



High-performance liquid chromatography of di- and trisubstituted aromatic positional isomers on *1,3-alternate* 25,27-dipropoxy-26,28-bis-[3-propyloxy]-calix[4]arene-bonded silica gel stationary phase

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Abstract

A new *1,3-alternate* 25,27-dipropoxy-26,28-bis-[3-propyloxy]-calix[4]arene-bonded silica gel stationary phase (*1,3-Alt CalixPr*) has been prepared and used for the separation of di- and trisubstituted aromatic positional isomers by HPLC. The effect of organic modifier content, pH and column temperature on retention and selectivity of the benzene derivatives were studied. The retention mechanism was also discussed. The results indicated that the stationary phase behaves like a reversed-phase packing. However inclusion, hydrophobic, hydrogen bonding and π - π interactions seem to be involved in separation process.

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1. Introduction

Calixarenes are macrocyclic molecules made up of phenolic units and *ortho* linked by methylene bridges. This interesting class of cavity-shaped cyclic compounds is known to have attractive structural properties and therefore are counted as the third generation of supramolecules, after cyclodextrin and crown ethers [1–3]. The cyclic tetramers known as calix[4]arene can exist in four distinctive conformations: first with all aryl groups *syn* to one another, second with three aryl groups *syn* and one *anti*, third with adjacent pairs of aryl groups *syn* and *anti*, and fourth with non-adjacent pairs of aryl groups *syn* and *anti*. These were later named by Gutsche as cone, partial cone, 1,2-alternate and 1,3-alternate respectively. Their properties are strongly influenced by conformation, which is fixed after introduction

of four bulky substituents at the phenolic oxygen atoms. The interest in calixarenes in analytical and separation chemistry have been increased in recent years because of their ability to form reversible complexes with neutral as well as charged molecules [4]. Calixarenes have been utilized in gas chromatography [5–8], solid-phase extractions [9], and capillary electrophoresis [10–12]. Calixarenes as stationary phases in liquid chromatography have attracted many researchers' attention. Glennon and coworkers [13–15] prepared silica-bonded calix[4]arene tetraester and silica-bonded calix[4]arene tetraethylamide stationary phases to separate metal ions and amino acid esters. Park et al. [16] synthesized calyx[6]arene-*p*-sulfonate-bonded silica stationary phase and carried out separation of aromatic positional isomers. Gebauer et al. [17–19] reported the chromatographic separation of disubstituted aromatics, nucleosides, uracil derivatives, estradiol epimers and *cis/trans* isomers of proline-containing peptides on calix[*n*]arene-bonded (*n* = 4, 5, 6, 8) silica gel. In the past few years the research group

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