Articles

Structure Optimization of Di-ionizable Calixarene Nano-baskets for Competitive Solvent Extraction of Alkali and Alkaline Earth Metals

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The competitive solvent extractions of alkali and alkaline earth metals by di-ionizable calix[4]arene nano-baskets were studied using nine conformers of calix[4]arene nano-baskets. The objective of this work is to assess the variation of macrocycle conformation, orientation and position of pendant moieties upon the extraction parameters (efficiency, selectivity and $pH_{1/2}$) of the complexes. The results revealed that alternation of ring conformation in calixarene scaffold affects the solvent extraction parameters towards alkali and alkaline earth metals, while changing the orientation of pendant moieties from *ortho*- to *para*- as well as *cis*- to *trans*-analogues depicted no changes in those extraction parameters.

Introduction

Nano-baskets of calixarenes are a versatile class of macrocycles, which have been subject to extensive research in development of many extractants, transporters and stationary phases (using gas chromatograph, Teif Gostar Faraz Co.) over the past four decades.[1-5] In the nineteenth century, Baeyer synthesized them *via* the reaction of formaldehyde with *p*-substituted phenols in basic or acidic environment.[6] In the 1940s, Zinke and Ziegler discovered that the products possessed cyclic tetrameric structures.[7] In 1975, Gutsche introduced the presently accepted name of calixarene.[8] The small calixarenic cycles, calix[4]arene, possess a bowl-shaped conformation[9] and those with pendent proton-ionizable groups, such as carboxylic acid,[10] phosphinoyl,[11] *N*-sulfonyl carboxamide[12] and hydroxyamic acid[13] have been utilized for solvent extraction of cations.

Ionizable calixarenes than non-ionizable analogues are more efficient in cation separation owing to charge matching within the resulted complex in the organic phase. There are two kinds of side chain in the calixarene skeleton that were studied including the ionizable sulfonyl carboxamide moieties and the crown ether moieties. The ionizable groups 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-ionizable function groups, *N*-phenyl-sulfonyl carboxamide, were incorporated into calix[4]arene scaffold. A special feature of such modification is that the hydrolysis of the *N*-phenyl-sulfonyl carboxamide moiety is tunable by changing the pH of solution. A wide range of pH environ-
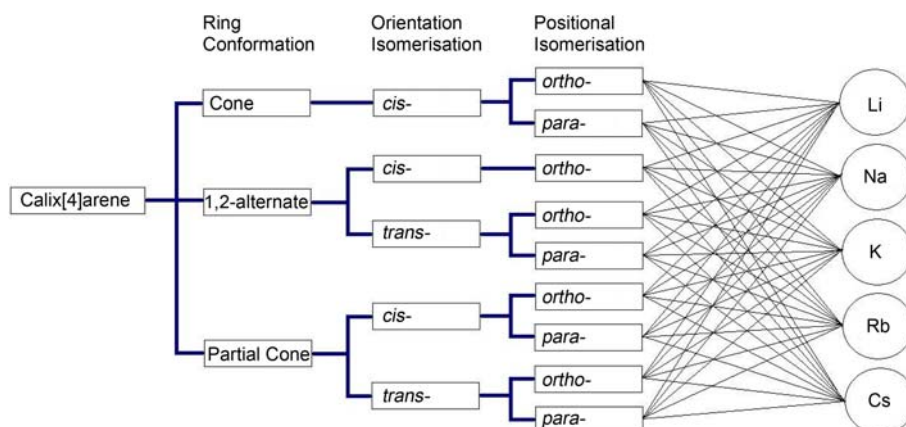
Figure 1. The hierarchical structures of complexes were investigated.

ments can be examined when these ionizable groups are incorporated into the calixarene skeleton. These extractants exhibit excellent extraction selectivity for alkali and alkaline earth metals.

Cations are transferred to the organic phase due to the production of a neutral complex and are analyzed quantitively in the aqueous phase after back extraction.[14-26] 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 alkali metals from aqueous solutions into chloroform by di-ionizable calix[4]arene derivatives were studied. Figure 1 shows the hierarchical structures of complexes were studied. Nine scaffolds were used to assess the isoconformations upon the extraction efficiency, selectivity and $pH_{1/2}$ of complexes.

Experimental

All of the experiments carried out using nine conformations of di-ionizable *p-tert*-calix[4]arene di-[*N*-(phenyl)sulfonyl carboxamide]. Two cone conformers (**1** and **2**), three 1,2-alternate conformers (**3-5**), and four partial-cone conformers (**6-9**) were synthesized to extract alkali metals. The *cis/trans* symbols refer to the direction of two di-ionizable moieties and the *ortho/para* depict the relative situation of two di-ionizable moieties.

Standard Solutions. Lithium chloride (99%), rubidium chloride (99+%) and cesium chloride (99+%) were obtained from Alfa Aesar (Ward Hill, MA). Potassium chloride (99%) and sodium chloride (99%) were purchased from Mallinckrodt (Phillipsburg, NJ). Magnesium chloride hexahydrate (99%), calcium chloride dihydrate (98%), barium chloride dihydrate (99%) and strontium chloride hexahydrate (99%) were obtained from Aldrich. Lithium hydroxide was purchased from Fisher Scientific (Fair Lawn, NJ). Barium hydroxide octahydrate (98%) was purchased from MCB, hydrochloric acid (1.0 N) from J. T. Baker, and sulfuric acid (2.0 N) was obtained from Mallinckrodt. Chloroform was purchased from EM Science and was shaken with deionized water to remove the stabilizing ethanol and stored in the dark.

Sample Preparation. The alkali metal cations were loaded into the aqueous solutions by adding stock solutions containing five alkali metal cations. The solutions of five alkali metal cations were made up as lithium, sodium, potassium, rubidium, and cesium chloride solutions (20.0 mM in each). The 20.0 mM lithium hydroxide and 0.01-1.0 M hydrochloric acid solutions were used to adjust the pH values of the aqueous phases.

The alkaline earth metal cations were loaded into the aqueous solutions by adding stock solutions containing 4 alkaline earth metal cations. The blend solutions of alkaline earth metal cations were made up as 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.

Extraction ability of calix[4]arene scaffolds were determined in thirteen solutions with pH range of 1.0-12.0. For each macrocyclic ligand, more than thirteen solutions for competitive solvent extraction of alkali or alkaline earth metals were prepared in 15 mL conical polypropylene centrifuge tubes. The samples contained 2.0 mL of the aqueous phase of 10.0 mM alkali or alkaline earth metals solution and 2.0 mL of 1.00 mM calixarene solution in chloroform.

Extraction Procedure. In this research, the solvent extraction procedure as a sample preparation and a pre-concentration method was used. The combined aqueous and organic phases were shaken for 5 minutes and were centrifuged for 5 minutes. 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 minutes of mixing and 5 minutes of centrifuging. After that, 1.0 mL of the aqueous phase was diluted to 10.0 mL for analysis by ion chromatography.

Ion Chromatographic Analysis. Determinations of alkali or alkaline earth metals were accomplished by Dionex DX-120 ion chromatographs with a CS12A column, a conductivity detection and membrane suppression. Nitrogen pressure for the eluent was set at 50 psi. The eluent was 0.011 M sulfuric 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 flowed through the column for 60 minutes and then, 2.0 mL of standard solutions were injected and they were repeated two other times. PeakNet software was used to manipulate the outputs from the ion chromatograph.

Results and Discussion

The proton-ionizable groups act as acidity tunable functions with functional group variation. The pH for half loading ($pH_{1/2}$) was used to measure qualitatively the ligand acidity. Alternating the orientation of pendant moieties from *cis-* to *trans-* as well as *ortho-* to *para-* analogues revealed no changes in the selectivity of macrocyclic ligands. Besides, the cone conformers were selective to sodium and the 1,2-alternate conformers showed a relative selectivity to potassium and rubidium. Figure 2 shows the chemical structure of those nine conformations **1-9** (R group was defined as: −NHSO2Phenyl. According to Figure 2, there were not any extractability towards cesium and rubidium in conformers **8** and **9**.

***ortho*-Cone Isoconformer 1.** Using the *ortho*-cone di-ionizable *p-tert*-butylcalix[4]arene **1**, the maximum loadings were in the range of 179-197%. The results of competitive solvent extractions by ligand derivative **1** in chloroform are presented in Figure 2. Because of the selective 1:1 binding of Na$^+$ with the ionizable moieties and unselective binding of other alkali cations with those moieties, the selectivity
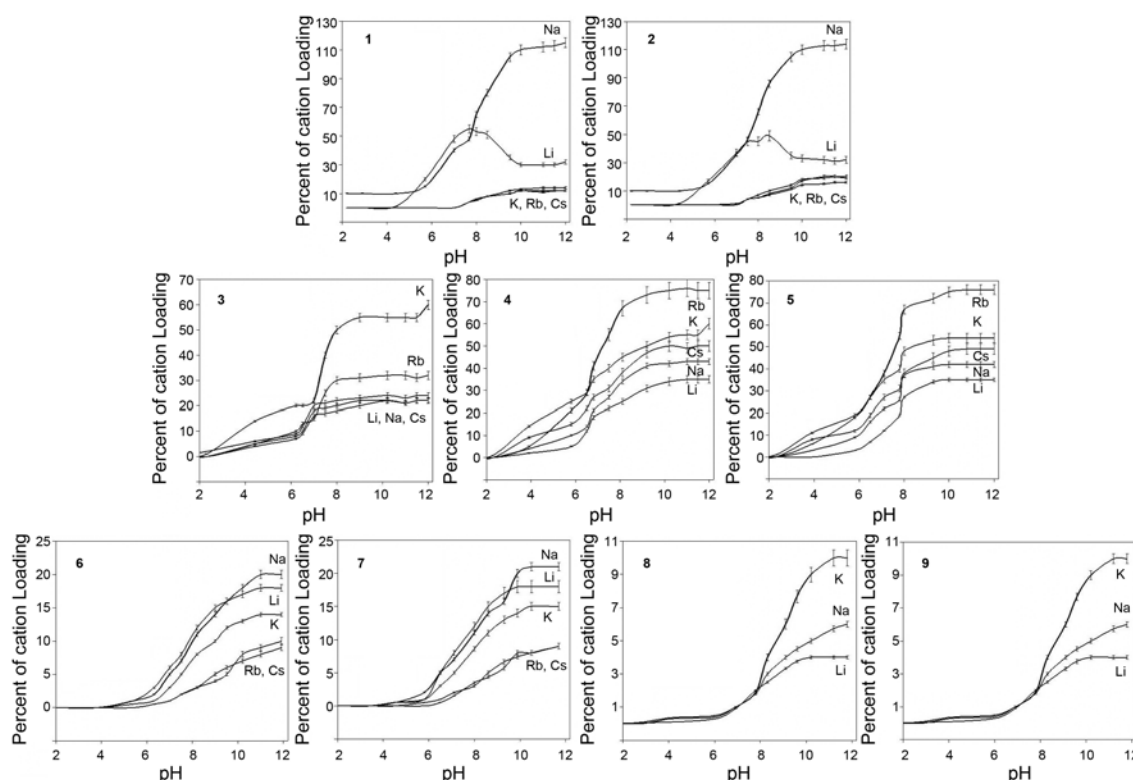
Figure 2. Loading traces for solvent extractions of alkali metals by isoconformers **1-9**. The cone conformations in the upper row, the 1,2-alternate conformations in the middle row and the partial-cone conformations in the lower row.

order for calix[4]arene derivative **1** at pH ≥ 8.0 was determined to be as Rb^+ & Cs^+ & K^+ < Li^+ << Na^+ and the maximum Na^+ loadings all exceeding 100%. This macrocycle presented a Na^+/Li^+ selectivity of 4 under conditions of high loading. This reveals that the binding of different alkali metal cation species by this derivative was influenced by the pH and the identity of the dangling proton-ionizable moieties. According to Figure 2 for derivative **1**, the amount of Li^+ extracted increased to its maximum loading at pH of 7.5, and then diminished as the pH increased.
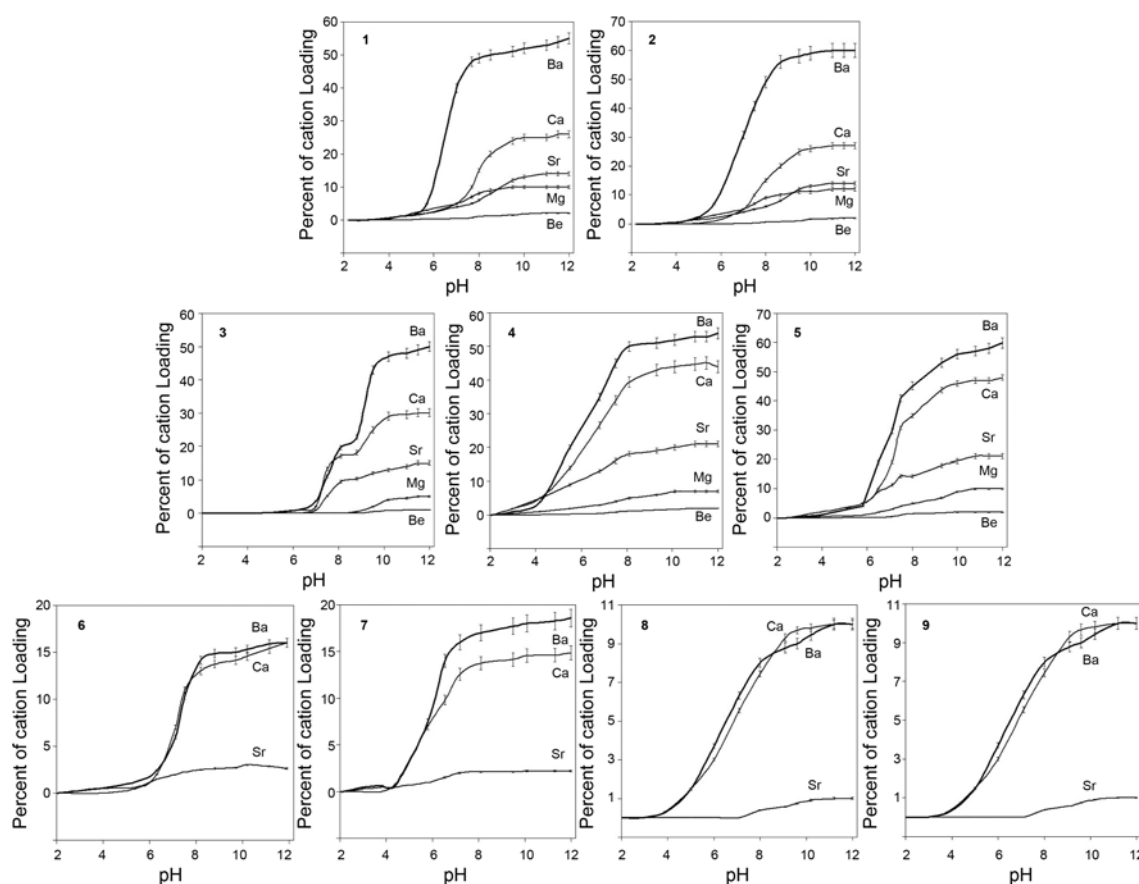
Using the *ortho*-cone di-ionizable *p-tert*-butylcalix[4]arene **1**, the maximum loadings were in the range of 85-107%. The results of competitive solvent extractions by ligand derivative **1** in chloroform are presented in Figure 4. Because of the selective 1:1 binding of Ba^{2+} with the ionizable moieties and unselective binding of other alkaline earth cations with those moieties, the selectivity order for calix-[4]arene derivatives **1** at pH ≥ 9.0 was determined to be as 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 2 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-ionizable moieties.

para-**Cone Isoconformer 2.** Using the *para*-cone di-ionizable *p-tert*-butylcalix[4]arene **2**, the maximum loadings were in the range of 197-224%. The results of competitive solvent extractions by this derivative in chloroform are depicted in Figure 2. Owing to the selective 1:1 binding of

Na^+ with the ionizable moieties and unselective binding of other alkali cations with those moieties, the selectivity order for calix[4]arene derivative **2** at pH ≥ 7.5 was determined to be as K^+ & Rb^+ & Cs^+ < Li^+ << Na^+ and the maximum Na^+ loadings all exceeding 100%. This macrocycle presented a Na^+/Li^+ selectivity of 4 under conditions of high loading. According to Figure 2, the amount of Li^+ extracted increased to its maximum loading at pH of 8.5.

Using the *para*-cone di-ionizable *p-tert*-butylcalix[4]arene **2**, the maximum loadings were in the range of 97-115%. The results of competitive solvent extractions by ligand derivative **2** in chloroform are depicted in Figure 4. Owing to the selective 1:1 binding of Ba^{2+} with the ionizable moieties and unselective binding of other alkaline earth metal cations with those moieties, the selectivity order for calix[4]arene derivative **2** at pH ≥ 9.0 was determined to be as 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 2 under conditions of high loading.

cis-**1,2-Alternate Isoconformer 3.** The results of competitive solvent extractions by ligand derivative **3** in chloroform are presented in Figure 2. Using the di-ionizable *cis*-1,2-alternate *p-tert*-butylcalix[4]arene **3**, the maximum loadings were in the range of 150-183%. Because of the selective 1:1 binding of Na^+ with the ionizable moieties and unselective binding of other alkali cations with those moieties, the selectivity order for calix[4]arene derivative **3** at pH ≥ 7.0 was determined to be as Li^+ & Na^+ & Cs^+ < Rb^+ << K^+ and the maximum K^+ loadings all exceeding 60%.

Figure 3. Loading traces for solvent extractions of alkaline earth metals by isoconformers **1-9**. The cone conformations in the upper row, the 1,2-alternate conformations in the middle row and the partial-cone conformations in the lower row.

This macrocycle presented a Na^+/Li^+ selectivity of 2.0 under conditions of high loading.

The results of competitive solvent extractions by ligand derivative **3** in chloroform are presented in Figure 3. Using the di-ionizable *cis*-1,2-alternate *p-tert*-butylcalix[4]arene **3**, the maximum loadings were in the range of 95-108%. Because of the selective 1:1 binding of Ba^{2+} with the ionizable moieties and unselective binding of other alkaline earth metal cations with those moieties, the selectivity order for calix[4]arene derivative **3** at pH ≥ 9.0 was determined to be as $Mg^{2+} Sr^{2+} < Ca^{2+} < Ba^{2+}$ and the maximum Ba^{2+} loadings all exceeding 50%. This macrocycle presented a Ba^{2+}/Ca^{2+} selectivity of 2 under conditions of high loading.

***ortho-trans*-1,2-Alternate Isoconformer 4.** Using the *ortho-trans*-1,2-alternate di-ionizable *p-tert*-butylcalix[4]arene **4**, the maximum loadings were in the range of 241-284%. The results of competitive solvent extractions by this derivative in chloroform are presented in Figure 2. Owing to the unselective binding of all alkali metal cations with the moieties, the low selectivity order for calix[4]arene derivative **4** at pH ≥ 7.5 was determined to be as $Li^+ < Na^+$ & $Cs^+ < K^+ < Rb^+$ and the maximum Rb^+ loadings all exceeding 80%. This macrocycle presented an Rb^+/K^+ selectivity of 1.5 in derivative **1** under conditions of high loading.

Using the *ortho-trans*-1,2-alternate di-ionizable *p-tert*-butylcalix[4]arene **4**, the maximum loadings were in the

range of 112-128%. The results of competitive solvent extractions by ligand derivative **4** in chloroform are presented in Figure 3. Owing to the unselective binding of all alkaline earth metal cations with the moieties, the low selectivity order for calix[4]arene derivative **4** at pH ≥ 7.0 was determined to be as $Mg^{2+} < Sr^{2+} < Ca^{2+} < Ba^{2+}$ 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.

***para-trans*-1,2-Alternate Isoconformer 5.** Using the *para-trans*-1,2-alternate di-ionizable *p-tert*-butylcalix[4]arene **5**, the maximum loadings were in the range of 240-294%. The results of competitive solvent extractions by this derivative in chloroform are presented in Figure 2. Due to the unselective binding of all alkali metal cations with the di-ionizable moieties, the poor selectivity order for calix[4]arene derivative **5** at pH ≥ 8.0 was determined to be as $Li^+ < Na^+$ & $Cs^+ < K^+ < Rb^+$ and the maximum Rb^+ loadings all exceeding 80%. This macrocycle showed an Rb^+/K^+ selectivity of 1.5 under conditions of high loading.

Using the *para-trans*-1,2-alternate di-ionizable *p-tert*-butylcalix[4]arene **5**, the maximum loadings were in the range of 125-140%. The results of competitive solvent extractions by ligand derivative **5** in chloroform are presented in Figure 3. Due to the unselective binding of all alkaline

earth metal cations with the di-ionizable moieties, the poor selectivity order for calix[4]arene derivative **5** at pH ≥ 8.0 was determined to be as $Mg^{2+} < Sr^{2+} < Ca^{2+} < Ba^{2+}$ 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.

ortho-cis-**Partial Cone Isoconformer 6.** Using the *ortho-cis* partial-cone di-ionizable *p-tert*-butylcalix[4]arene **6**, the maximum loadings were in the range of 57-115%. The results of competitive solvent extractions by this derivative in chloroform are presented in Figure 2. The unselective binding of alkali metal cations with the ligand shows no selectivity order for calix[4]arene derivative **6**. The maximum Na^+ loading was exceeding 25%.

This derivative did not show any binding tendency towards Mg^{2+} and Be^{2+}. Using the *ortho-cis*-partial cone di-ionizable *p-tert*-butylcalix[4]arene **6**, the maximum loadings were in the range of 34-35%. The results of competitive solvent extractions by ligand derivative **6** in chloroform are presented in Figure 3. The unselective binding of alkaline earth metal cations with the ligand shows no selectivity order of calix[4]arene derivative **6** for Ba^{2+} versus Ca^{2+} and the selectivity of Ba^{2+}, Ca^{2+} versus Sr^{2+} was about 5. The maximum Ba^{2+} loadings all exceeding 15%.

para-cis-**Partial Cone Isoconformer 7.** Using the *para-cis* partial-cone di-ionizable *p-tert*-butylcalix[4]arene **7**, the maximum loadings were in the range of 59-112%. The results of competitive solvent extractions by this derivative in chloroform are presented in Figure 2. Using this macrocycle, the maximum Na^+ loading was exceeding 25% and there was a poor selectivity towards the cations.

This derivative did not show any binding tendency towards Mg^{2+} and Be^{2+}. Using the *para-cis*-partial cone di-ionizable *p-tert*-butylcalix[4]arene **7**, the maximum loadings were in the range of 33-37%. The results of competitive solvent extractions by ligand derivative **7** in chloroform are presented in Figure 3. Using this macrocycle, the maximum Ba^{2+} loadings all exceeding 15% and there is a good selectivity toward Sr^{2+} and a poor selectivity towards Ba^{2+} and Ca^{2+} cations.

ortho-trans-**Partial Cone Isoconformer 8.** Using the *ortho-trans* partial-cone **8**, the maximum loadings were in the range of 17-24%. The results of competitive solvent extractions by this derivative in chloroform are presented in Figure 2. These derivatives did not show any binding tendency towards Cs^+ and Rb^+. Due to the selective 1:1 binding of K^+ with the ionizable moieties and unselective binding of other alkali cations, the selectivity order for calix[4]arene derivative **8** at pH ≥ 8.0 was determined to be as $Li^+ < Na^+ < K^+$ and the maximum K^+ loadings all exceeding 12%. This macrocycle presented a K^+/Li^+ selectivity of 3, K^+/Na^+ selectivity of 2.0, and Na^+/Li^+ selectivity of 1.5 under conditions of high loading. This reveals that the binding of different alkali metal cation species by this derivative was influenced by the pH and the identity of the dangling proton-ionizable moieties.

Using the *ortho-trans*-partial cone **8**, the maximum loadings were in the range of 20-21%. The results of competitive solvent extractions by ligand derivative **8** in chloroform are presented in Figure 3. 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 ionizable moieties and unselective binding of other alkaline earth cations, the selectivity of calix[4]arene derivative **8** at pH ≥ 4.0 was Sr^{2+} in the presence of Ba^{2+} and Ca^{2+}. the maximum Ba^{2+} and Ca^{2+} loadings all exceeding 10%.

para-trans-**Partial Cone Isoconformer 9.** Using the *para-trans* partial-cone di-ionizable *p-tert*-butylcalix[4]-arene **9**, the maximum loadings were in the range of 17-22%. The results of competitive solvent extractions by this derivative in chloroform are presented in Figure 2. These derivatives did not show any binding tendency towards Rb^+ and Cs^+. owing to the selective 1:1 binding of K^+ with the ionizable moieties and unselective binding of other alkali cations, the selectivity order for calix[4]arene derivative **9** at pH ≥ 8.0 was determined to be as $Li^+ < Na^+ < K^+$ and the maximum K^+ loadings all exceeding 12%. This macrocycle presented the K^+/Li^+, K^+/Na^+, and Na^+/Li^+ selectivities of 3, 2, and 1.5 under high loading conditions, respectively.

Using the *para-trans*-partial cone di-ionizable *p-tert*-butylcalix[4]arene **9**, the maximum loadings were in the range of 20-23%. The results of competitive solvent extractions by ligand derivative **9** in chloroform are presented in Figure 3. 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 ionizable moieties and unselective binding of other alkaline earth metal cations, the selectivity order for calix[4]arene derivative **9** at pH ≥ 4.0 was determined to be as Ba^{2+}, $Ca^{2+} < Sr^{2+}$ and the maximum Ba^{2+}, Ca^{2+} loadings and Sr^{2+} loading all exceeding 10% and 1%, respectively.

Conclusion

Changing the orientation of pendant moieties from *cis*- to *trans*- as well as *ortho*- to *para*- analogues revealed no changes in the selectivity, extraction efficiency and pH$_{1/2}$ of calix[4]arene complexes towards alkali and alkaline earth metals. Besides, alternation of ring conformation (cone, 1,2-alternate and partial cone) showed a pronounced influence upon the solvent extraction of alkali and alkaline earth metal cations.

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