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REVIEW ARTICLE

Calixarene-engineered surfaces and separation science

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Abstract After their discovery, calixarenes have attracted the attention of many researchers from various disciplines. This group of supramolecules has an increasing popularity and this is most probably related with the flexibility of calixarene chemistry. Owing to their multifunctional character and stability, calixarenes became important precursors in separation science to derive new-type of sorbents or stationary phases. Immobilization of calixarenes to a suitable solid support (e.g. silica, synthetic polymers, magnetite nanoparticles, etc.) is a very popular concept being used for this purpose, and various immobilization methodologies have been proposed in the literature. In the present work, some state-of-the-art researches and developments published in the past are reviewed in a collective manner, and thus fundamentals of calixarene-immobilization and the application of the obtained materials in sorption and high performance liquid chromatography are represented.

Keywords Adsorption · Calixarene · Chromatography · Immobilization · Supramolecules · Purification

Introduction

Calixarene is a generic name which defines a class of macrocyclic compounds consisted of phenolic units connected by methylene bridges. Their discovery goes back to 1872 when Adolph von Baeyer [1] was introduced the synthesis of these supramolecules as products of the reaction of phenols with aldehydes in presence of strong acids. In the beginning of 20th century, Baekeland [2] patented a process where a small amount of base was used to yield resinous materials (obtained from the reaction of phenol and formaldehyde) he called Bakelite. This discovery made their large-scale production possible. Despite their early discovery, the structural details were not clear until the studies of Zinke and his coworkers in 1944 and 1952 [3, 4]. They proposed a cyclic tetrameric structure for the product of the base-induced condensation of *p-tert*-butylphenol and formaldehyde. In the late 1970s, the studies of Gutsche and coworkers [5] had a synergistic effect on the chemistry of phenol–formaldehyde products, and they were also the scientists who named such products as *calixarenes*.

Today, there is a well-recognized nomenclature for calixarenes. A bracketed number, n, positioned between calix and arene (i.e. calix[*n*]arene) indicates the number of phenolic units linked to each other by methylene bridges to form the cavity of the molecule. Substitution on the aromatic rings is specified by appropriate prefixes. Calixarenes containing four, six, and eight aryl units (the “major” calixarenes) can be easily prepared in good to excellent yields with high states of purity. Calixarene skeleton possesses a well-defined cavity with polar (lower-rim) and nonpolar (upper-rim) properties. Also, they can be derivatized in terms of cavity size and functional group to yield analyte-selective compounds.

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A series of books and reviews have been published which discuss in length the calixarenes and its substituted derivatives being used for the recognition of cation, anion, neutral molecules, and organic compounds [6–11]. Reversible interaction of calixarenes with different types of solutes and their adaptability to various applications made this group of supra-molecules very popular in sorption and chromatography as sorbent or stationary phase [12].

Application of calixarene-based materials as stationary phase begins with the studies performed in 1990s [13–16] where separation of different types of chemical species such as alkali metal ions and amino acid esters, nitroaniline regioisomers, nucleosides and proline-containing dipeptides on the prepared stationary phases was studied. The range of applications is, today, extended to magnetic separations and calixarene-embedded nanofibers. In this kind of applications, immobilization of calixarenes to a solid support is one of the most applied processes and it is deemed important to obtain stable calixarene-based materials suitable for particular application.

As a matter of fact, the literature contains valuable reviews [17–22] concentrated on the application of calixarenes in separation processes (especially chromatography) and their other analytical applications. Nevertheless, most of the published reviews deal with the application of calixarene-immobilized materials in chromatography as stationary phase, and there is still a big demand for a compact review of the methodologies used in immobilization of calixarenes and the usability of the obtained materials in separation processes based on liquid–solid interfaces; especially sorption and high performance liquid chromatography (HPLC). Moreover, rapid developments and progress in the calixarene chemistry (and calixarene-immobilized materials), and their incredible use in separation processes made it necessary recollecting some important works published in the past. The present mini review not only pictures past and present of the issue, but also represents a good understanding of the topic. The aim of this work is not to collect all the related studies; instead it aims at representing the issue through a clear view point and thus assessing the current situation.

Immobilization of calixarenes

Immobilization is a process through which a ligand (i.e. molecule, macromolecule) is fixed to a solid support (e.g. silica, polymeric particles, etc.) as homogeneously as possible through a suitable reaction. It is actually an art of surface modifications to obtain stable functional materials. The process may involve attachments based on chemical or physical interactions between ligand and support material; however, due to the poor stability of the obtained materials, the immobilization processes based on physical interactions are not preferable. For this reason, this kind of so-called immobilization processes will not be considered in the present study. The immobilization process incorporates inherent advantages (and perhaps disadvantages) of a support and a molecule (or macromolecule, i.e. ligand) through a carefully designed reaction. Therefore, immobilization is, usually, a mutually-beneficial process for ligand and support, because the obtained material bears the mechanical (and sometimes chemical) stability of the support and the functionality (i.e. interaction capability) of the ligand. It is a widely employed process in different fields to obtain stable and functional materials suitable for particular application. From the perspectives of separation science, the goal of an immobilization process can be summarized as follows:

(i) Obtaining a material which is, at least, stable under the studied conditions (i.e. good chemical and mechanical stability).
(ii) Obtaining a material which is of use (i.e. high capacity and selectivity, reversible interaction with species, interaction with species through explainable (understandable) manners, a desirable morphology, high efficiency, etc.).

In general, it is nearly impossible to obtain a material which bears all the desirable properties. However, by a carefully designed immobilization process, the desired aspects can prevail on the obtained material. Hence, overall success of an immobilization process is closely related with the following:

(i) The chemistry of support material and ligand,
(ii) The spacer arm used, and
(iii) The method of immobilization.

Analogically, “brain” functions on a “body”. In other words, both ligand to be immobilized and support material have almost equal importance in immobilization and separation processes. However, sometimes, the role of support material in immobilization and separation processes is, unfortunately, ignored; whereas the chemistry and the morphology of the support is crucial for efficiently performing both processes.

Silica which carry at least half of the whole “burden” of chromatography on its “shoulders”, probably by far the most widely used support material in separation science. Some of its desirable properties, such as high mechanical stability, controllable particle size and shape, adaptability to further functionalization, easy separation from suspensions, and etc., have made silica an unrivaled support, especially, in chromatography. Moreover, silica does not swells or shrink in water and organic solvents and thus it offers a good environment as a support. Despite the mentioned desirable properties, poor chemical (hydrolytic) stability of silica is considered as an important problem that should be taken into account when working at highly acidic (pH <3) and alkaline (pH >8) conditions [23, 24]. In other words, when it comes into contact with highly acidic and basic aqueous solutions, silica and silica-derived materials can hydrolyze and thus the ligand immobilized on the silica is loosen. This property restricts the use of silica in separation processes where highly acidic and basic aqueous solutions are sometimes needed.

Polymeric materials are very popular in immobilization and they are being used in different separation processes like chromatography and membrane separation. Polymeric supports usually exhibit higher chemical stability (i.e. hydrolytic stability) compared to silica while their mechanical stability may be poorer. Anyway, the interest on polymeric supports is drastically increasing.

Another group of support materials used in calixarene immobilization is magnetic nanoparticles. In the past decade, separation processes based on an external magnetic field became a well-recognized concept. Recently, there has been a tremendous increment in the number of studies dealing with the immobilization of calixarenes to magnetic nanoparticles. Superparamagnetic iron oxide nanoparticles are by far the most widely used magnetic nanoparticles as support material. This group of supports can easily be prepared by co-precipitation of Fe(II) and Fe(III) and subsequent formation of Fe_3O_4 (magnetite) nanoparticles. Before calixarene immobilization, the surface of Fe_3O_4 is usually activated through a reaction with silylating agent (e.g. 3-aminopropytriethoxysilane).

In practice, two manners are followed before immobilization of calixarene to a solid support:

(i) The surface of the support is activated through a suitable reaction and in this way its surface is turned into a more attractive and/or reactive form for calixarene.

(ii) The ligand (calixarene) is reacted with a chemical species and is turned into an active form which can easily react with the support.

Depending on the chemistry of support and calixarene, both methodologies can be followed. An example of the second strategy has been applied on some calix-crowns by preparing their triethoxysilane derivatives before immobilization to silica. Triethoxysilane derivatives have been prepared in toluene by reacting calix-crowns with triethoxysilane in presence of catalytic amount of H_2PtCl_6 [25]. In another example, calix[6]arene-*p*-sulfonate was immobilized to aminopropyl silica after preparing the bromobutoxy derivative of the calixarene through its reaction with 1,4-dibromobutane [26]. Considering probable secondary reactions of silylating agent with other functionalities may be present on the calixarene, and difficulties may be encountered to separate the product [27], the first strategy (surface-activation of the support) seems to be more profitable.

As a rule of thumb, in an immobilization process, the chemistries of the ligand and the support must fit to each other; in other words, suitable functionalities should be present on the calixarene and support. For this purpose, a process called *surface-activation* is usually performed before immobilization. Through this process, the surface of the solid support is decorated with electron-donor or electron-acceptor groups and thus turned into a more attractive form for calixarene.

Various methodologies have been used in immobilization of calixarenes, such as amide-bond formation, epoxide-activation, nucleophilic substitution reactions, diazonium method, click chemistry, and etc (Fig. 1). These strategies are sometimes named according to the underlying chemical reaction, the spacer arm used and the type of bond formed. In most of the proposed immobilization methodologies, a spacer arm is used to improve the immobilization yield. A spacer arm (i.e. linker, coupling agent) is a molecular linker that attaches the ligand under consideration (e.g. calixarene) to support material (e.g. silica). Without a spacer arm, sometimes, the immobilization yield can be significantly low, due to steric effects which make the ligand and the support unable to find a suitable position to interact efficiently over the functional groups. By using a suitable spacer arm, overall efficiency of the immobilization process can be improved substantially.

Amide-bond formation method

The principle of this method is based on the formation of an amide bond between calixarene and support. The process can be performed in aqueous or anhydrous medium, depending on the physicochemical properties of calixarene and support material under consideration. However, in case of calixarenes, this process has been almost completely performed in anhydrous media.

In a typical procedure, the surface of the support is usually activated by using aminopropyltriethoxysilane (APTES). For example, amine-activation of silica can be performed according to the procedure described in the literature [28]. A very similar procedure have been applied in surface activation of magnetite nanoparticles (MNP) with APTES before immobilization of calix[4]arene [29]. In the mentioned study, calixarene has been immobilized to aminated-MNP over its ester groups, resulting in formation of an amide-bond between calixarene and the support (Fig. 2). A similar concept has been applied in immobilization of L-alanine methylester derivative of calix[4]arene

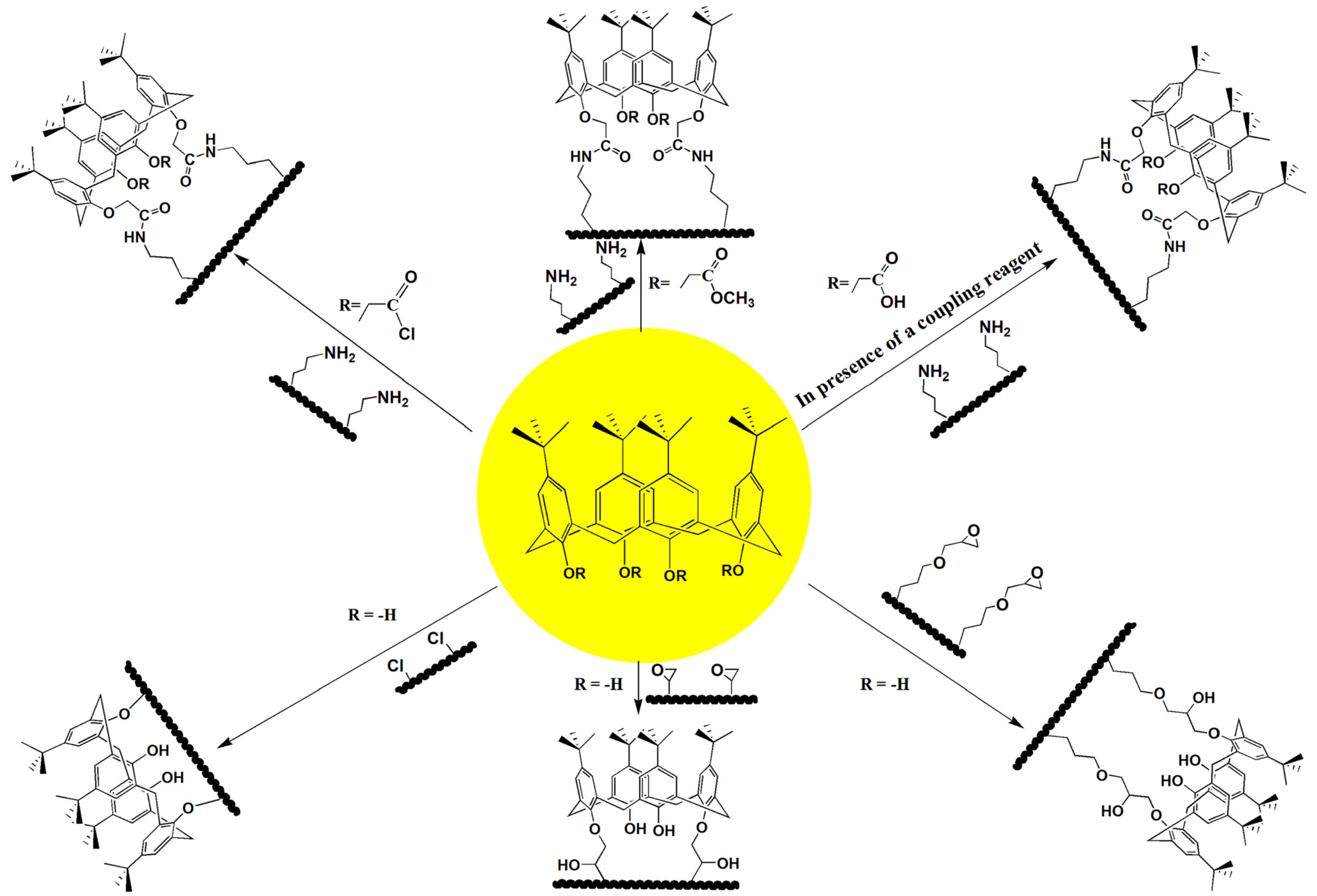

Fig. 1 The concept of some popular methods of calixarene immobilization

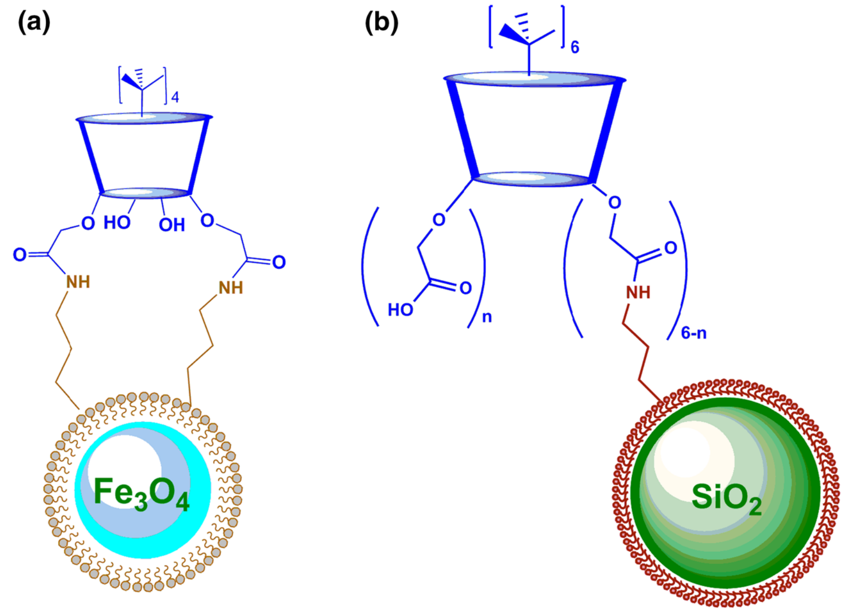

Fig. 2 Some materials obtained through amide-bond formation method **a** immobilization of *p-tert*-butyl-calix[4]arene methyl ester to aminopropylsilane activated MNP [29], **b** immobilization of *p-tert*-butyl-calix[6]arene to 3-aminoproyl silica in presence of a carbodiimide coupling reagent [35]

to aminopropyl silica [30], and immobilization of semicarbazone derivative of calix[4]arene to aminopropylsilane-activated MNP [31] through reaction of ester and amine groups. Like ester groups, acid chloride derivatives of calixarenes are good precursors for immobilization of calixarenes through amide-bond formation mechanism. In the study of Gezici et al. [32], monoacyl chloride derivative of a calix[4]arene with nitrile groups was prepared through a reaction of the monocarboxylic acid derivative of the calix[4]arene with oxalyl dichloride in tetrahydrofuran. Afterwards, calix[4]arene was immobilized to 3-aminopropyl silica through amide-bond formation mechanism. Immobilization of diacyl chloride derivative of calix[4]arene to 3-aminopropyltriethoxysilane activated silica was performed in a very similar procedure [33]. The studies of Xiao et al. [27, 34] are examples of this concept where 1,3-substituted acid chloride derivative of a *p-tert*-butyl calix[4]arene is reacted with γ-(ethylenediamino)-propyltriethoxylsilane to form triethoxysilane derivative. Since acid chlorides are very sensitive to moisture, special care is needed during this kind of reactions, and for this reason the given steps are performed in dry solvents (e.g. toluene, dichloromethane) under dry N_2. Note that a weak Lewis base like triethylamine in the reaction medium takes role as an "HCl scavenger", because during the immobilization reaction HCl is produced and this should be removed from the reaction medium or inactivated.

An example of calixarene immobilization over amide-bond formation in presence of a coupling reagent was reported by Tabakci [35]. In the reported study a hexacarboxylate derivative of *p-tert*-butyl-calix[6]arene was immobilized to 3-aminopropyl silica in presence of N,N'-diisopropyl carbodiimide (DIC) in dichloromethane (Fig. 2).

Epoxide-activation method

In this method, the surface of the support is activated by reacting it with epichlorohydrin which is a reactive organochlorine compound. For epichlorohydrin activation of silica, very useful receipts are available in the literature [36]. The immobilization of calixarene to epoxide-activated support can be processed in aqueous or anhydrous media depending on the chemistry of calixarene and solid support, using base- or acid-catalyzed reaction conditions. Calixarene skeleton can easily be immobilized to a surface containing epoxide group, owing to good reactivity of epoxide group. In this method, the main problem would be the hydrolysis of epoxide groups bonded to the support in aqueous media. However, according to the findings of Santodonato et al. [37], half-life for the hydrolysis of epichlorohydrin in distilled water at pH 7 (at 20 °C) is 8 days [38]. Nevertheless, there is a risk of hydrolysis for epoxide groups in aqueous media especially at elevated temperatures and at acidic and basic conditions.

In calixarene immobilizations over epoxide groups, the support material or calixarene are usually activated by using some spacer arms which contain epoxide group rather than epichlorohydrin. In the study of Xu et al. [39], 3-Glycidyloxypropyl trimethoxysilane was used as a spacer arm to immobilize calixarene to silica. The procedure is based on the preparation of 3-Glycidyloxypropyl trimethoxysilane derivative of calixarene, and then interacting it with the silica in dry toluene. The same spacer arm has been used by some other researchers [40, 41], too, with some differences in the immobilization method followed so that epoxide-activated silica has been prepared (through reaction with 3-Glycidyloxypropyl trimethoxysilane) instead of preparing the trimethoxysilane derivative of calixarene first. The method is based on a typical silylation procedure that involves refluxing the acid-treated and purified silica with 3-Glycidyloxypropyl trimethoxysilane in anhydrous toluene for 16 h. Final step of the procedure is to wash the obtained product thoroughly with organic solvents [40]. There are similar concepts based on surface activation of silica with 3-Glycidyloxypropyl trimethoxysilane before calixarene immobilization [42]. In Fig. 3, an example of calix-crown immobilization to 3-Glycidyloxypropyl trimethoxysilane activated-silica is shown [41].

3-Glycidyloxypropyl trimethoxysilane activation process has been successfully applied to activate the surface of MNP, too. By using tetraethyl orthosilicate in the reaction medium, a dendritic silica-MNP composite material has been obtained [43]. A material obtained in this way was used as a support for immobilization of *N*-methylglucamine derivative of calix[4]arene and 5,11,17,23-tetra-tert-butyl-25,27-di(benzhydrazidylmethoxy)-26,28-dihydroxycalix[4]arene [44, 45].

Immobilization of calixarenes over epoxide-containing polymers is another attracting methodology; because the epoxide groups are already present on the polymeric support and thus it is not necessary to perform a surface activation process. The concept has been applied in immobilization of *N*-methylglucamine derivative of calix[4]arene to poly[(phenyl glycidyl ether)-co-formaldehyde] resin (Fig. 3) [46].

Nucleophilic substitution reactions

Nucleophilic substitution reactions have been widely utilized in calixarene immobilization. In this method, a releasing group (or anion) on the support is replaced by a good ligand, resulting in formation of a covalent bond between the support and ligand. In general, thiol, amine, phenolic hydroxyl (and etc.) are good ligands which can replace a weak Lewis base (e.g. Cl^-, Br^-) on the support. For example, bromobutoxy derivative of calix[6]arene-*p*-sulfonate was successfully immobilized to aminopropyl silica on the basis of substitution reactions [26].

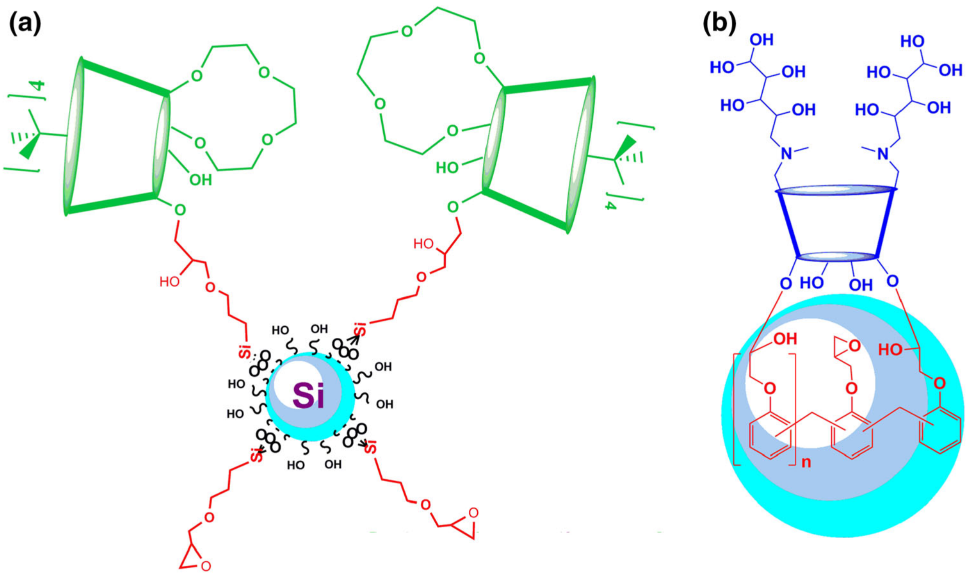

Fig. 3 Some materials obtained through epoxide method **a** immobilization of a calix-crown to 3-Glycidyloxypropyl trimethoxysilane-activated silica [41], **b** immobilization of *N*-methylglucamine derivative of calix[4]arene to a polymeric support containing epoxide groups [46]

Another example for immobilization of calixarenes to silica through nucleophilic substitution mechanism is the attachment of *p*-*tert*-butyl-calix[8]arene to chloropropyltriethoxysilane-activated silica. The immobilization proceeds via the attack of deprotonated phenolic –OH groups of calixarene to alkyl carbon and thus substituting chloride [47].

Immobilization of calixarenes to polymeric supports is promising and beneficial to obtain materials having good hydrolytic stability. Merrifield resin, which is a co-polymer of styrene and chloromethylstyrene, is one of the most widely studied polymeric support in calixarene immobilization. In the past, the concept was employed for immobilization of various types of calixarenes [48 and references therein]. This polymeric support is still very popular in calixarene immobilization due to the stability of the materials obtained after immobilization. For example, in the study of Bhatti et al. [49], calix[4]arene was immobilized to Merrifield resin. The resin contains Cl atom on the benzylic position which is very suitable for substitution reactions. A calixarene with piperidine groups was immobilized to Merrifield resin over the formation of an ether bond between the resin and calixarene [50]. A very similar concept was applied to prepare *p*-tetraaminocalix[4]arene- and *p*-tetrathioureacalix[4]arene-resins. Both resins were prepared by (i) immobilization of *p*-tetranitrocalix[4]arene to Merrifield resin and afterwards (ii) modification of the bonded calixarenes through reactions of nitro groups [51].

Other methods of immobilization

In a method proposed by de Gaetano et al. [52], a calixarene derivative having *p*-aminoethyl-phenoxypropyl and 6-methylene-[6′-methyl-2,2′-bipyridine]yl groups was immobilized to Wang benzaldehyde resin over an imine-bond formation mechanism (Fig. 4).

Immobilization of monopropargyl thiacalixarene via click-chemistry has been successfully applied on a chitosan azide-coated MNP. The coating was found to be uniform and the particles being spherical [53].

Immobilization of calix[4]arene to a diazonium-modified XAD-4 resin was reported by Qureshi et al. [54]. The proposed procedure is based on electrophilic attack of diazonium groups on the surface of the modified XAD-4 to aromatic units of calixarene (preferably to para position) and thus a C-N bond is formed between calixarene and the support.

A very interesting support material used in calixarene immobilization is magnetoferritin which is a naturally-occurring iron storage protein called ferritin. 25,27-Bis[(3-carboxypropyl)-oxy]calix[4]arene-crown-6 was immobilized to magnetoferritin over its acyl fluoride derivative (Fig. 4) [55]. In the study, acyl fluoride derivative of the calixarene preferred due to its much lower hydrolysis compared to other acyl halides.

Finally, direct immobilization of calixarene derivatives to silicon tetrachloride ($SiCl_4$)-activated silica has also been reported. In the proposed method, –OH groups on the surface of silica is turned into active $–OSiCl_3$ groups, and calixarene is attached to the surface over the nucleophilic attack of lower-rim phenolic –OH groups of calixarene [56]. As can be seen, in this methodology no spacer arm was used.

The following can be drawn as a conclusion of this section:

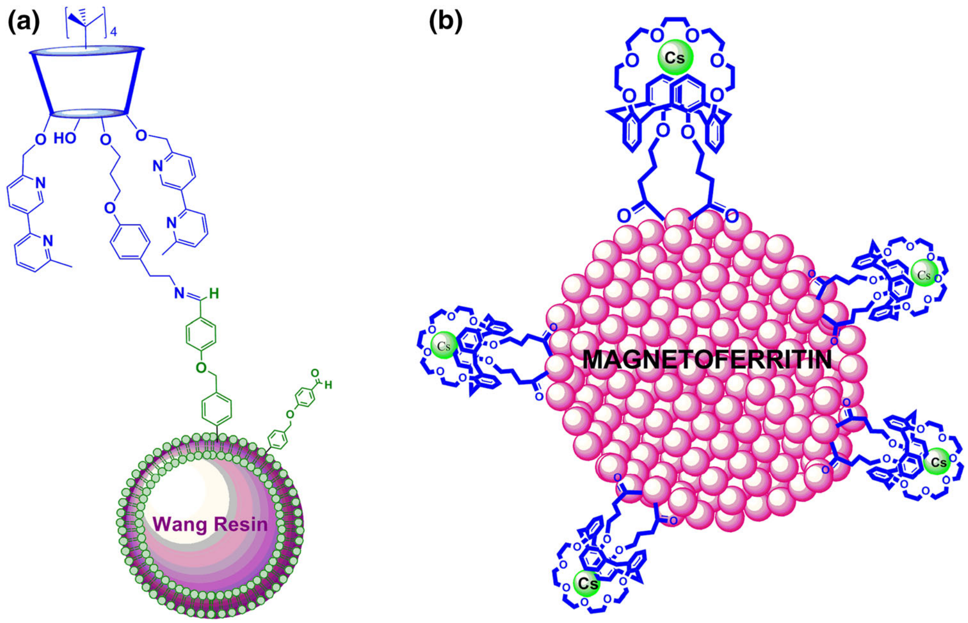

Fig. 4 Immobilization of calixarenes to two different supports **a** immobilization of a calix[4]arene derivative with *p*-aminoethyl-phenoxypropyl and 6-methylene-[6′-methyl-2,2′-bipyridine]yl groups to Wang resin over imine-bond formation mechanism [52], **b** immobilization of an acyl fluoride derivative of calixarene to magnetoferritin [55]

(i) Despite the fact that silica-based calixarene stationary phases exhibit good mechanical stability, they suffer from their poor hydrolytic stability. Hence, for the separation processes to be performed at pH values below 3 and above 8, polymeric supports can be preferred to silica as well as to materials activated by silylation processes.

(ii) The immobilization can be performed on the basis of formation of amide, ether, thioether, amine, imine, and etc. bonds between calixarene and support. The strategy to be followed in immobilization is defined according to the chemistries of calixarene and support.

(iii) Different types of support materials, such as silica-based, polymeric, MNP, have been used in calixarene immobilization.

(iv) In calixarene immobilization, particle-based support materials are more popular than monolithic materials. This interesting field (calixarene immobilization to monolithic supports) is missing in the literature while it is straightforward to obtain calixarene-immobilized materials that can be used as stationary phase in separation of high-molecular weight species (e.g. proteins).

(v) The presence of spacer arm-activated support materials with various functional groups in the market, is a big facility which enables performing immobilization of the ligand to the support directly. However, it is always not possible to find a suitable surface-activated support which is ready for the ligand immobilization. For this reason, most of the surface activation and ligand modification processes, which are generally time-consuming and labor-intensive, are done by the researcher.

(vi) The length and the chemistry of the spacer arm is one of the most important factors influencing the immobilization yield and the performance of a stationary phase in separation processes [57]. Actually, there is no rule of thumbs to select the best spacer arm, and therefore the role of the mentioned aspects can be best evaluated experimentally.

Calixarene-based sorbents and HPLC stationary phases

Separation can be evaluated as an “eternal struggle” of human-being against entropic forces. Due to the entropic driving-forces, a mixture is usually a more favorable environment for the components in a mixture. This must be the reason why mixtures exist in the environment much more than pure substances. However, in practice, the components in a mixture are usually separated from each other before a specific application, and this can be done by simple or very sophisticated separation processes. Separation processes are being widely employed in diverse applications ranging from wastewater treatment to purification of drugs. The cost associated with these processes sometimes becomes very high as in the case of biopharmaceuticals [24]. For this reason, separation scientists strive for developing efficient separation processes and/or improving the performance of the present ones.

Sorption and chromatography are the two most widely used methods of separation, and both of them have very close relation with each other. In both processes, mass-transport phenomena takes place between the two immiscible phases called *mobile phase* (or bulk solution) and *stationary phase* (or solid phase, sorbent). The stationary phase or sorbent used in chromatography or sorption are the key factors defining the efficiency of these processes. Hence, there is a big demand for efficient solid/stationary phases. Calixarene-based materials have been widely used as solid/stationary phase in chromatography and sorption of a wide range of chemical species. A great part of the studies in this context deal with mass-transport at liquid–solid interfaces. Therefore, in this section, some special applications of calixarene-immobilized materials as sorbent and stationary phase in sorption and HPLC are introduced.

Sorption

Sorption is a fundamental field which deals with mass-transfer phenomena at gas–solid and liquid–solid interfaces. This interesting field is applied in many chemical processes and industrial applications to separate chemical species especially from aqueous media [58]. In practice, sorption process can be conducted in *batch* and *column* modes. The first involves equilibration of the sorbent with bulk solution by mixing the suspension. The column mode is based on a process of bringing into contact the sorbent fixed in a column with fresh solution containing analyte by pumping the solution through the column (or by means of gravity). Removal and recovery of various types of chemical species by calixarene-immobilized sorbents have been extensively studied, as can be seen below. The performance of the sorbents obtained by immobilization of calixarenes to different support materials (such as silica, synthetic polymers, MNP) has been studied.

Some calixarene-silica materials prepared by immobilization of different calix[4-6] arene derivatives and they were used as sorbent for removal of *n*-butanol from dilute aqueous solutions [56]. As reported, the adsorption became more favorable with increasing the number of hydrophobic groups on the upper-rim of calixarene derivative. Therefore, butanol adsorption was mainly attributed to van der Waals interactions with contributions of CH-π and OH-π interactions. Except for a thiacalixarene derivative immobilized to silica, adsorption of *n*-butanol was reported to be reversible, and desorption was successfully performed at around 150 °C. This temperature was below the decomposition temperature limit (<300 °C) of the studied calixarenes, and thus the obtained materials were proposed as reversible sorbents for butanol removal [56].

The sorbents obtained by immobilization of calixarenes to MNP have recently become a springboard for application of calixarenes in sorption process. Separation of sorbent particles from suspensions by using an external magnet eliminates time-consuming filtration steps. Hence, separations based on MNP are straightforward [59].

Calix[4]arene-bonded MNP were used as sorbent for removal of dichromate anions from aqueous solutions. The material was found to be efficient in the pH range 2.5–4.5 [29]. A material obtained by immobilization of *N*-methylglucamine derivative of calixarene to silica-MNP composite support was used as a sorbent for removal of dichromate and arsenate ions from aqueous solutions (Fig. 5). Removal efficiencies of 66 % (at pH 1.5) and 86 % (at pH 3.5) were obtained for dichromate and arsenate, respectively [44]. 5,11,17,23-Tetra-tert-butyl-25,27-di(benzhydrazidylmethoxy)-26,28-dihydroxycalix[4]arene-immobilized silica-MNP was used as a sorbent for removal and/or recovery of dichromate, arsenate and uranyl ions [45] (Fig. 5). Sorption of dichromate and arsenate ions was studied on sulfo- and fosfo-calixarenes-immobilized MNP [60] as well as *N*-methylglucamine derivative of calixarene immobilized to a polymeric support [46]. Removal of dichromate anion from aqueous solution was studied on a sorbent obtained by immobilization of semicarbazone derivative of calix[4]arene to MNP, and equilibrium binding data was modelled on the basis of the Langmuir and the Freundlich models [31]. Calixarene-immobilized MNP were found to be nice carriers for lipase encapsulation, and the obtained material was found to exhibiting good enantioselectivity compared to free enzyme [61]. In another application, a naturally-occurring support material called magnetoferritin was used as a sorbent for removal of radioactive cesium(I) ions from aqueous solutions [55].

The materials obtained by immobilization of calixarenes to polymeric materials have also been used as sorbent. Sorption of perchlorate was studied by using a mini-column packed with a calix[4]arene-Merrifield sorbent. The sorption was ascribed to the interaction between piperidine groups on the calixarene and perchlorate anion. Maximum sorption was obtained at pH 3.0 [49]. The same concept was used in sorption of dichromate [50]. In another application, a material obtained by immobilization of calixarene to a Wang benzaldehyde resin was used as a chelating material for Cu(I) and Zn(II) [52]. Heavy metal sorption to a thiacalixarene-immobilized chitosan-MNP composite material was studied, and the binding data was evaluated in terms of isotherm models [53]. Sorption of Eu(III) on a thiacalixarenes-immobilized Merrifield resin

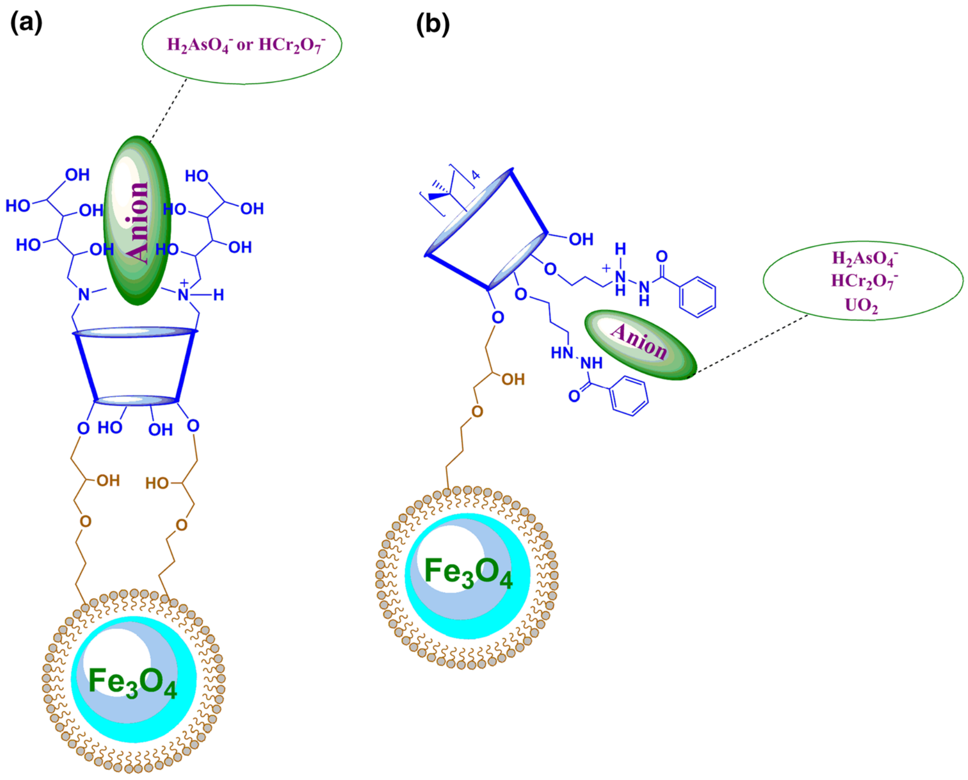

Fig. 5 Calixarene-MNP sorbents for removal of some anions **a** removal of arsenate and dichromate anions by *N*-methylglucamine derivative of calix[4]arene-bonded MNP [44], **b** removal of arsenate, dichromate and uranyl by 5,11,17,23-tetra-tert-butyl-25,27-di(benzhydrazidyl-methoxy)-26,28-dihydroxy-calix[4]arene-immobilized silica-MNP [45]

was studied, and Eu(III) ions were quantitatively extracted from aqueous solutions [62]. Fluoride sorption to *p*-tetraaminocalix[4]arene- and *p*-tetrathioureacalix[4]arene-immobilized Merrifield resins was studied and the equilibrium binding data was modeled on the basis of some common adsorption isotherm models. The mechanism of fluoride sorption was related with the hydrogen-bond formation, and the material was found to be reusable after several regeneration steps comprised of acid–base washing [51]. Another polymeric support used in calixarene immobilization is XAD-4 resin. The resin was modified into a diazonium form before immobilization of calix[4]-arene, and the obtained material was used as a sorbent in removal of As(III) [54].

The following can be listed as a conclusion of this section:

(i) Removal and/or recovery of different types of chemical species, such as *n*-butanol, arsenate, dichromate, perchlorate, fluoride, heavy metal ions, have been studied.
(ii) The majority of the sorption studies have been conducted in batch-mode.
(iii) A great part of the studies focused on the performance of the obtained sorbents with respect to removal efficiency and capacity; whereas the number of studies dealing with the isotherm modeling was found to be very few.

High performance liquid chromatography

HPLC, is, certainly, the most widely employed chromatographic technique, because of its efficiency and its flexibility to a wide variety of applications. Development of sub-2 µm stationary phase particles led evolution of HPLC systems into more efficient forms (e.g. Ultra Performance Liquid Chromatography, UPLC, or Ultra High Performance Liquid Chromatography, UHPLC). Despite the technological improvements in HPLC equipment, the efficiency of HPLC is, still, mostly related with the stationary phase used, and thus the stationary phase is deemed as a key factor in HPLC separations [32]. This is the reason why huge amount of stationary phases have been developed, and (probably) hundreds of them being under investigation.

Chromatography is one of the most sophisticated processes where calixarene-derived materials have been extensively (and successfully) used as stationary phase. The range of applications varies from gas chromatography [63, 64] to HPLC, and numerous valuable works have been performed during the past several decade. In this context, various immobilization processes have been extensively applied to prepare calixarene-derived stationary phases as discussed in previous sections.

Calix[6]arene-*p*-sulfonate-bonded silica was used as a stationary phase, and the retention behavior of some monosubstituted phenol regioisomers (i.e. cresol, methoxyphenol, nitrophenol, aminophenol and chlorophenol) and positional isomers of some aromatic compounds (i.e. nitroanilines, nitrotoluenes, bromo-nitrobenzenes and dichlorobenzenes) was investigated. Nitrophenol, aminophenol and methoxyphenol isomers, which have polar and hydrogen-bonding groups, were separated while the separation was not good in the case of other isomers having nonpolar groups. The effect of polar groups was attributed to the formation of host–guest inclusion complexes. The studied positional isomers were well separated on the stationary phase. The obtained chromatographic behaviors imply the role of the chemistry of the test compounds (e.g. their polarity, solubility in mobile phase, etc.) and that of the stationary phase [26]. 1,3-Alternate 25,27-dipropoxy-26,28-bis-[3-propyloxy]-calix[4]arene-bonded silica gel stationary phase exhibited good performance for separation of some positional isomers, and elution order of the substituted benzoic acids was found to be decreasing in order of ortho > metha > para. The retention mechanism was related with multiple interactions [65]. Chromatographic performance of a *p*-*tert*-butyl-calix[6]arene-silica stationary phase was studied by using some disubstituted benzenes, polycyclic aromatic hydrocarbons and nucleosides, and the studied stationary phase exhibited a typical reversed-phase behavior towards disubstituted benzenes. The separation selectivity was observed to be better for the compounds containing amino groups, and this was ascribed to the interactions between phenol units of calixarene and amine groups of the test compounds. The observed chromatographic behavior was related with inclusion, π–π and charge-transfer interactions (especially for nitroanilines) [39]. The performance of the same stationary phase in separation of sulfonamides and quinolones was also studied. Despite the fact that reversed-phase behavior of the stationary phase for the studied compounds was observed, the retention mechanism of sulfonamides was found to be different than that observed on C18 and a diamino-bonded stationary phase. The observed discrepancies were related with multiple interaction pathways (e.g. hydrophobic, polar, charge and inclusion complexation interaction) in the case of calixarene-silica stationary phase [34]. For polyaromatic hydrocarbons, reversed-phase behavior of *p*-*tert*-butyl-calix[4]arene-silica stationary phase was reported. In the case of nucleosides and nucleobases, the retention on this stationary phase was ascribed to electrostatic, π–π, hydrogen-bonding and partial inclusion interactions [27]. Very similar conclusions were reported by Huai et al. [33] for the retentive behavior of some polar and nonpolar aromatic compounds, basic aromatic compounds and polycyclic aromatic hydrocarbons (PAH) on *p*-*tert*-butyl-calix[4]arene silica stationary phase. Despite its lower carbon loading (compared to C18), base-line separation of phenanthrene and anthracene was achieved on the calixarene-silica stationary phase. In another study, chromatographic separation of some aromatic carboxylic acids on *p*-*tert*-butyl-calix[8]arene-silica stationary phase was studied by Li et al. [42], and the studied calixarene-silica stationary phase was found to be superior in terms of capacity and selectivity in comparison to C18. Some discrepancies observed on both stationary phases were related with different retention mechanisms of the solutes. The retention mechanism was attributed to a combination effect of multiple interactions such as hydrophobic, hydrogen bonding, π–π and inclusion interactions. In another study of the same group [66], retentive behaviors of nucleosides and nucleobases on the same stationary phase (*p*-*tert*-butyl-calix[8]arene-silica) were studied, in detail. According to the results, hydrophobic, hydrogen-bonding, and dipole–dipole were thought to be the main interactions defining the chromatographic behavior of the studied compounds. The same calix[8]arene-silica stationary phase has been used to study chromatographic behavior of some water soluble vitamins, and retention mechanism of the vitamins on the stationary phase was again attributed to multiple interactions [67]. The performance of a calix[4]arene-bonded silica stationary phase for separation of some water soluble vitamins was studied (Fig. 6). At high pH values, calix[4]arene immobilized stationary phase was found to behave totally different than that observed at lower pH values, and this behavior was related with ionization of phenolic –OH groups on the calixarene [68].

The separation of some steroids on calix[8]arene-silica stationary phase was studied, and the chromatographic behavior was compared with a cyclodextrine-bonded silica stationary phase. Hydrophobicity and π–π interaction of calixarene-silica stationary phase were found to be stronger when compared with cyclodextrine-silica. On the other hand, inclusion complexation ability of cyclodextrine-silica was found to be stronger than that of calixarene-silica [47].

Separation of alkali metal ions is another interesting field where functional calixarene-based stationary phases have been used. Calix-crown based stationary phases exhibited selectivity towards some alkali metal ions like Na^+, K^+ and Cs^+. The size of calix-crowns was found to influencing the selectivity of the stationary phase towards alkali metals; two studied calixcrown-6 derivatives exhibited selectivity towards cesium ion while calixcrown-5 was selective for potassium ion [25].

The stationary phase behavior of 12 different 1,3-alternate calix[4]arene-silica bonded stationary phases was

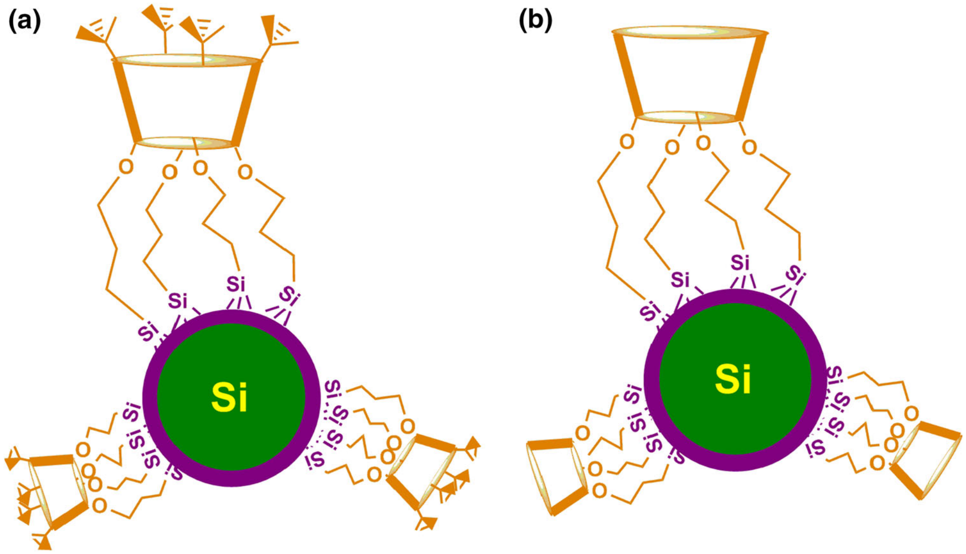

Fig. 6 Calix[4]arene-bonded silica stationary phases for separation of some water soluble vitamins [69]

investigated [69]. Functional groups on the 1,3-alternate positions range from alkyl chains to substituted aromatic groups. The stationary phase behavior of the studied materials has been evaluated in terms of surface coverage, hydrophobic selectivity, and shape selectivity, hydrogen bonding capacity, ion-exchange capacity and aromatic selectivity. There was a good relation between the chemistry of functional groups on the mentioned positions of bonded-calixarene and the retentive behavior. With increasing electron deficiency in the phenyl rings as a consequence of the presence of electron-withdrawing groups like Cl, NO_2 and F, the aromatic selectivity parameters increased. As a general behavior, hydrophobic retention capacity of the studied stationary phases was found to be lower than that of C18 [70]. In another study of the same research group, retention behavior of some polyaromatic hydrocarbons was studied on some of the above mentioned 1,3-alternate calix[4]arene-silica bonded stationary phases. The results, again, emphasized the importance of the chemistry of the functionalities on the studied calixarene. However, it is difficult to relate the retention behavior of the studied analyte on the studied calixarene-bonded stationary phases with a unique interaction mechanism [70].

Bis and tetra L-alanine-methylester derivative of *tert*-butyl-calix[4]arene were used as stationary phase and their chromatographic performance was investigated using PAH, disubstituted benzene isomers, and mono-substituted benzenes as solute probes [30]. Both stationary phases were found to exhibiting weaker character in terms of hydrophobicity and hydrophobic selectivity; *tetra*-substituted derivative exhibiting higher hydrophobicity and hydrophobic selectivity compared to bis-substituted derivative for the studied compounds. Another interesting result was the observed better stereo-selectivity of the bis- and tetra-substituted calix[4]arene stationary phases compared to commercially available phenyl and C18 phases. Aniline, *N*-methyl aniline, and *N*,*N*-dimethyl aniline were base-line separated on the same order using the two studied calixarene-based stationary phases. The retention behavior was related with π–π interactions between anilines and the stationary phase. One of the most important finding was the opposite elution orders observed for some phenols (i.e. phenol, 1,3-dihydroxybenzene, and 1,3,5-trihydroxybenzene) on bis- and tetra-substituted calixarene stationary phase. The results are clearly indicating the role of lower-rim –OH groups (or lower-rim substitution) of calixarenes on stationary phase behavior of calixarene-based materials [30]. Therefore, hydrogen-bonding and hydrophobic interactions are the two important interaction types which define the retention behavior of chemical species on calixarene-derived stationary phases. For more detailed information about stationary phase behavior of calixarene-derived materials and host–guest interactions in chromatography, it is strongly suggested to refer valuable studies of Sokoließ et al. [12, 71].

The presence of *p*-*tert*-butyl group substituent was found to be an important parameter influencing phenyl and methylene selectivity of the stationary phase [72]. Likewise, a cyclodextrine-functionality on the calixarene was found to have role in retention behavior. Stationary phase behavior of a calixarene-derived stationary phase with cyclodextrine functionality on the calixarene, was studied [73]. Hydrophobic interactions were thought to be the predominant factor defining the retentive behavior of the analytes (some antihypertensive drugs) on the studied calixarene stationary phase and C18. However, different interaction mechanisms, such as inclusion, hydrogen-bond formation, π–π interactions, steric selectivity and ionic selectivity, were also thought to participate in the case of calixarene-derived stationary phase; whereas hydrophobicity was thought to be the main effect in the case of C18. Most of the proposed interaction mechanisms are in consistence with those proposed for *p-tert*-butyl-calix[4]-arene-1,2-crown-4 bonded silica towards some polycyclic aromatic hydrocarbons, phenols, aromatic amines, benzoic acid and its derivatives being the test compounds [41]. Two factors were found to be important when studying with calixarene- and crown ether-derived stationary phases: (i) Competition between buffer cations and basic compounds to enter the cavity of calixarene, and (ii) ion-pair formation between analyte and counter anion [74, 75]. In another application, the performance of two stationary phases (i.e. *p-tert*-butyl-calix[6]arene-bonded silica and *p-tert*-butyl-calix[6]-1,4-benzocrown-4-bonded silica stationary phases) was studied and the separation of some neutral, acidic and basic compounds was investigated. Both stationary phases were found to exhibiting reversed-phase behavior while the calix-crown stationary phase exhibited different selectivity towards some aromatic compounds. Hence, a crown substituent was found to have effect on retention behavior. The retention mechanism was related with corporation of hydrophobic and hydrogen-bonding interactions as well as conformational and synergistic effects of cavities and ether-bridges [76].

Though it is sometimes omitted, an end-capping step, which deactivates residual silanol groups (or any other reactive groups) on the silica, is of crucial to improve the stability of the stationary phase and reproducibility of the results to be obtained on the stationary phase. Because, residual silanol groups on the surface may lead secondary interactions between analyte and stationary phase, and this effect is usually understood through observed peak-tailings which are undesirable. A typical end-capping process is done by reacting a calixarene-bonded stationary phase with a low-molecular weight silylating agent like trimethylchlorosilane. As reported in Ref. [33], no peak tailing was observed after performing an end-capping step on a calixarene-silica stationary phase.

As a conclusion of this section, the following statements can be drawn:

(i) The usability of different calixarene-derivatives with various core size (i.e. n = 4, 5, 6 and 8) as HPLC stationary phase has been extensively studied [14, 27, 39, 42, 77, 78].

(ii) The test compounds ranges from aromatic compounds to nucleosides, nucleobases, PAH, fullerenes, drugs, alkali metal ions, vitamins, steroids, etc.

(iii) As a general character, the retention mechanism on calixarene-based stationary phases cannot be rigorously explained by one-type interactions; instead it is more reasonable to relate the overall retention behaviors with combination effect of multiple interactions such as inclusion, hydrogen-bond formation, π–π interactions, steric selectivity, ionic selectivity, and etc. For example, an analyte possessing both hydrophobic and hydrophilic groups can interact with a *p-tert*-butyl-calix[*n*]arene immobilized silica through various interactions over (a) aromatic moieties as well as *p-tert*-butyl groups of the calixarene via hydrophobic, π–π and inclusion interactions, and (b) etheric oxygens of the calixarene via polar–polar, hydrogen-bonding interactions [12].

(iv) Cone size of the immobilized calixarene influences the stability of the inclusion complexes formed. For example, the stability for toluene inclusion complexation was found to be higher in the case of *p-tert*-butyl-calix[4]arene when compared with those observed on larger calixarenes [12].

(v) The upper-rim substituent can influence interactions between analyte and stationary phase [73]. For example, presence of *p-tert*-butyl group prevents separation of ethylbenzene and naphthalene. This group was thought to have a stabilizing effect for inclusion of some species [12].

(vi) The type of organic modifier in the mobile phase may influence retention interactions especially those based on π–π. For example, acetonitrile diminishes the degree of π–π interactions, and for this reason, methanol is preferred [69], especially if an extra-selectivity is needed.

(vii) In application of calixarene-immobilized HPLC stationary phases, silica (and silica derivatives) is by far the most widely used support material. Therefore, there is a lack of knowledge about the performance of calixarene-immobilized polymeric HPLC stationary phases (both particle-packed columns and monolithic columns) in the literature.

Other types of calixarene-derived materials and some interesting applications

In the previous sections, the most common methodologies used to immobilize calixarenes to solid supports and their applications in sorption and HPLC have been drawn. Both aspects refer to wide range of applications and thus it is actually difficult to discuss all of them in the present review. In this section, some other interesting applications related with calixarene-based materials (i.e. calixarene-based polymers and co-polymers, nanoporous colloidal films, calixarene-nanofiber composite material, etc.) and their use in diverse applications are given.

A calix[4]arene-based copolymer obtained through Mannich reaction, and subsequent co-polymerization of the obtained material in presence of dibromoxylene was used as a sorbent in sorption of azodyes and aromatic amines [79].

Nanoporous colloidal films constitute another field which benefits from calixarene immobilization. Mollard et al. [28] studied the transport of two redox-active species, ferrocene dimethanol and iron tris(bipyridyl) hexafluorophosphate, through the films prepared by immobilization of thiacalix[4]arene to colloidal films assembled from 200 nm silica sphere (Fig. 7). In the literature, there are some other interesting studies focused on thiacalixarene-derived materials [80, 81].

Another very interesting application of calixarene-based materials has been reported by Adhikari et al. [82]. The researchers report a material which has been synthesized by direct radicalic polymerization of an upper-rim vinyl-containing calixarene with carboxylic acid groups (on the lower-rim). Despite its low porosity, the polymeric resin exhibited selectivity towards lead ion. In another study, Adhikari et al. [83] report the preparation of methylene-cross-linked calix[4]arene and calix[6]arene resins, and their application in sorption of indium.

A very interesting field where a composite material prepared by physical immobilization of calixarenes to nanofibers has been recently reported by Bayrakci et al. [84]. In the study, calixarene-embedded nanofibers were prepared by electrospinning process. The obtained material was used in removal of some toxic heavy metals. The study is actually promising and the idea drawn in this pioneering study will probably be employed in various range of applications.

Host–guest sensing technology is another important field which benefits from immobilization of calixarenes to support materials. For this important field, readers are advised to refer valuable works already present in the literature ([85] and references therein).

Interaction mechanisms

Calixarene-immobilized materials have been used as sorbent or stationary phase for separation of a broad range of chemical species such as inorganic ions (i.e. alkali metal ions, heavy metal ions, dichromate, arsenate, uranyl, perchlorate, fluoride, etc.), organic species (i.e. aromatic compounds and their isomers, PAH, *n*-butanol, sulfonamides and quinolones, thioxhantene, etc.) and some biologically-important species (i.e. nucleosides, nucleobases, water-soluble vitamins, steroids, antihypertensive drugs, etc.). Despite the presence of a very rich literature, it is still controversial to explain interaction types of calixarene-immobilized materials with chemical species, comprehensively. This is mainly arisen from multiple effects related with the molecular structure of calixarenes. In this section, the interaction types of calixarene-based sorbents and

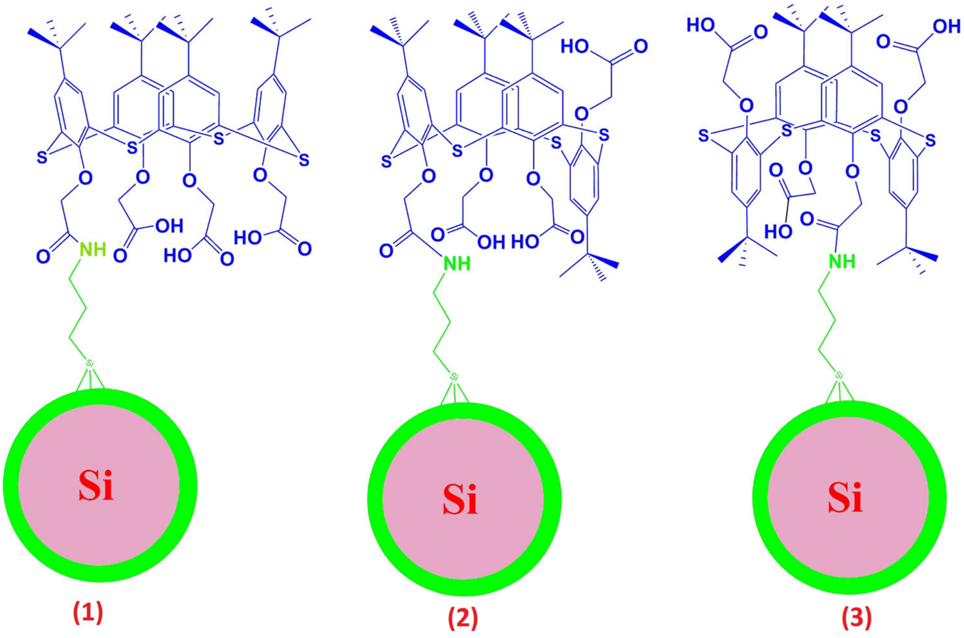

Fig. 7 Nanoporous colloidal films prepared by immobilization of thiacalix[4]arene derivatives to aminopropyl silica [28]

stationary phases with chemical species is discussed in light of the literature knowledge.

The molecular structure of calixarenes lends them interacting with different classes of chemical- and/or biologically-important species through diverse interaction types. Interaction of calixarenes with species is generally explained by host–guest interactions which are mainly attributed to the formation of inclusion complexes. Despite the fact that inclusion complexes of calixarenes are sometimes solely ascribed to the hydrophobic cavity of calixarenes, it is well known that the functional groups at the rims contribute to overall chromatographic behavior when using calixarene-based stationary phases. Hence, even small changes in the molecular structure of calixarenes may influence the capacity and selectivity of the solid/stationary phases, significantly. For example, carboxylic acid groups on *p-tert*-butyl-calix[*n*]arenes ($n = 6$, 8) were found to have major role in hydrogen bonding and ionic interactions between the calixarene-immobilized material and aromatic amines [86, 87]. Together with some common experimental parameters like temperature, composition of the mobile phase, etc., ring-size, functional groups at the rims and spacer arm used to fix calixarenes to the support are very important parameters which directly influence the interaction types of calixarene-based materials. Therefore, depending on the chemistry of analyte, calixarene-immobilized stationary phases can interact with species through various interactions like π–π, π-electron transfer, dipole–dipole, hydrogen-bond formation, ionic interactions, etc. In addition to the above mentioned interaction types, calixarenes which contain chiral groups or molecules can lead designing stationary phases which exhibit extreme selectivity. Hence, calixarene-immobilized stationary phases offer a broad range of interaction spectrum which can lead further selectivity [91].

As mentioned before, the size of the calixarene cavity is another important parameter influencing retentive behavior. For example, the cavity of *p-tert*-butyl-calix[4]arene is big enough to include Na^+, UO_2^+ and Ag^+ ions while it may not be suitable for some nucleosides and nucleobases [27]. In the case of ionic dyes, the electrostatic interactions were found to be prevailing in removal of some dyes having sulfonic acid groups by using a calix[4]arene-based sorbent which bears amine groups [80]. Another interesting conclusion is the role of hydrogen-bonding in sorption of fluoride [51], oxoanions (e.g. dichromate and arsenate) [46, 88] to calixarene-based sorbents. In this kind of interactions, the presence of functional groups capable of forming hydrogen-bonds (such as amine, amide and protonated imine as well as nitrile groups) in the calixarene structure are deemed important [50, 89]. Thus, binding mechanism of ionic species to calixarene-based sorbents/stationary phases can follow different pathways depending on the chemistry of analyte and the calixarene immobilized to the support.

Notestein et al. [89] reported important findings about the interactions of calixarene-immobilized stationary phases with aromatic compounds. As reported by the researchers, calixarenes bind small aromatic compounds over 1:1 stoichiometry, and calixarene upper-rim composition was found to have role in binding. Moreover, considering interactions of small aromatics, the interior of calixarene cavity is a more preferred environment compared to the outside. The sorption from water to the hydrophobic cavity of calixarenes was understood to be enthalpy-driven, and the nature of sorption was mainly ascribed to van der Waals forces arising from hydrophobic calixarene cavity. The phenolic –OH groups were thought to contribute interaction of small aromatics with calixarenes. Another very interesting result was the presence of a competition between water molecules and aromatic species for interacting with the mentioned hydrophobic cavity. Accessibility of hydrophobic calixarene cavity to different types of sorbates, makes this class of supramolecules useful for separation processes to be performed in different solvents [90].

As a general behavior, the influence of hydrophobic interactions on retention decreases with increasing methanol concentration in the mobile phase. The methanol content in the mobile phase influences both selectivity and retention of some solutes when using calixarene-bonded stationary phase [91]. In another study, which reports the hydrophilic interaction liquid chromatography (HILIC) behavior of a calixarene-immobilized stationary phase, the influence of mobile phase on the stationary phase behavior has been emphasized [92]. The retention of some basic compounds exhibited a *U-shaped* curve which is an indicative of the presence of two different retention mechanisms (at relatively low acetonitrile concentrations: RPLC; at higher acetonitrile concentrations: HILIC) depending on the mobile phase composition. The observed major change in retention mechanism from RPLC to HILIC (both mechanism are orthogonal) implies a multimodal character of 1,3-alternate 25,27-bis-[cyanopropyloxy]-26,28-bis-[3-propyloxy]-calix[4]arene-silica stationary phase [92]. Hence, the type and concentration of the organic modifier in the mobile phase may have a significant effect on chromatographic behavior of the solutes on calixarene-based stationary phases.

As a matter of the fact, more comprehensive studies are needed to fully understand interaction phenomena on calixarene-immobilized materials. For a complex environment like calixarenes, this is, actually, not an easy task; however, the results reported in the literature are promising. The authors of this work are in the opinion that the composition of the mobile phase may have greater impact than what we imagine when working with the calixarene-immobilized materials.

Conclusions and recommendations

Owing to their functionality associated with conformational stability, calixarenes are evaluated as very suitable supramolecules for production of straightforward sorbents and stationary phases. Immobilization is one of the most widely used methods to obtain calixarene-based sorbents and stationary phases, and various methodologies based on covalent bond formation between the supports and calixarenes have been proposed in the literature. As it is drawn throughout the present work, silica (and/or silica derivatives) is by far the most widely used support material for calixarene immobilization. Calixarene-silica based materials were, usually, utilized as HPLC stationary phase. In the case of sorption process, greater emphasize has recently been given to MNP as support material. Together with the mentioned supports, immobilization of calixarenes to synthetic polymers was also studied. In the related sections, the hydrolysis of silica (and silanized supports) was emphasized as an important point which threats the stability of the sorbents and stationary phases.

Calixarene-immobilized materials have been used in sorption and HPLC of various types of chemical species ranging from metal ions to drugs. The mechanism of interaction between the obtained sorbents/stationary phases and chemical species was understood to be related with the chemistry of immobilized calixarene and the analytes. Depending on the mentioned aspects, the separation of analyte is usually attributed to a combination effect of diverse interactions such as inclusion complexation, π–π interactions, hydrogen-bonding, van der Waals, polar–polar and ionic interactions (and etc.); one (or some) of them being predominant in the system. In all cases, calixarene-immobilized materials are promising candidates for the development of new (and/or alternative) sorbents/stationary phases.

As a conclusion, calixarene immobilization to a support is deemed an important concept to develop efficient solid/stationary phases exhibiting good selectivity and capacity. The studies on the issue will probably continue in the future, and perhaps, future studies will focus on calixarene-based solid/stationary phases exhibiting multimodal character. Moreover, though it is still a dream, in development of *universal solid/stationary phases*, calixarenes (and resorcinarenes) may be good precursors owing to their interesting structure. Finally, immobilization of calixarenes is a promising concept in various fields (e.g. separation science, sensing technology, catalysis) to develop novel materials.

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