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Preparation and evaluation of 2-methylimidazolium-functionalized silica as a mixed-mode stationary phase for hydrophilic interaction and anion-exchange chromatography

Beibei Yang[a,b], Houmei Liu[b], Jia Chen[b], Ming Guan[a,*], Hongdeng Qiu[a,b,*]

[a] Laboratory on Pollution Monitoring and Control, College of Chemistry and Chemical Engineering, Xinjiang Normal University, Urumqi, 830054, China
[b] Key Laboratory of Chemistry of Northwestern Plant Resources and Key Laboratory for Natural Medicine of Gansu Province, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou, 730000, China

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ABSTRACT

In this paper, a novel 2-methylimidazolium-functionalized silica stationary phase was prepared and further used for hydrophilic interaction and anion-exchange mixed-mode chromatography. The stationary phase was characterized by elemental analysis and Fourier transform infrared spectrometry. The chromatographic properties of this stationary phase were investigated by hydrophilic chromatography for the separation of nucleosides, nucleobases, water soluble vitamins, sulfonamides and saccharides, and ion chromatography for the separation of inorganic anions. The effect of acetonitrile content, salt concentration and pH values of the mobile phase on the retention of the stationary phases was also investigated. Compared with 1-methylimidazolium-functionalized silica stationary phase, this new stationary phase demonstrated similar or better separation selectivity. This new column demonstrated good performance and separation selectivity even better than a commercial hydrophilic column. Besides, 2-methylimidazolium-functionalized silica is possible to be modified again and used as a precursor to derivate some new stationary phases from the 3-position nitrogen.

1. Introduction

Mixed-mode chromatography (MMC), is a type of chromatography in which the stationary phase interacts with solutes through more than one interaction mode, can offer more selectivities for simultaneous separation of diverse compounds [1,2]. Through MMC, one mixed-mode column can be used to replace two or more single-mode columns, avoiding the consumption of stationary phase materials [3]. The key to develop MMC lies in the improvement of stationary phases with mixed-mode or multiple interactions. So far, two or more than two modes stationary phases have been reported, such as reversed-phase liquid chromatography (RPLC)/hydrophilic interaction chromatography (HILIC) [4–6], RPLC/ion-exchange chromatography (IEC) [7–9], HIILC/IEC [10,11], RPLC/HIILC/IEC [12,13], etc. However, the literatures of HIILC/IEC mixed-mode stationary phase are relatively less.

Ionic liquids (ILs), are a class of ionic, non-molecular solvents, consist of relatively large asymmetric organic cations and inorganic or organic anions [14–16]. ILs have been widely used in two aspects in high performance liquid chromatography (HPLC), which are either added in mobile phase as additives to shelter the adverse effect of residual silanols on separation of basic compounds [17–19] or bonded to stationary phases for chromatographic packing. Different with conventional stationary phases, ILs stationary phases can exhibit more interactions with solutes, including hydrophobic, π–π, electrostatic, hydrogen bonding and ion-dipole interactions [20], so it is very important for the development of mixed-mode chromatography.

Imidazolium is a kind of cations in the composition of ILs, which is a good and familiar ligand of stationary phase because it has a nitrogen ring atom with a localized pair [21]. For the moment, there have been a number of studies about imidazolium ILs modified silica as stationary phases of packed columns by different methods in HPLC [22–27]. Our research group firstly prepared a 1-methylimidazolium (*N*-methylimidazolium) modified silica stationary phase (Sil-1-MIm) for the separation of organic and inorganic anions and some basic compounds, finding that the phase displayed a strong anion-exchange

* Corresponding authors at: Laboratory on Pollution Monitoring and Control, College of Chemistry and Chemical Engineering, Xinjiang Normal University, Urumqi, 830054, China.
E-mail addresses: guanm@xjnu.edu.cn (M. Guan), hdqiu@licp.cas.cn (H. Qiu).

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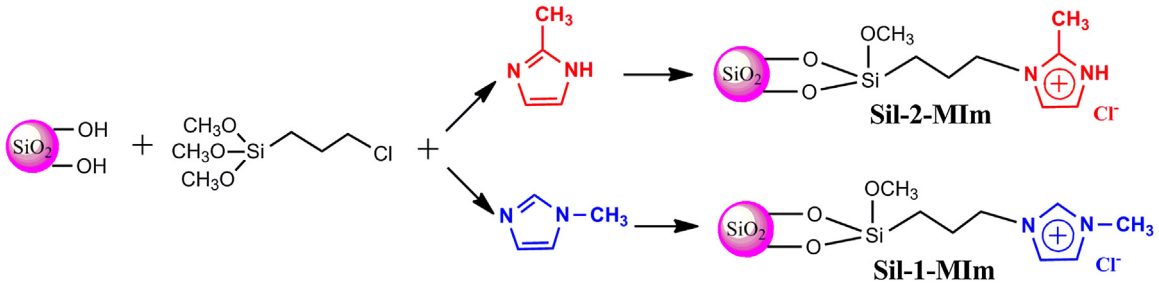

Fig. 1. Schematic diagram for the preparation of Sil-2-MIm and Sil-1-MIm.

mechanism and coexistent reverse-phase interaction [28]. Later, Zhang et al. successfully prepared 1-methylimidazolium functionalized monolithic silica column for performing capillary liquid chromatography and evaluated the characteristics of the column by separating some compounds including inorganic anions, aromatic acids, nucleotides, phenols, alkylbenzenes and polycyclic aromatic hydrocarbons. They concluded that the column had the mixed interactions including anion-exchange, hydrophilic, π–π, dipole–dipole, and hydrophobic interactions [29]. The only difference between 2-methylimidazolium and 1-methylimidazolium is methyl substituted site, so it can be deduced that the 2-methylimidazolium modified silica stationary phase (Sil-2-MIm) would have a good chromatographic performance. In addition, most of the surface-confined IL stationary phases are obtained by imidazole derivatives prepared through *N*-alkylation [30]. Compared to 1-methylimidazolium, 2-methylimidazolium remained 3-position nitrogen which could continue to be functionalized to create some new ionic liquid functionalized silica materials.

In this paper, a novel hydrophilic interaction/anion-exchange mixed-mode stationary phase based on 2-methylimidazolium modified silica was synthesized. The new phase was evaluated in hydrophilic chromatography for the separation of nucleosides, nucleobases, water soluble vitamins, sulfonamides and saccharides, and performed in ion chromatography for the separation of some inorganic anions. The effects of different chromatographic conditions were investigated by variation of acetonitrile content, salt concentration and pH in the mobile phase. Compared with Sil-1-MIm, Sil-2-MIm exhibited very similar or better chromatographic separation abilities.

2. Experimental

2.1. Apparatus

The vast majority of tests were run on a Shimadzu Essentia system (Kyoto, Japan) assembled with an injector with 20 μL sample loop, a column oven, a binary pumps and a UV–vis detector. The five saccharide tests was investigated with Agilent 1100 series with a quaternary pumps, a 20 μL sample loop and a UV–vis detector. The flow-rate was set as 1 mL min^{-1}. Elemental analysis was performed on a Vario EL III elementary analyzer (Hanau, Germany). The FTIR spectra were collected from IFS 120HR Fourier transform infrared spectrometer (Bruker, Germany).

2.2. Reagents and materials

Spherical porous silica was purchased from Fuji Silysia Chemical Ltd. (Aichi, Japan), with 5 μm particle size, 90 Å pore size and 306 m^2 g^{-1} surface area. 2-Methylimidazole, 1-methylimidazole and toluene were all analytical grade and without purification before use. The silylant agent, 3-chloropropyltrimethoxysilane (98%) was obtained from Energy Chemistry. Ammonium acetate, dipotassium hydrogen phosphate was purchased from Sinopharm Chemical Reagent Factory (Shanghai, China). Acetonitrile of HPLC grade from Mreda (USA) and deionized water purified by Milli-Q purification equipment (Millipore, Billerica, MA, USA) were degassed ultrasonically prior to be used as mobile phases. The inorganic salts including potassium iodate, sodium chloride, sodium nitrite, potassium bromide, sodium nitrate and potassium iodide used in anion-exchange chromatographic tests and some polar compounds including nucleosides, nucleobases, vitamins, sulfonamide drugs and saccharides used in hydrophilic chromatographic tests were of analytical reagent grade and were purchased from various reagent suppliers. Separations were carried out using stainless steel columns of 150 mm × 4.6 mm i.d. Inspire 5 μm HILIC column (150 mm × 4.6 mm i.d.) was purchased from Dikma Technologies Inc (China).

2.3. Preparation of stationary phase and column packing

The synthesis procedure of Sil-2-MIm as follow. Firstly, spherical porous silica (3.0 g) was placed in a round-bottomed flask with a branched outlet, and suspended in anhydrous toluene (20 mL). Then, 2-methylimidazole (0.6 g) and 3-chloropropyltrimethoxysilane (1.2 g) was successively added to the above solution. The mixture was heated at 110 °C with a magnetic stirring and refluxed for 48 h. After the completion of the reaction, the resulting silica suspension was cooled to room temperature and centrifuged. The product was washed in sequence with ethanol, ethanol-water (1:1, v/v) mixture, distilled water and ethanol. Finally, the product was dried under vacuum at 60 °C, ready for use.

The only difference of synthesis procedure of Sil-1-MIm was that 2-methylimidazole was replaced with 1-methylimidazole. The preparation schemes of the 2-methylimidazolium- and 1-methylimidazolium- modified silica particles were both shown in Fig. 1.

2.4. Column packing

The resulting modified silica materials were packed into stainless-steel columns (150 mm × 4.6 mm i.d.), which were downward packed using a 40 MPa packing press (6752B-100, Beijing, China) with CCl_4 as slurry solvent and hexane as the propelling solvent.

3. Results and discussion

3.1. Characterizations

3.1.1. Elemental analysis

To quantitate the elemental composition of two stationary phases above mentioned, the silica, Sil-2-MIm and Sil-1-MIm were submitted for elemental analysis. The resultant data were listed