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REVIEW

Applications of Nano-Baskets of Calixarenes in Chromatography

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Abstract Nano-baskets of calixarenes have been subject to extensive research in the construction of liquid chromatographic phases, extractants, transporters, electrode ionophores, and optical and electrochemical sensors over the past 4 decades. There has long been interest in calixarene-based liquid chromatographic phases. Owing to the recent rapid growth in the number of publications on calixarene-based liquid chromatographic phases, this review paper focuses on their different applications in the main fields of molecular and ionic species as well as liquid chromatographic mobile and stationary phases. Although the recent reports have focused on the optimization and application of one kind or a unique group of calixarenic mobile or stationary phases, this review is a collection and comparison of a variety of research data dealing with the synthesis, preparation and behavior of calixarene-based liquid chromatographic phases.

Keywords Chromatography · Calixarene · Nano-basket · Mobile phase · Stationary phase

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Introduction

Calixarenes are a class of cyclic oligomers or macrocycles based on a hydroxyalkylation product of an aldehyde and a phenol. The word calixarene was derived from chalice (or calix), because this type of molecule resembles a vase, and from the word arene, which refers to the aromatic building blocks. Calixarenes have hydrophobic cavities that can hold smaller ions or molecules and belong to the class of host-guest chemistry.

Calixarenes were first introduced in 1872, but the discovery of calixarenes was attributed to Zinke in 1940 and fully interpreted by Gutsche in 1970 [1]. Calixarenes were obtained by the oligomerization of phenol and formaldehyde, and their moieties can be easily varied at least from 1 to 8, while the stereochemical orientation of the ligating arms can be properly tuned by shaping. According to the relative orientation of *para* and phenolic sites, calix[4]arene has four different conformations [2]. Baldini et al. [3] illustrated the calix[4]arene conformations including: cone, partial cone, 1,2-alternate and 1,3-alternate. Figure 1 presents the common structure of calix[4]arenes.

Various methods for functionalizing calixarenes have been developed, and numerous calixarene derivatives have been synthesized in the past 2 decades. Because of lower rim phenolic hydroxyls, they can be easily functionalized to provide a variety of donor groups by comparatively straightforward reactions. Calixarenes under intensive study in host-guest chemistry are mainly those that are functionalized on the lower rim with hydrogen or *p-tert*-butyl groups on the upper rim. Identities of the para substituents on the upper rim (i.e., substituents in parapositions relative to the phenolic oxygens) also influence the ionophoric propensities of these ligands. However, this feature has been much less explored because of the lack of suitable

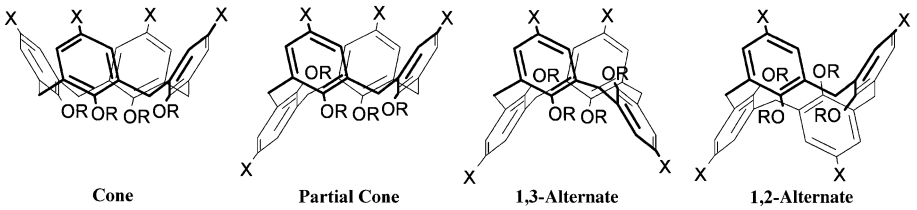

Fig. 1 Illustration of four common conformations of calix[4]arenes. From [3], copyright 2007, Royal Society of Chemistry

functionalization on the upper rim. Different complexing groups at the upper rim of calixarenes are able to attract desirable molecules with pre-defined selectivity. The lower rim functional groups of calixarenes are usually responsible for the physical properties of calixarene molecules [4].

The relative simplicity of chemical modification and the easy preparation of calixarenes have produced increased interest in host-guest chemistry over the last few years. Moreover, their ion-binding properties are highly dependent upon the conformation of the calixarene moieties as well as the number and the nature of donor groups. Based on these factors, calixarenes have demonstrated an outstanding complex ability concerning ions, neutral molecules, etc., and are considered the third best host molecules after cyclodextrins and crown ethers [5]. Various applications of calixarenes are used in purification, chromatography, catalysis, enzyme mimics, ion selective electrodes, phase transfer, transport across membranes, ion channels and self-assembling monolayers [6]. The poor solubility of most calixarenes precludes their applications as additives in aqueous eluents of chromatographic systems [7]. Study of calixarene binding to alkali and alkaline earth metal cations (Fig. 2) [8–21], transition metal ions (Fig. 3) [22–37], molecular compounds (Fig. 3) [38–58] and anions (Fig. 3) [59–65] shows an increase in the ability of calixarene derivatives in solvent extraction of alkaline earth metal cations [66–77], transition metal ions [78–90], molecular compounds [91–105] and anions [106–108].

Meyer and Jira [109] reviewed and summarized the application possibilities and interactions of calixarenes as the stationary phase in liquid chromatography (LC). Sliwka-Kaszynska [110] in a short review focused on recent advances in the synthesis and characterization of calixarene, calixresorcinarene and calixpyrrole stationary phases, chemically bonded or dynamically adsorbed onto silica gel or used as mobile phase additives, and their application to separate the organic and inorganic solutes by high performance liquid chromatography. Iki [86] reviewed thiacalixarene compounds as pre-column derivatization reagents for the highly selective and sensitive determination of Ni^{2+}, Fe^{3+}, Al^{3+} and Ti^{4+} at sub-*ppb* levels with reversed-phase LC.

Nowadays, much macrocyclic research is focused on the separation of neutral and ionic species as well as enantiomers by chromatographic methods. Calixarenes represent a

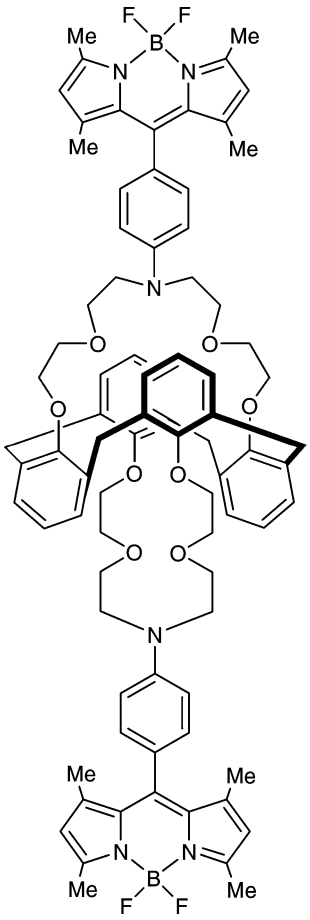

Fig. 2 Molecular structure of a typical calixarene with binding affinity to the alkali and alkaline earth metal cations. From Ref. [8], with permission

new class of chiral selectors applied in chiral chromatography. Gübitz and Schmid reviewed the chiral separation of calixarenes in chromatographic [111] and capillary electrophoresis (CE) techniques [112]. They assessed the gas chromatographic methods in two parts of indirect and direct separations. In the direct separation methods, they studied chiral separation of chiral stationary phases (CSPs) based on calixarenes as well as that of CSPs based on the metal complexes, the cyclodextrins (CDs) and the cyclocholates. Moreover, they reviewed the chiral separation by CE in two categories of indirect and direct separations. In the direct separation techniques, they studied chiral separation of calixarenes as well as cyclodextrins, neutral

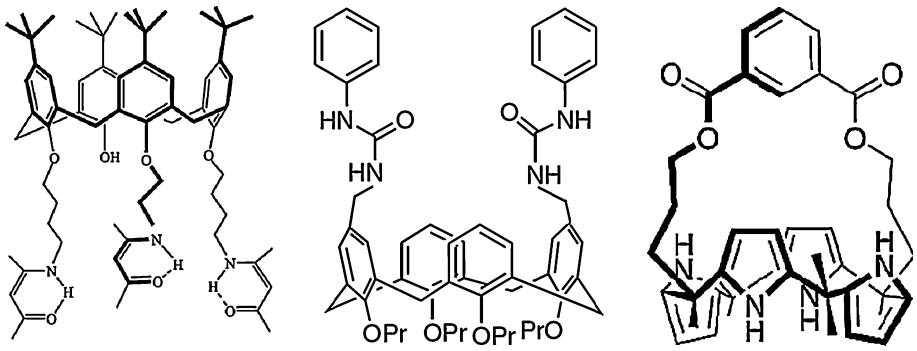

Fig. 3 Molecular structure of a typical calixarene with binding affinity to the transition metal cations (left), the molecular compounds (middle) and the anions (right). From Refs. [37, 54, 63], with permission

CD derivatives, negatively charged CDs, positively charged CDs, amphoteric CDs, CDs and non-chiral additives, carbohydrates, neutral mono-, oligo- and polysaccharides, charged polysaccharides, chiral crown ethers, macrocyclic antibiotics and proteins.

In the first step of this review paper, the application of calixarenes in gas chromatography stationary phases and electrokinetic chromatography is briefly reviewed. Then the paper focuses on the application of calixarene-based stationary phases as well as calixarene-based mobile phases in LC systems. The comparative study of this work was arranged based upon the recognition of molecular or ionic species as well as calixarene applicability in stationary or mobile phases.

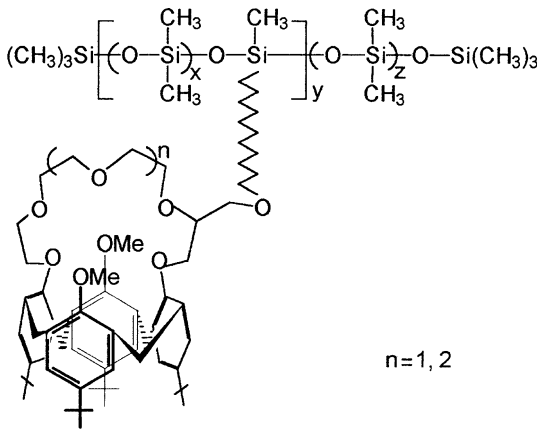

Fig. 4 Molecular structure of two calixacrown ether polysiloxanes. From [113], copyright 1999, Elsevier

GC Stationary Phases

Zhang et al. [113] examined the column efficiency, polarity and selectivity of two calixacrown ether polysiloxanes (Fig. 4) and discussed the mechanism of specific selectivity for position isomers based on the ether ring of the stationary phase, the molecular size of the solute and its shape in capillary gas chromatography. They hydrosilylated ω-undecenyloxymethyl dimethyl calix[4]-15C5 (PSOC[4]-11-15C5) and ω-undecenyloxymethyl dimethyl calix[4]-18C6 (PSOC[4]-11-18C6) with dichloromethane.

They compared the selectivity and average polarity of new synthesized stationary phases with three commercially available stationary phases including: ω-undecyloxymethyl-18-crown-6 (PSO-11-18C6), 2,3-benzo-9-propyloxymethyl-15-crown-5 (PSOB-3-15C5) and 2,3-benzo-11-propyloxymethyl-18-crown-6 (PSOB-3-18C6). The selectivity and average polarity were represented by McReynold's constants. This showed that the calixcrown ether polysiloxanes yielded a lower polarity compared to PSO-11-18C6, PSOB-3-15C5 and PSOB-3-18C6. This indicated that aromatic calixarenes play an influential role in the contribution to the polarity of the stationary phase.

The range of operating temperatures of the stationary phases is related to the glass transition temperature (T_g) and column bleeding. Hence, T_g was determined by the slope change of the log k' versus l/T plot for naphthalene. PSOC[4]-11-18C6 and PSOC[4]-11-15C5 columns demonstrated the changes of the grades at 107 and 100 °C, respectively, which corresponded to phase changes in the columns and was 57 or 62 °C below that of POS-11-18C6. This indicated that PSOC[4]-11-18C6 and PSOC[4]-11-15C5 had lower minimum operating temperatures than PSO-11-18C6, PSOB-3-15C5 and PSOB-3-18C6. Moreover, the column bleeding was measured by heating the columns from 120 to 330 °C at a rate of 6 °C min^{-1}. The column began to bleed at 308 or 306 °C. This revealed that the calixcrown ether polysiloxanes retained their capability at a higher operating temperature range than crown ether poly siloxane and benzocrown ether polysiloxane stationary phases, which started bleeding at 200 or 246 °C.

Pfeiffer and Schurig [114] synthesized a polymeric chiral resorc[4]arene stationary phase for enantiomer separation of amino acid derivatives in capillary gas chromatography.

Mňuk and Feltl [115] and Mňuk et al. [116] studied the inclusion properties of *p-tert*-butylcalix[4]arene towards alicyclic and aliphatic alkanes, alicyclic and aliphatic alkenes, aromatics, halo derivatives, alcohols and ethers in gas-solid chromatography. In their experiments,

Table 1 The list of calixarenes used in electrokinetic chromatography

Type of calixarene	Analytes used	References
p-Sulfonate calix[6]arene	Chlorinated phenols, benzenediols and toluidines	[120]
(*N*-L-Alaninoacyl)calix[4]arene, (*N*-L-Valinoacyl)calix[4]arene	Three binaphthyl derivatives	[121]
Calix[4]arene-bearing sulfonate groups	Positional isomers of nitrophenols, dinitrobenzenes, and benzenediols	[122]
p-(Carboxyethyl)calix[n]arenes	PAHs	[123]
(*N*-L-Valinoacyl)calix[4]arene, (*N*-L-Alaninoacyl)calix[4]arene	Enantioseparation of three binaphthyl derivatives	[124]
p-Sulfonic calix[4]arene	Positional isomers of nitrophenol, benzenediol and aminophenol	[125]
p-(quaternary ammonium) calix[4]arene	Positional isomers of aminophenol and benzenediol	[126]

p-tert-butylcalix[8]arene exhibited selectivity toward chloromethanes.

Lin et al. [117] and Lai et al. [118] synthesized 5,11,17,23-tetra-*tert*-butyl-25,27-bis(isopropylcarbamoylmethoxy)-26,28-diundecenyloxycalix[4]arene and 25,27-dibutoxy-5,11,17,23-tetra-*tert*-butyl-26,28-diundecenyloxycalix[4]arene, and used them with capillary columns containing 14% cyanopropylphenyl methylpolysiloxane (OV-1701) as stationary phases in capillary gas chromatography. They showed wide operating temperature ranges, high column efficiencies, good thermal stability and excellent selectivity for aromatic isomers (especially phenol compounds). Yu et al. [119] mixed three calix[4]arene derivatives with OV-1701 to prepare gas chromatographic stationary phases. They used 5,11,17,23-tetra-*tert*-butyl-25,27-dibutoxy-26,28-diundecenyloxycalix[4]arene, and *25,27*-dibutoxy-26,28-diundecenyloxycalix[4]arene and 5,11,17,23-tetra (*N,N*-diethylaminomethyl)-25,26,27,28-tetra(*ω*-undecenoxy) calix[4]arene. There is a discussion about the relationship between the structure and chromatographic properties of these calixarene stationary phases.

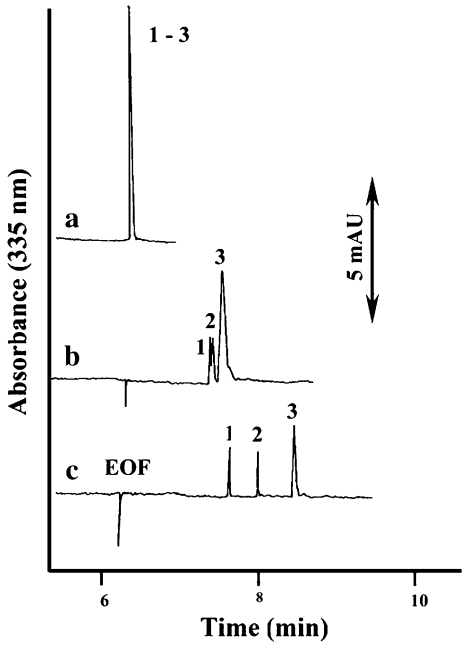

Fig. 5 Electropherograms obtained from the nitrophenols (1 mM) in the presence of **a** 0 mM, **b** 1.5 mM and **c** 10 mM calixarene derivative. From Ref. [122], with permission

Electrokinetic Chromatography

Electrokinetic chromatographic techniques are based on the differential distribution of analytes between an electrophoretically mediated calixarene and a running buffer phase, which is transported by electroosmotic flow. The size of the calixarene influences separation performance, illustrating the importance of cavity size and geometry in the complexation process. Table 1 presents a summary of the research in electrokinetic chromatography using calixarenes. The table contents are then discussed briefly.

Shohat and Grushka [120] studied the applicability of *p*-sulfonate calix[6]arene on the retention behaviors of chlorinated phenols, benzenediols and toluidines in capillary electrophoresis. Moreover, Sirit and Yilmaz [121] reported the applicability of (*N*-L-alaninoacyl)calix[4]arene and (*N*-L-valinoacyl)calix[4]arene for chiral separations of three binaphthyl derivatives (BNHP, BNA and BINOL) in capillary electrophoresis. Mori et al. [122] used calix[4]-arene with sulfonate groups on the lower rim for separation of positional isomers of nitrophenols, dinitrobenzenes and benzenediols by capillary electrophoresis.

All the isomers were co-eluted under electrophoretic conditions with no additives. Figure 5a presents the related electropherogram. In contrast, the isomers were resolved as the concentration of calixarene derivative in the running buffer was increased. Figure 5b, c shows the effect of calixarene concentration on the buffer. They illustrate the electropherograms obtained from dinitrobenzenes (1: *m*-dinitrobenzene, 2: *p*-dinitrobenzene and 3: *o*-dinitrobenzene) in the presence of 7.5 mM calixarene derivative. Moreover, they presented the electropherograms obtained from benzenediols (1: *p*-benzenediol, 2: *m*-benzenediol and

3: *o*-benzenediol) in the presence of 10 mM calixarene derivative. Finally, they showed that the size-selective host:guest interactions between analytes and calixarenes played a prominent role in determining the separation behavior.

Sun et al. [123] studied the behavior of *p*-(carboxyethyl)calix[n]arenes stationary phases in capillary electrokinetic chromatography to separate native and substituted polycyclic aromatic hydrocarbons (PAHs). Pena et al. [124] synthesized two chiral acylcalix[4]arene amino acid derivatives including (*N*-L-valinoacyl)calix[4]arene and (*N*-L-alaninoacyl)calix[4]arene. They used them for enantioseparation of three binaphthyl derivatives by electrokinetic capillary chromatography and compared them.

By capillary electrophoresis, Zhao et al. [125] separated positional isomers of nitrophenol, benzenediol and aminophenol with the addition of *p*-sulfonic calix[4]arene to the running buffer, and they found that the resolution of such separations increased with increasing calixarene concentration. Yang et al. [126] used *p*-(quaternary ammonium) calix[4]arene in a capillary electrophoresis coupled with an electrochemical detector to separate the positional isomers of aminophenol and benzenediol. They compared the electrochemical detector and the UV detector in the separation of those analytes.

LC Stationary Phases for Molecular Recognition

The simplicity of chemical modification, easy preparation of calixarenes, and strong and variable ion binding abilities (by changing the conformations, the moieties, the number of donor groups and the nature of them) led to calixarenes, following cyclodextrines and crown ethers, being the third

Table 2 The list of calixarenes used in LC stationary phases for determination of molecular species

Type of calixarene	Analytes used	References
Calix[4,6,8]arene	PAHs	[7]
CalixBzCl, CalixBzF_5, CalixBzNO_2, LiChrosorb, CalixBn, CalixBph, CalixBnOMe	Pentylbenzene, butylbenzene, triphenylene, *o*-terphenyl, caffeine, phenol, benzylamine	[127]
Caltrex AI-calix[4]aren, Caltrex AII-calix[6]aren, Caltrex AIII-calix[8]aren, Caltrex BI-*p*-*tert*-butyl-calix[4]aren, Caltrex BII-*p*-*tert*-butyl-calix[6]aren, Caltrex BIII-*p*-*tert*-butyl-calix[8]aren, Caltrex Science-calix[4]aren, *p*-*tert*-butyl-calix[4]aren and resorcinarene-bonded phase (Caltrex resorcinaren)	Benzene, toluene, ethylbenzene, naphthalene, propylbenzene, anthracene, phenanthrene, bipheny, *o*-terpheny, triphenylene, promazine, propranolol, chlorpromazine, promethazine, amitriptyline, nortriptyline, *o*-cresol, phenol, dimethylacetamide, benzoic acid, naproxen, diclofenac, benzoic acid, salicylic acid, procaine and ephedrine	[128]
p-*tert*-Butyl-calix[8]arene	Steroids	[129]
Naphthyl-calix[4]arene and *t*-butyl-calix[4]arene	Caffeine	[130]
Calix[6]arene-*p*-sulfonate	Nitrophenol, methoxyphenol, cresol, aminophenol and chlorophenol	[131]
C-Tetraundecylcalix[4]resorcinarene	Cytosine, uracil and thymine	[132]
Calix[8]arene	Tricyclic neuroleptic	[133]
Calix[4]arenes	Benzene or uracil derivatives	[134]
Caltrex BIIE	Paracetamol, caffeine and acetylsalicylic acid	[135]
Caltrex AIII	Celecoxib	[136]
Fluorinated calix[4]arene	Fluorine compounds	[137]
p-*tert*-Butyl-calix[8]arene	Aromatic carboxylic acids	[138]
9-Amino(9-deoxy)-epiquinine calix[4]arene, 9-amino(9-deoxy)-quinine calix[4]arene	Cyclic amino acids	[139]
Caltrex AI, Caltrex AII, Caltrex AIII, Caltrex BI, Caltrex BII and Caltrex BIII	PAHs, phenols, substituted aromatics, xanthines, barbituric acid, benzoic acid esters	[140]
Calix[4]arene tetradiethylamide	Amino acid ester hydrochlorides	[141, 142]
Calix[4]resorcinarene and calix[4,6,8]arene	Flupentixol, chlorprothixene, clopenthixol and doxepin	[143]
p-*tert*-Butylcalix[4,6,8]arene	Disubstituted aromatics, uracil derivatives and estradiol epimers	[144]
p-*tert*-Butylcalix[4,6,8]arene	Peptide bond isomers of proline	[145]
p-*tert*-Butyl-calix[4]arene	Nucleosides, PAHs and bases	[146]
Calix[6]arene	nucleosides and PAHs	[147]
p-*tert*-Butyl-calix[4]arene	Basic aromatic compounds, polar and non-polar aromatic compounds, and PAHs	[148]

generation of macrocycles used in LC as stationary phases [109]. Table 2 summarizes the recent research carried out using calixarenes in liquid chromatography. The table contents are discussed briefly in the following section.

Chromatographic performance of six calixarene-bonded silica gel stationary phases was investigated by using PAHs, aromatic positional isomers and *E*- and *Z*-ethyl 3-(4-acetylphenyl) acrylate isomers as probes [7]. Ding et al. discussed a separation mechanism based on the different interactions among calixarenes and analytes, chromatographic behaviors of these analytes on the calixarene and the effect of polar groups in the aromatic isomers on separation selectivity. Figure 6 presents the preparation of these stationary phases.

They separated six PAHs on three stationary phases including calix[4]arene-bonded silica gel stationary phase (CBS4), Waters Xterra RP-18 (ODS) and calix[8]arene-bonded silica gel stationary phase (CBS8). The elution orders of PAHs on calixarene columns were the same as that obtained on ODS, implying that the calixarene bonded phases and *p-tert*-butyl-phenyl ether bonded silica gel stationary phase (BPBS) have strong hydrophobic selectivity, which plays an important role in the separation. At the same time, the capacity factors of PAHs on the calixarene-bonded phases are also related to the cavity size of calixarenes.

Moreover, they separated three dinitrobenzene isomers in three stationary phases including CBS4, *p-tert*-butylcalix[6]arene-bonded silica gel stationary phase (BCBS6) and ODS. A better separation of dinitrobenzene isomers was achieved on the BPBS column and the calixarene bonded phases than on the ODS column. Their k' values on the calixarene columns were larger than those on the ODS column. This means that there were additional interactions, with the exception of the hydrophobic interaction between calixarene and dinitrobenzene, which included hydrogen bonding and π–π interactions. This leads to the opposite elution order for dinitrobenzene isomers on the ODS columns and these calixarene derivatives. They attributed such an elution order on calixarene columns to the different field effects for three dinitrobenzene isomers. The field effect order ortho > meta > para was consistent with the hydrogen bonding interaction order between the phenolic OH group of calixarene and NO_2 of dinitrobenzene.

Furthermore, they separated α- and β-naphthol derivatives on two stationary phases including calix[6]arene-bonded silica gel stationary phases (CBS6) and ODS. Their separation chromatograph using CBS6 is shown in Fig. 7. They showed that naphthylamines and naphthols gave comparatively weaker retention on the ODS than on the calixarene columns. This means that there were additional interactions with the exception of the hydrophobic

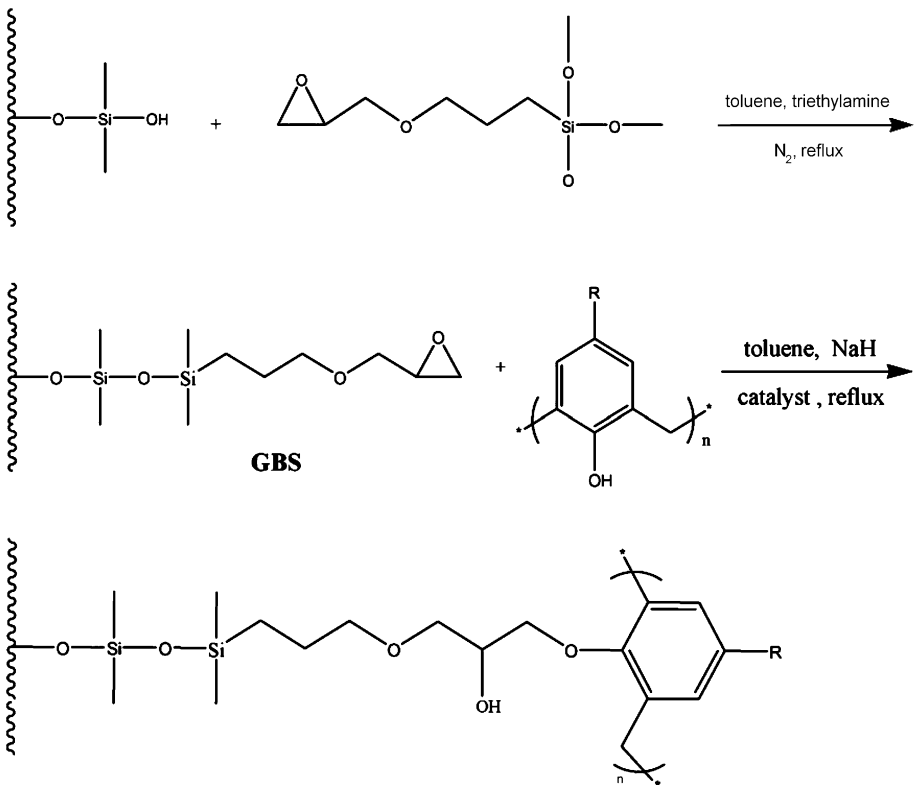

Fig. 6 Preparation scheme of calix[4,6,8]arene-bonded silica-gel stationary phases (R= H, *tert*-butyl). From [7], copyright 2007, Elsevier

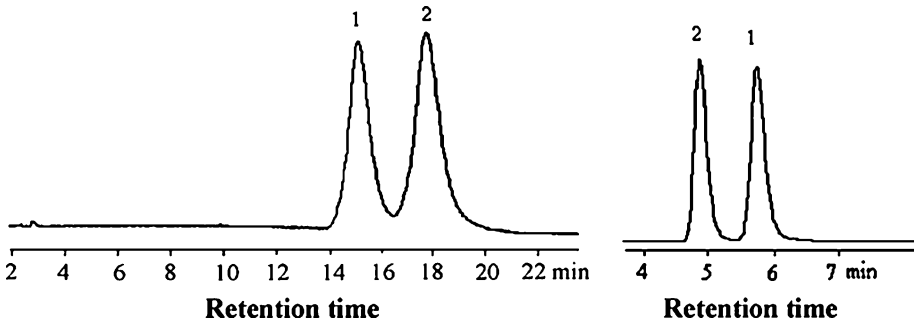

Fig. 7 The chromatograms for separation of α-naphthol (2) and β-naphthol (1) derivatives using CBS6 (*left*) and ODS (*right*) columns. From [7], copyright 2007, Elsevier

interaction between calixarene and naphthalene, which included hydrogen bonding and π–π interactions.

Sliwka-Kaszynska et al. [127] used six aspects, including surface coverage, hydrophobic selectivity, aromatic selectivity, shape selectivity, hydrogen bonding capacity and ion-exchange capacity, to study 12 calix[4]arene stationary phases (Fig. 8), which had been synthesized before by them. Figure 9 shows the chemical structures of investigated silica-based 1,3-alternate disubstituted calix[4]arene stationary phases.

There are some comparisons between commercially available stationary phases and calix[4]arene stationary phases. Such comparisons between 12 calix[4]arene stationary phases and some phenyl, fluorophenyl and fluoroalkyl columns were reported by the authors.

According to their results, calixarene phases generally exhibited a lower hydrophobic retention capacity than the LiChrosorb (C_{18}) phase; however, the CalixBzNO$_2$ column was the exception. Moreover, the results imply that only the C_{18} phase gave a selectivity factor above 1, whereas on all the calixarene phases *o*-terphenyl was retained longer than pentylbenzene. The aromatic selectivity parameters of CalixBzCl, CalixBzF$_5$ and CalixBzNO$_2$ columns increased in order of increasing electron deficiency in the phenyl rings derivatized by electron-withdrawing moieties. The calixarene phases showed better separation properties for alkylbenzenes than can be expected from their hydrophobic retention capacity. Different sites of the calixarene phases contributed to the selectivities toward the tested solutes. The calixarene phases had significant differences in hydrogen bonding capacities, which did not correspond to the degree of their surface coverage. CalixBn, CalixBzF$_5$, CalixBph and CalixBnOMe columns exhibited the highest total silanol activity among calixarene phases [127].

In order to characterize the chromatographic behavior of calixarene-bonded stationary phases and to test the applicability of established models predicting retention factors, Schneider and Jira [128] analyzed 31 solutes of highly various molecular structures at different composition mobile phases from 0 to 98% (*v/v*) methanol. The solutes included: benzene, toluene, ethylbenzene, propylbenzene, naphthalene, anthracene, phenanthrene, bipheny, *o*-terpheny,

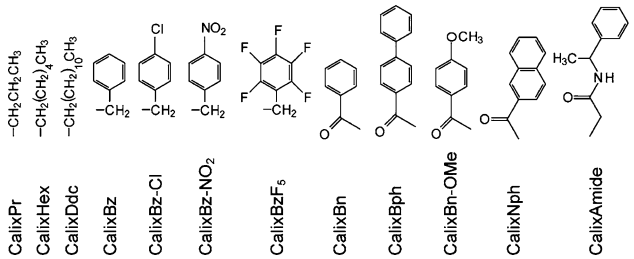

Fig. 8 Chemical structure of 12 calix[4]arene stationary phases. From [127], copyright 2010, Elsevier

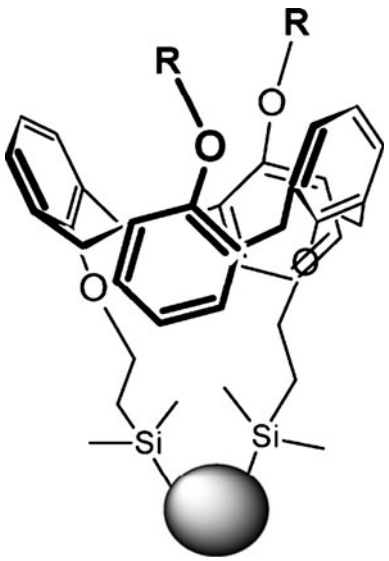

Fig. 9 Chemical structures of 12 silica-based calix[4]arene stationary phases including Calixper (R=*n*-propyl), CalixHex (R=*n*-hexyl), CalixDdc (R=*n*-C_{12}), etc. From [127], copyright 2010, Elsevier

triphenylene, propranolol, promazine, chlorpromazine, promethazine, amitriptyline, nortriptyline, dimethylacetamide, phenol, *o*-cresol, benzoic acid, naproxen, diclofenac, benzoic acid, salicylic acid, procaine and ephedrine. They examined seven calixarene-bonded phases including Caltrex AI-calix[4]aren, Caltrex AII-calix[6]aren, Caltrex AIII-calix[8]aren, Caltrex BI-*p-tert*-butyl-calix[4]aren, Caltrex BII-*p-tert*-butyl-calix[6]aren, Caltrex BIII-*p-tert*-butyl-calix[8]aren, Caltrex Science-calix[4]aren and *p-tert*-butyl-

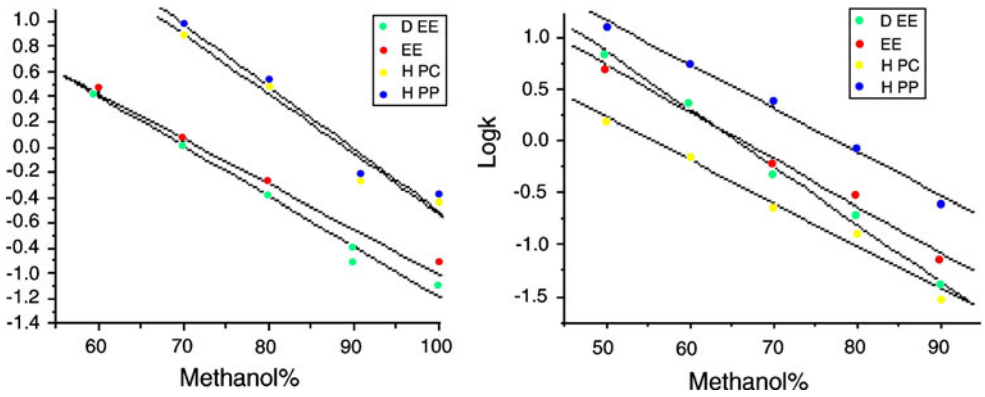

Fig. 10 Influence of methanol content on the retention factors of steroids on CBS (*left*) and *β*-CD-BS (*right*) columns. From [129], copyright 2005, Elsevier

calix[4]aren as well as a resorcinarene-bonded phase (Caltrex resorcinaren). They showed the influence of methanol content for non-polar, polar and ionic solutes and differences in their behavior on the differing column types.

Liu et al. [129] prepared four bonded silica stationary phases including chloropropyl bonded silica (CPS), *p-tert*-butyl-calix[8]arene bonded silica (CBS), *β*-cyclodextrin bonded silica (*β*-CD-BS) and ODS and applied them to separate steroid hormone medicines. Steroid samples included ethinylestradiolum (EE), nandrodone phenylpropionate (NPP), dexamethasoni natrii phosphas (DNP), hydroxyprogesterone caproate (HPC) and diethylstilbestroum (DEE).

They showed that the retention mechanisms of the four stationary phases for steroids were obviously different, and excellent separation was achieved on *β*-CD-BS. The retention process on *β*-CD-BS exhibited inclusion complexation, hydrogen-bonding and weak hydrophobic interaction, while for CBS hydrogen-bonding and π–π in addition hydrophobic interaction played an important role. Moreover, the effect of mobile phase composition on the retention of steroids was examined by changing the ratio of methanol:water. Figure 10 presents the influence of methanol content on the retention factors of solutes on CBS and *β*-CD-BS columns. This figure shows that the retention of steroids decreased with increasing methanol content of the mobile phase.

To find the best chromatographic separation of steroids, the smallest resolution between adjacent peaks, $R_{s,min}$, and the retention factor of the last eluted peak, k_{max}, was simultaneously compared. Figure 11 shows the separation chromatograms of steroids on the CBS column. They showed that the optimum separation was achieved on *β*-CD-BS having smaller k_{max} preferably under $R_{s,min}$.

Kimiko et al. [130] compared naphthyl-calix[4]arene and *t*-butyl-calix[4]arene bonded silica in the retention of caffeine and showed that naphthyl-calix[4]arene bonded silica strongly retained caffeine, similar to calix[4]arene bonded silica. Lee et al. [131] prepared a calix[6]arene-*p*-sulfonate stationary phase (Fig. 12) and separated the

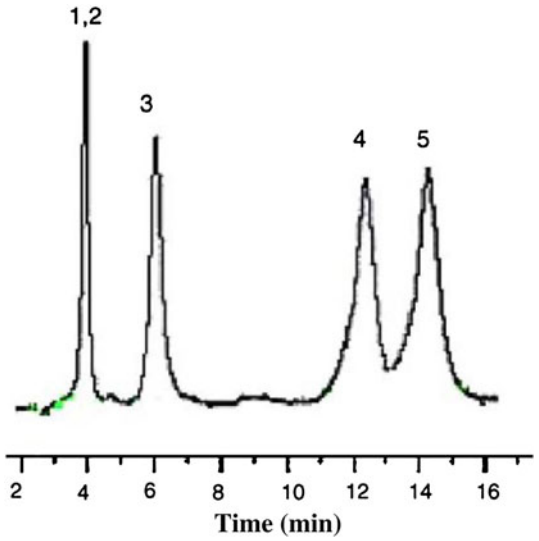

Fig. 11 Separation chromatograms of steroids on the CBS column; (1) EE, (2) DEE, (3) DNP, (4) HPC, (5) NPP. From [129], copyright 2005, Elsevier

regioisomers of mono-substituted phenol (nitrophenol, methoxyphenol, cresol, aminophenol and chlorophenol) and some other aromatic positional isomers.

Pietraszkiewicz et al. [132] studied the influence of the modification of the RP-18 phase on the partition and selectivity coefficients of pyrimidine bases (cytosine, uracil and thymine) in various eluents. They carried out the modification by passing the solution of lipophilic *C*-tetraundecylcalix[4]resorcinarene in acetonitrile through the analytical LC column filled with RP-18 phase. Figure 13 presents the chromatograms of cytosine, uracil and thymine on the coated column using a water solvent at different pHs. Figure 14 shows that the chemical structure of lipophilic *C*-tetraundecylcalix[4]resorcinarenes was used.

Hashem and Jira [133] studied the effects of different chromatographic conditions on the separation of nine tricyclic neuroleptics and the effect of structural differences of analytes with a new LC stationary phase with calixarenes. They showed that chemical the structure and pK_a of

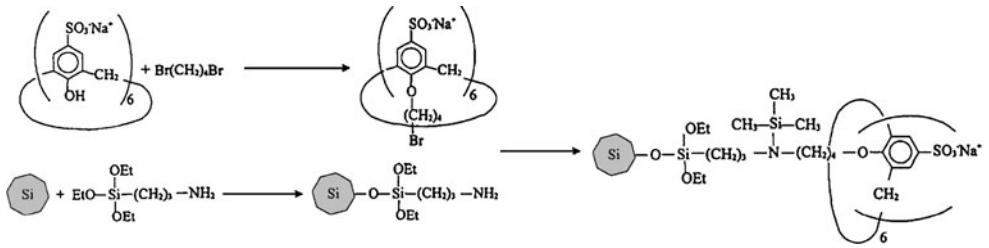

Fig. 12 Preparation of Lee's calix[6]arene-*p*-sulfonate stationary phase. From Ref. [131], with permission

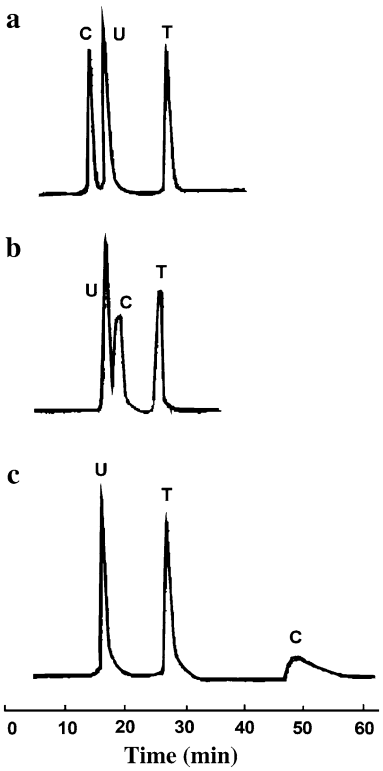

Fig. 13 Separation of cytosine (C), thymine (T) and uracil (U) on the coated column: **a** pH= 2, **b** pH= 4, **c** pH= 7. From Ref. [132], with permission

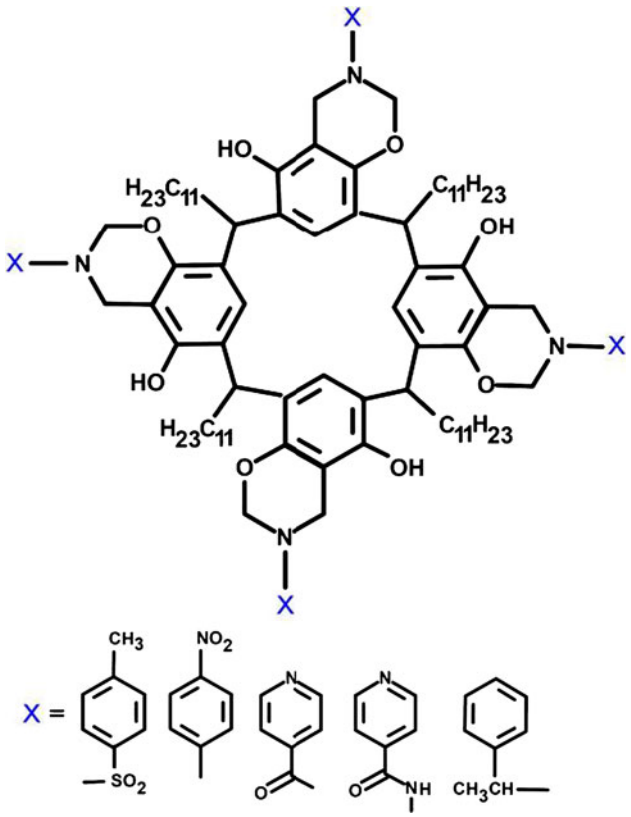

Fig. 14 The chemical structure of lipophilic *C*-tetraundecylcalix[4]resorcinarenes. From Ref. [132], with permission

neuroleptics influenced their separation on the calix[8]arene stationary phase. Addition of calix[4]arenes to mobile phases improves the chromatographic separation of benzene or uracil derivatives [134]. In this regard, Kalchenko et al. discussed the structure of the calixarenes and their complexes with benzene or uracil derivatives (benzene, benzoic acid, *m*-aminobenzoic acid, *m*-toluic acid, *o*-bromotoluene, *o*-nitrobenzoic acid, *o*-phthalic acid, *p*-aminobenzoic acid, *p*-aminophenol, *p*-bromotoluene, *p*-cresol, phenol, *p*-nitrobenzoic acid, *p*-phthalic acid, *p*-toluic acid and toluene) in the context of chromatographic separation. They used MeCN:H_2O and MeOH:MeCN:THF:H_2O mobile phases to improve the chromatographic separations on Separon SGX C_{18} or Separon SGX NH_2 supports. They explained the potential mechanism for the separation of benzene or uracil derivatives as follows: Ethyluracyl is included in the calixarene hydrophobic cavity by its ethyl group. The hydrophobic part C(O)–NH–C(O) of the ethyluracil is oriented outside the calixarene cavity. The complex is stabilized by C–H π bonds of the methyl group (in 5-ethyluracyl) with calixarene benzene rings, solvatophobic interactions and van der Waals forces. The complexation transforms the flattened cone conformation of the calixarene into a regular cone one. Other abilities of calixarenes in mobile phases have been discussed in another section.

Simultaneous determination of paracetamol (PAR), caffeine (CAF) and acetylsalicylic acid (ASA) in the Excedrin tablet formulation was done by Hashem [135] using

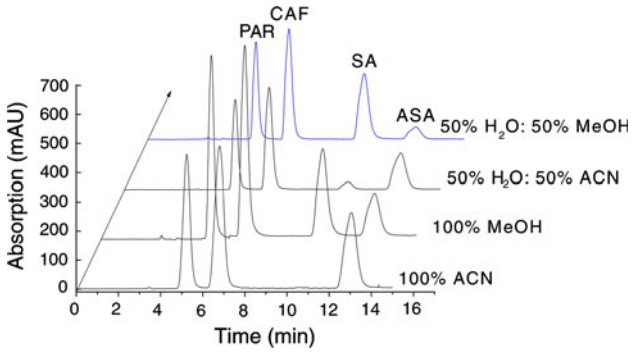

Fig. 15 The effect of the extracting solvent composition on the stability of analytes in Excedrin tablets. From Ref. [135], with permission

calixarene stationary phases (Caltrex BIIE column) with detection limits of 0.488, 0.977 and 7.813 ng μL^{-1}, respectively. The effect of the extracting solvent composition on the stability of analytes is presented in Fig. 15. He et al. [136] used the Caltrex AIII column for extraction and quantification of celecoxib in tablets with a detection limit of 0.122 $\mu g\ mL^{-1}$. They assessed the method selectivity by sample degradation using evaluation of peak purity. The first three degradation conditions did not affect celecoxib, while UV radiation strongly affected its solution. However, there was no interference between the celecoxib peak and those of degradation products.

In Poland, a new fluorinated calix[4]arene-bonded silica gel stationary phase ($CalixBzF_{10}$) was synthesized, structurally characterized and used as a selector in liquid chromatography for fluorine-containing compounds and non-fluorinated analytes. Barc and Sliwka-Kaszynska [137] showed that the retention time of basic analytes depends on the mobile phase pH, and fluorine-fluorine interactions are involved in the separation process of fluorine-containing analytes.

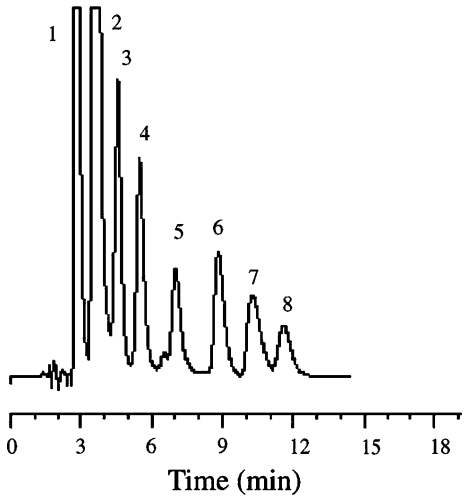

Fig. 17 The chromatograms of aromatic carboxylic acids on the *p-tert*-butyl-calix[8]arene-bonded silica gel stationary phase (1: *p*-amino benzoic acid; 2: *o*-amino benzoic acid; 3: *p*-fluorobenzoic acid; 4: phthalic acid; 5: 2,4-dihydroxyl benzoic acid; 6: *o*-chlorobenzoic acid; 7: *o*-bromobenzoic acid; 8: *p*-nitrobenzoic acid). From [138], copyright 2004, Elsevier

Li et al. [138] used the *p-tert*-butyl-calix[8]arene-bonded silica gel stationary phase to separate aromatic carboxylic acids and compared it with conventional ODS columns. The procedure for preparation of *p-tert*-butyl-calix[8]arene-bonded silica gel was described briefly as illustrated in Fig. 16. The chromatogram of tested acids on the *p-tert*-butyl-calix[8]arene-bonded silica gel stationary phase is shown in Fig. 17. They investigated the influence

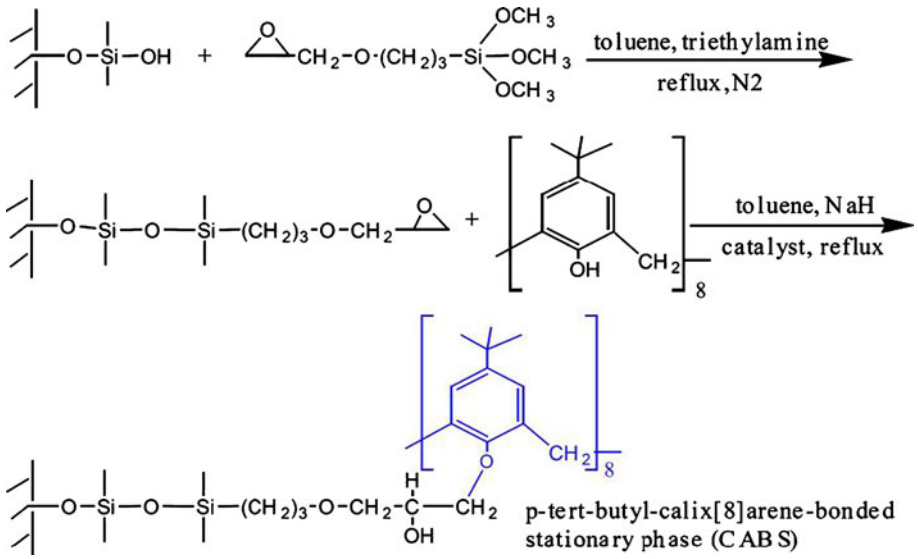

Fig. 16 Preparation of *p-tert*-butyl-calix[8]arene-bonded silica gel. From [138], copyright 2004, Elsevier

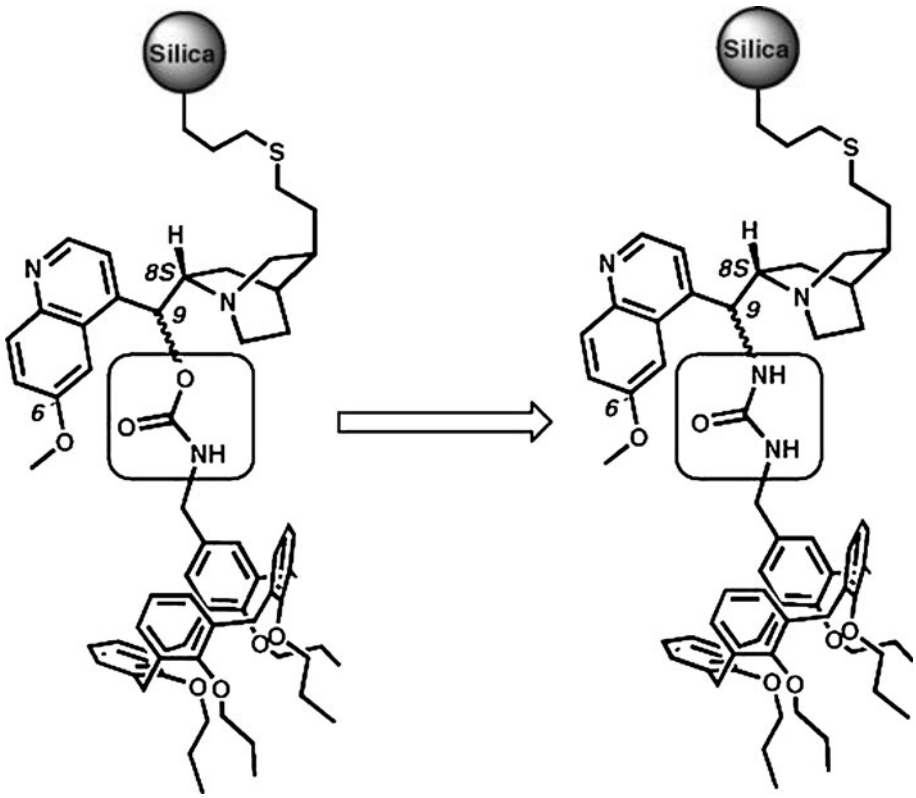

Fig. 18 Chemical structures of carbamate-linked and urea-linked cinchona-calixarene hybrid type. From [139], copyright 2004, Elsevier

of several mobile parameters on the chromatographic behavior of the solutes. The better separation of carboxylic acids on *p-tert*-butyl-calix[8]arene-bonded silica gel was achieved in methanol-phosphate buffer without any ion pair reagent. Moreover, the retention mechanism of the acids on the calix[8]arene-bonded phase was discussed. The calix[8]arene-bonded phase exhibited a better selectivity than ODS, which was due to some interaction, such as hydrophobia, hydrogen bonding, π–π and inclusion.

According to Fig. 18, Krawinkler et al. [139] synthesized two diastereomeric cinchona-calixarene hybrid-type receptors (SOs) including 9-amino(9-deoxy)-epiquinine calix[4]arene (eAQN-calixarene) and 9-amino(9-deoxy)-quinine calix[4]arene (AQN-calixarene). In the column of these stationary phases, high levels of enantioselectivity for benzyloxycarbonyl (Z)-, *tert*-butoxycarbonyl (Boc)- and fluorenylmethoxycarbonyl (Fmoc)-protected cyclic amino acids were achieved. Due to the crucial contributions of hydrogen bonding to chiral recognition, increasing amounts of acetic acid compromised enantioselectivity.

Sokoließ et al. [140] compared the chromatographic behavior of six calixarene-bonded stationary phases including Caltrex AI, Caltrex AII, Caltrex AIII, Caltrex BI, Caltrex BII and Caltrex BIII. They examined their selectivity on the PAHs, phenols, substituted aromatics, xanthines, barbituric acid (Fig. 19) and benzoic acid esters derivatives as the analytes. Moreover, they assessed the

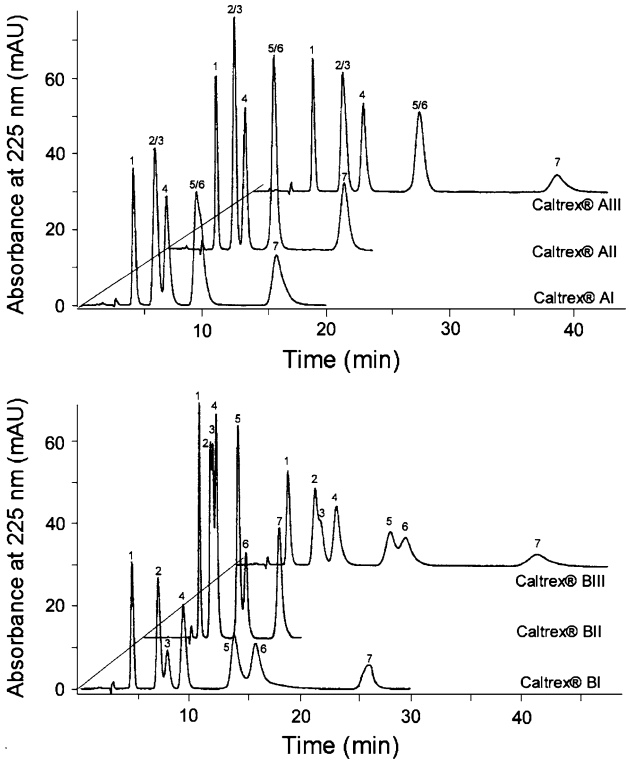

Fig. 19 Comparison of isocratic separations of barbituric acid derivatives including related compounds (primidone, phenytoine) on calixarene phases. Analytes: 1: barbital, 2: primidone, 3: crotylbarbital, 4: phenobarbital, 5: hexobarbital, 6: pentobarbital, 7: phenytoine. From [140], copyright 2000, Elsevier

role of the ring size of the calix[4,6,8]arenes and the substitution at the upper rim with *para-tert*-butyl groups on the interaction behavior of stationary phases and analytes. Furthermore, they compared the influences of several organic solvents on retention variations of solutes for reversed-phase columns, phenyl and calixarene phases. A comparison with conventional reversed-phase columns shows a predominantly reversed-phase character with remarkable selectivities of these phases.

Glennon et al. [141, 142] examined the chromatographic behavior of amino acid ester hydrochlorides on a silica-bonded macrocyclic calix[4]arene tetradiethylamide phase. A series of amino acid ester hydrochlorides were shown to be retained in order of their hydrophobicity on the silica bonded phase. They found that the retention of organic solutes on these silica-bonded functionalized calixarene phases was dependent on the organic modifier concentration.

Sokoließ et al. [143] separated *cis*- and *trans*-isomers of three thioxanthene (flupentixol, chlorprothixene, clopenthixol) and one benz[*b*,*e*]oxepin derivative (doxepin) on one calix[4]resorcinarene- and six calix[4,6,8]arene-bonded LC stationary phases. Moreover, they assessed the influences of MeOH and MeCN as two different organic modifiers. Based on the experiments, different selectivities of the stationary phases were reported to be the function of the ring size and the substitution at the upper rim with *p-tert*-butyl groups. Furthermore, they compared the selectivity of the calixarene and resorcinarene stationary phases with a RP-C_{18} phase containing the same base silica.

Gebauer et al. separated the regio/stereo isomers of disubstituted aromatics, uracil derivatives and estradiol epimers [144], and the *cis/trans* peptide bond isomers of proline [145] using *p-tert*-butylcalix[4,6,8]arene-bonded silica gels. As shown in Fig. 20, Xiao et al. [146] attached the *p-tert*-butyl-calix[4]arene to silica gel via the silane coupling reagent γ-(ethylenediamino)-propyl-triethoxyl-silane and characterized the bonded phase by ^{29}Si and ^{13}C cross polarization/magic angle spinning solid-state nuclear magnetic spectrometry. After that, they assessed the retention behavior of nucleosides, polycyclic aromatic hydrocarbons (PAHs) and bases on the bonded phase, while a reversed-phase mode was used. The chromatogram of the mixture of bases is presented in Fig. 21.

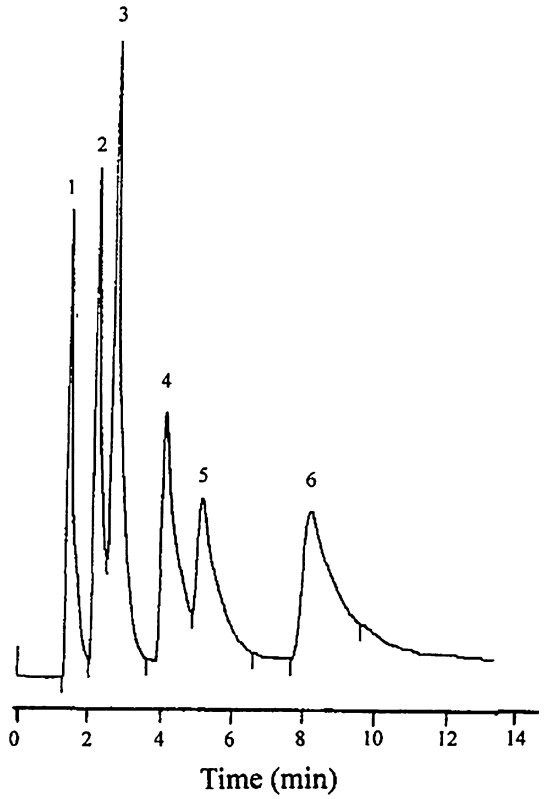

Fig. 21 Chromatogram of a mixture of bases: *1* cytosine, *2* 5-flurouracil, *3* purine, *4* 5-iodouracil, *5* 6-mercaptopurine, *6* caffeine. From Ref. [146], with permission

Xu et al. [147] attached the calix[6]arene to a silica gel via a longer spacer to separate the positional isomers, some nucleosides and polycyclic aromatic hydrocarbons in a reversed-phase mode by use of methanol and water as mobile phase. They examined the chromatographic performance of the prepared bonded phase and reported its highly hydrophobic characteristics. According to Fig. 22, Huai et al. [148] prepared end-capped *p-tert*-butyl-calix[4]arene-bonded silica phases using the end-capping agent of trimethylchlorosilane. They reported good separations of basic aromatic compounds, polar and non-polar aromatic compounds, polycyclic aromatic hydrocarbons and some isomers. They observed that the end-capped phase was more selective toward alkylbenzenes than

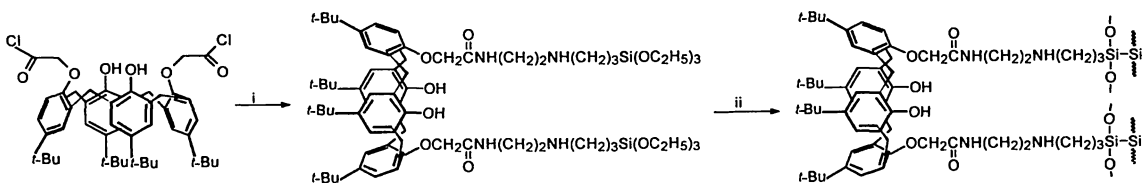

Fig. 20 Synthesis procedure for *p-tert*-butyl-calix[4]arene bonded silica gel stationary phase. (*i*) = γ-(ethylenediamino)-propyl-triethoxyl-silane, Et_3N and toluene under reflux, (*ii*) = silica gel, Et_3N and toluene under reflux. From Ref. [146], with permission

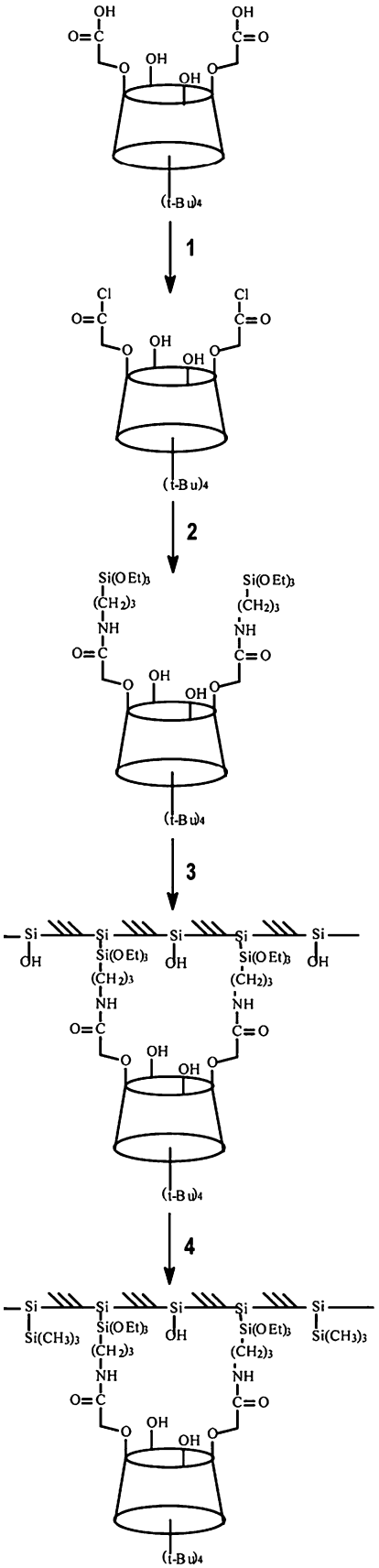

Fig. 22 Preparation steps of end-capped *p-tert*-butyl-calix[4]arene-bonded-silica phases by means of the end-capping agent of trimethylchlorosilane. From Ref. [148], with permission

kromasil-C_{18}-SiO_2. Hence, they reported that the retention mechanisms involved strong π–π interaction, strong hydrophobic interaction and host-guest interaction.

LC Stationary Phases for Recognition of Ionic Species

Table 3 summarizes research topics based on calixarenes in ionic liquid chromatography. The table contents are discussed briefly in the following section.

Glennon et al. [141, 142] studied the chromatographic behavior of alkali and alkaline earth metal ions on a silica-bonded macrocyclic calix[4]arene tetradiethylamide phase. They found the selective retention of Na^+ over other alkali metal ions and of Ca^{2+} over Mg^{2+} ions. They reported that retention of metal ions on these silica-bonded functionalized calixarene phases was related to the concentration of the organic modifier in mobile phase.

Zhang et al. [149] prepared a setup, which is shown in Fig. 23, and used the extraction chromatography process to propose a partitioning and recovery of two heat generators (strontium and cesium) from acidic high activity liquid waste (HLW). They synthesized two macroporous silica-based polymeric materials, *N,N,N′,N′*-tetraoctyl-3-oxapentane-1,5-diamide and 1,3-[(2,4-diethyl-heptylethoxy)oxy]-2,4-crown-6-calix[4]arene (Fig. 24), immobilized into the pores of

Table 3 The list of calixarenes used in ionic liquid chromatography for determination of ionic species

Type of calixarene	Analytes	References
Calix[4]arene tetradiethylamide	Na^+ and Ca^{2+}	[141]
Calix[4]arene tetradiethylamide	Na^+ and Ca^{2+}	[142]
N,N,N′,N′-Tetraoctyl-3-oxapentane-1,5-diamide and 1,3-[(2,4-diethyl-heptylethoxy)oxy]-2,4-crown-6-calix[4]arene	Cs^+ and Sr^{2+}	[149]
p-tert-Butylcalix[6]arene hexacarboxylate	Cr^{6+}	[150]
2-Pyridylcalix[4]arene	Ag^+	[151]
Calix[6]arene derivatives	Pu, Am and U	[152]
Octacarboxymethyl-*C*-methylcalix[4]resorcinarene	La^{3+}, Ce^{3+} and Y^{3+}	[153]
2,3-[(2,4-Diethyl-heptylethoxy)oxy]-2,4-crown-6-calix[4]arene	Cs^+	[154]
Calix[4]arene-R14	Cs^+ and Sr^{2+}	[155]

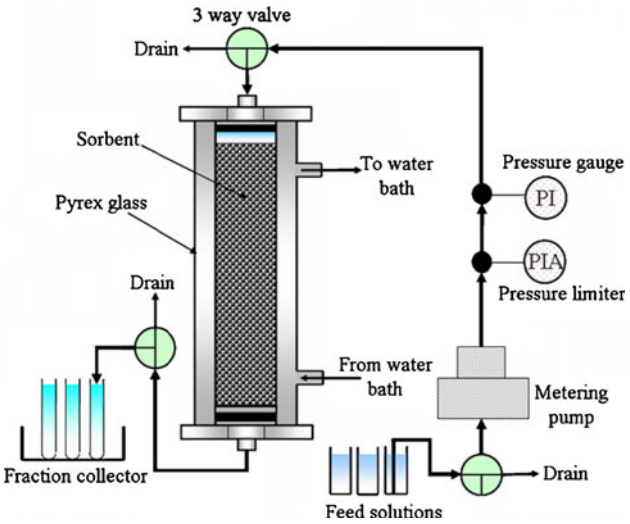

Fig. 23 Apparatus of the chromatographic partitioning of the simulated solution. From [149], copyright 2007, Elsevier

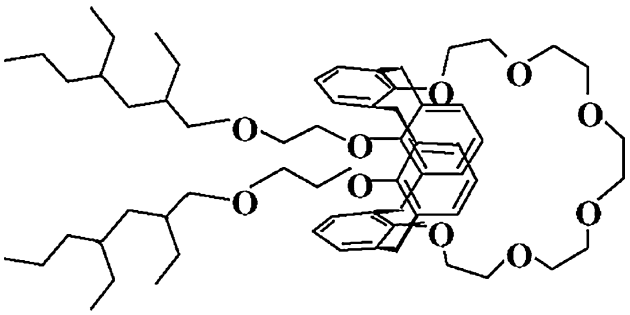

Fig. 24 Molecular structure of 1,3-[(2,4-diethyl-heptylethoxy)oxy]-2,4-crown-6-calix[4]arene. From [149], copyright 2007, Elsevier

SiO_2 particle support. They showed them by TODGA/SiO_2-P and Calix[4]arene-R14/SiO_2-P, respectively. In the Calix[4]arene-R14/SiO_2-P column, they found that all of the simulated elements were separated effectively into two groups, the Sr group and Cs group. The first group contained Na(I), K(I), Sr(II), Fe(III), Ba(II), Ru(III), Pd(II), Zr(IV) and Mo(VI), while the second consisted of Cs(I) and Rb(I). Based on their observations, they revealed that Cs(I) flowed into the Cs group along with Rb(I) because of their close sorption and elution properties towards Calix[4]arene-R14/SiO_2-P, while Sr(II) showed no sorption and flowed into the Sr group. Moreover, in the TODGA/SiO_2-P column, they observed that the Sr group was separated into four groups, including a non-sorption group and three sorption groups. They contained (1) Ba(II), Ru(III), Na(I), K(I), Fe(III) and Mo(VI); (2) Sr(II); (3) Pd(II) and (4) Zr(IV).

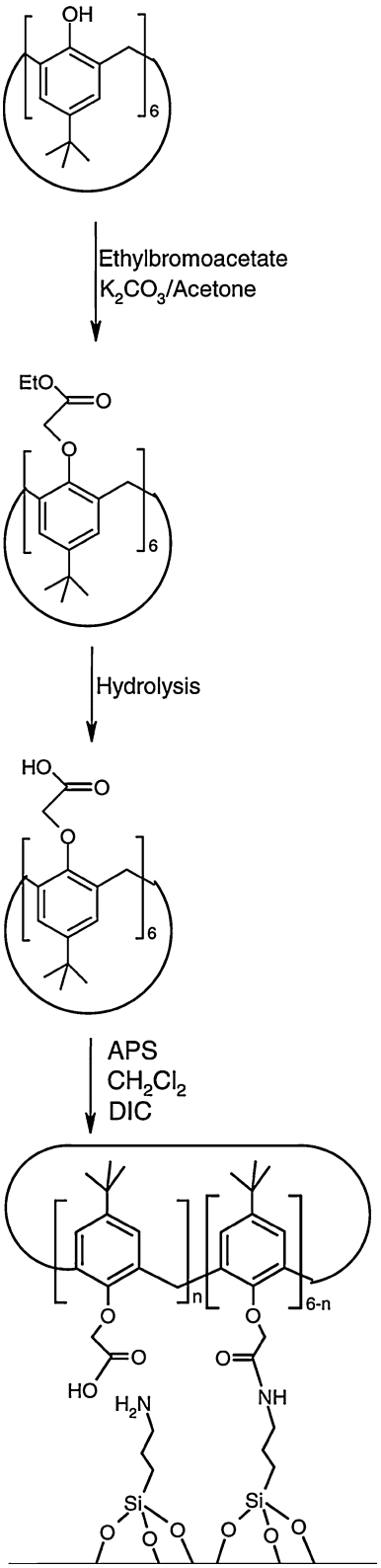

Fig. 25 The synthesis procedure of Tabakci's stationary phase. From Ref. [150], with permission

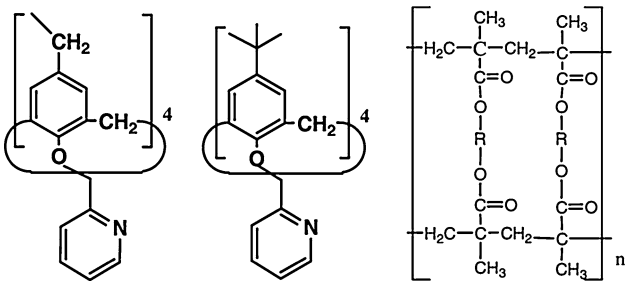

Fig. 26 The chemical structures of the reagents employed in the methylene crosslinked resins. From left to right: ideal structure of methylene crosslinked resin (MC resin), 2-pyridylcalix[4]arene impregnated reagent resin (2Py-IR resin) and Amberlite XAD-7 (macroporous polymer matrix). From Ref. [151], with permission

Tabakci [150] used *p-tert*-butylcalix[6]arene hexacarboxylate containing both amide and acid moieties, and immobilized it on the aminopropyl silica gel surface. Figure 25 shows the synthesis procedure of the stationary phase as well as the chemical structure of amide and acid moieties. The prepared sorbent was highly effective for Cr^{6+} at pH 1.5. They also studied the effect of pH, contact time, sorbent dosage, initial Cr^{6+} concentration and temperature on Cr^{6+} sorption and the sorption isotherms.

Japanese chemists [151] synthesized three different resins by methylene crosslinking of 2-pyridylcalix[4]arene and investigated their adsorption behavior towards the metal ions existing in photographic waste. The chemical structures of reagents employed in their study are shown in Fig. 26. The resins showed absolute efficiency for adsorption of Ag^+ with no affinity for other coexisting ions (such as sodium, potassium and lead ions). The range of maximum loading capacity of Ag^+ on the resins was found to be 0.69–1.29 mol kg^{-1}. Column chromatographic separation of Ag^+ in the presence of excess of Na^+ was carried out, and selective adsorption of Ag^+ was achieved.

The high selectivity of prepared resins towards Ag^+ was attributed to the chelating effect of soft donor atoms in which the silver ion is encapsulated within the cavity composed by pyridyl groups forming a 1:1 complex. Although Ag^+ and Na^+ have similar ionic radii, their experimental results indicated that the cavity size of calixarene was not an evident factor for complexation with Ag^+. The chelating effect and preorganization of functional groups were reported as the absolute factors for Ag^+ adsorption. The maximum loading capacity of crosslinked resins for Ag^+ was determined to be higher than that of impregnated resin.

Bouvier-Capely et al. [152] investigated the applicability of calix[6]arene columns for actinide analysis in urine samples and drinking water using a radiochemical procedure for analysis of Pu, Am and U ions. Gok et al. [153] proposed the procedure of separation and preconcentration of cerium, lanthanum and yttrium using octacarboxymethyl-*C*-methylcalix[4]resorcinarene impregnated onto a polymeric matrix (Amberlite XAD-16). The preconcentration factors and RSD were determined to be 125, 83, 100 and 2.27, 1.97, 2.01 for La^{3+}, Ce^{3+} and Y^{3+}, respectively. Zhang et al. [154] proposed the separation of Cs^+ from highly active liquid waste by a novel silica-based 1,3-[(2,4-diethylheptylethoxy)oxy]-2,4-crown-6-calix[4]arene impregnated polymeric composite by extraction chromatography.

They [155] synthesized two kinds of macroporous silica-based polymeric materials, Calix[4]arene-R14/SiO_2-P and TODGA/SiO_2-P, and used them to partition Cs^+ and Sr^{2+} effectively from a highly active liquid waste by extraction chromatography. In a packed column of Calix[4]arene-R14, all of the simulated elements were separated effectively into two groups: Sr group (Na, K, Sr, Fe, Ba, Ru, Pd, Zr, Mo) and Cs group (Cs, Rb). The harmful element Cs^+ flowed into the second group along with Rb^+ because of their close sorption and elution properties towards Calix[4]arene-R14/SiO_2-P, while Sr^{2+} showed no sorption and flowed into the Sr-containing group. In the packed column of TODGA, the Sr group was separated into four groups: the non-sorption (Ba, Ru, Na, K, Fe, Mo), Sr, Pd and Zr groups. The packed TODGA column showed excellent separation efficiency compared to others.

Table 4 The list of calixarenes used as modifier in chromatographic mobile phases for determination of molecular species

Type of calixarene	Analytes used	References
Calix[6]arene-*ρ*-sulfonate	Methoxyphenol, aminophenol and nitrophenol	[156]
p-Sulfonatocalix[4]arene	Amino acids	[157]
4-Sulphonic calix[4,6]arenes	2-,3- and 4-Nitrophenols	[158]
Calix[4]arenes	Benzene and uracil derivatives	[134]
4-Sulfonic calix[6]arene, *p*-(*N,N*-Diallylaminomethyl)calix[6]arenes	Naphthalene, anthracene, phenanthrene, fluoranthene, pyrene, acid red 8, acid red 88, acid red 114, acid blue 45, 1-aminonaphthalene, 5-amino-1-naphthol and 3-amino-2-naphthol	[159]

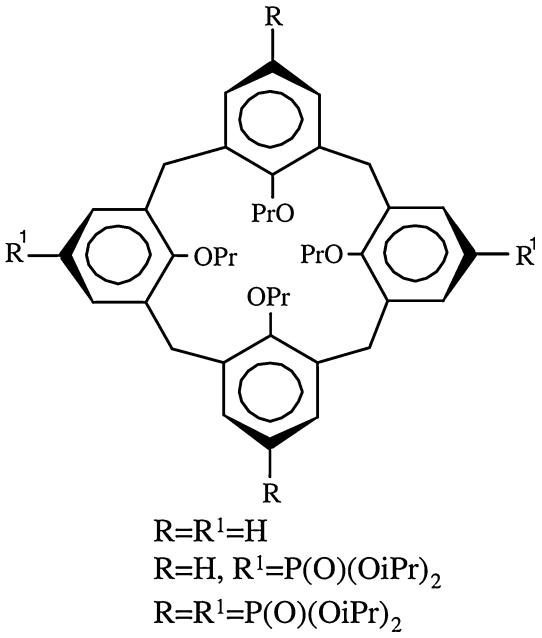

Fig. 27 Molecular structure of three tetrapropoxycalixarenes in Kalchenko's experiments. From Ref. [134], with permission

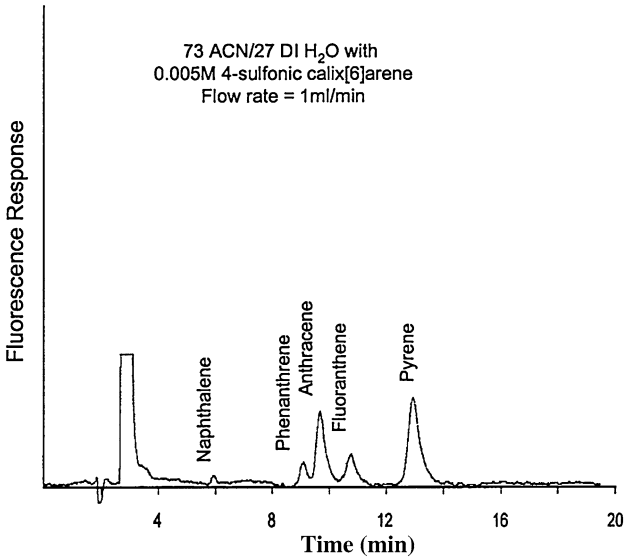

Fig. 28 The chromatographs for separation of PAHs with 4-sulfonic calix[6]arene. From Ref. [159], with permission

Chromatographic Mobile Phases

In LC and electrokinetic chromatography, only the soluble calixarenes are used as mobile phase additives. Moreover, calixarene-bonded stationary phases are preferably used in LC, because the UV detection of analytes is hindered by the strong absorbance of calixarenes [7]. Therefore, there have been few investigations of calixarenes as mobile phase modifiers because of the limited availability of

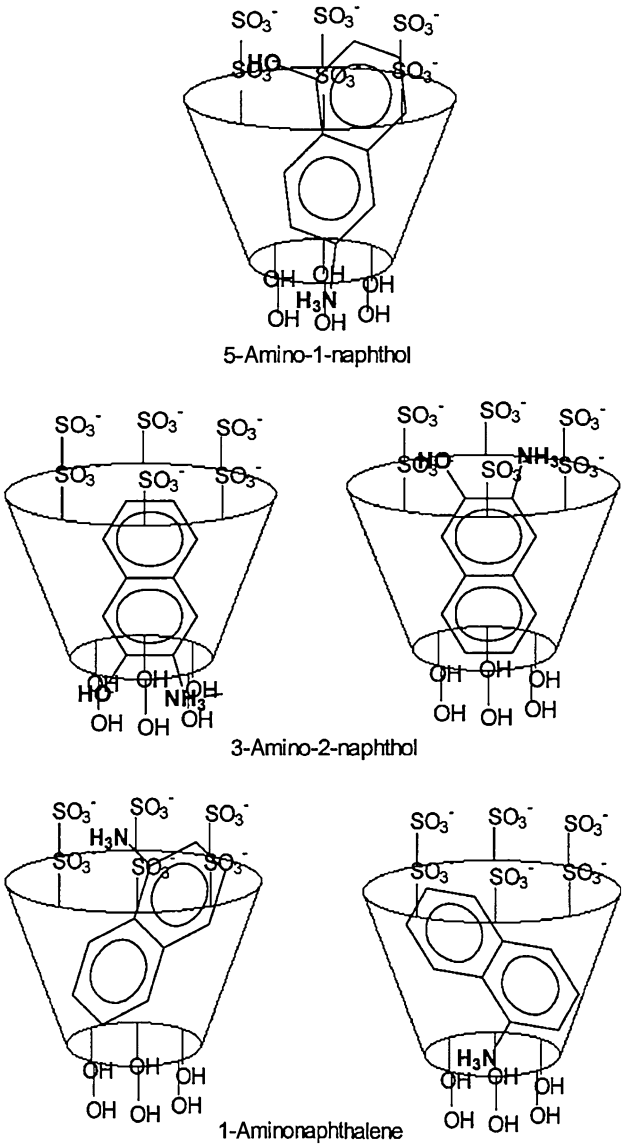

Fig. 29 A schematic for inclusion of amino-naphthols with 4-sulfonic calix[6]arenes. From Ref. [159], with permission

water-soluble calixarenes and their ability to be strong ultraviolet absorbers. Table 4 presents the topics of research based on calixarenes that were used as modifiers or additives in chromatographic systems. The table contents are discussed briefly in the following section.

Park et al. [156] examined the calix[6]arene-ρ-sulfonate as a mobile phase additive to separate regioisomers of methoxyphenol, aminophenol and nitrophenol via reversed phase liquid chromatography. They revealed that the addition of calix[6]arene-ρ-sulfonate to the mobile phase (acetonitrile:water and methanol:water) caused a reduction in the retention of the phenol isomers but increased the separation between them. Kalchenko et al. [157] studied the host-guest complexation of *p*-sulfonatocalix[4]arene with amino acids as the guest. The formation of the

inclusion complexes resulted in changes in the retention times of amino acids. They explained the variations in stability constants in terms of hydrophobia, ion pairing, electrostatic and aromatic-aromatic interactions.

Millership et al. [158] used 4-sulphonic calix[4, 6]arenes as mobile phase additives in reversed phase LC to separate 2-, 3- and 4-nitrophenols. Their results indicated that the reduction in the LC capacity factors of nitrophenols was primarily a function of the pH and did not result from complexation between the calixarenes and the phenols. Kalchenko et al. [134] improved LC separation of benzene and uracil derivatives on Separon SGX NH_2 or Separon SGX C_{18} supports by the addition of calix[4]arenes (Fig. 27) to the mobile phases.

The similarities in host-guest complex formation between the calixarenes and the cyclodextrins have led to the belief that calixarenes will form significant host-guest interactions with solute molecules during chromatography. Interactions have been determined to take place by the reduction of capacity factors of solutes when a calixarene additive is introduced to the mobile phase. One problem associated with the use of calixarenes (as mobile phase modifiers) is their strong absorbance in the UV region of the spectrum, which has been circumvented by Vis absorbance and fluorescence detection of solutes. Lowe [159] examined the separation of PAHs (naphthalene, anthracene, phenanthrene, fluoranthene and pyrene), sulfonated azo dyes (acid red 8, acid red 88, acid red 114 and acid blue 45) and amino-naphthols (1-aminonaphthalene, 5-amino-1-naphthol and 3-amino-2-naphthol) with and without calixarene additives. Figure 28 presents the separation chromatograph of PAHs using 4-sulfonic calix[6]arene stationary phase. Figure 29 illustrates the inclusion of amino-naphthols with *4*-sulfonic calix[6]arenes.

As discussed above, calixarenes are often used as the mobile phase additives or the chemically bonded stationary phases. Calixarene-bonded stationary phases are preferably used in LC, because the UV detection of analytes is hindered by the strong absorbance of calixarenes. Furthermore, the poor solubility of most calixarenes precludes their applications as additives in aqueous eluents of chromatographic systems.

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