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Ionic liquids-assisted fabrication of silica-based monolithic columns

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ABSTRACT

The mesopores of a monolithic silica column are very important and useful for chromatographic separation since they can offer sufficiently large surface area. In this paper, a novel method with the assistance of an ionic liquid (1-butyl-3-methylimidazolium tetrafluoroborate ([bmin]BF_4)) was developed for the preparation of a C18-modified monolithic silica column for the first time, in which, the through pores and mesopores were formed simultaneously during the sol–gel reaction. The method is effective to simplify the preparation process of the silica-based monolithic columns. The factors influencing the sol–gel process, including the content of methanol and pH, were studied. The chromatographic performance of the prepared monolithic column was evaluated by the separation of alkylbenzenes.

1. Introduction

The applications of capillary liquid chromatography (CLC) in the fields of pharmaceutical and biochemical research have grown tremendously because of its attractive features such as low sample and reagent consumptions, good compatibility with mass spectrometry, and the possibility of a high degree of automation [1]. The chromatographic columns play a crucial role in CLC since the separation of analytes is based on the interaction between the analytes and stationary phases in columns. So far, the columns are classified as packed, open-tubular and monolithic columns. Open-tubular columns have relatively low sample loading capability. Monolithic column is a good alternative to packed column since its continuous stationary phase has higher permeability at a similar column efficiency and it does not need end frits [2]. Therefore, the development of monolithic columns has become a fascinating research field in chromatographic area [2–9]. Up to date, the protocol for the preparation of silica-based monolithic columns usually included pretreatment of a capillary, sol–gel reaction, aging of gel, mesopores-tailoring of silica monolith, calcination, and modification of the silica monolith. Obviously, the aforementioned process for the preparation of silica monolithic columns is not only complicated, but also takes too much time. Therefore, it is necessary to develop a new method for the preparation of silica-based monolithic columns, which can reduce the preparation steps and shorten the time without compromising the separation efficiency.

Ionic liquids (ILs) containing relatively large asymmetric organic cations and inorganic or organic anions have aroused considerable scientific interest in various disciplines due to their advantages over conventional solvents [10–12]. Some researchers have reported that ILs can act as pore templates in the sol–gel reaction [13–19]. Deng et al. [20] synthesized a silica gel with a mesopores sizes (5–12 nm) using 1-alkyl-3-methylimidazolium tetrafluoroborate as a template. Also, Zhou et al. have reported that the monolithic mesoporous silica was prepared by using various alkyl side chain lengths on the imidazoliun of ILs as mesopores tailor. And the mesopore sizes increased slightly when the number of the carbon chain atoms of the ILs increased under comparable reaction conditions [13–15]. Based on the characteristic of ILs as mesopores template, Yan and co-workers reported an IL-mediated non-hydrolytic sol–gel method for the synthesis of molecularly imprinted monoliths, in which methacrylic acid was used as a functional monomer, methacryloxypropyltrimethoxysilane as a crosslinker, and an IL (1-butyl-3-methylimidazolium hexafluorophosphate) as a pore template. The column was used for the chiral separation of racemic mixtures of naproxen [21] and zolmitriptan [22] in capillary electrokinetic chromatography. ILs were also used to assist the preparation of the poly(dimethylsiloxane), poly(ethyl glycol), poly (tetrahydrofuran), and bis[(3-methyldimethoxysilyl)propyl] polypropylene oxide coatings in capillaries [23]. These open tubular columns were utilized as the solid-phase microextraction media. Based on these reports, the feasibility to fabricate monolithic columns assisted with ILs for tailoring the mesopores can be anticipated.

The mesopores of a monolithic silica column are very important and useful for chromatographic separation since they can offer sufficiently large surface area. In this paper, a novel method with the

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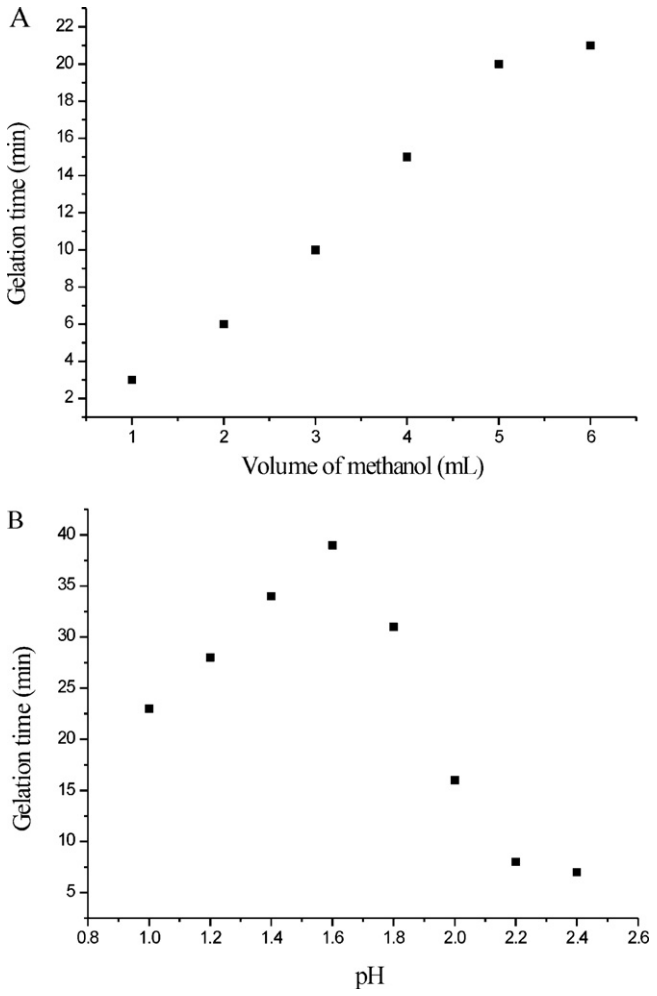

Fig. 1. Effect of (A) the volume of methanol, and (B) the pH value of HCl solution on the gelation time.

assistance of an IL (1-butyl-3-methylimidazolium tetrafluoroborate ([bmin]BF_4)) was developed for the preparation of a monolithic silica column for the first time, in which, the through pores and mesopores were formed simultaneously during the sol–gel reaction. The conditions for the preparation of the monolithic silica column with the addition of an IL were investigated. The characterization of the column was carried out using scanning electron microscopy (SEM) and size exclusion chromatography (SEC). The separation efficiency of the column was evaluated through the separation of alkylbenzenes.

2. Experimental

2.1. Reagents and chemicals

Ammonium hydroxide ($NH_3{\cdot}H_2O$ (25%, w/w)), sodium hydroxide (NaOH), hydrochloric acid, and acetic acid were purchased from Guangzhou Chemical Regent Factory (Guangzhou, China). Polyethylene glycol (PEG, MW 10,000) was obtained from Sinopharm Chemical Reagent Company (Shanghai, China). [bmin]BF_4 was purchased from Center for Green Chemistry and Catalysis, Lanzhou Institute of Chemical Physics, China Academy Sciences (Lanzhou, China). Tetramethoxysilane (TMOS) was purchased from Acros Organics (Geel, Belgium). Methylbenzene, ethylbenzene, propylbenzene, and butylbenzene were obtained from Alfa Aesar (Heysham, UK). Dimethyloctadecylchlorosilane was purchased from Fluorochem Company (Derbyshire, UK). Polystyrene standards with molecular masses ranging from 1300 to 2×10^6 were purchased from Alfa (Tianjin, China). Tetrahydrofuran (THF), methanol and acetonitrile (HPLC grade) were purchased from SK Chemicals (Ulsan, South Korea). Water used in the experiments was obtained from an Elga water purification system (ELGA, London, UK).

2.2. Instrumentation

The CLC system was comprised of a microflow pump, an UV detector (TriSep-2100, Unimicro Technologies, Pleasanton, CA, USA), a manual injection valve (Valco VICI, Switzerland) with an internal sample loop of 100 nL, and a lab-made splitter with a PEEK tube (65 μm i.d. × 150 cm). The column was inserted into the body of the splitter as near as possible to the rotor. Chromatographic data acquisition was performed with the software HW-2000 workstation (Qianpu Software Company, Shanghai, China). All separations were carried out at room temperature, which was kept at 25 °C using air conditioning system. A fused-silica capillary, 2 cm × 50 μm i.d., was used as a transfer tubing between the column and the detection window. For column fabrication, temperature-controlling process was carried out using a gas chromatography (GC) system 7890 II (Techcompany, Shanghai, China).

Fused-silica capillaries (100 μm i.d. × 365 μm o.d.) were purchased from Hebei Yongnian Ruipu Chromatogram Equipment Company (Handan, China). SEM of the silica monolith was carried out on XL-30 scanning electron microscope (Philips, Netherland).

2.3. Column preparation

2.3.1. Pretreatment of capillary

In order to clean and activate the inner surface of a fused-silica capillary, the capillary was first rinsed with 1 M NaOH for 2 h, and then was placed in a thermostated water bath at 40 °C for 3 h. Next the capillary was rinsed with water for 30 min, 1 M HCl for 1 h, water for 30 min, respectively. Then, it was dried with nitrogen at 170 °C in a GC oven for 3 h prior to use.

2.3.2. Preparation of monolithic columns with [bmin]BF_4

TMOS (3.13 mL), PEG (0.625 g), hydrochloric acid at different pH (7 mL) [bmin]BF_4 (0.371 g), and different volumes of methanol were mixed by stirring for 40 min at 0 °C. Then, the solution was sonicated for 1 min. After the sol was injected into a pretreated capillary, the capillary was placed in a 30 °C water bath overnight. Then, the column was washed with water and methanol in sequence to remove the remnant unreacted substances.

2.3.3. Chemical modification of monolithic silica columns with C18 chain

After a silica column was washed with toluene for 1 h, a solution consisting 10% (w/v) dimethyloctadecylchlorosilane in toluene was pushed through the silica monolith, and reacted at 120 °C for 10 h before it was sealed with a rubber septum. Then, the column was rinsed by toluene and methanol in sequence. After preparation, both ends of the capillary about 10 cm were cut off.

In the abbreviations of the columns in Table 1, MS, stands for monolithic silica followed by the capillary diameter in parentheses, M, methanol followed by the volume of methanol in the sol solution and the pH value of hydrochloric acid solution. A series of columns designed as MS(100)-IL-M4-pH1.6, MS(100)-IL-M4-pH1.8, MS(100)-IL-M4-pH2.0, and MS(100)-IL-M3-pH2.0, were prepared with [bmin]BF_4 in the starting sol solutions.