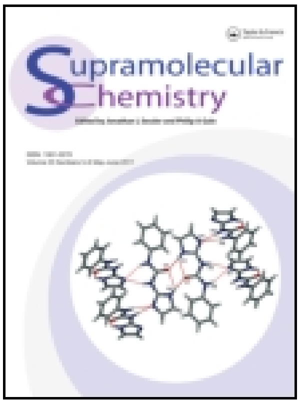

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# Competitive solvent extraction of alkaline earth metals by ionizable nano-baskets of calixarene

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The competitive solvent extraction of alkaline earth metals using different nano-baskets was investigated. The novelty of this work is to study the correlations between the isomer structure of calixarenes and their extraction properties. The objective was to quantify the effects of aryl groups in the ionisable pendant moieties, calixarene conformation, steric orientations (*cis*- and *trans*-) and relative positions (*ortho*- and *para*-) of pendant moieties upon the extraction efficiency, $pH_{1/2}$ and the selectivity of calix[4]arene complexes. Alkaline earth metals were extracted from aqueous solutions into chloroform by di-ionisable calix[4]arenes and were measured using ion chromatography. The results revealed that alternation of aryl group in the pendant moieties, changing their orientation from *cis*- to *trans*-analogues as well as from *ortho*- to *para*- analogues, showed no changes in the selectivity, the extraction efficiency and the $pH_{1/2}$ of calix[4]arene complexes. Changing the scaffold of calixarene's ring to the cone, 1,2-alternate and partial-cone conformers altered their complexation ability towards alkaline earth metals and their extraction efficiency.

**Keywords:** nano-basket; calix[4]arene; alkaline earth metal; solvent extraction

## 1. Introduction

Nano-baskets of calixarenes as a versatile class of macrocycles have been subjected to extensive research in the development of many extractants, transporters, stationary phases, electrode ionophores and optical and electrochemical sensors over the past four decades (*1–7*). In the nineteenth century, Baeyer synthesised them via the reaction of formaldehyde with *p*-substituted phenols in basic or acidic environment (*8*, *9*). However, the limited analytical methods and instruments at that time were unable to interpret the structure of the new synthesised products. In the 1940s, Zinke and Ziegler (*10*) discovered that the products possessed cyclic tetrameric structures. In 1975, Gutsche (*11*, *12*) introduced the currently accepted name of calixarene.

The small calixarenic cycles, those with a bowl-shaped conformation (*13*) and those with pendant proton-ionisable groups, such as carboxylic acid (*14*), phosphinoy (*15*), *N*-(X)-sulphonyl carboxamide (*16*) and hydroxyamic acid (*17*), have been utilised for solvent extraction of metal cations. Ionisable calixarenes are more efficient than non-ionisable analogues in metal cation separation owing to charge matching within the resulting complex in the organic phase. The metal cations are transferred to the organic phase due to the production of a neutral complex. Different complexing groups at the upper rim of calixarenes attract species with predefined selectivity, while the lower rim moieties are usually responsible for physical properties of calixarenes (*2*). Calixarene isoconformers including cone, 1,2-alternate, 1,3-alternate and partial-cone have been synthesised and investigated in other works (*18–21*).

In solvent extraction, two immiscible liquid phases are mixed with the calixarene as an extractant in the organic phase, and a stripping aqueous acidic solution is used in the back extraction. The metal cation extracted by the calixarene ligands is analysed quantitatively in the aqueous phase after back extraction (*22*). Different analytical methods such as atomic absorption, inductively coupled plasma spectroscopy, UV–vis and ion chromatography are routinely used to determine the metal cation concentrations after back extraction. The loading percentage is equal to the ratio of the extracted amount of metal cation over the initial macrocycle concentration in the organic phase.

In this paper, the competitive solvent extractions of alkaline earth metals from aqueous solutions into chloroform by di-ionisable calix[4]arene derivatives were studied. Figure 1 shows the structures of complexes, which were studied. In nine scaffolds, 34 calix[4]arene derivatives were used to assess the effect of variation of pendant groups and isoconformations (conformation, orientation and position) on the extraction efficiency, selectivity and $pH_{1/2}$ of complexes.

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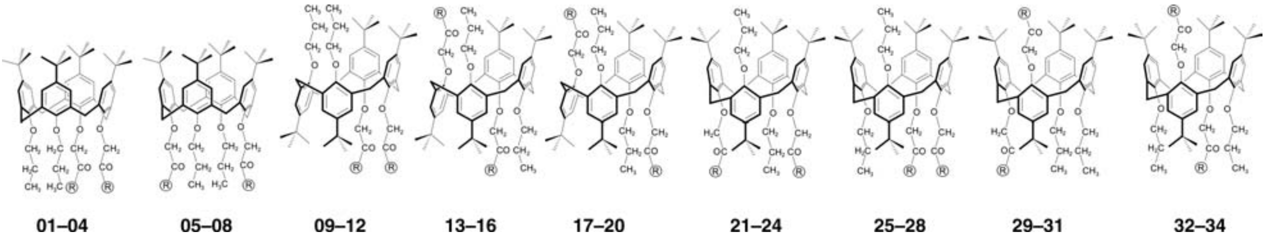

Figure 1. The hierarchical structures of complexes were investigated. R group was defined as —$NHSO_2$Phenyl; —$NHSO_2$($p$-$CH_3$Phenyl); —$NHSO_2$($p$-OHPhenyl) and —$NHSO_2$($p$-$NO_2$Phenyl).

## 2. The logic for choosing the side chains

There are two kinds of side chain in the calixarene skeleton which were studied including the ionisable sulphonyl carboxamide moieties and the ether moieties. The ionisable moieties not only participate in cooperative metal ion coordination, but also eliminate the need to transfer the anions from the aqueous phase into the organic phase by operating in a cation-exchange mode with the metal cation. In this work, two proton-ionisable function groups, *N*-(X)sulphonyl carboxamide, were incorporated into calix[4]arene scaffold. A special feature of such modification is that the acidity of the *N*-(X)sulphonyl carboxamide moiety is tunable by changing the X group from phenyl to nitrophenyl group due to different electron-withdrawing abilities of X group. A wide range of pH environments can be examined when these ionisable groups are incorporated into the calixarene skeleton. These extractants exhibit excellent extraction selectivity for alkali and alkaline earth metals.

The ether moieties contain oxygen atoms, which participate in cooperative cation coordination and regulate the solubility of calixarene platform or its distribution between the organic and the aqueous phases. The long alkyl chains in the ether moieties lead to increase in the solubility of calixarene towards organic phases, and the short chains shift the solubility to the aqueous phases. Here, a propyl ether moiety was selected to optimise the calixarene distribution between the two phases.

## 3. Experimental method

### *3.1 Standard solutions*

Beryllium chloride (99%), magnesium chloride hexahydrate (99%), calcium chloride dihydrate (98%), barium chloride dihydrate (99%) and strontium chloride hexahydrate (99%) were obtained to prepare the work solutions. Barium hydroxide octahydrate (98%), hydrochloric acid (1.0 N) and sulphuric acid (2.0 N) was obtained to adjust the pH of solutions. Chloroform was shaken with deionised water to remove the stabilising ethanol and was stored in the dark.

### *3.2 Calix[4]arene isoconformers*

All the experiments were carried out using four derivatives of di-ionisable *p-tert*-calix[4]arene di-[*N*-(phenyl)sulphonyl carboxamide], di-ionisable *p-tert*-calix[4]arene di-[*N*-(*para*-hydroxy phenyl)sulphonyl carboxamide], di-ionisable *p-tert*-calix[4]arene di-[*N*-(*para*-nitro phenyl)sulphonyl carboxamide] and di-ionisable *p-tert*-calix[4]arene di-[*N*-(*para*-methyl phenyl)sulphonyl carboxamide]. Two conformers for each four of di-ionisable cone derivatives (**01**–**04** and **05**–**08**), three conformers for each four of di-ionisable 1,2-alternate derivatives (**09**–**12**, **13**–**16** and **17**–**20**) and four conformers for each four of the partial cone (**21**–**24**, **25**–**28**, **29**–**31** and **32**–**34**) conformation were synthesised to extract alkaline earth metal cations. The cis/trans symbols refer to the direction of two di-ionisable moieties and the *ortho-/para-*depict the relative situation of two di-ionisable moieties. Calix[4]arenes **01**–**34** were prepared separately by organic chemistry research group. The proton-ionisable groups act as acidity tunable functions with functional group variation.

### *3.3 Sample preparation*

The alkaline earth metal cations were loaded into the aqueous solutions by adding stock solutions containing five alkaline metal cations, 20.0 mM barium chloride solution and 20.0 mM barium hydroxide solution. The blend solutions of alkaline earth metal cations were made by beryllium, magnesium, calcium, barium and strontium chloride solutions (20.0 mM in each). The pH values of the aqueous phases were adjusted using 4.0 mM barium hydroxide and 0.01 M hydrochloric acid solutions. The extraction ability of eight distinct dangling moieties was examined on five conformations of calix[4]arene scaffold, in 13 solutions with a pH range of 1.0–12.0. For each macrocyclic ligand, 13 solutions for competitive solvent extraction of alkaline earth metal cations were prepared in 15 ml conical polypropylene centrifuge tubes. The samples contained 2.0 ml of the aqueous phase of 10.0 mM alkaline earth metals solution and 2.0 ml of 1.00 mM calixarene solution in chloroform.

### 3.4 Extraction procedure

The combined aqueous and organic phases were shaken for 5 min and were centrifuged for 5 min. The pH of the aqueous phase was measured using pH meter with a Corning 476157 combination pH electrode. In the stripping step, 1.5 ml of the organic phase was transferred to a capped conical centrifuge tube containing 3.0 ml of 0.10 M HCl. The stripping involved 5 min of mixing and 5 min of centrifuging. After that, 1.0 ml of the aqueous phase was diluted to 10.0 ml for analysis by ion chromatography.

### 3.5 Ion chromatographic analysis

Determinations of alkaline earth metal cation were accomplished by Dionex DX-120 ion chromatographs with a CS12A column, a conductivity detection and a membrane suppression. The eluent was 0.011 M sulphuric acid after filtration through a Millipore 0.22 μm filtration membrane, while the pump flow rate at 1700 psi was about 1 ml/min. To obtain a stable baseline, the eluent was made to flow through the column for 60 min and then 2.0 ml of standard solutions was injected, and this procedure was repeated twice.

## 4. Results and discussions

The results of complexation ability for the cone, the 1,2-alternate and the partial-cone conformations of calix[4] arene derivatives are discussed. The cone conformers in two categories of *trans*-cone and *cis*-cone isomers are discussed first. It is followed by presenting the results of three isomers of 1,2-alternate conformer including *cis*-1,2-alternate, *ortho*-*trans*-1,2-alternate and *para*-*trans*-1,2-alternate. After that, four isoconformers of *ortho*-*cis*-partial cone, *para*-*cis*-partial cone, *ortho*-*trans*-partial cone and *para*-*trans*-partial cone are discussed. The identities of the dangling proton-ionisable moieties affect the acidity of macrocycle derivatives and their ability to extract alkaline earth metal cations. Hence, the pH for half loading, which is defined as $pH_{1/2}$, is used to measure the ligand acidity qualitatively.

The percent (%) of cation loading assumes a 1:1 complex and additional binding such as 2:1 to give the results more than 100%.

### 4.1 Two cone conformations

The total loading of metal:macrocycle complexes was determined by the sum of individual complexes to be about 100%, which depict a 1:1 ratio of metal:macrocycle and is expected for complexation of di-ionisable calixarenes towards divalent cations. The extraction characteristics of cone isoconformers (*ortho*-cone and *para*-cone) are discussed in this section.

#### 4.1.1 ortho-Cone isoconformers

For all four of the *ortho*-cone di-ionisable *p*-*tert*-butylcalix[4]arenes **01–04**, the maximum loadings were in the range of 85–107%. In derivatives **01–04**, the $pH_{1/2}$ values were computed to be 7.0, 6.9, 8.3 and 7.3, respectively. The results of competitive solvent extractions by ligand derivatives **01–04** in chloroform are presented in the upper row of Figure 2. Because of the selective 1:1 binding of $Ba^{2+}$ with the ionisable moieties and unselective binding of other alkaline earth cations with those moieties, the selectivity order for calix[4]arene derivatives **01–04** at $pH \geq 9.0$ was determined to be $Mg^{2+} < Sr^{2+} < Ca^{2+} < Ba^{2+}$ and the maximum $Ba^{2+}$ loadings all exceeding 40%. This macrocycle presented a $Ba^{2+}/Ca^{2+}$ selectivity of two under conditions of high loading. This reveals that the binding of different alkaline earth metal cation species by this derivative was influenced by the pH and the identity of the dangling proton-ionisable moieties.

#### 4.1.2 para-Cone isoconformers

For all four of the *para*-cone di-ionisable *p*-*tert*-butylcalix[4]arenes **05–08**, the maximum loadings were in the range of 97–115%. In derivatives **05–08**, the $pH_{1/2}$ values were determined to be 7.3, 7.2, 8.1 and 7.3, respectively. The results of competitive solvent extractions by ligand derivatives **05–08** in chloroform are depicted in the lower row of Figure 2. Owing to the selective 1:1 binding of $Ba^{2+}$ with the ionisable moieties and unselective binding of other alkaline earth metal cations with those moieties, the selectivity order for calix[4]arene derivatives **05–08** at $pH \geq 9.0$ was determined to be $Mg^{2+} < Sr^{2+} < Ca^{2+} < Ba^{2+}$ and the maximum $Ba^{2+}$ loadings all exceeding 45%. This macrocycle presented a $Ba^{2+}/Ca^{2+}$ selectivity of two under conditions of high loading.

### 4.2 Three 1,2-alternate conformations

The total loading of metal:macrocycle complexes was determined to be about 110%, which depict a 1:1 ratio for 1,2-alternate conformers. In the following, the extraction characteristics of *cis*-, *ortho*-*trans* and *para*-*trans*-1,2-alternate isoconformers are discussed.

#### 4.2.1 cis-1,2-Alternate isoconformers

The results of competitive solvent extractions by ligand derivatives **09–12** in chloroform are depicted in the upper

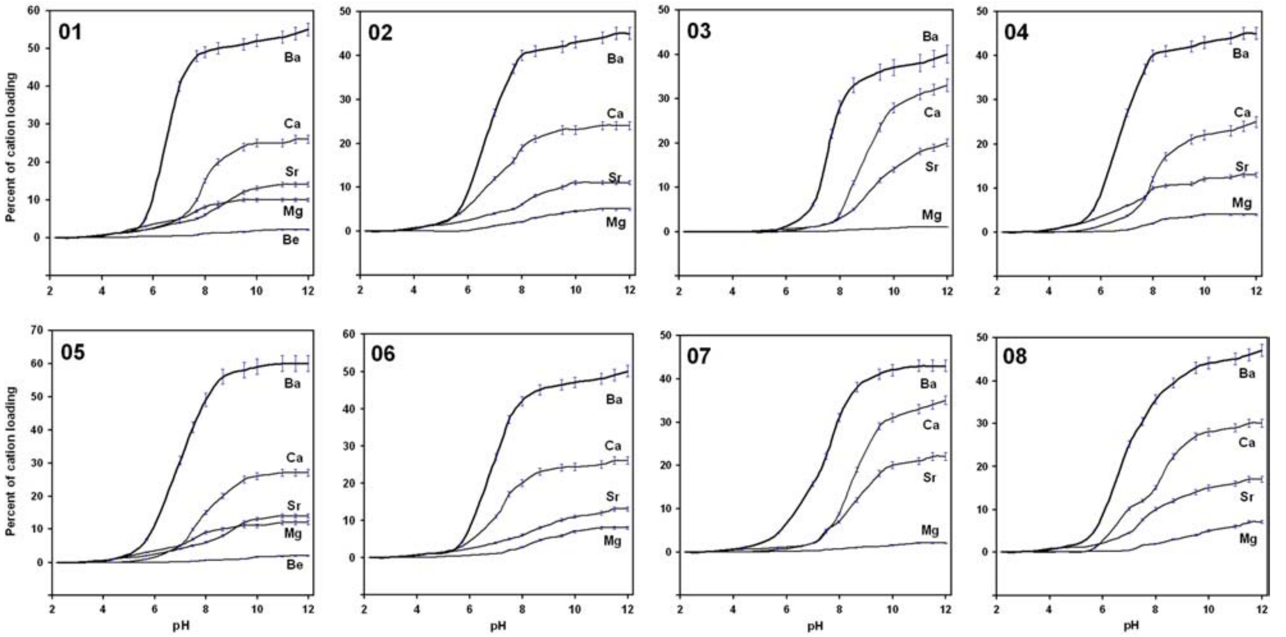

Figure 2. Competitive solvent extractions of alkaline earth metal cations by *ortho*-cone isoconformers **01–04** (upper row) and by *para*-cone isoconformers **05–08** (lower row).

row of Figure 3. For all four of di-ionisable *cis*-1,2-alternate *p-tert*-butylcalix[4]arenes **09–12**, the maximum loadings were in the range of 95–108%. In derivatives **09–12**, the $pH_{1/2}$ values were computed to be 8.2, 8.3, 7.9 and 7.9, respectively. Because of the selective 1:1 binding of $Ba^{2+}$ with the ionisable moieties and unselective binding of other alkaline earth metal cations with those moieties, the selectivity order for calix[4]arene derivatives **09–12** at $pH \geq 9.0$ was determined to be $Mg^{2+} \approx Sr^{2+} < Ca^{2+} < Ba^{2+}$ and the maximum $Ba^{2+}$ loadings all exceeding 50%. This macrocycle presented $Ba^{2+}/Ca^{2+}$ selectivity of two under conditions of high loading. According to Figure 3 for derivatives **10** and **11**, the amount of $Ca^{2+}$ extracted increased to its maximum loading at pH 10.0 and then diminished as the pH increased.

### 4.2.2 ortho-trans-1,2-Alternate isoconformers

For all four of the *ortho-trans*-1,2-alternate di-ionisable *p-tert*-butylcalix[4]arenes **13–16**, the maximum loadings were in the range of 112–128%. In derivatives **13–16**, the $pH_{1/2}$ values were calculated to be 6.3, 6.2, 6.2 and 6.3, respectively. The results of competitive solvent extractions by ligand derivatives **13–16** in chloroform are presented in the middle row of Figure 3. Owing to the unselective binding of all alkaline earth metal cations with the moieties, the low selectivity order for calix[4]arene derivatives **13–16** at $pH \geq 7.0$ was determined to be $Mg^{2+} < Sr^{2+} < Ca^{2+} < Ba^{2+}$ and the maximum $Ba^{2+}$ loadings all exceeding 50%. This macrocycle presented no $Ba^{2+}/Ca^{2+}$ selectivity but a good $Ba^{2+}$, $Ca^{2+}$ versus both $Sr^{2+}$ and $Mg^{2+}$ selectivity under conditions of high loading to be 3 and 6, respectively.

### 4.2.3 para-trans-1,2-Alternate isoconformers

For all four of the *para-trans*-1,2-alternate di-ionisable *p-tert*-butylcalix[4]arenes **17–20**, the maximum loadings were in the range of 125–140%. In derivatives **17–20**, the $pH_{1/2}$ values were computed to be 7.2, 7.0, 7.0 and 7.0, respectively. The results of competitive solvent extractions by ligand derivatives **17–20** in chloroform are presented in the lower row of Figure 3. Due to the unselective binding of all alkaline earth metal cations with the di-ionisable moieties, the poor selectivity order for calix[4]arene derivatives **17–20** at $pH \geq 8.0$ was determined to be $Mg^{2+} < Sr^{2+} < Ca^{2+} < Ba^{2+}$ and the maximum $Ba^{2+}$ loadings all exceeding 55%. This macrocycle presented small $Ba^{2+}/Ca^{2+}$ selectivity and a good $Ba^{2+}$, $Ca^{2+}$ versus both $Sr^{2+}$ and $Mg^{2+}$ selectivity under conditions of high loading to be 3 and 6, respectively.

## 4.3 Four partial-cone conformations

The total loading of metal:macrocycle complexes was determined to be about 34 and 17% for *cis*- and *trans*-isomers of partial-cone conformers, respectively. These percentages depict a 1:1 ratio of metal:macrocycle and were expected for complexation of di-ionisable calixarenes

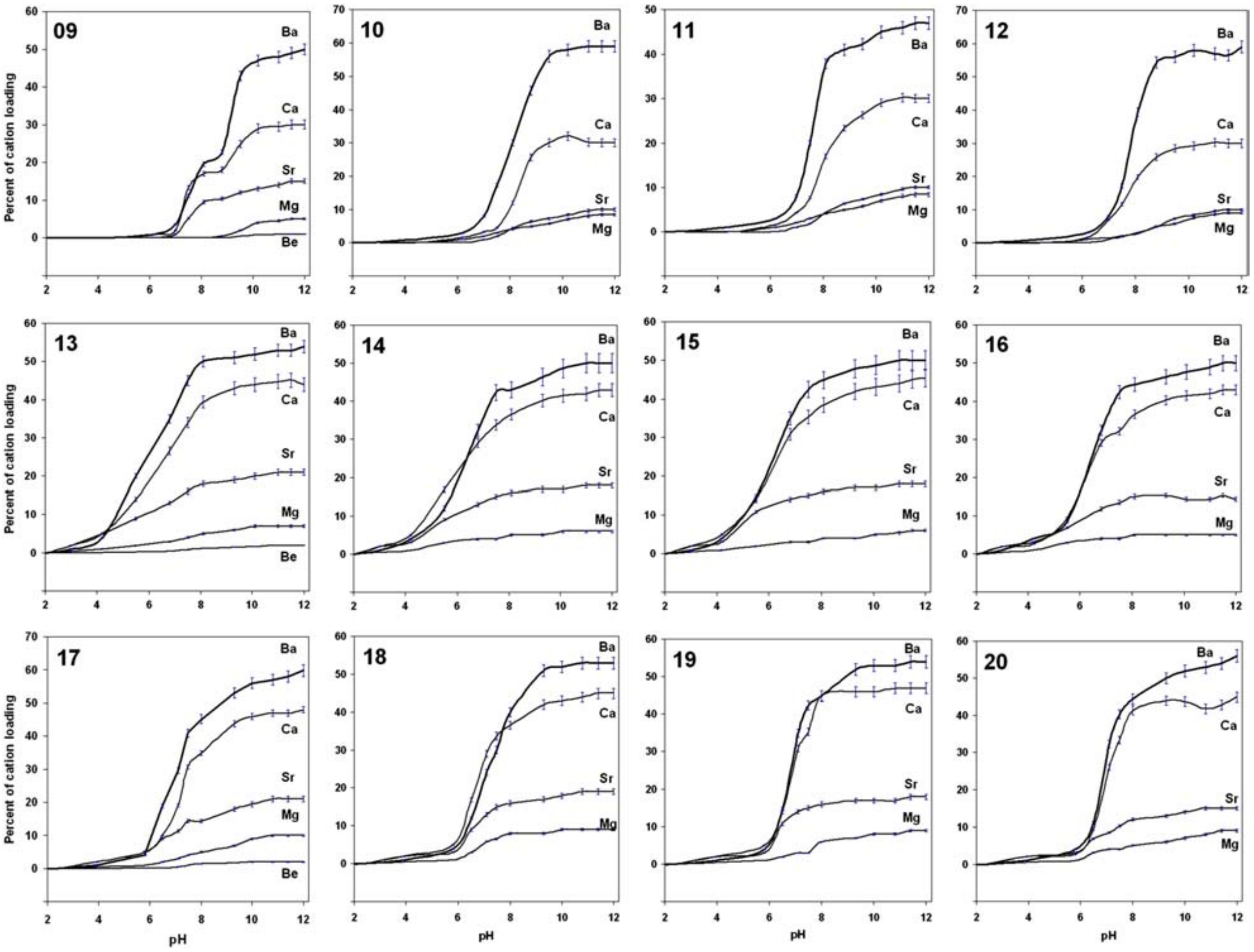

Figure 3. Competitive traces for solvent extractions of alkaline earth metal cations by *cis*-1,2-alternate isoconformers **09**–**12** (upper row), by *ortho-trans*-1,2-alternate isoconformers **13**–**16** (middle row) and by *para-trans*-1,2-alternate isoconformers **17**–**20** (lower row).

towards divalent cations. The extraction characteristics of partial cone isoconformers (*cis*- and *trans*-) are discussed in the following.

### 4.3.1 ortho-cis-Partial cone isoconformers

These derivatives did not show any binding tendency towards $Mg^{2+}$ and $Be^{2+}$. For all four of the *ortho-cis*-partial cone di-ionisable *p-tert*-butylcalix[4]arenes **21**–**24**, the maximum loadings were in the range of 34–35%. In derivatives **21**–**24**, the $pH_{1/2}$ values were computed to be 7.2 for all. The results of competitive solvent extractions by ligand derivatives **21**–**24** in chloroform are presented in the first row of Figure 4.

### 4.3.2 para-cis-Partial cone isoconformers

These derivatives did not show any binding tendency towards $Mg^{2+}$ and $Be^{2+}$. For all four of the *para-cis*-partial cone di-ionisable *p-tert*-butylcalix[4]arenes **25**–**28**, the maximum loadings were in the range of 33–37%. In derivatives **25**–**28**, the $pH_{1/2}$ values were computed to be 6.2, 6.3, 6.0 and 6.1, respectively. The results of competitive solvent extractions by ligand derivatives **25**–**28** in chloroform are presented in the second row of Figure 4. Using this macrocycle, the maximum $Ba^{2+}$ loadings are all exceeding 15% and there is a good selectivity towards $Sr^{2+}$ and a poor selectivity towards $Ba^{2+}$ and $Ca^{2+}$ cations.

### 4.3.3 ortho-trans-Partial cone isoconformers

The di-ionisable *ortho-trans*-partial cone *p-tert*-butylcalix[4]-arenes with di-[*N*-(*para*-nitro phenyl)sulphonyl carboxamide] moieties could not be synthesised. For all three of the *ortho-trans*-partial cone **29**–**31**, the maximum loadings were in the range of 20–21%. In derivatives

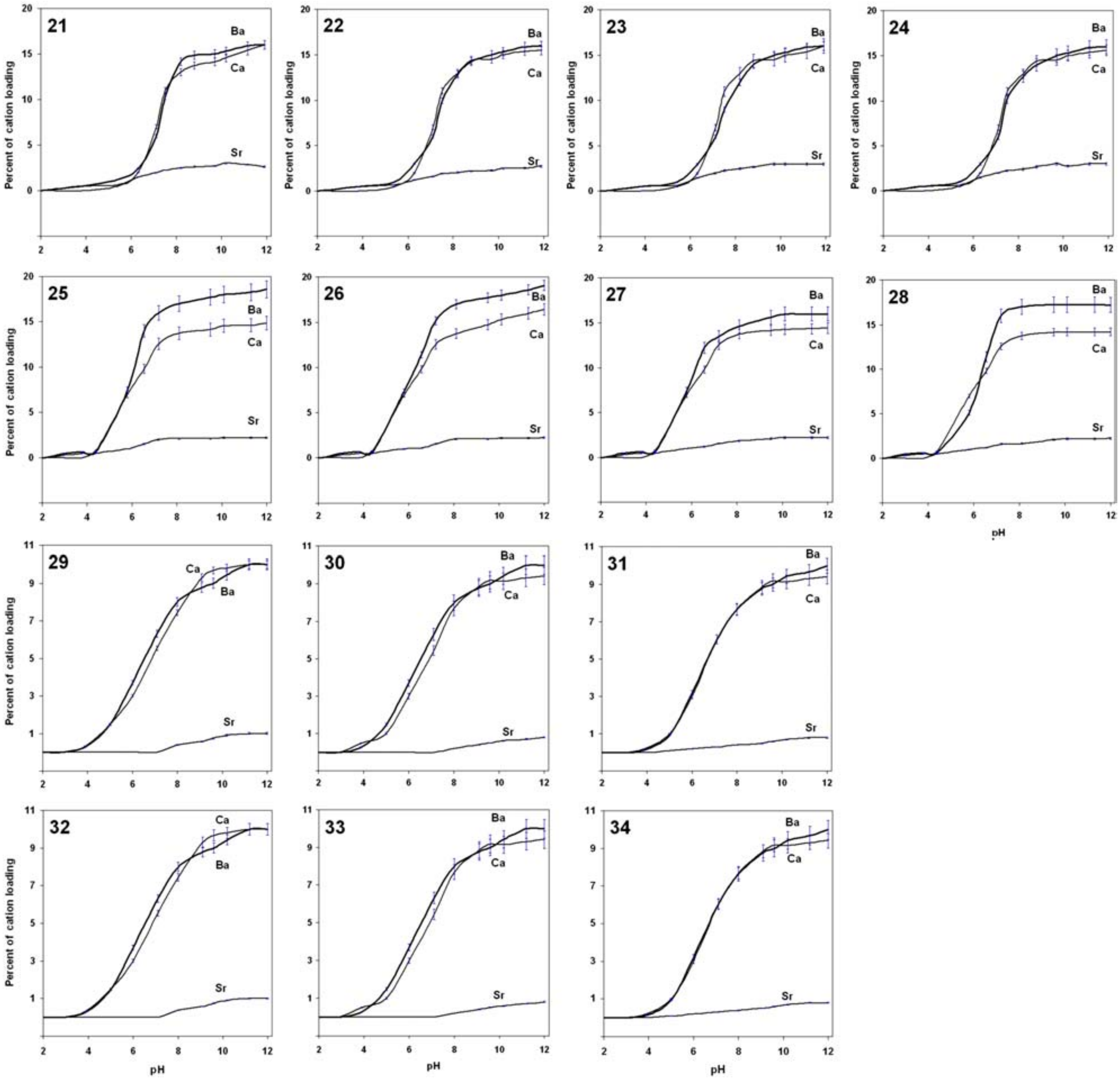

Figure 4. Solvent extractions of alkaline earth metal cations by *ortho-cis*-partial cone isoconformers **21–24**, (first row), by *para-cis*-partial cone isoconformers **25–28** (second row), by *ortho-trans*-partial cone isoconformers **29–31** (third row) and by *para-trans*-partial cone isoconformers **32–34** (fourth row).

**29–31**, the $pH_{1/2}$ values were computed to be 7.0, 6.9 and 6.9, respectively. The results of competitive solvent extractions by ligand derivatives **29–31** in chloroform are presented in the third row of Figure 4. These derivatives did not show any binding tendency towards $Mg^{2+}$ and $Be^{2+}$. Due to the selective 1:1 binding of $Ba^{2+}$ with the ionisable moieties and unselective binding of other alkaline earth cations, the selectivity of calix[4]arene derivatives **29–31** at pH ≥ 4.0 was $Sr^{2+}$ in the presence of $Ba^{2+}$ and $Ca^{2+}$ with the maximum $Ba^{2+}$ and $Ca^{2+}$ loadings all exceeding 10%.

### 4.3.4 *para-trans-Partial cone isoconformers*

The third derivative with di-[*N*-(*para*-nitro phenyl)sulphonyl carboxamide] moiety could not be synthesised. For all three of the *para-trans*-partial cone di-ionisable *p-tert*-butylcalix[4]arenes **32–34**, the maximum loadings were in the range of 20–23%. In derivatives **32–34**, the $pH_{1/2}$

values were computed to be 7.1, 7.0 and 7.2, respectively. The results of competitive solvent extractions by ligand derivatives **32–34** in chloroform are presented in the fourth row of Figure 4. These derivatives did not show any binding tendency towards $Mg^{2+}$ and $Be^{2+}$. Owing to the selective 1:1 binding of $Sr^{2+}$ with the ionisable moieties and unselective binding of other alkaline earth metal cations, the selectivity order for calix[4]arene derivatives **32–34** at pH $\geq$ 4.0 was determined to be $Ba^{2+}$, $Ca^{2+} < Sr^{2+}$ and the maximum $Ba^{2+}$, $Ca^{2+}$ loadings and $Sr^{2+}$ loading all exceeding 10% and 1%, respectively.

## 5. Conclusions

In this paper, the effects of four independent variables including calixarene conformations (cone, 1,2-alternate and partial-cone), aryl groups (in the ionisable pendant moieties), steric orientations (*cis*- and *trans*-) and relative positions (*ortho*- and *para*-) of pendant moieties on three dependent variables including extraction efficiency, $pH_{1/2}$ and selectivity of calix[4]arene complexes were assessed and quantified.

The lower extraction efficiency and selectivity of partial-cone conformers than their cone and 1,2-alternate analogues demonstrated that conformation variation had a pronounced influence upon the complexation of alkaline earth metals. But alternation of aryl groups in the ionisable pendant moieties, changing the orientation (from *cis*- to *trans*-) and the position (from *ortho*- to *para*-) of pendant moieties, did not cause any dominant change in the extraction efficiency, $pH_{1/2}$ and the selectivity of calixarenes.

The relatively higher extraction efficiency of *cis*-isomers than their *trans*- analogues revealed that the orientation variation of ionisable pendant moieties has a pronounced influence upon the complexation of alkaline earth metals. Among the conformers, the 1,2-alternate scaffold showed the widest range of extraction efficiency and $pH_{1/2}$ (6.2–8.1).

## Acknowledgements

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