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Calixarene ionic liquid modified silica gel: A novel stationary phase for mixed-mode chromatography



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ABSTRACT

A novel calixarene ionic liquid functionalized silica material was synthesized by the preparation of a new calixarene monomer and its grafting on mercaptopropyl modified silica gel. The material was characterized by infrared spectra, elemental analysis, and thermogravimetric analysis. To explore the retention mechanism of the stationary phase, linear solvation energy relationships (LSER) equation as an effective mathematical model was used. In addition to this, the distinct separation mechanisms were outlined by selected examples of chromatographic separations in the different modes. In reversed-phase liquid chromatography, this new stationary phase presented specific chromatographic performance when evaluated using alkylbenzenes, PAHs and phenols as solutes. Due to the existing polar functional groups, this stationary phase can also be used in hydrophilic interaction chromatography, six nucleosides and four ginsenosides were separated successfully in hydrophilic mode. Furthermore, anions can be separated on the column in anion exchange mode. Thus, this new material was can be applied as a new kind of mixed-mode stationary phase in liquid chromatography, which allows an exceptionally flexible adjustment of retention and selectivity by tuning the experimental conditions.

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1. Introduction

Recently, mixed-mode chromatography (MMC) has emerged as a flexible and versatile technique that can offer more than one retention modes with solutes to improve the selectivity [1–3]. The main advantage of MMC over conventional single-mode chromatography (reversed-phase or ion-exchange stationary phase, et al. is that it can offer more selectivities for simultaneous separation of different groups of compounds, and gives additional selectivity for unresolved peaks. However, the advancement of liquid chromatography has mainly depended on the improvement of stationary phases [4–6]. Therefore, more and more chromatographic scientists have paid the exceptional attention to the exploitation of stationary phases with mixed-mode or multiple interactions.

Calixarene, as a typical representative of the third-generation supramolecule after crown ether and cyclodextrin, possesses tunable cavities and exhibits versatile complexation abilities [7].

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The outstanding recognition ability of host to guest makes it widely used in the field of analytical science [8–10]. Nowadays, calixarene stationary phase with multiple interactions was successfully applied to separate polycyclic aromatic hydrocarbons (PAHs) [11,12], aromatic positional isomers [13,14], sulphonamides [15], amino acid esters [16], flavonoids [17,18], nucleosides [19], and so on. A variety of interaction mechanisms, including hydrophobic, π - π , hydrogen bonding and inclusion interactions were existed in the separation process, indicating it has advantages over conventional reversed- or normal-phase stationary phases.

Ionic liquid (IL) [20] was another powerful ligand that has been widely investigated in the field of chromatographic science. By immobilizing onto silica gel, IL stationary phases were emerging to be an another high effectively separation means for HPLC [6,21–27], which have been demonstrated extraordinary selectivity in the analysis of polycyclic aromatic compounds (PAHs), alkylbenzene, anions, bases, nucleosides, peptides, etc. [25–27]. Different with conventional stationary phases, IL stationary phases can provide hydrophobic, π - π , hydrogen bonding and ion-dipole interactions.

Along with the advances in the field of calixarenes, many researches were involved in design and synthesis of supramolecules

with special properties using calixarenes as building blocks. Lately, calixarene ionic liquids have been emerging as a type of novel calixarene derivatives and they exhibit unique, versatile structures and molecular recognition properties [28,29]. On the opinion of the structural analysis, calixarene ionic liquids might exhibit excellent recognition abilities for organic molecular in water due to their good solubility in water based on ions groups, and good complexation abilities for organic molecules and anions based on the cavities of calixarene skeleton. The cooperation effect of the calixarene and ionic liquid groups on the enhancement of the chromatographic selectivity is eagerly anticipated. Herein, we report the first synthesis of calixarene ionic liquid stationary phase and its excellent separation property.

Therefore, a new calixarene ionic liquid was synthesized and immobilized onto silica gel by using a surface-initiated radical chain-transfer reaction. This newly prepared stationary phase not only can present an enhanced selectivity to alkylbenzene and phenols in reversed-phase liquid chromatography, but also can be used to separate nucleosides and ginsenosides in HILIC mode. Additionally, anions were also can be separated on the same column in ion-exchange modes.

2. Experimental

2.1. Apparatus and materials

All experiments were carried out on an Agilent 1260 series (Agilent Technologies, Germany) equipped with a 1200 model quaternary pump, a G1315A model diode array detector and a G1316A model thermostatic column compartment. An Agilent LC ChemStation (Rev. B.04.03) was used for the data analysis and instrumental control. Fourier transform infrared spectroscopy (FT-IR) of the materials was obtained on an FT-IR spectrometer (Bruker Vector 22) in the region of 4000–400 cm^{-1} . The carbon, hydrogen and nitrogen contents of the MPS-Sil and CalixILSP were determined by elemental analysis performed on a Flash EA 1112 elemental analyzer (Thermo Electron Corporation). Thermal gravimetric analysis (TGA) was applied to evaluate thermo stability of the stationary phase in the range of 40–600 °C.

Silica gel (particle size of 5 μm , pore size of 100 Å and specific surface area of 300 $\text{m}^2 \text{g}^{-1}$) was provided by Lanzhou Institute of Chemical and Physics of CAS (Lanzhou, China). 1-allylimidazole (99%), 3-mercaptopropyltrimethoxysilane and azobisisobutyronitrile (AIBN) were purchased from J&K Scientific Company (Beijing, China). HPLC-grade acetonitrile and methanol were purchased from Tianjin Kermel Chemical Reagent (Tianjin, China). All other chemicals and solvents used in this study were of analytical grade unless specially mentioned. Deionized water was purified by using Milli-Q purification equipment (Millipore, Bedford, USA). The analytes were all of analytical grade, and dissolved in the mobile phase at a concentration in the range of 5–50 $\mu\text{g}/\text{mL}$, and 5 μL of the solution was injected onto the chromatographic column.

2.2. Synthesis of calix[4]arene ionic liquid

1,3-Butyldibromo *p*-tert-butyl calix[4]arene was prepared in good yield according to the previous literature [30]. First, 1-Allylimidazole (0.59 g, 5.5 mmol) and 1,3-butyldibromo *p*-tert-butyl calix[4]arene (2.50 g, 2.75 mmol) were added into 60 mL acetonitrile. The mixture was stirred at 80 °C for 72 h under the atmosphere of nitrogen. After rotary evaporation of the solvent, the residue was treated in desiccator under reduced pressure for a week to dryness. The calix[4]arene ionic liquid was obtained as soft straw yellow solid. ^1H NMR (400 MHz, CDCl_3 , ppm): δ ppm: 0.89 (s, 18 H, $\text{C}(\text{CH}_3)_3$), 1.31 (s, 18 H, $\text{C}(\text{CH}_3)_3$), 1.80–2.31 (m, 8 H,

CH_2), 3.31(d, 4 H, ArCH_2Ar), 4.10 (d, 4 H, ArCH_2Ar), 4.86 (s, 2 H, NCH_2), 5.15 (t, 4 H, $\text{NCH}_2\text{-CH}_2$), 5.40 (d, 4 H, $\text{CH}=\text{CH}_2$), 5.96 (m, 2 H, $\text{CH}=\text{CH}_2$), 6.71 (s, 4 H, ArH), 6.86 (s, 2 H, ImH), 7.11 (s, 4 H, ArH), 7.46(s, 2 H, ImH), 7.45 (s, 2 H, ImH), 8.08 (s, 2H, OH), 10.21 (s, 2 H, ImH).

2.3. Preparation of CalixILSP

Activated silica gel (3.5 g) was placed in a dried flask and dispersed in anhydrous toluene (30 mL). Then, 3-mercaptopropyltrimethoxysilane (5 mL) was added and the reaction mixture was refluxed under nitrogen atmosphere for 72 h. The resulting 3-mercaptopropyltrimethoxysilane modified silica (MPS-Sil) was filtered, and washed in sequence with toluene, methanol and distilled water. Finally, the product of MPS-Sil was dried under vacuum at room temperature.

The calix[4]arene ionic liquid modified silica gel (CalixILSP) was obtained through a surface radical chain-transfer reaction [31] (Fig. 1). Details of the bonding procedure are as follows: a mixture of calix[4]arene ionic liquid (3.0 g), MPS-Sil (3.5 g) was dissolved in 30 mL of acetonitrile. Then, AIBN (40 mg) was added to the above solution. Then, the mixture was stirred at 50 °C for 12 h under argon atmosphere. After the completion of the reaction, the precipitates were filtered and washed in sequence with acetonitrile, dichloromethane, acetone, methanol and distilled water. Subsequently, the calix[4]arene ionic liquid modified silica material (CalixILSP) was dried under vacuum at 60 °C for 24 h before packing and characterization.

The prepared CalixILSP was packed into a stainless-steel column (150 mm \times 4.6 mm i.d.) using methanol as displacing agent (40 MPa, 30 min) according to a slurry packing method.

3. Results and discussion

3.1. Characterization of CalixILSP

The synthesis procedures of CalixILSP are outlined in Fig. 1. In brief, the CalixILSP was obtained by the reaction of calixarene ionic liquid and 3-mercaptopropyl-modified silica via a surface-initiated radical chain-transfer reaction [31].

Elemental analysis results showed that the content of C and H in Sil-MPS was 3.51% and 0.87%, respectively; the C, H and N in CalixILSP was 14.28%, 2.18% and 0.79%, respectively. The degree of surface coverage for MPS-Sil and CalixILSP was calculated according the previous methods [4], based on the change of carbon content. The bonding amount which indicating the quantity of mercaptopropyl and calixarene moieties that attached to the silica surface can thus be calculated as 3.40 $\mu\text{mol m}^{-2}$ for Sil-MPS and 0.56 $\mu\text{mol m}^{-2}$ for CalixILSP.

Thermo gravimetric analysis was usually used for the determination of thermal stability and to confirm the total amount of immobilized compounds on the silica surface. The weight loss between 200 and 600 °C is considered to represent the loss of organic material attached to silica surface [32]. The mass loss of MPS-Sil was of 5.65% at 200–600 °C. After covalently bonding with calixarene ionic liquid, a considerably higher mass loss of 17.7% was observed over the same temperature range, indicating a considerable increase in organic content. The mass losses were attributed to the breakage of calixarene derivatives group bonded on the silica-gel surface together with the condensation of remaining silanol groups.

Infrared spectroscopy is another method that used to identify the chemical modifications of materials. Significant differences of were observed between the IR spectra of MPS-Silica and CalixILSP as shown in Fig. 1S (Supplementary material). For MPS-Sil, the

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