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Metal ion separations with proton-ionizable crown ethers and their polymers

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Lipophilic crown ethers with pendent proton-ionizable groups are novel complexing agents for use in metal ion separations by solvent extraction. For a series of structurally related, lipophilic dibenzocrown ether carboxylic acids, the efficiency and selectivity of competitive alkali metal cation extraction for aqueous solution into chloroform is found to be strongly influenced by the crown ether ring size and the lipophilic group attachment site. Reaction of dibenzocrown ether carboxylic acids with formaldehyde in formic acid produces condensation polymers which possess both ion-exchange and cyclic polyether binding sites for metal ion complexation. These resins exhibit excellent exchange kinetics for competitive alkali metal cation sorption from aqueous solution and subsequent stripping and may be used in concentrator columns for the recovery of these metal ions from very dilute aqueous solution. Cation selectivity in the sorption and stripping steps is controlled by the structure of the crown ether monomer unit.

INTRODUCTION

The synthesis of new organic complexing agents with good metal specificity may lead to the development of improved separation systems for aqueous metal ions. Thus, the preparation and introduction of highly lipophilic hydroxyoximes led to the current utilization of these compounds as commercial extractants for the hydrometallurgy of non-ferrous metals.

As first described by Pedersen,¹ cyclic polyethers (crown ethers) form stable complexes with a variety of metal salts. With hard donor atoms (oxygen) crown ethers would be anticipated to exhibit the strongest association with hard metal ion species, i.e. alkali metal, alkaline earth, lanthanide and actinide cations.

The potential of crown ethers as the next generation of specific extracting agents for metal ions was markedly enhanced by the introduction of crown ethers which bear pendent proton-ionizable groups.²⁻⁶

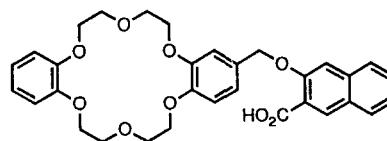
Metal ion extraction by such proton-ionizable crown ethers involves ion exchange of the metal ion for a proton and therefore does not require concomitant transfer of the aqueous phase anion into the organic medium. This factor is of immense importance to potential practical applications of crown ethers for metal ion separations in which hard aqueous phase anions (chloride, nitrate and sulphate) would be involved. In addition, the combination of ion binding cavities with fixed dimensions and proton-ionizable groups creates novel bifunctional chelating agents. The ease with which extracted metal ions may be stripped from the organic phase by shaking with aqueous mineral acid is a final factor.

In this paper the influence of structural variations within the lipophilic dibenzocrown ether carboxylic acids on the selectivity and efficiency of competitive alkali metal cation extraction into chloroform is summarized. Also condensation polymers formed from dibenzocrown ether carboxylic acids are utilized as novel ion exchange resins for competitive alkali metal cation sorption.

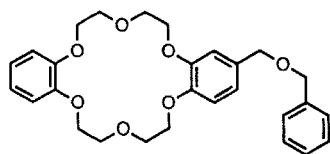
RESULTS AND DISCUSSION

Comparison of solvent extractions by closely-related proton-ionizable and neutral crown ethers

Macrocyclic polyethers **1** and **2** are benzo-18-crown-6 compounds with side arms. In **1** there is a pendent



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2

carboxylic acid function, whereas in **2** there is no proton-ionizable group. Figure 1 presents results for the competitive solvent extraction of five alkali metal chlorides from aqueous solution (0.25 M in each) with an equal volume of 0.050 M crown ether in chloroform. For the neutral crown ether **2**, the metal ion loading of the organic phase is very low and there was no apparent influence of the aqueous phase pH upon the extraction efficiency. Only small amounts of potassium chloride were extracted into the organic phase by the crown ether. On the other hand, alkali metal cation loading of the chloroform phase for extractions with crown ether carboxylic acid **1** is strongly dependent upon the aqueous phase pH. When the aqueous solution is neutral or basic, the crown ether carboxylate efficiently transfers alkali metal cations into the organic phase. When the aqueous phase is strongly alkaline (pH > 11) the metal loading in the chloroform phase is quantitative, assuming formation of a 1:1 metal ion-crown ether carboxylate complex. The results presented in Figure 1 dramatically demonstrate the benefit of employing a proton-ionizable crown

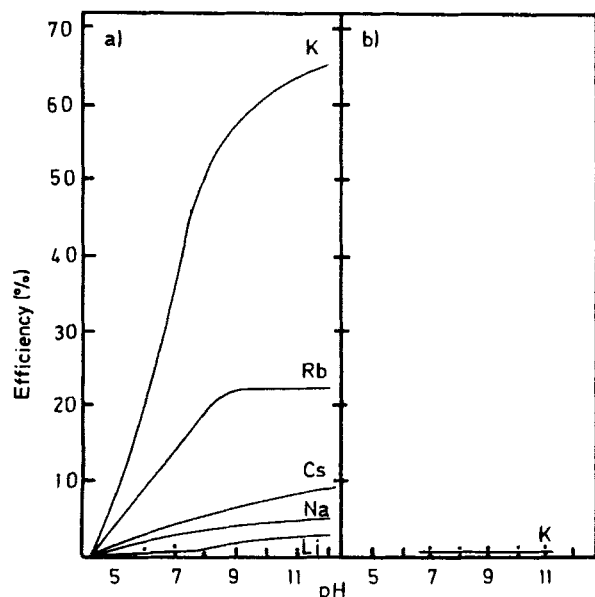


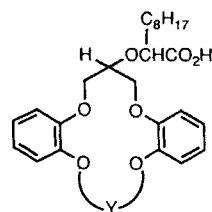
Figure 1 Extraction efficiency for competitive solvent extraction of aqueous alkali metal cations (each 0.25 M) with 0.050 M chloroform solutions of substituted benzo-18-crown-6 compounds (a) **1** and (b) **2**.

ether for metal ion extraction from aqueous solutions containing hard anionic species such as chloride.

Influence of structural variation of dibenzocrown ether carboxylic acids on solvent extraction of alkali metal cations

Dibenzocrown ethers with an alcohol group attached to the polyether ring are conveniently prepared by reaction of appropriate bis-phenols with epichlorohydrin.⁸ By reaction of the dibenzocrown ether alcohols with sodium hydride and 2-bromodecanoic acid, dibenzocrown ether carboxylic acids **3–6** were prepared. In **3–6** the side arm contains a lipophilic octyl group to prevent loss of the crown ether carboxylates from an organic phase into a contracting highly alkaline aqueous phase during solvent extraction.^{7,9}

To investigate the influence of crown ether ring size in **3–6** upon extraction selectivity, competitive solvent extractions of aqueous solutions of the five alkali metal chlorides (with hydroxide added for pH adjustment) with chloroform solutions of **3–6** were performed.^{9,10} The results are recorded in Figure 2. The crown ether ring sizes in **3–6** are 14-crown-4, 16-crown-5, 19-crown-6 and 22-crown-7, respectively. Based upon the polyether ring sizes, extraction selectivities for Li⁺, Na⁺, K⁺ and Cs⁺ would be anticipated for crown ether carboxylic acids **3–6**, respectively. In agreement, the dibenzo-16-crown-5 compound **4** and the dibenzo-19-crown-6 compound **5** exhibit good extraction selectivities for Na⁺ (Fig 2b) and K⁺ (Fig 2c), respectively. On the other hand, the dibenzo-14-crown-4 carboxylic acid **3** shows extraction selectivity for Na⁺ instead of Li⁺ (Fig 2a) and the dibenzo-22-crown-7 analogue **6** exhibits poor differentiation among the alkali metal cations for solvent extraction into chloroform (Fig 2d). The very poor selectivity noted for **6** compared with **3–5** suggests that the polyether ring is not planar, but provides three-dimensional 'wrap-around' complexation of alkali metal cations.



- Y
- 3** -CH₂CH₂CH₂-
 - 4** -CH₂CH₂OCH₂CH₂-
 - 5** -CH₂(CH₂OCH₂)₂CH₂-
 - 6** -CH₂(CH₂OCH₂)₃CH₂-

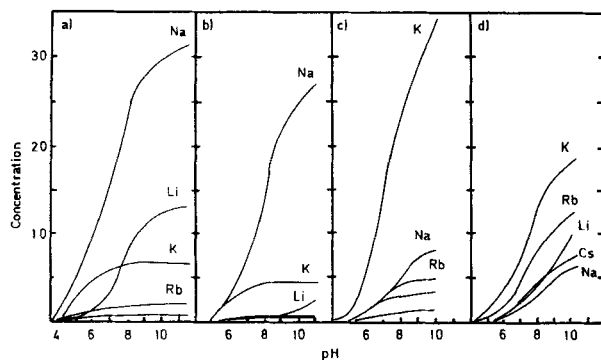


Figure 2 Concentrations of metals ($M \times 10^3$) in the chloroform phase vs. the equilibrium pH of the aqueous phase for competitive extraction of 0.25 M alkali metal cations by 0.050 M chloroform solutions of dibenzocrown ether carboxylic acids (a) **3**, (b) **4**, (c) **5** and (d) **6**.

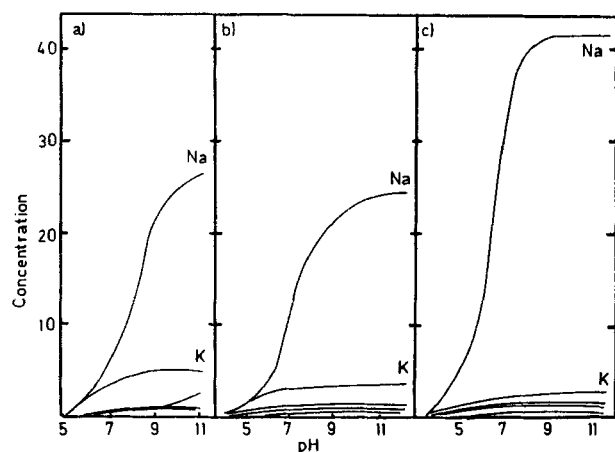
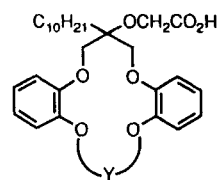
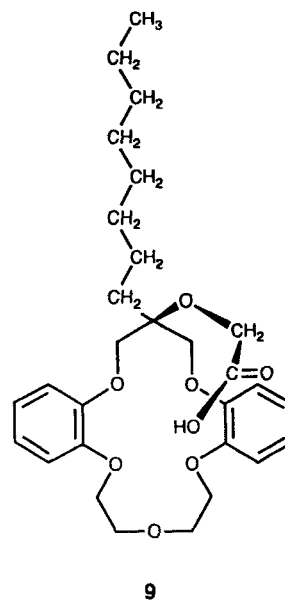
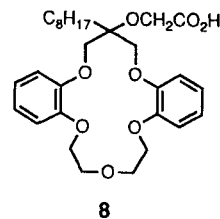
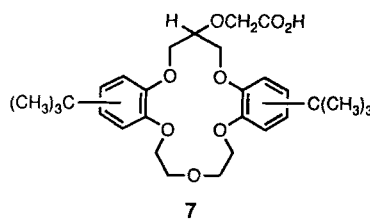


Figure 3 Concentrations of metals ($M \times 10^3$) in the chloroform phase vs. the equilibrium pH of the aqueous phase for competitive extraction of 0.25 M alkali metal cations by 0.050 M chloroform solutions of dibenzo-16-crown-5-oxyacetic acids (a) **4**, (b) **7** and (c) **8**.

For dibenzocrown ether carboxylic acid extractants, the next structural variation to be examined was the attachment site for the lipophilic group. Crown ethers **4**, **7**¹¹ and **8**¹² are structural isomers with a common dibenzo-16-crown-5-oxyacetic acid structure, but different lipophilic group attachment sites. Results for the competitive solvent extraction of aqueous solutions of the five alkali metal cations as the chlorides and hydroxides with chloroform solutions of structural isomers **4**, **7** and **8** are shown in Figure 3. The Na^+ extraction selectivities for **4** (Fig 3a) and **7** (Fig 3b) are similar. Thus it seems to make little difference whether there is one 8-carbon lipophilic group attached to the carboxylic acid group-containing side arm or one, 4-carbon group attached to each of the two benzene rings. However, the Na^+ extraction selectivity observed for **8** (Fig 3c) is much higher than that found for either **4** or **7**. Examination of CPK

space-filling models reveals that when the lipophilic octyl group in **8** points away from the polar polyether ring, the carboxylic acid group is positioned directly over the polyether cavity, as depicted in **9**. Hence the much higher Na^+ selectivity of **8** is ascribed to preorganization of the binding site.¹³

A new series of lipophilic crown ether carboxylic acids **10–12** was prepared in which a decyl group is



- Y**
- 10** $-\text{CH}_2\text{CH}_2\text{CH}_2-$
 - 11** $-\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2-$
 - 12** $-\text{CH}_2(\text{CH}_2\text{OCH}_2)_2\text{CH}_2-$

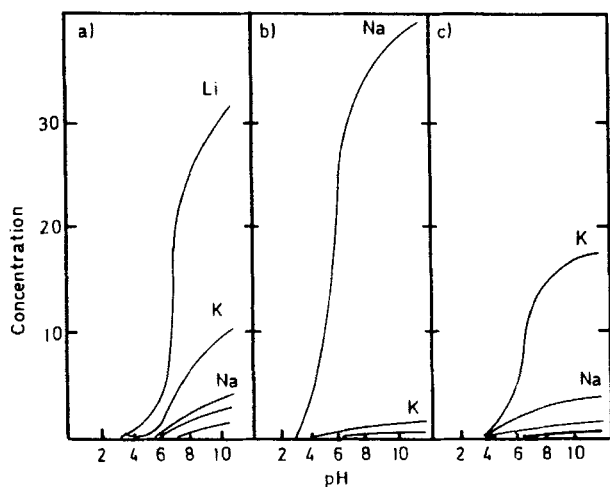


Figure 4 Concentrations of metals ($M \times 10^3$) in the chloroform phase vs. the equilibrium pH of the aqueous phase for competitive extraction of 0.25 M alkali metal cations by 0.050 M chloroform solutions of dibenzocrown ether carboxylic acids (a) 10, (b) 11 and (c) 12.

utilized to orient the carboxylic acid function and the dibenzocrown ether ring size is systematically varied from 14-crown-4 to 16-crown-5 to 18-crown-6, respectively. Results for competitive solvent extraction of alkali metal chloride and hydroxide solutions with chloroform solutions of 10–12 are presented in Figure 4. As can be seen, lipophilic dibenzocrown ether carboxylic acids 10–12 exhibit extraction selectivity for Li^+ , Na^+ and K^+ , respectively. Thus for the preorganized binding sites in dibenzocrown ether carboxylic acids 10–12 the alkali metal cation which is expected to best fit the polyether cavity is preferentially extracted.

Competitive alkali metal cation sorption by condensation polymers of dibenzocrown ether carboxylic acids

By polymerization or immobilization on support materials, crown ethers may be adapted to continuous separation processes and their toxicity alleviated.¹⁴ Blasius and co-workers¹⁵ synthesized a series of crown ether resins by polycondensation reactions of dibenzocrown ethers with formaldehyde. These resins were used as stationary phases for the chromatographic separation of alkali metal and alkaline earth cations. Retention behaviour of a given metal ion was found to be highly dependent upon the identity of the counteranion.

Condensation polymers 13–15 were formed by refluxing the acyclic or cyclic polyether carboxylic acid monomers 16–18, respectively, with formaldehyde in formic acid for 24 h.¹⁶ The precipitated polymer was washed, dried, and ground to finer than 100 mesh.

The absence of monomer decomposition during polymerization was verified by infrared spectroscopy.¹⁶

Structural representations 13–15 imply polymers with no crosslinking. This is most certainly an oversimplification since some level of crosslinking is anticipated. The elemental analysis results agreed with a partially crosslinked structure in which there is one methylene group crosslink for every six dibenzo polyether carboxylic acid monomer units.

Aqueous solutions of the five alkali metal cations (0.10 M in each) as the chlorides and hydroxides were shaken with the polyether carboxylic acid resin. In control experiments conducted with resin 14, no significant variation in alkali metal cation sorption was noted for sorption times which ranged from 60 min to 12 h. More than 85% of alkali metal cation sorption was observed after a shaking time of only 5 min. The resin was filtered, washed with water, and dried. Of the dried resin a portion was shaken with 0.10 M HCl to strip the alkali metal cations from the resin into an aqueous solution for analysis. In control experiments conducted with resin 14, complete stripping was noted for times which ranged from 0.5 to 120 min. Thus in contrast to the condensation polymers prepared from neutral dibenzocrown ethers, which showed slow exchange kinetics for metal ion salts,¹⁵ dibenzo polyether carboxylic acid resins 13–15 exhibit both rapid sorption of alkali metal cations and stripping. The reproducibility of this alkali metal cation sorption and stripping procedure for different batches of resin 15 was demonstrated.¹⁶

For comparison with a commercially available carboxylic acid ion-exchange resin, competitive alkali metal cation sorption from aqueous solution by Amberlite CG-50, a poly(methacrylic acid) resin, was investigated.¹⁶ When the pH of the aqueous alkali metal cation solution was greater than 7, the sorption selectivity was $\text{Li}^+ > \text{Na}^+ > \text{K}^+$, $\text{Rb}^+ > \text{Cs}^+$.

Dibenzo polyether carboxylic acid resins 13–15 differ from Amberlite CG-50 in that they have not only an ion-exchange site but also a polyether binding site for metal ion complexation.

Results for competitive alkali metal cation sorption from aqueous solution by dibenzo polyether carboxylic acid resins 13–15 are given in Figure 5.¹⁶ In the pH region of 7–12.5, the sorption selectivity for the acyclic polyether dicarboxylic acid resin 13 (Fig 5a) is $\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Rb}^+$, Cs^+ which closely resembles that for Amberlite CG-50 resin that contains carboxylic acid groups, but no ether linkages. In contrast, the sorption selectivities for the cyclic polyether carboxylic acid resins 14 (Fig 5b) and 15 (Fig 5c) are $\text{Na}^+ > \text{Li}^+$, $\text{K}^+ > \text{Cs}^+ > \text{Rb}^+$ and $\text{Na}^+ \gg \text{Li}^+ > \text{K}^+$, $\text{Cs}^+ > \text{Rb}^+$, respectively. Clearly the sorption selectivity is influenced by the presence

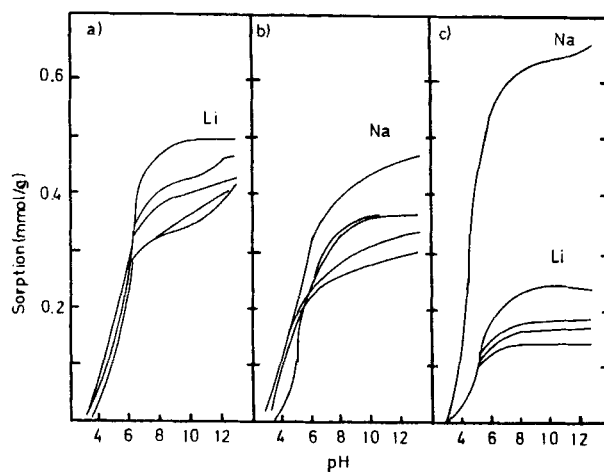
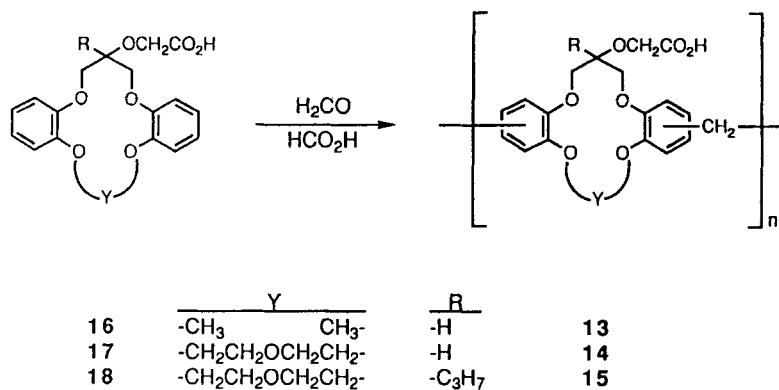


Figure 5 Sorption of alkali metal cations by dibenzo polyether carboxylic acid resin vs. the equilibrium pH of the aqueous phase for resins (a) 13, (b) 14 and (c) 15.

of crown ether rings in the resin. Based upon the relative diameters between alkali metal cations and the polyether cavities in resins 14 and 15, Na⁺ sorption selectivity would be predicted. Compared with resin 14, much higher Na⁺ selectivity is observed for resin 15. Examination of CPK space-filling models reveals that when a lipophilic propyl group in 15 extends away from the polar crown ether cavity, the carboxylic acid group is oriented directly over the crown ether cavity. Thus the much higher Na⁺ sorption selectivity observed for crown ether carboxylic acid resin 15 is attributed to preorganization of the binding site.¹³ This is the first instance in which conformational positioning of an ion-exchange group in a resin has shown an important influence on metal ion recognition.

To explore the influence of crown ether ring size variation within the polyether carboxylic acid unit upon alkali metal cation sorption selectivity, dibenzo-14-crown-4 carboxylic acid resins 19 and 20 were prepared.¹⁷ Results for competitive alkali metal cation

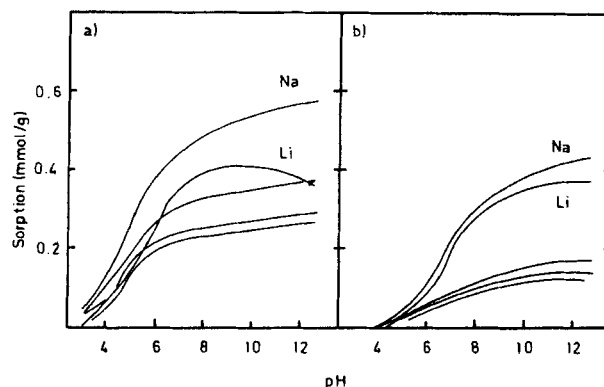
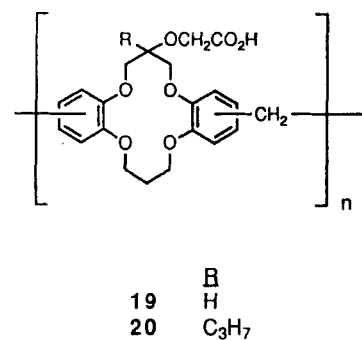


Figure 6 Sorption of alkali metal cations by dibenzo-14-crown-4 carboxylic acid resin vs. the equilibrium pH of the aqueous phase for resins (a) 19 and (b) 20.

sorption from aqueous solutions by crown ether carboxylic acid resins 19 and 20¹⁷ are presented in Figure 6. The sorption selectivities for resins 19 and 20 are Na⁺ > Li⁺ > K⁺ > Rb⁺, Cs⁺ and Na⁺, Li⁺ ≫ K⁺, Rb⁺, Cs⁺, respectively. Once again the sorption selectivity orders are found to be different from the Li⁺ sorption selectivities observed for Amberlite CG-50 resin and the acyclic polyether carboxylic acid resin 13. The sorption selectivity of the dibenzo-14-crown-4 carboxylic acid 19 for Na⁺, a metal ion which is too large to fit within the crown ether cavity, suggests formation of a complex in which

Na^+ perches on the crown ether oxygens while associating with one or more of the oxygen atoms in the side arm. The enhancement in Li^+ sorption, which is noted on going from resin **19** to resin **20**, is attributed to preorganization of the binding site in the latter which enhances recognition of that alkali metal cation that should be best accommodated within the crown ether cavity.

The rapid sorption and desorption alkali metal cations from dibenzocrown ether carboxylic acid resins suggest that such resins could be utilized as stationary phases for columns chromatographic concentration of alkali metal cations from dilute aqueous solution. In a preliminary study of this potential application, column concentration of alkali metal cations from dilute aqueous solution was investigated with dibenzocrown ether carboxylic acid resin **15** which showed good Na^+ sorption selectivity in batch sorption experiments. An aqueous solution (1.00 l, pH 10.2) with the concentration for each of the five alkali metal cations at 6.00×10^{-5} M was passed through a 0.42 cm internal diameter column of resin **15** (0.10 g) at a flow rate of 8.0 ml/min. The column was washed with 100 ml of water at the same flow rate and then stripped with 5.0 ml of 0.10 M HCl. The stripping solution was analysed and it was found that the recovery of Na^+ was 79%, while the recoveries of Li^+ , K^+ , Rb^+ and Cs^+ were all in the range of 22–27%.¹⁶ Defining the concentration factor (CF) as the ratio of the concentration of M^+ in the stripping solution to the initial concentration of M^+ in the sample solution, the concentration factor for Na^+ was 157, whereas those for Li^+ , K^+ , Rb^+ and Cs^+ were all in the range of 43–54. Thus dibenzo-16-crown-5 carboxylic acid resin **15** was demonstrated to provide efficient and selective column concentration of Na^+ from a dilute aqueous solution of five alkali metal cations.

Subsequently the stripping of alkali metal cations sorbed on a column of dibenzo-16-crown-5 carboxylic acid resin **15** was examined in detail by determination of the alkali metal cation concentrations in eluted fractions of the 5.0 ml of 0.10 N HCl.¹⁸ Results are presented in Figure 7. Most of the resin-bound alkali metal cations were eluted in the first 3.0 ml of stripping solution. The maximum CF values were 200–350 except with Na^+ for which the maximum value was nearly 700. Apparently a stronger binding ability of resin **15** for Na^+ retards the stripping of this section.

Since elution of the other alkali metal cations from dibenzo-16-crown-5 carboxylic acid resin **15** is relatively rapid when compared with the more strongly bound Na^+ , the Na^+ separation efficiency might be enhanced by varying the eluent strength. To examine this possibility, a sample solution (1.0 l, pH 10.4, 6.0×10^{-5} M in each alkali metal cation) was passed

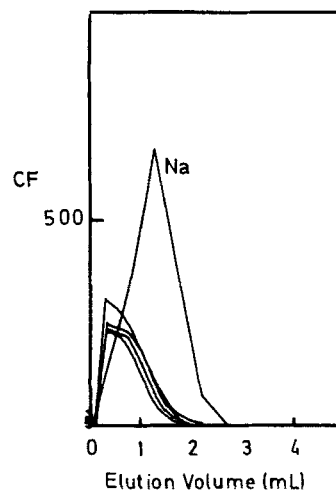


Figure 7 Concentration factors (CF) for alkali metal cations from sample solutions (1 l, pH 10.4, 6.0×10^{-4} M of each alkali metal cation) vs. the elution volume of 0.10 M HCl with a 0.10 g column of dibenzo-16-crown-5 carboxylic acid resin **15**.

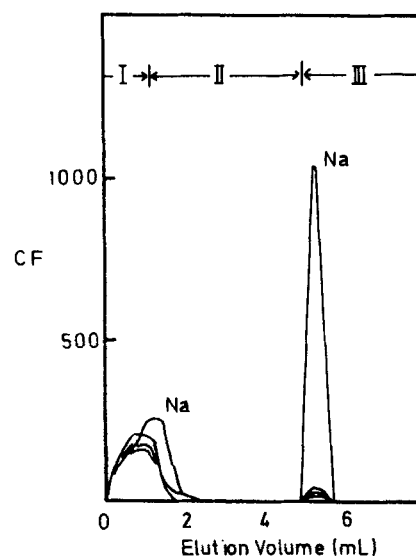


Figure 8 Concentration factors (CF) for alkali metal cations from a sample solution (1 l, pH 10.4, 6.0×10^{-4} M of each alkali metal cation) with a 0.10 g column of dibenzo-16-crown-5 carboxylic acid resin **15** vs. the elution volume of (I) 0.05 M HCl, (II) water and (III) 0.50 M HCl.

through a 1.0 g column of resin **15**, and unbound metal ions were removed by washing with water. The stripping was performed with 1.14 ml of 0.050 M HCl (weak acid strippant), then 3.80 ml of water, and then 0.50 M HCl (strong acid strippant). The results presented in Figure 8 show marked improvement in the separation of Na^+ . The maximum CF value for Na^+ in the second peak is 1030, and Na^+ comprises 84% of the alkali metal cations in the second peak. Of the Na^+ recovered from the dilute aqueous sample solution by resin **15**, 57% is in the second peak.

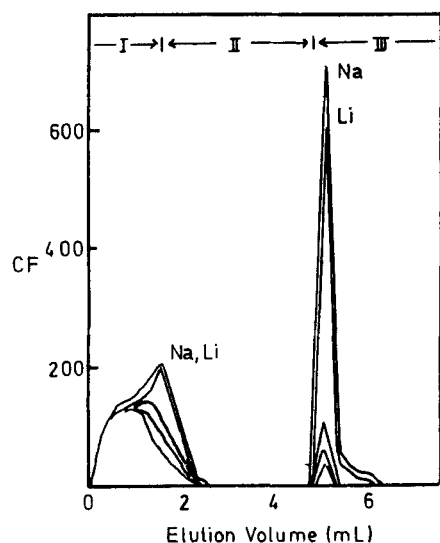


Figure 9 Concentration factors (CF) for alkali metal cations from a sample solution (1 l, pH 10.4, 6.0×10^{-4} M of each alkali metal cation) with a 0.10 g column of dibenzo-14-crown-4 carboxylic acid resin **20** vs. the elution volume of (I) 0.05 M HCl, (II) water and (III) 1.0 M HCl.

Step gradient elution of sorbed alkali metal cations was also examined for the dibenzo-14-crown-4 carboxylic acid resin **20** which exhibited Na^+ and Li^+ selectivity in batch sorption experiments.¹⁸ The sample solution (1.0 l, pH 10.4, 6.00×10^{-5} M in each alkali metal cation) was passed through a column which contained 0.10 g of resin **20**, and unbound metal cations were removed by washing with water. Stripping was performed with 1.06 ml of 0.050 M HCl, then 3.2 ml of water, and then 1.0 M HCl. The elution profile is shown in Figure 9. Of the second peak, 84% is comprised of Li^+ and Na^+ , and the maximum CF values for Li^+ , Na^+ , K^+ , Rb^+ and Cs^+ were 605, 712, 104, 35 and 70, respectively, in the second peak. Of the Li^+ and Na^+ recovered from the dilute aqueous sample solution, 46% of Li^+ and 54% of Na^+ were in the second peak.

Conventional solvent extraction systems are usually inappropriate for metal ion recovery from dilute aqueous solution due to losses of slightly soluble diluents and extractants into the sample solution. The type of concentrator column described above possesses excellent potential for the efficient and selective recovery of metal ions from such solutions.

MATERIALS AND METHODS

The procedures for competitive solvent extraction of alkali metal cations by chloroform solutions of proton-ionizable crown ethers¹⁹ and for competitive alkali metal cation sorption by proton-ionizable crown ether resins¹⁶ have been reported. Procedures for the preparation of the dibenzocrown ether carboxylic acids^{8,11,12} and their polymerization^{16,17} have been described.

ACKNOWLEDGMENTS

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