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## Research Article

# Polycyclic aromatic hydrocarbons as test probes to investigate the retention behavior of 1,3-*alternate* calix[4]arene silica-bonded stationary phases

A series of polycyclic aromatic hydrocarbons (PAHs) of different size and shape has been used to characterize the chromatographic behavior of five calix[4]arene stationary phases in 1,3-*alternate* conformation synthesized in our laboratory. The selection of linear, four-ring nonlinear, and five-ring PAHs gave data on selectivity changes across range of the calix[4]arene columns. Retention of the 12 aromatic solutes has been evaluated at various methanol contents in the mobile phase (70–100% v/v) and column temperatures (20–45°C). The thermodynamic parameters underlying the retention mechanisms revealed that each of the five calix[4]arene columns exhibited variation in selectivity and retention of PAHs caused by enthalpy and entropy effects. The calixarene stationary phases substituted with electron-withdrawing groups exhibit enhanced selectivity toward PAHs in comparison to the rest of the investigated columns. The observed divergences are due to differences in solute–stationary phase interactions and originate in  $\pi$ – $\pi$  and  $\pi$ -electron transfer specific to the analytes and the type of calix[4]arene functionalization at the upper rim, as well as steric and sorption phenomena.

**Keywords:** Calix[4]arene stationary phases / Column characterization / Polycyclic aromatic hydrocarbons / Retention behavior / Thermodynamics  
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## 1 Introduction

LC is most often accomplished on alkyl- and phenyl-bonded stationary phases in RP mode [1]. In recent years, macrocycle-bonded stationary phases have received great attention owing to their specific selectivity based on supramolecular interactions. Calixarenes, among other macrocycles, occupy a distinguished place owing to their host–guest interactions with analytes determined by their hydrophobic cavities and additional functional groups attached at their rims. Alterations

of these macrocycles also include the conformation in which the calixarene molecules are blocked and the calixarene ring size [2, 3].

Chromatographic stationary phases are characterized using various spectroscopic techniques, mathematical and statistical methods (e.g. principal component analysis), thermodynamic measurements, theoretical calculations, and chromatographic methods. The last evaluation includes systematic investigation of the retention behaviors of a certain group of solutes, usually arbitrarily selected, which are supposed to reflect a specific column property [4]. The most widely used and acceptable approaches for the characterization of RP columns were systemically applied to investigate the chromatographic properties of calixarene-bonded stationary phases. The multiple-term linear equation developed by Dolan and Snyder has been adapted to fit the properties of calixarene-bonded columns [5, 6]. The chromatographic tests described by Tanaka, Lindner and Horak as well as Standard Reference Material 870 of the National Institute of Standards Technology were used to characterize several novel calixarene stationary phases [7–9].

Extensive studies on the shape selectivity of alkyl- and phenyl-bonded stationary phases have been performed using polycyclic aromatic hydrocarbons (PAHs) [10–16]. Sander and

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**Abbreviations:** CalixNph, 25,27-bis[naphthoyloxy]-26,28-bis-[3-propyloxy]calix[4]arene; CalixHex, 25,27-bis[hexyloxy]-26,28-bis-[3-propyloxy]calix[4]arene; CalixBzF<sub>5</sub>, 25,27-bis(pentafluorobenzyloxy)-26,28-bis-(3-propyloxy)calix[4]arene; CalixBzNO<sub>2</sub>, 25,27-bis[*p*-nitrobenzyloxy]-26,28-bis-[3-propyloxy]calix[4]arene; CalixBzCl, 25,27-bis[*p*-chlorobenzyloxy]-26,28-bis-[3-propyloxy]calix[4]arene; L/B, length-to-breadth; PAH, polycyclic aromatic hydrocarbon