Magdalena Śliwka-Kaszyńska[1]
Katarzyna Jaszcołt[1,2]
Iwona Anusiewicz[3]

[1]Department of Organic Chemistry, Chemical Faculty, Gdansk University of Technology, Narutowicza, Gdansk, Poland
[2]Ziaja Ltd., Pharmaceutical Factory, Jesienna, Gdansk, Poland
[3]Department of Chemistry, Quantum Chemistry Group, University of Gdansk, Sobieskiego, Gdansk, Poland

Original Paper

1,3-*Alternate* calix[4]arene-bonded silica stationary phases. Effect of calixarene skeleton substituents on the retention mechanism and column selectivity

Four novel 1,3-*alternate* calix[4]arene-bonded silica gel stationary phases possessing different aromatic and aliphatic substituents at the upper rim (CalixNph, CalixBph, CalixHex, and CalixDdc) were prepared and structurally characterized. The comparison and selectivity of these phases were done by using alkylbenzenes, fatty acid *p*-bromophenacyl esters, aromatic positional isomers, and polynuclear aromatic hydrocarbons as analytes. Quantum chemistry calculations have also been performed (using an *ab initio* method) to support the experimental findings. The effect of the type and content of organic modifier on the retention and selectivity of the alkylbenzenes was studied. The retention mechanism is also discussed. The results indicate that the stationary phases behave like RP packings. However, inclusion complex formation and hydrophobic and $\pi-\pi$ interactions seem to be involved in the separation process.

Keywords: Alkylbenzenes / Aromatic positional isomers / Calix[4]arene stationary phase / Retention mechanism / PAH

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1 Introduction

RP-LC is the most important mode of LC, and it is extensively used for analytical separations [1]. A variety of RP stationary phases, *e.g.*, C-18, C-8, phenyl, and others, are commercially available. However, their selectivity is limited in some cases, mainly due to nonspecific solute-stationary phase interactions. Therefore, the search for more efficient stationary phases has led manufacturers to synthesize new materials that comply with the requirements of good stability, sufficient selectivity, and high efficiency.

In recent years, macrocyclic molecule-bonded stationary phases based on supramolecular interactions have received great attention due to their specific separation selectivity. Calixarenes, among other macrocycles, occupy a prominent place due to their ready access, easy chemical transformation, and complexing properties toward charged and neutral molecules, which make them important hosts. The host–guest interactions of calixarenes with solutes are not determined solely by their hydrophobic cavities but also by additional functional groups attached at their rims, which can contribute to potential variations in these interactions. Several functionalized calixarenes have been utilized as selectors in LC [2, 3]. The modifications to these macrocycles include conformations in which the calixarene molecules are blocked, the type of functional groups and substituents present at their upper and lower rims, the calixarene ring-size, and the type of spacer fixing the macrocycles to the solid support. Calix[*n*]arenes [*n* = 4, 6, 8] in the cone conformation functionalized at the upper rim by *tert*-butyl [4, 5] or other substituents [6], including chiral residues [7, 8], have attracted great attention. However, some examples of calix[4]arenes in 1,3-*alternate* conformations have also been successfully used as selectors in RP-HPLC separations [9–11]. The preparation of an appropriate stationary phase for a given chromatographic analysis is facilitated by adequate knowledge of the mutual relations between the chemical structure and physical properties of the packings and the nature of the analytes [12, 13]. On the other hand, it is obvious that even small changes in the surface structure of the stationary phase can influence its properties, retention power, and selectivity.

Correspondence: Dr. Magdalena Śliwka-Kaszyńska, Department of Organic Chemistry, Chemical Faculty, Gdansk University of Technology, Narutowicza 11/12, 80-952 Gdansk, Poland
E-mail: kaszynski@interia.pl
Fax: +48-583472694

Abbreviations: CalixBph, 25,27-bis-[biphenyl-4-carbonyl]-26,28-bis-[3-propyloxy]-calix[4]arene; **CalixDdc**, 25,27-bis-[dodecyloxy]-26,28-bis-[3-propyloxy]-calix[4]arene; **CalixHex**, 25,27-bis-[hexyloxy]-26,28-bis-[3-propyloxy]-calix[4]arene; **CalixNph**, 25,27-bis-[naphthoyloxy]-26,28-bis-[3-propyloxy]-calix[4]arene; **HF**, Hartree-Fock; **PAH**, polynuclear aromatic hydrocarbon