



A new stationary phase for high performance liquid chromatography: Calix[4]arene derivatized chitosan bonded silica gel[☆]



Jing Lu^a, Wenfen Zhang^a, Yanhao Zhang^a, Wenjie Zhao^{a,b}, Kai Hu^c, Ajuan Yu^a, Pu Liu^{a,*}, Yangjie Wu^a, Shusheng Zhang^{d,*}

^a College of Chemistry and Molecular Engineering, Zhengzhou University, Zhengzhou 450001, PR China

^b School of Chemistry and Chemical Engineering, Henan University of Technology, Zhengzhou 450001, PR China

^c Henan University of Traditional Chinese Medicine, Zhengzhou 450008, PR China

^d Key Laboratory of Chemical Biology and Organic Chemistry of Henan, Zhengzhou University, Zhengzhou 450052, PR China

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ABSTRACT

In the present paper, a new calix[4]arene derivatized chitosan bonded stationary phase (CCS4) for high performance liquid chromatography (HPLC) was synthesized and characterized. Its chromatographic performance and retention mechanism were evaluated in reversed-phase mode compared with ODS using different solute probes including mono-substituted benzenes, phenols and nucleosides. The results showed that CCS4 stationary phase could provide various interactions with solutes, such as hydrophobic, hydrophilic, π - π , and inclusion interactions. It could perform the mixed-mode separation including RP and HILIC.

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1. Introduction

Traditionally, HPLC separation is mainly based on single mechanism, such as hydrophobic interaction for separating nonpolar compounds on reversed-phase packing material and ion-exchange interaction for separating ions on ion-exchange stationary phase [1]. However, the development of newly mixed-mode bonded stationary phases such as ionic liquid [2,3] and macrocyclic [4,5] stationary phases with the multiple interactions has become a significant direction in HPLC.

Recently, many chromatographic scientists [6–9] have paid the exceptional attention to calixarenes because of their unique structures. Calixarenes, cavityshaped cyclic molecules consisting of phenol units linked via methylene bridges, are known as a typical representative of the third-generation host after crown

ethers and cyclodextrins [10,11]. The distinctive configurations lead to the formation of typical host–guest interaction between calixarenes and numerous compounds, and result in widely varied applications in ion-selective membranes and electrodes [12–17], electrophoresis [18–23] and chromatography [24–35]. Chitosan (Fig. 1) is one of the most abundant optically active biopolymers and consists of β -(1 \rightarrow 4)-linked D-glucosamine units. It is produced by N-deacetylation of chitin obtained from shrimp or crab shells. Chitosan has excellent binding capacity because it possesses active primary amino group and hydroxyl group.

In the present work, a new calix[4]arene derivatized chitosan bonded silica stationary phase (CCS4) was prepared by calixarene and chitosan, which made the stationary phase not only has the hydrophobic characteristics of the traditional calixarene stationary phase, but also features hydrophilicity. The chromatographic behaviors of different types of aromatic compounds (mono-substituted benzenes and phenols) and nucleosides were investigated by HPLC on CCS4. The influences of methanol concentration in the mobile phase and temperature on the *k* (retention factor) values of these solutes were also investigated. Using the mono-substituted benzenes and phenols as solute probes, we found that the CCS4 mainly features hydrophobicity with solute. Using the strong polar nucleosides as solute probes, the CCS4

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* Corresponding authors at: Daxue Road 75, Zhengzhou 450052, PR China.

Tel.: +86 371 67763224.

E-mail addresses: liupu@zzu.edu.cn (P. Liu), zhangshusheng@371.net, sszz@126.com (S. Zhang).

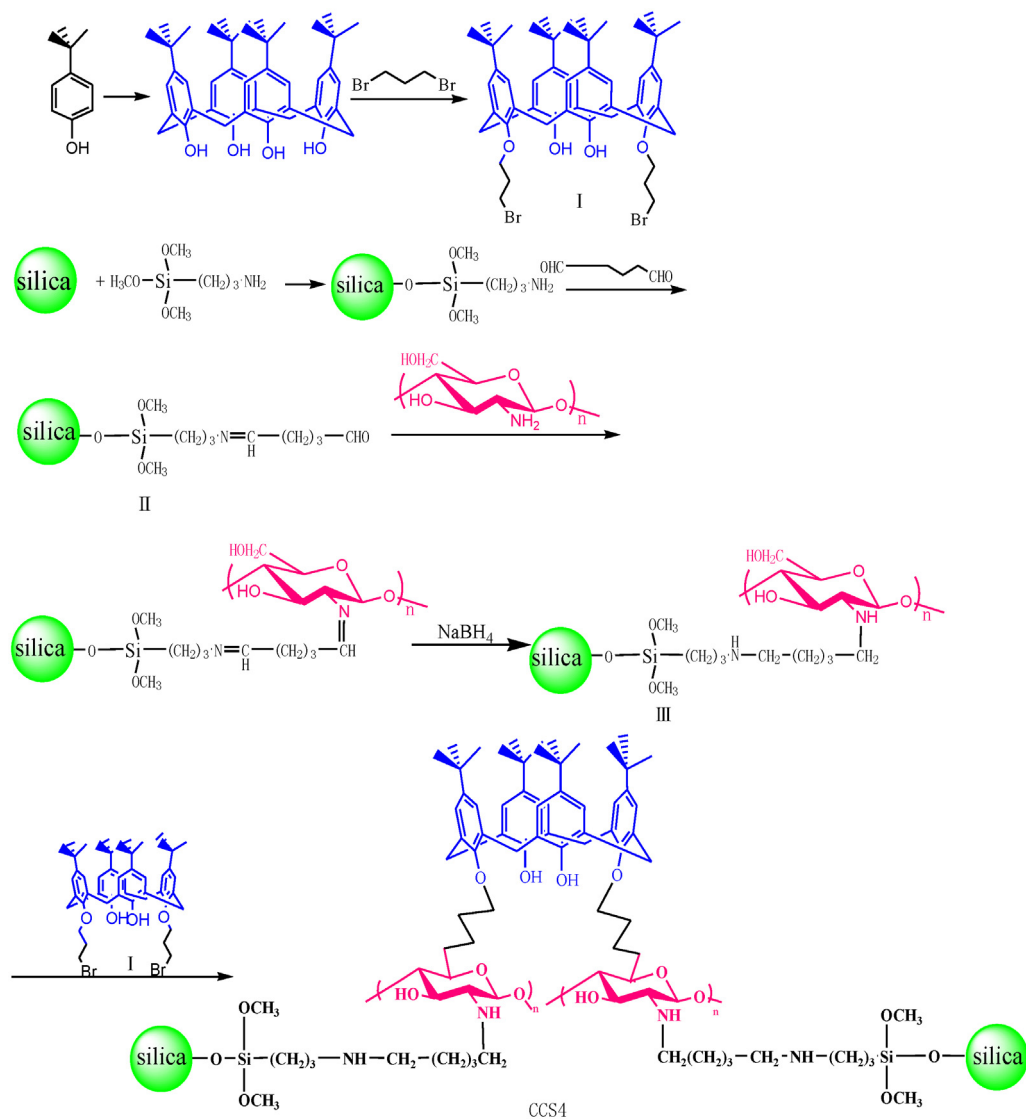


Fig. 1. RepARATION scheme of chitosan derivatized calix[4]arene bonded stationary phase (CCS4).

features certain hydrophilicity. Therefore, this new CCS4 is both hydrophobic and hydrophilic, and could play multiple interactions with the solutes.

2. Experimental

2.1. Apparatus and materials

All chromatographic separations were performed on an Agilent 1260 series (Santa Clara, CA, USA) equipped with an autosampler and a UV detector. The home-made CCS4 column was filled using a packing machine (Kerui Tech. Co. Ltd., Dalian, China) under the pressure of 45 MPa. An Eclipse XDB-C18 column (Agilent, 150 mm × 4.6 mm i.d., 5 μm) was used as a comparison with the home-made CCS4 column. Elemental analysis (EA) was performed with a Flash EA 1112 elemental analyzer. Thermal gravimetric analysis (TGA) was carried out with a Shimadzu DT-40 thermal analyzer, the analysis was performed from 20 °C to 640 °C at heating rate of 10 °C/min in argon atmosphere with a gas flow rate of 20 mL/min. Silica gel (with molecular weight of 1000, particle size of 5 μm, pore size of 100 Å and specific surface area of 300 m²/g) was provided by Lanzhou Institute of Chemical Physics, Chinese Academy of

Science (Lanzhou, China). 3-Aminopropyltriethoxysilane (KH-550) was purchased from Jingchun Chemical Reagent Co. Ltd. (Shanghai, China). Water was purified by using Milli-Q purification equipment. The other reagents are of analytical grade unless indicated otherwise. All syntheses, tests and measurements were performed in triplicate.

2.2. Synthesis of 5,11,17,23-tetra-tert-butyl-25,27-bis(3-bromopropoxy)-26,28-dihydroxycalix[4]arene

Fig. 1 shows the synthesis scheme of 5,11,17,23-tetra-tert-butyl-25,27-bis(3-bromopropoxy)-26,28-dihydroxycalix[4]arene (compound I). Para-tert-butylcalix[4]arene was prepared in good yield according to the previous literature. Compound I was obtained by the following procedures in details. 3.24 g (5 mmol) para-tert-butylcalix[4]arene, 5.2 ml (50 mmol) 1,3-dibromopropane and 1.66 g (12 mmol) K₂CO₃ was added in 125 mL dry acetonitrile. The mixture was stirred and heated to reflux under nitrogen atmosphere for 48 h. The resulting solution was evaporated to dryness and the residue was taken up with aqueous HCl (5%, 25 mL), extracted with methylene chloride (50 mL) for three times. The organic layer was combined and dried by anhydrous Mg₂SO₄ and evaporated to dryness. The

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