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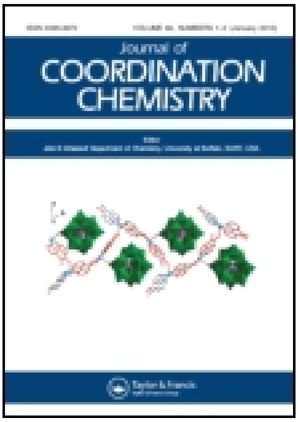

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gcoo20

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Published online: 07 Sep 2011.

To cite this article: Bahram Mokhtari & Kobra Pourabdollah (2011) Effect of crown size and upper moieties in nano-baskets of diacid calix[4]arene-1,2-crowns-3,4,5,6 on the extraction of s-block metals, Journal of Coordination Chemistry, 64:17, 3081-3091, DOI: 10.1080/00958972.2011.613462

To link to this article: http://dx.doi.org/10.1080/00958972.2011.613462

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Journal of Coordination Chemistry
Vol. 64, No. 17, 10 September 2011, 3081–3091

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Effect of crown size and upper moieties in nano-baskets of diacid calix[4]arene-1,2-crowns-3,4,5,6 on the extraction of s-block metals

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(*Received 4 June 2011; in final form 18 July 2011*)

Eight proton di-ionizable diacid conformers of cone 25,26-di(carboxymethoxy)calix[4]arene crown-3,4,5,6 were synthesized and characterized by ^{1}H, ^{13}C NMR, infrared spectroscopies, and elemental analysis. Competitive solvent extractions of alkali and alkaline earth metal cations were studied using these nano-baskets. This study includes three binding units of the calixarene bowl, crown ether ring, and electron-donor ionizable moieties in a unique scaffold to assess the binding tendency toward cations. The results of solvent extraction experiments indicated that these compounds were effective extractants of alkali and alkaline earth metal cations. The selectivities were greatly influenced by acidity of solution and conformation of the calixcrown. One conformer was selective to Na^+ in $pH \geq 4$, while the other was highly selective to Ba^{2+} in pH=6 and above.

Keywords: Nano-basket; Solvent extraction; Calixcrown; Upper rim; s-Block metals

1. Introduction

Nano-baskets of calixarenes and calixcrowns are a versatile class of macrocycles, which have been subject to extensive research in development of extractants, transporters, and stationary phases [1–5]. Calixarene scaffolds without structural modification have weak metal ion affinity and poor selectivity [6]. Functionalization of calix[4]arenes at both the upper rim and the lower rim has been extensively studied. Attaching donors to the lower rim of a calix[4]arene improves the binding strength of the parent calixarene dramatically. One modified scaffold was synthesized by Deligoz and Erdem introducing diazo groups on the calixarene structure [7]. The selective liquid extraction of alkaline, alkaline earth, and transition metals using diazo coupled calix[4]arenes showed no selectivity toward alkaline and alkaline earth metals but some selectivity toward Ag^+, Hg^+, and Hg^{2+}. The two main groups of lower rim functionalized calix[4]arenes are calix[4]arene podands and calixarene-crown ethers [8, 9].

Among the modified calixarene scaffolds, calixcrown derivatives receive attention for a crown ether ring on the lower rim, which increases the cation-binding ability of the calixarenic scaffold and enhances selectivity through modulation of the crown

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Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2011 Taylor & Francis
DOI: http://dx.doi.org/10.1080/00958972.2011.613462

ring size [10–12]. Two types of crown ethers bridging on the lower rim of calixarenes have been studied, 1,2-bridging of proximal phenolic units and 1,3-bridging of distal phenolic units. Investigations have focused mainly on the 1,3-bridged ones since they show high binding affinity and selectivity in solvent extraction of both alkali and alkaline earth metals [13, 14]. Arduini *et al.* [15] studied calix-1,2-crowns (*p-tert*-butylcalix[4]arene-1,2-crown-5 and *p-tert*-butylcalix[4]arene-1,2,3,4-biscrown-5) in 1990, and assessed the binding toward alkali metals with poor selectivity [16].

Combining crown ethers with calix[4]arenes increases the cation-binding ability of the parent calixarenes; control of the selectivity is obtained through modulation of the crown ether size. Attachment of proton-ionizable groups to calixcrowns can further improve their extraction properties because the ionized group participates in metal ion coordination and eliminates the need to transfer aqueous phase anions into the organic phase. Ungaro *et al.* [17] reported the first di-proton-ionizable calix[4]crown-5 in 1984 and it showed efficiency in extraction of divalent cations from water into dichloromethane. Combining crown ethers with calix[4]arenes increases the cation-binding ability of the parent calixarenes [18–20]. The selectivity can be affected by the crown ether size, the identity of donors on the crown ether moiety, and the conformation of the calixarene platform. To further explore the influence of these factors on the extraction of metal ions with *p-tert*-butylcalix[4]arene-1,2-crown ethers, di-ionizable *p-tert*-butylcalix[4]arene-1,2-crown-3 compounds in the cone conformation and the 1,2-alternate conformation, as well as *p-tert*-butylcalix[4]arene-1,2-thiacrown-3 in the cone conformation have now been synthesized.

There are two kinds of side chains in the calixcrown skeleton that were studied, including two ionizable carboxylic acid moieties and crown-ether moieties. The ionizable moieties participate in cooperative metal ion coordination and eliminate the need to transfer 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 functional groups were incorporated into the calix[4]arene scaffold. A special feature of such modification is that the acidity of the ionizable moiety can be tuned by changing the functional group from hydroxyl to other groups with different electron-withdrawing abilities. A wide range of pH environments can be examined when these ionizable groups are incorporated into the calixcrown skeleton. These extractants exhibit excellent extraction selectivity for alkali and alkaline earth metals.

In this work, eight diacid proton-ionizable calixcrowns were synthesized, *p-tert*-butyl-25,26-di(carboxymethoxy)calix[4]arene-1,2-crown-3 (**10**), cone *p-tert*-butyl-25,26-di(carboxymethoxy)calix[4]arene-1,2-crown-4 (**11**), cone *p-tert*-butyl-25,26-di(carboxymethoxy)calix[4]arene-1,2-crown-5 (**12**), cone *p-tert*-butyl-25,26-di(carboxymethoxy)calix[4]arene-1,2-crown-6 (**13**), cone 25,26-di(carboxymethoxy)calix[4]arene-1,2-crown-3 (**23**), cone 25,26-di(carboxymethoxy)calix[4]arene-1,2-crown-4 (**24**), cone 25,26-di(carboxymethoxy)calix[4]arene-1,2-crown-5 (**25**), and cone 25,26-di(carboxymethoxy)calix[4]arene-1,2-crown-6 (**26**). Competitive solvent extractions of alkali metal cations and alkaline earth metal cations were performed using $1.0\,\mathrm{mmol\,L^{-1}}$ solutions of di-ionizable calix[4]crown ligands in chloroform as well as plots of cation loading of the organic phase *versus* the equilibrium pH of the aqueous phase. Synthesis and extraction procedures of eight conformers are presented. Figure 1 depicts structure of eight calixcrown scaffolds used as extractants.

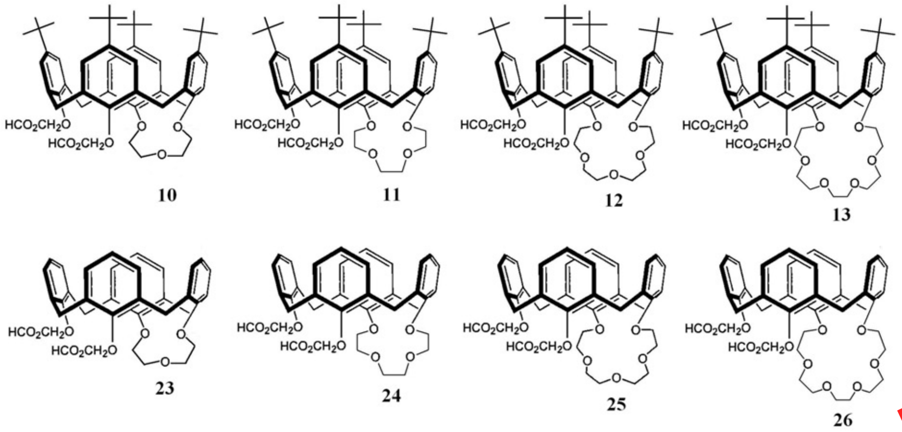

Figure 1. The chemical structure of eight calixcrown scaffolds synthesized and studied.

2. Experimental

2.1. *Synthesis procedure*

Reagents were obtained from commercial suppliers and used directly, unless otherwise noted. Acetonitrile (MeCN) was dried over CaH_2 and distilled immediately before use. Tetrahydrofuran (THF) was dried over sodium with benzophenone as an indicator and distilled just before use. Cs_2CO_3 was activated by heating at 150°C overnight under high vacuum and stored in a desiccator. Melting points were determined with a Mel-Temp melting point apparatus. Infrared (IR) spectra were recorded with a Perkin-Elmer Model 1600 FT-IR spectrometer as deposits from CH_2Cl_2 solution on NaCl plates. The ^{1}H and ^{13}C NMR spectra were recorded with a Varian Unity INOVA 500 MHz FT-NMR (^{1}H 500 MHz and ^{13}C 126 MHz) spectrometer in $CDCl_3$ with Me_4Si as internal standard. Chemical shifts (δ) are given in ppm downfield from TMS and coupling constants (J) are in Hz. The synthesis scheme for the preparation of cone *p*-*tert*-butyl-25,26-di(carboxymethoxy)calix[4]arene-1,2-crown-3,4,5,6 (**10–13**) and cone 25,26-di(carboxymethoxy)calix[4]arene-1,2-crown-3,4,5,6 (**23–26**) are presented in figure 2. Detailed syntheses are given in "Supplementary material".

2.2. *Extraction procedures*

Upon ionization, the cone calix[4]crowns form metal complexes with two anionic centers on the same side of the crown unit. Competitive solvent extractions of alkali metal cations (Li^+, Na^+, K^+, Rb^+, and Cs^+) and alkaline earth metal cations (Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+}) were performed in $1.0\,\mathrm{mmol\,L^{-1}}$ solutions of di-ionizable calix[4]crown ligands **10–13** and **23–26** in chloroform, and plots of metal ion loading of the organic phase *versus* the equilibrium pH of the aqueous phase were obtained, as depicted in figures 3–6. All extraction experiments were repeated three times and the mean value of the extraction loadings are presented in the plots.

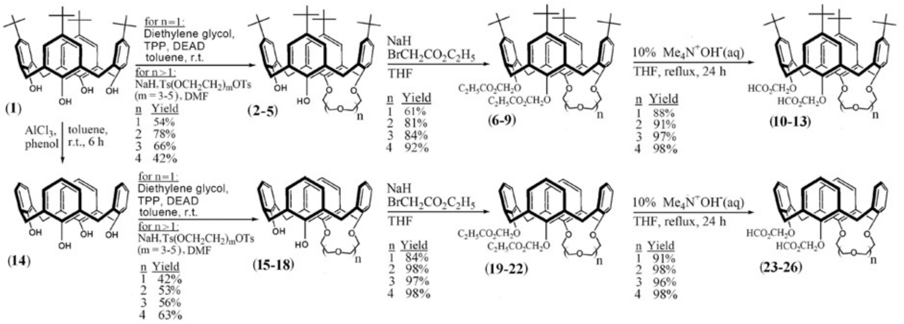

Figure 2. Synthesis of cone *p-tert*-butyl-25,26-di(carboxymethoxy)calix[4]arene-1,2-crown-3,4,5,6 (**10–13**) and cone 25,26-di(carboxymethoxy)calix[4]arene-1,2-crown-3,4,5,6 (**23–26**).

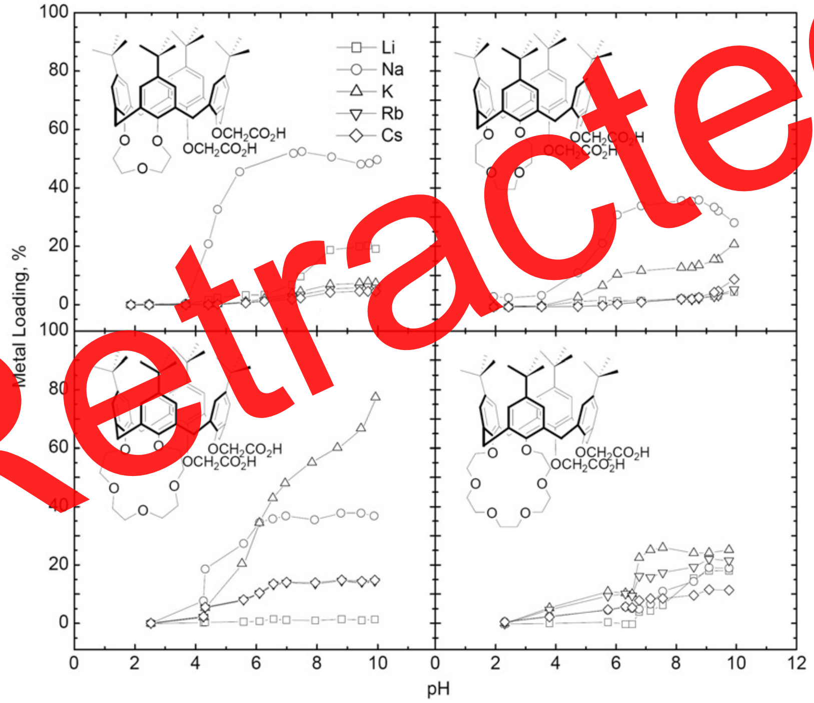

Figure 3. Percentage of metal loading *vs*. equilibrium pH of the aqueous phase for competitive solvent extraction of alkali metal ions into chloroform by **10–13**.

2.2.1. Competitive solvent extraction by 10. Competitive extraction of metal cations with **10** have different selectivity from **11–13**. All five alkali metal cations and four alkaline earth metal cations were extracted into the chloroform phase with selectivity order $Na^+ >> Li^+ > K^+$, Rb^+, Cs^+ and $Mg^{2+} > Ba^{2+} \approx Ca^{2+} > Sr^{2+}$. The pH for half loading, $pH_{1/2}$, is a measure of the ligand acidity. For **10**, the $pH_{1/2}$ was 4.5 for binding to Na^+ and 7.5 for binding to Li^+, K^+, Rb^+, and Cs^+. The $pH_{1/2}$ values for binding to alkaline earth metal cations were 9.0–9.5. Figures 3 and 4 depict plots of alkali and

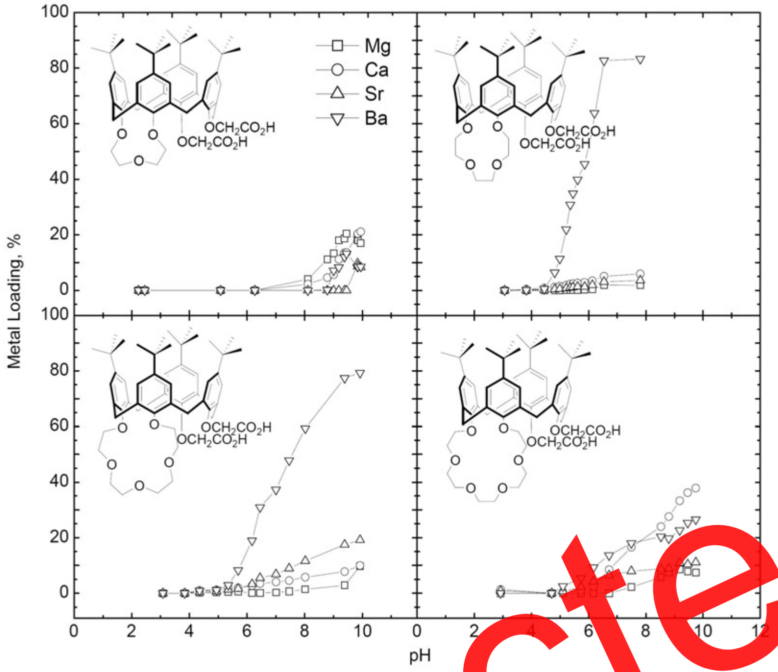

Figure 4. Percentage of metal loading *vs.* equilibrium pH of the aqueous phase for competitive solvent extraction of alkaline earth metal ions into chloroform by **10–13**.

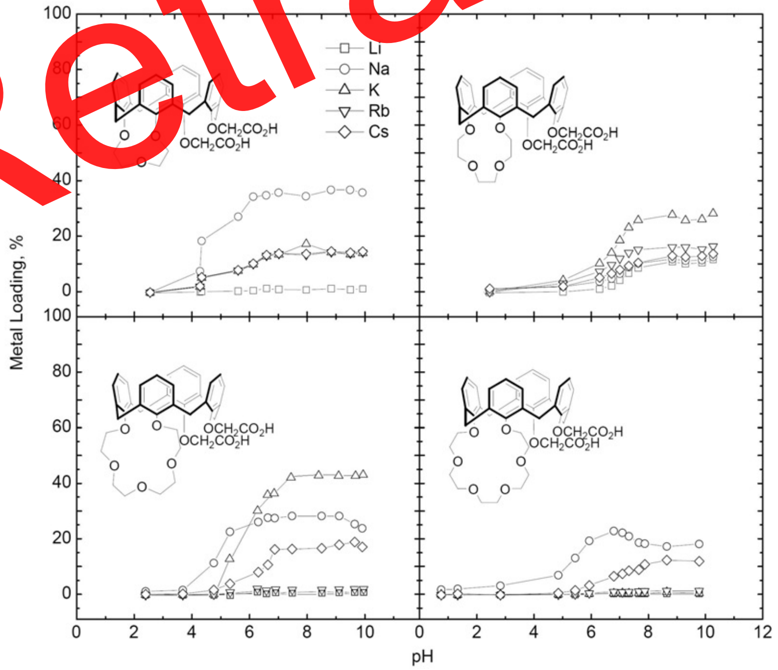

Figure 5. Percentage of metal loading *vs.* equilibrium pH of the aqueous phase for competitive solvent extraction of alkali metal ions into chloroform by **23–26**.

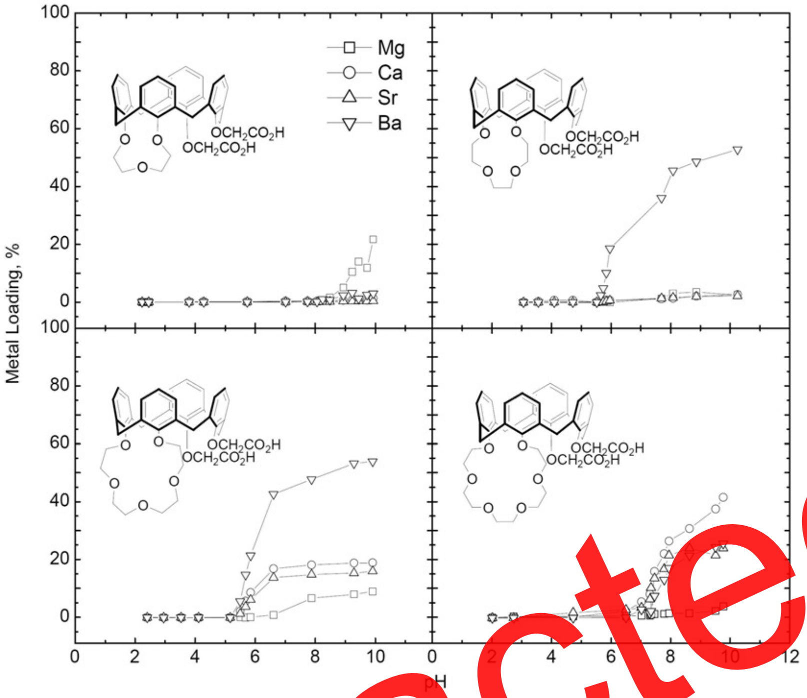

Figure 6. Percentage of metal loading *vs.* equilibrium pH of the aqueous phase for competitive solvent extraction of alkaline earth metal ions into chloroform by **23**–**26**.

alkaline earth metal ions loading of the organic phase *versus* equilibrium pH of the aqueous phase using **10**.

2.2.2. Competitive solvent extraction by 11. Competitive extractions of aqueous alkali and alkaline earth metal cations (10.0 mmol L^{-1} in each) solutions by 1.0 mmol L^{-1} solutions of **11** in chloroform have plots of metal ion loading of the organic phase *versus* the equilibrium pH of the aqueous phase, presented in figures 3 and 4, respectively.

All five alkali metal cations and four alkaline earth metal cations were extracted into the chloroform phase. The selectivity order was $Na^+ > K^+ > Li^+$, Rb^+, Cs^+ and $Ba^{2+} >> Ca^{2+}$, Sr^{2+}, Mg^{2+}. $pH_{1/2}$ values were 5.5 for binding to both the alkali and the alkaline earth metal cations.

2.2.3. Competitive solvent extraction by 12. Compound **12** also exhibits different selectivity from **10**, **11** and **13**. Metal cations were extracted into the chloroform phase with selectivity order $K^+ > Na^+ > Rb^+ \approx Cs^+ > Li^+$ and $Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+}$. The $pH_{1/2}$ values were 4–6 for binding to alkali metal cations and 7 for alkaline earth metal cations. Figures 3 and 4 show the loading plots of alkali and alkaline earth metal cations in the organic phase *versus* the equilibrium pH of the aqueous phase using **12**.

2.2.4. Competitive solvent extraction by 13.

For competitive solvent extractions by **13** in chloroform, plots of metal ion loading of the organic phase *versus* the equilibrium pH of the aqueous phase are presented in figures 3 and 4. Compound **13** exhibits selectivities $K^+ > Rb^+ > Na^+ \approx Li^+ > Cs^+$ and Ba^{2+}, $Ca^{2+} > Sr^{2+}$, Mg^{2+}. The $pH_{1/2}$ value was 7 for binding to alkali and alkaline earth metal cations.

2.2.5. Competitive solvent extraction by 23.

For competitive extraction of alkali and alkaline earth metal cations, **23** has different selectivity than **24–26**. The cations were extracted into chloroform in the order $Na^+ > K^+$, Rb^+, $Cs^+ > Li^+$ and $Mg^{2+} > Ba^{2+}$, Ca^{2+}, Sr^{2+}. The $pH_{1/2}$ was 5 and 9 for binding to alkali and alkaline earth cations, respectively. Figures 5 and 6 depict plots of metal ion loading of the organic phase *versus* equilibrium pH of the aqueous phase using **23**, respectively.

2.2.6. Competitive solvent extraction by 24.

For competitive extractions of aqueous alkali and alkaline earth cations ($10.0\,mmol\,L^{-1}$ in each) by $1.0\,mmol\,L^{-1}$ solutions of **24** in chloroform, plots of metal ion loading of the organic phase *versus* equilibrium pH of the aqueous phase are presented in figures 5 and 6. **24** has selectivity order $K^+ > Rb^+ > Na^+$, Li^+, Cs^+ and $Ba^{2+} > Ca^{2+}$, Sr^{2+}, Mg^{2+}. The $pH_{1/2}$ value was 7 for binding to alkali and alkaline metals.

2.2.7. Competitive solvent extraction by 25.

For **25**, plots of metal ion loading of the organic phase *versus* equilibrium pH of the aqueous phase are presented in figures 5 and 6. The $pH_{1/2}$ was 5–6 for binding to alkali metals and 6 for alkaline earth cations. The selectivity order was $K^+ > Na^+ > Cs^+$, Li^+, Rb^+ and $Ba^{2+} > Ca^{2+} > Sr^{2+} > Mg^{2+}$.

2.2.8. Competitive solvent extraction by 26.

For **26**, plots of metal ion loading of the organic phase *versus* equilibrium pH of the aqueous phase are presented in figures 5 and 6. The selectivity order was $Na^+ > Cs^+ > Li^+$, K^+, Rb^+ and $Ca^{2+} > Ba^{2+}$, $Sr^{2+} > Mg^{2+}$ and $pH_{1/2}$ was 5.5–6.5 for alkali metals and 7.5 for binding to alkaline earths.

3. Results and discussion

3.1. *The role of crown ether moiety*

Arduini *et al.* [15, 16, 21–24] showed 1,2-bridged calix[4]crown compounds have poor binding ability and selectivity toward metal cations. Arnaud-Neu *et al.* [22, 23] continued this work, synthesizing cone, partial cone, and 1,2-alternate *p-tert*-butylcalix[4]arene-1,2-crown-4,5,6 ethers bearing a lower rim α-picolyl and tested their metal picrate extraction from water into dichloromethane. The results also showed poor extraction levels for alkali, alkaline earth, and heavy metal picrates. Their selectivities varied from K^+ for the cone conformer to both K^+ and Rb^+ for the partial cone isomer and Cs^+ for the 1,2-alternate conformer.

This study focusing on the cone conformation of 1,2-bridging calixcrowns confirms the work of Arduini *et al.* [15, 16, 21–24] regarding a poor ability of complexation for 1,2-bridged calix[4]crowns toward alkali, alkaline earth, and other metal cations. However, such complexation and binding abilities were enhanced in comparison with calixarenes without crown ether modification. For alkali metals, tuning the ring size of crown ether led to increase and decrease of K^+ and Na^+ selectivity, respectively. For alkaline earth metals, increasing the size of crown ether enhanced the Ba^{2+} selectivity. In comparison to the work of Arnaud-Neu *et al.* [22, 23], in which lower rim α-picolyl group was introduced, poor extraction efficiency for alkali and alkaline earth metals was confirmed. High selectivity toward K^+ using 1,2-bridged calix[4]crowns bearing lower rim di-carboxylic acid (in this study) and bearing lower rim α-picolyl group (in the Arnaud-Neu studies) reveal that changing the lower rims does not affect selectivity. Arnaud-Neu *et al.* did not investigate extraction efficiency and selectivity of selected calixcrown derivatives toward alkaline earth metals.

3.2. *The role of ionizable acid moieties*

Introducing one or two phenolic groups in calix[4]crowns provides proton-ionizable groups under strongly basic conditions. Calix[4]crowns-5,6 bearing one phenolic group showed high selectivities toward K^+ over alkali metals and toward Ca^{2+} over alkaline earth metals, while calix[4]crowns-5,6 bearing two phenolic moieties exhibited no selectivity toward alkali metals but remarkable selectivity toward Ca^{2+} [25–28]. Introduction of pendant proton-ionizable moieties into a calixcrown scaffold increases the extraction efficiency by forming electro-neutral complexes during extraction [29–33]. Ungaro and coworkers [17] reported the first example of a proton-ionizable calix[4]crown. Based upon their later results, calix-1,3-crowns bearing two carboxylic acid groups exhibited high efficiency for solvent extraction of divalent metals except Mg^{2+} from water into dichloromethane. The extraction selectivities for Pb^{2+} and Ca^{2+} were reported to be better than those of non-ionizable analogs. They did not study the extraction efficiency and selectivity toward alkali metals.

In comparison to the work of Ungaro *et al.* and according to the results of this work, di-carboxylic acid calix-1,2-crowns were selective to Ba^{2+}, while di-carboxylic acid calix-1,3-crowns showed high selectivity toward Ca^{2+}.

Other types of proton-ionizable functions, *N*-(X)sulfonyl carboxamide groups, have been introduced into calixcrowns by Pourabdollah [34] and Talanov *et al.* [35, 36]. These ligands exhibit enhanced extraction efficiency, while retaining high selectivity toward Cs^+ compared with a non-ionizable analog.

In comparison to the works of Talanov *et al.*, the extraction efficiency of calixcrowns bearing two *N*-(X)sulfonyl carboxamide moieties and the efficiency of calixcrowns bearing two carboxylic acid groups (in this study) exhibited marked enhancement. However, the selectivities are different, in which the *N*-(X)sulfonyl carboxamide groups shifted the selectivity of alkali metal extraction to Cs^+, while the carboxylic acid groups moved the selectivities to K^+. Talanov *et al.* did not discuss the selectivity of calix-1,3-crowns bearing *N*-(X)sulfonyl carboxamide groups toward alkaline earths, but selectivity using carboxylic acids was toward Ba^{2+} at $pH = 6$ and higher.

Zhou *et al.* [14] synthesized three conformations of proton ionizable *p*-*tert*-butylcalix[4]crown-6 bearing sulfonyl carboxamide groups including cone, partial-cone and

1,3-alternate and studied the effect of ionizable groups and scaffold conformation on the efficiency and selectivity of solvent extraction for divalent metals, revealing that the cone conformer had high extraction efficiency and selectivity for Ba^{2+} over Mg^{2+}, Ca^{2+}, and Sr^{2+}. In similar work, they [37] reported the synthesis of proton ionizable *p-tert*-butylcalix[4]crown-5 bearing sulfonyl carboxamide groups in the cone, partial-cone and 1,3-alternate conformations and their application as extractants for alkaline earth metals. They also showed that all conformers have high extraction efficiency and selectivity for Ba^{2+} over Mg^{2+}, Ca^{2+}, and Sr^{2+}.

In comparison to the work of Zhou *et al.*, extraction efficiency of calixcrowns bearing two sulfonyl carboxamide groups exhibit marked enhancement over those bearing two carboxylic acid groups. Their selectivities are the same, with both favoring Ba^{2+} over Mg^{2+}, Ca^{2+}, and Sr^{2+}. Zhou *et al.* did not report alkali metal extractions.

Chen and coworkers [38] synthesized the cone *p-tert*-butylcalix[4]crown-6 bearing two carboxylic acid moieties and two hydroxamic acid moieties and showed a high selectivity toward Ra^{2+} over alkaline earth metals. No other conformers were studied and complexation and the extraction of alkali metal cations were not examined.

3.3. *The role of upper rim moieties*

Singh *et al.* [39] synthesized some tetrathiacalix[4]arene tetraethylacetate derivatives with upper rim *p-tert*-butyl and without such upper rim substituents. They examined the extraction ability of the new calixarenes toward alkali and alkaline earth metals as well as the oxyanions but did not report the extractions by calixarenes without upper rim substituents.

In this study, introducing upper rim moieties of *p-tert*-butyl improved the binding tendency and the extraction ability of alkali and alkaline earth metals. Such upper rim moieties enhance the inductive charges from aromatic rings to the crown and acid's oxygen atoms.

4. Conclusions

Proton di-ionizable diacid conformers of cone 25,26-di(carboxymethoxy)calix[4]arene-27,28-crown-3,4,5,6 (**23–26**), and their analogs including *p-tert*-butyl moieties in the upper rim (**10–13**), were synthesized as potential extractants for alkali and alkaline earth metal cations. The conformations and regio-selectivities of the new ligands were verified by ^{1}H, ^{13}C NMR, IR spectroscopies, and elemental analysis. The upper rim moieties (*p-tert*-butyl) gave an enhancement in the binding tendency and extraction ability of alkali and alkaline earth cations, attributed to inductive charges from aromatic rings to the oxygens in the crown ether and acid moieties. By increasing the ring size of crown ether moieties from crown-3 to crown-6, increasing K^{+} selectivity was observed. It passed through a maximum for crown-5 and decreased on further increasing in ring size. A similar but inverse trend was obtained for Na^{+} selectivity. By increasing the ring size of crown ether, increase in Ba^{2+} selectivity was observed, also decreasing on further increasing in ring size.

Ligand **10** and its analog (**23**) with crown-3 showed the most selectivity toward Na^+ at $pH = 4$ and higher, while **11** and **24** with crown-4 showed the most selectivity toward Ba^{2+} at $pH = 6$ and higher. The $pH_{1/2}$ values, in a broad range of 4–9, depended mainly on conformer's structure and less to the trapped cation.

Acknowledgments

This work was supported by Islamic Azad University (Shahreza branch) and Iran Nanotechnology Initiative Council.

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