

Magdalena Śliwka-Kaszyńska¹
 Kamila Łępicka¹
 Marek Ślebioda²

¹Department of Organic Chemistry, Gdansk University of Technology, Gdańsk, Poland

²Perlan Technologies Sp. z o.o., Warszawa, Poland

Received April 19, 2010

Revised June 15, 2010

Accepted July 11, 2010

Research Article

Chromatographic behavior of a new hybrid type RP material containing silica bonded 1,3-alternate 25,27-bis-[cyanopropoxy]-26,28-bis-[3-propyloxy]-calix[4]arene

A novel 1,3-alternate 25,27-bis-[cyanopropoxy]-26,28-bis-[3-propyloxy]-calix[4]arene-bonded silica gel stationary phase (CalixPrCN) was prepared and its structure was confirmed by ATR-FTIR spectroscopy and elemental analysis. The CalixPrCN phase was characterized in terms of its surface coverage, hydrophobic selectivity, aromatic selectivity, shape selectivity, hydrogen bonding capacity, residue metal content, and silanol activity based on Tanaka, Lindner, and SMR 870 test protocols. The effect of the acetonitrile content on the retention and selectivity of the selected neutral, basic, and acidic solutes was studied. The neutral and acidic analytes exhibited classical RP behavior, in which retention time decreases with increasing acetonitrile content. In contrast, basic analytes showed an increase in retention at low and high percentages of acetonitrile, forming “U-shaped” retention profiles. The new calixarene phase was compared with previously reported 1,3-alternate 25,27-bis-[propyloxy]-26,28-bis-[3-propyloxy]-calix[4]arene stationary phase and commercial cyanopropyl column. The results indicate that the CalixPrCN stationary phase behaves like RP packing; however, inclusion complex formation, dipole–dipole, and π – π interactions seem to be involved in the separation process. The selectivity of this phase was demonstrated in separation of polynuclear aromatic hydrocarbons, non-steroidal anti-inflammatory drugs, and sulfonamides as analytes.

Keywords: Calix[4]arene stationary phase / Column characterization / Retention mechanism

DOI 10.1002/jssc.201000263



1 Introduction

Reversed stationary phases are by far the most widely used packing materials and numerous chemically bonded phases differing in ligand types and bonding procedures are presently commercially available. The most often applied adsorbents are based on silica gel modified with various selectors, e.g. hydrocarbon chains of different length (C₈, C₁₈, C₃₀), aromatic substituents (phenyl, biphenyl, pyrene), or other functional groups (cyano, amino, hydroxyl) [1–3].

Correspondence: Dr. Magdalena Śliwka-Kaszyńska, Department of Organic Chemistry, Chemical Faculty, Gdansk University of Technology, Narutowicza 11/12, 80-952 Gdańsk, Poland

E-mail: kaszynski@interia.pl

Fax: +48-583472694

Abbreviations: CalixPr, 25,27-bis-[propyloxy]-26,28-bis-[3-propyloxy]-calix[4]arene stationary phase; CalixPrCN, 25,27-bis-[cyanopropoxy]-26,28-bis-[3-propyloxy]-calix[4]arene-bonded silica gel stationary phase; HILIC, hydrophilic interaction chromatography; PAH, polynuclear aromatic hydrocarbon; PrCN, cyanopropyl stationary phase; TFA, tailing factor of amitriptyline

The continuous growth in the use of RPLC techniques has furthered the need for new generation of stationary phases offering not only the chemical stability but also improved selectivity and efficiency with the possible widest spectrum of application. For that reason, many researchers and academic groups are still making efforts to synthesize stationary phases with specific structural properties that could meet these requirements, the macrocycle bonded stationary phases occupying presently a prominent place. Calixarenes, amongst other macrocycles, became very popular due to their interesting architecture, easy chemical transformations, and complexing properties toward cations, anions, and neutral molecules. The host–guest interactions of calixarenes with solutes are determined not solely by their hydrophobic cavities but also by additional functional groups attached at their rims that can contribute to these interactions. Several functionalized calixarenes have been utilized as selectors in LC [4, 5]. The modifications to these macrocycles include conformations in which the calixarene molecules are blocked, the type of substituents present at their upper or lower rims, the calixarene ring size, and the type of spacer fixing the macrocycles to the solid support.