors that influence rebinding of the imprinted polymer were explored. The result demonstrated that the cyclic voltammetry was an efficient approach to explore interactions between template and imprinted polymers.

Keywords: Molecular imprinted polymer, copper(II)–dipyridyl complex, carbon paste electrode, cyclic voltammetry.

Molecular imprinted polymers(MIPs) have attracted considerable attention due to their high affinity and selectivity to template molecule, as well as their applications in stationary phases[1] of highly selective chromatographic, antibody and receptor mimics[2], artificial enzymes[3]and sensor components[4]. The principal paradigm of the molecular design of such materials involves the preorganization of binding sites of the host system (receptor) around complementary binding sites of the guest molecule (template) through covalent or noncovalent hydrogen bonding and electrostatic interactions. Although noncovalent interactions provide polymers faster rebinding kinetics, the recognition capability is limited by the weak nature of individual interactions. Due to its relatively high strength and selectivity, metal-ligand coordination is well-suited to molecular recognition and biological molecules, as exemplified by metal-affinity chromatographic purification of proteins[5]. As it is electrochemically reactive, the metal-complex can be detected by electrochemical methods. To our knowledge, electrochemical evaluation of MIPs has never been reported. Realizing that chromatography is currently employed as the main implement to evaluate imprinted materials, we propose that cyclic voltammetry can also be a very effective one when electrochemically active chemicals are involved in the recognition process.

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Experimental

2 mmol 2, 2′-dipyridyl and 2 mmol cupric acetate were dissolved in 10 mL of methanol. Then, 4-vinylpyridine (4-Vpy) (2 mmol), ethylene glycol dimethacrylate (EGDMA) (20 mmol), and azo-bis-isobutyronitrile (AIBN) (48 mg) were added, the mixture was transferred to a 18 × 180 mm borosilicate glass test tube, and purged with nitrogen for 10 min. The tube was sealed under vacuum at liquid nitrogen temperature. The polymerization was initiated at 60°C and the reaction was allowed to continue for 24 h at the same temperature. Non-imprinted polymer was produced under the same conditions in the absence of 2, 2′-dipyridyl and cupric acetate. The resulting bulk polymer was ground and sieved to collect particles less than 30 μm. The template was extracted with 10% acetic acid in methanol for 48 h until no dipyridyl was detected. For the non-imprinted polymer, the same extracting procedure was employed.

Graphite powder was immersed in 8 mol/L hydrochloric acid solution for 8 h, then washed by deionized water until no Cl^- could be detected, and then kept in alcohol. The treated graphite powder was filtered and dried in air. The polymer particles, carbon powder and 25% of solid wax were thoroughly mixed in a mortar with a pestle, then heated on a hot plate at 55°C to make a paste. While hot, a portion of the paste was packed into a teflon tube, 1.6 mm in diameter, until it contacted a copper wire placed in the distal end of the tube. The surface of the electrode was polished to finish the preparation of polymer containing paste electrode. The graphite paste electrode, used for comparison, was prepared in exactly the same manner and wax content, except for the absence of polymer.

Electrochemical measurements were performed on a CHI 812 electrochemical system with a saturated calomel electrode as reference electrode, a platinum wire as counter electrode and a carbon paste electrode as working electrode. Absorption of cupric acetate, 2, 2′-dipyridyl or copper-dipyridyl (1:1) complex on electrode was achieved by soaking the carbon paste electrodes in 5 mmol/L methanolic solution and rinsing with methanol to wash off weakly absorbed solute. Electrochemical characteristics of absorbed compounds can be investigated by cyclic voltametric scanning of these electrodes in 20 mmol/L pH=7 phosphate buffer solution from 1.0 V to –1.0 V at a scan rate of 100 mVs^{-1}. The buffer solution was purged with nitrogen for 10 min before experiment.

Results and Discussion

The effect of soaking time was investigated by soaking electrodes in 1 mmol/L cupric acetate-2, 2′-dipyridyl (1:1) methanolic solution for 2, 6 and 12 h, respectively. After 2 h soaking, graphite paste electrode, imprinted polymer electrode and non-imprinted polymer electrode have a weak reductive peak at –0.2 V, which is identified as the reduction of cupric acetate absorbed on the electrode by comparing with the cyclic voltammograms of cupric acetate in aqueous solution using the above electrodes. There is no discernible difference between these three kinds of electrodes in either magnitude or position of the peak, showing that absorption was a physical process at relatively low concentration and short soaking time. When soaking time is extended to 6 h, the reductive peaks of cupric acetate on both imprinted and non-imprinted polymer electrodes appears more negative with significant increases in magnitude, while the peak on carbon electrode remains unchanged. Although at almost the same potential, the peak on imprinted polymer has a current much larger than that on the non-imprinted polymer. The peak shifting towards negative indicates the stabilization of electrochemically reactive copper(II) on the electrodes, which is supposed to be achieved by the forming of covalent bonds between copper ion and nitrogen atoms in the polymer matrices. Since the stabilization of copper ion is a chemical absorption process, it is usually slower than physical absorption and will reasonably take a longer time. The increases of current on polymer electrodes show that the amount of cupric acetate absorbed is increased and the imprinted polymer has a higher absorption capacity. No significant changes can be observed after increasing the soaking time further to 12 h, suggesting that 6 h would be long enough for the adsorption to reach equilibrium.

No peaks of copper-dipyridyl complex appear anticipatedly under above experimental conditions, probably due to the relatively low concentration of metal-complex. This is verified by increase the concentration to 5 mmol/L. After 6 h soaking, the imprinted polymer electrodes have a reductive peak at –0.5 ~ –0.7 V corresponding to the reduction of copper-dipyridyl.

The composition of imprinted polymer electrode is studied. The optimal composition was found to be 15% polymer, 60% carbon and 25% solid wax. **Figure 1** shows the cyclic voltametric graphs of imprinted and non-imprinted polymer electrodes at the optimal composition above and carbon electrode. **Figure 2** shows the cyclic voltametric graphs of optimized polymer electrodes and carbon electrode after soaking in 5 mmol/L methanolic solution of cupric acetate for 6 h. The reductive peak of copper-dipyridyl complex appears at –0.75 V for the imprinted polymer electrode, which is 0.35 V more negative than that on the non-imprinted polymer electrode. Although 2, 2′-dipyridyl is usually electrochemically reactive, no significant peak is observed on either polymer electrode or carbon electrode after the same soaking procedure. Probably it is because covalent

Figure 1 Cyclic voltammograms of Cu-2, 2′-dipy absorbed on different electrodes

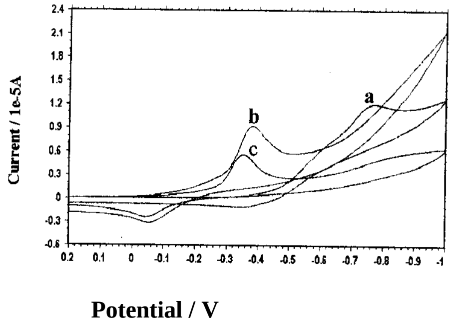
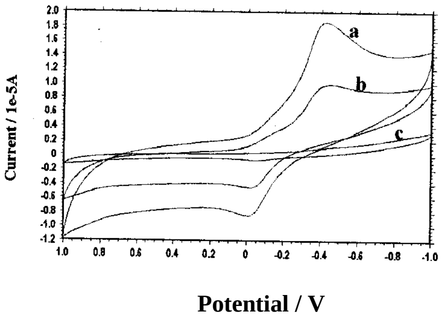


Figure 2 Cyclic voltammograms of cupric acetate absorbed on different electrodes



a control polymer electrode; **b** imprinted polymer electrode; **c** carbon electrode bonds are less likely to form between 2, 2′-dipyridyl and polymer or carbon particles. The negative peak shifting (**Figure 1**) is due to the specific recognition of imprinted polymer to template, thus the value of association constant can be calculated as 10^{15} based on the 0.35 V peak potential difference between imprinted and non-imprinted polymer electrodes[6].

The effect of the ratio of dipyridyl to Cu was investigated by increasing the concentration of dipyridyl from 5 to 15 mmol/L, while keeping the concentration of Cu constant as 5 mmol/L. First, the peak current and the background increase with the peak potential remains the same. After increase the concentration of dipyridyl to 15 mmol/L, the peak current drops steadily. This shows that by varying the ratio of dipyridyl to Cu, the predominant species in the solution was changed. The Cu-dipyridyl dominates when the ratio is about 3. Increasing or decreasing dipyridyl will lead to the decreasing of Cu-dipyridyl; thus the peak current will decrease subsequently. This indicates that the key species in molecular imprinting process is Cu-dipyridyl.

The specificity to Cu-dipyridyl was further investigated by soaking the electrodes in 5 mmol/L 1:1 methanol solution of Cu and other ligands of similar structure to 2, 2′-dipyridyl: 4, 4′-dipyridyl, 1, 10-phenanthroline, 4, 4′-dimethyl-2, 2′-dipyridyl and 2, 9-dimethyl-1, 10-phenanthroline, respectively. No significant difference was observed between the cyclic voltametric graphs from imprinted and non-imprinted electrodes. This shows that the complex of Cu and other ligands have much lower interaction to imprinted polymer, comparing to the Cu-dipyridyl complex.

In summary, this letter reports a very simple method for the evaluation of the interactions between MIP and its template. Compared with commonly used HPLC method, the present one is fast, simple and sample saving. It provides an alternative method for the systems where electrochemically active species are involved.

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