Critical Reviews in Analytical Chemistry, 37:211–224, 2007

ISSN: 1040-8347 print / 1547-6510 online
DOI: 10.1080/10408340701244672

Calixarenes as Stationary Phases in High Performance Liquid Chromatography

Magdalena Śliwka-Kaszyńska
Gdansk University of Technology, Chemical Faculty, Department of Organic Chemistry, Gdańsk, Poland

Calixarenes are a class of host molecules with three-dimensional cavity capable of accepting guest molecules. The interest of calixarenes in analytical and separation chemistry has increased in recent years because of their ability to form reversible complexes with both neutral and charged molecules. Calixarenes have been utilized in gas chromatography, solid-phase extraction, capillary electrophoresis and overall in high performance liquid chromatography. This short review is focused on recent advances in synthesis and characterization of calixarene, calixresorcinarene and calixpyrrole stationary phases, chemically bonded or dynamically adsorbed onto silica gel or used as mobile phase additives, and its application to separation of organic and inorganic solutes by high performance liquid chromatography.

Keywords calixarene, calixresorcinarene, calixpyrrole, stationary phase, separation, analytes, high performance liquid chromatography

INTRODUCTION

Since identification and rationalization of calixarenes and the structurally related calixresorcinarenes (resorcinarenes) and calixpyrroles syntheses, they have been of interest in almost all fields of chemistry. Starting from pioneering work of Gutsche, the chemistry of these metacyclophanes has been extensively discussed in several books concerning synthesis (1, 2) structural features and host-guest interactions (3–5). Many review articles deal with more specific applications of calixarenes, e.g., in separation chemistry (6–8). In the subject of application of these macromolecules in chromatography, relatively recent literature has been available. There are several reasons for the current widespread interest in calixarenes in chromatography. One of them is the remarkably simple way of synthesis and modification of the parent compounds. In addition, lower and upper rim functionalization of these macrocycles resulted in massive expansion in the range of derivatives available. The properties of calixarenes are also strongly influenced by its conformation, which is fixed after introduction of bulky substituents at the phenolic oxygen atoms.

To summarize, calixarenes represent compounds with great potential for chemical alternation through variation of the ring-size and by insertion of functional groups at the upper and lower rim of the macrocycle. The interest in calixarenes as stationary phases in chromatography resulted from unique opportunities to influence the specificity and selectivity of the macrocycles. However, in contrast to crown ethers and cyclodextrin, the host-guest interactions of calixarenes with solutes are not determined solely by their hydrophobic cavities, but are also influenced by additional functional groups attached at their rims. It can contribute to potential variation in these interactions. The great potential of this class of macrocyclic compounds has been shown for several applications e.g., in gas chromatography (9–16), capillary electrophoresis (17–30), solid phase microextraction (31–38) and overall high-performance liquid chromatography.

Until now, calixarenes have been chemically bonded or dynamically adsorbed onto silica gel or used as mobile phase additives in reversed-phase liquid chromatography.

The present review dealing with recent advances in synthesis and characterization and HPLC application of calixarene, calixresorcinarene and calixpyrrole stationary phases. The paper is organized according to the structures and cavity size of calixarene derivatives used as selectors in HPLC and type of anchor molecule immobilizing macromolecules to the solid support.

CALIXARENE AND CALIXRESORCINARENE STATIONARY PHASES CHEMICALLY BONDED ONTO SILICA GEL

Calixarene in *Cone* Conformation

Calix[n]arenes (n = 4,5,6,8) with tert-Butyl Substituents at the Upper Rim. Historically first p-*tert*-butyl calix[4]arene HPLC stationary phase **1a** (Figure 1) was synthesized by Friebe

Address correspondence to Magdalena Śliwka-Kaszyńska, Gdansk University of Technology, Narutowicza str. 11/12, 80-952 Gdańsk, Poland. E-mail: pestka@chem.pg.gda.pl