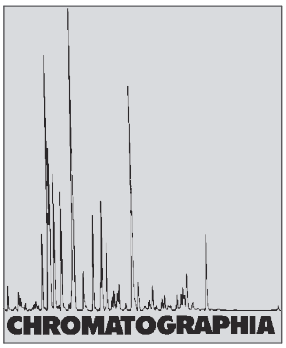
Preparation and Evaluation of *1,3-alternate* 25,27-Bis-[*p*-nitrobenzyloxy]-26,28-bis-[3-propyloxy]-calix[4]arene-bonded Silica Gel Stationary Phase for LC



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Katarzyna Jaszczołt, Magdalena Śliwka-Kaszyńska✉

Department of Organic Chemistry, Gdansk University of Technology, Narutowicza St. 11/12, 80-952, Gdansk, Poland;
E-Mail: kaszynski@interia.pl

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Abstract

A novel *1,3-alternate* 25,27-bis-[*p*-nitrobenzyloxy]-26,28-bis-[3-propyloxy]-calix[4]arene-bonded silica gel stationary phase has been prepared and used for separating various selected analytes by HPLC. The effect of organic modifier and pH of the mobile phase on retention and selectivity were studied using aromatic positional isomers as an example. Application examples have been provided for separation of alkylbenzenes, PAHs, xanthine derivatives, and purine and pyrimidine bases. A selectivity comparison of the novel phase versus CalixBz and Backerbond PhenylEthyl phases has been performed.

Keywords

Column liquid chromatography
Aromatic positional isomers
Purine and pyrimidine bases
Polycyclic aromatic hydrocarbons
1,3-alternate Calix[4]arene

Introduction

The creation of an ideal model of a stationary phase capable of concurrently separating the highest number of compounds is still a great challenge in organic and analytical chemistry. Separation of compounds characterized by similar structure and chemical properties is particularly difficult and encounters many obstacles. The choice of a proper stationary phase becomes a decisive factor that should allow the most effective separation.

Presently, there are many commercially available stationary phases e.g.,: RP-C_{18}, RP-C_8, RP-Phenyl and others. In recent years, also hybrids, nanomaterials and biomolecular materials are often used as alternative phases for liquid chromatography to improve column efficiency, stability and selectivity [1]. These interesting materials comprise two or more integrating components, which combine at the molecular and nanometer level. However, their application is limited, to a large degree, due to the specific features such as, hydrophobicity and ionic or polar properties. There are no universal columns, which would be selective towards all classes of organic compounds. Therefore the search for more efficient stationary phases with the widest possible spectrum of application has become a significant direction in studying compound separation by HPLC techniques.

Macrocyclic compounds that are capable of forming inclusion complexes with guest molecules are more commonly used in modern chromatography. Cyclodextrins, crown ethers and recently also calixarenes are the main focus of attention. An increasing interest in this last class of compounds observed in recent years results, to a large degree, from the fact that they can be easily synthesized and modified [2, 3]. Opposite to crown ethers and cyclodextrins, in calixarenes the host–guest interaction types do not result only from the macrocyclic structure or the presence of hydrophobic cavity [4–6]. Additional substituents and functional groups that are easily introduced into the molecule's structure modify the existing interactions and increase their diversity, which in turn constitutes good basis for their potential application, e.g., in separation techniques [7, 8].

The great potential of this class of macrocyclic compounds was shown for several applications e.g.,: in gas chromatography, capillary electrophoresis or solid phase microextraction [9]. In the case of HPLC [10, 11], calixarenes were in general chemically bonded to the silica gel. Their use as an additive to the mobile phase in reversed-phase liquid chromatography was strongly limited due to the strong absorption in the UV range and

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