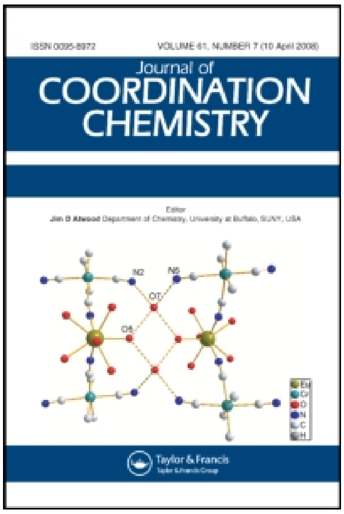

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# Selective Transport of Alkali Metal Cations in Solvent Extraction by Proton-Ionizable Dibenzocrown Ethers

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# SELECTIVE TRANSPORT OF ALKALI METAL CATIONS IN SOLVENT EXTRACTION BY PROTON–IONIZABLE DIBENZOCROWN ETHERS

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Lipophilic crown ethers with pendant proton-ionizable groups are novel metal complexing agents for use in solvent extraction of alkali metal cations. A variety of dibenzocrown ether carboxylic acids and dibenzo crown phosphonic acid monoesters have been examined to probe the effect of structural variation within the complexing agent upon selectivity and efficiency in solvent extraction. Results from competitive solvent extractions of alkali metal cations from aqueous solutions into chloroform are summarized.

Keywords: Macrocyclic polyethers, alkali metal cations, solvent extraction

## 1. INTRODUCTION

The importance 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 pendant proton-ionizable groups.[1–5] In this case metal ion extraction does not involve concomitant transfer of the aqueous phase anion into the organic phase.[6,7] This factor is very important to potential practical applications of these proton-ionizable crown ethers in which hard aqueous phase anions like chloride, nitrate and sulfate would be involved. Recently McDowell[8] has reviewed crown ethers as solvent extraction reagents. He points out that when a proton-ionizable group is attached to the crown ether framework the crown ether molecule is both a cation exchanger and a coordinator. This arrangement has the susceptibility for providing more efficient and selective extractant system than those in which an lipophilic acid is simply mixed with a crown ether.

In an earlier study[9] the effect of the polyether cavity size on competitive solvent extraction of alkali metal cations from aqueous solutions into chloroform by dibenzocrown ether carboxylic acids **1**, **2**, and **3** was examined (Figure 1). It was found that these ionizable ionophores which possess different ring sizes of 14-crown-4, 16-crown-5, and 19-crown-6, respectively, were of insufficient lipophilicity to remain completely in the organic phase. Thus, the effect of polyether cavity size on extraction selectivity for proton-ionizable crown ethers **1–3** could not be deduced. Therefore, a second generation of highly lipophilic ionizable dibenzocrown ethers **4–18** is being examined (Figure 1).

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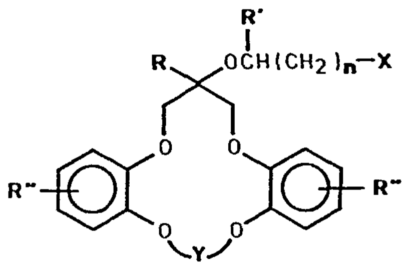

| | R | R' | R'' | n | X | Y |
|---|---|---|---|---|---|---|
| **1** | H | H | H | 0 | -COOH | $(CH_2)_3$ |
| **2** | | | | | | $(CH_2)_2O(CH_2)_2$ |
| **3** | | | | | | $(CH_2)_2O(CH_2)_2O(CH_2)_2$ |
| **4** | H | $C_8H_{17}$ | H | 0 | -COOH | $(CH_2)_3$ |
| **5** | | | | | | $(CH_2)_2O(CH_2)_2$ |
| **6** | | | | | | $(CH_2)_2O(CH_2)_2O(CH_2)_2$ |
| **7** | | | | | | $(CH_2)_2O(CH_2)_2O(CH_2)_2O(CH_2)_2$ |
| **8** | H | H | $-C(CH_3)_3$ | 0 | -COOH | $(CH_2)_2O(CH_2)_2$ |
| **9** | $C_8H_{17}$ | H | H | 0 | -COOH | $(CH_2)_2O(CH_2)_2$ |
| **10** | $C_4H_9$ | | | | | |
| **11** | $C_{10}H_{21}$ | | | | | |
| **12** | $C_{14}H_{29}$ | | | | | |
| **13** | $C_{10}H_{21}$ | H | H | 0 | -COOH | $(CH_2)_3$ |
| **14** | | | | | | $(CH_2)_2O(CH_2)_2O(CH_2)_2$ |
| **15** | $C_{10}H_{21}$ | H | H | 0 | $-\underset{\underset{OC_2H_5}{\vert}}{\overset{\overset{O}{\Vert}}{P}}-OH$ | $(CH_2)_2O(CH_2)_2$ |
| **16** | | | | 1 | | |
| **17** | | | | 2 | | |
| **18** | | | | 3 | | |

FIGURE 1 Structures of proton-ionizable dibenzocrown ethers studied.

We now report results for the competitive solvent extraction of alkali metal cations from aqueous phases into chloroform solutions of ionophores **4–18**. Effects of structural modification upon the efficiency and selectivity of solvent extraction are assessed.

## 2. EXPERIMENTAL

*Reagents.* Sources of inorganic reagents and chloroform were the same as previously described.[9] Synthetic routes to ionophores **4–14** have been described.[5,10] The preparation of crown ethers **15–18** have not been published yet.[11]

*Apparatus and procedure.* For crown carboxylic acids **4–14** the extraction procedure has been described previously and is shown in Figure 2.[9] For competitive extractions of aqueous alkali metal chloride solutions by crown ether phosphonic acid monoesters **15–18** in chloroform, a microscale extraction technique was developed.

Concentrations of alkali metal cations in aqueous solutions were determined with a Dionex Model 2000i ion chromatograph. Organic complexing agent concentrations in the chloroform phases were measured by a Cary Model 17 or Shimadzu Model 260 spectrophotometer. Measurements of pH where made with a Fischer Accumet Model 620 pH meter.

## 3. RESULTS AND DISCUSSION

In a previous investigation of alkali metal cations extraction by crown ether carboxylic acids,[9] it was shown that the selectivity orders and efficiencies for competitive extractions in multiion systems were quite different from extrapolations based on the results of single ion extractions. Therefore, competitive extractions were utilized in this study. For all of the dibenzocrown ethers studied there was no detectable loss of the ionophores from the organic phase during extraction. The cavity diameters for studied ionophores can be estimated from CPK models. The cavity diameters are compared with those for alkali metal cations in Table I. Selectivity orders and

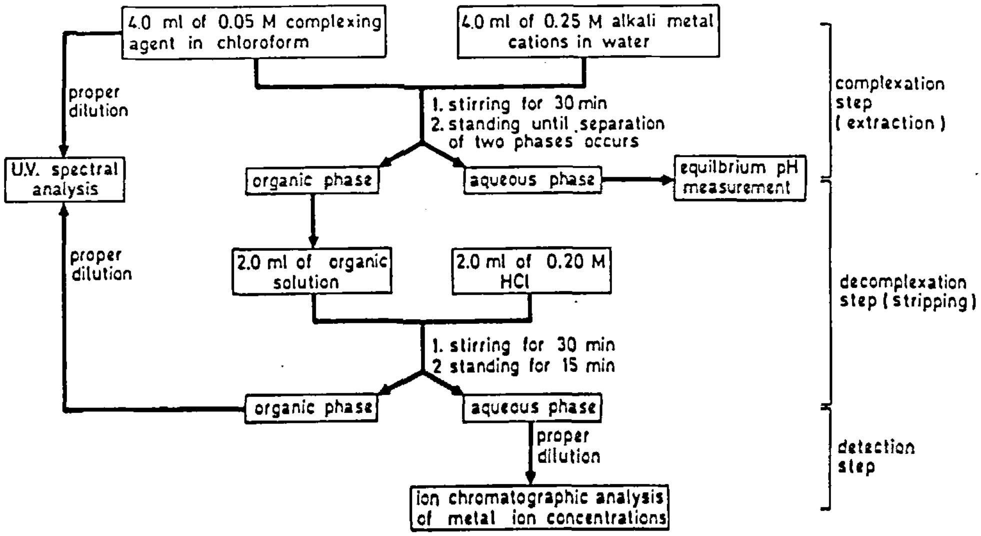

FIGURE 2 Solvent extraction technique flow chart.

TABLE I
Diameters of alkali metal cations and crown ether cavities.

| Cation | Diameter (A([12] | Crown ether | Diameter (A)[13] |
|---|---|---|---|
| $Li^+$ | 1.20 | 14-crown-4 | 1.2–1.5 |
| $Na^+$ | 1.90 | 16-crown-5 | 2.0–2.4 |
| $K^+$ | 2.66 | 19-crown-6 | 3.0–3.5 |
| $Rb^+$ | 2.96 | 22-crown-7 | 4.2–5.0 |
| $Cs^+$ | 3.38 | | |

selectivity coefficients (the ratio of the chloroform phase concentration of the best extracted metal ion to the indicated metal ion) for these ionophores are presented in Table II.

### *Effect of Ring Size Variation for Dibenzocrown Ether Carboxylic Acids with Lipophilic Octyl Groups*

Ionophores **4**, **5**, **6** and **7** provide a series dibenzocrown carboxylic acids which have the same lipophilic group, i.e. octyl, but possess different cavity sizes of 14-crown-4, 16-crown-5, 19-crown-6, and 22-crown-7, respectively. Data for concentrations of metal cations extracted into chloroform in competitive solvent extractions by **4**–**7** are shown in Figure 3.

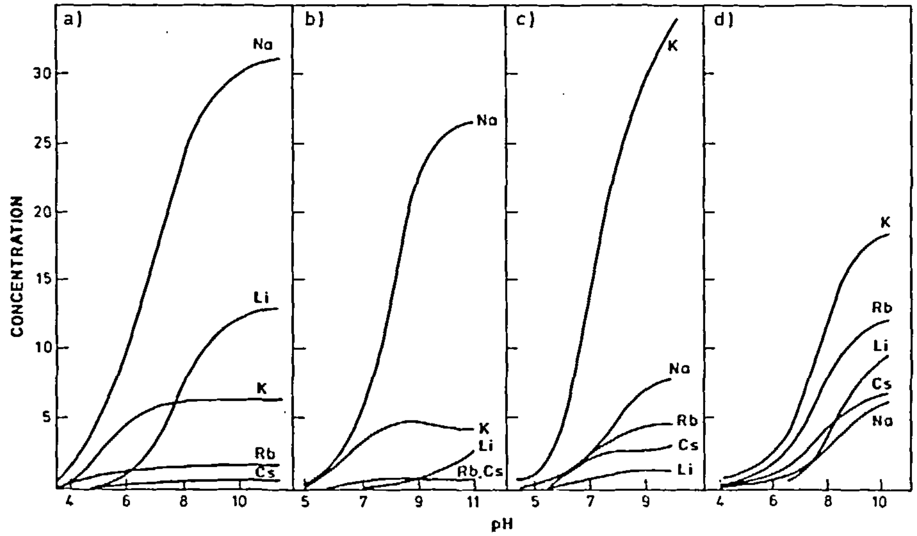

FIGURE 3 Molar concentrations of metal cations ($\times 10^3$) in the chloroform phase *vs* the equilibrium pH of the aqueous phase for competitive extraction of 0.25 M alkali metal cations by 0.050 M. (a) **4**, (b) **5**, (c) **6**, and (d) **7**.

TABLE II

Selectivity and efficiency of competitive alkali metal cation extraction from aqueous solution into chloroform by proton-ionizable dibenzocrown ethers **4–18**.

| Crown ether | Selectivity order and selectivity coefficients at pH = 10.0 | Maximal metal loading, % |
|---|---|---|
| 4 | Na > Li > K > Rb > Cs<br>2.5 5 19 60 | 100 |
| 5 | Na > K > Li > Rb > Cs<br>5 17 36 83 | 68 |
| 6 | K > Na > Rb > Cs > Li<br>4 7 11 | 100 |
| 7 | K > Rb > Li > Cs,Na<br>1.5 1.9 2.9 | 100 |
| 8 | Na > K > Li > Rb > Cs<br>5 10 17 30 | 100 |
| 9 | Na > K > Rb > Cs > Li<br>27 51 62 90 | 93 |
| 10 | Na > K > Li,Rb,Cs<br>9.4 ND* | 96 |
| 11 | Na > Li > K > Rb,Cs<br>101 168 ND | 97 |
| 12 | Na > K > Rb > Cs > Li<br>12 17 27 34 | 97 |
| 13 | Li > Na > K > Rb > Cs<br>3 7 12 13 | 100 |
| 14 | K > Na > Rb > Li > Cs<br>4 14 21 67 | 48 |
| 15 | Na > K > Li > Rb,Cs<br>21 60 ND | 100 |
| 16 | Na > K > Li > Rb,Cs<br>28 43 ND | 99 |
| 17 | Na > K > Li > Rb,Cs<br>4.6 6.5 17 | 75 |
| 18<br>(pH = 9.3) | Na > K > Li > Rb > Cs<br>1.5 1.7 3.7 4.6 | 74 |

* ND = not detected.

The alkali metal cation extraction selectivities for macrocycles **5** and **6** are in agreement with the crown cavity size concept. Thus, these ionophores are selective for sodium and potassium, respectively, as would be predicted from the relationship between the metal cation and crown cavity diameters. On the other hand, the structurally-related macrocycles with a smaller 14-crown-4 ring and a larger 22-crown-7 ring do not exhibit the anticipated extraction selectivity. Compound **4** is selective for sodium instead of lithium. Ionophore **7** exhibits poor overall selectivity compared with the other dibenzocrown carboxylic acids **4–6**. The maximal metal loadings of organic phase is equal to 100% for all the crown ether carboxylic acids in this series with the exception of **5** for which the maximal loading is 68%.

## *Effect of Lipophilic Group Attachment Site*

To determine the influence of varying the lipophilic group attachment site upon extraction selectivity and efficiency, dibenzocrown ether carboxylic acids **9**, **5**, and **8** are compared. These three compounds are structural isomers which have a common dibenzo-16-crown-5 ring. The eight-carbon lipophilic group, *i.e.* octyl, is attached to the side arm in **5** and to the polyether ring in **9**. In the case of **8**, one four-carbon lipophilic group, *i.e.* tert-butyl, is attached to each benzene ring. Results for competititve solvent extractions of alkali metal cations into chloroform by **9**, **5**, and **8** are shown in Figure 4 and in Table II.

All three ionophores are selective for sodium as would be predicted for the 16-crown-5 ring size. The selectivity is the highest for **9** in which the lipophilic group is attached to the same polyether ring carbon as the side arm. The sodium/potassium selectivity coefficient for **9** is equal to 27, while for **5** and **8** this selectivity coefficient is 5.

Examination of CPK models reveals that when the lipophilic group in **9** points away from the polar polyether ring, the ionizable group is oriented directly over the crown ether cavity. Thus, the enhanced extraction selectivity observed for **9** may be attributed to preorganization of the binding site.[13]

## *Effect of Lipophilic Group Size*

Ion complexing agents **9**, **10**, **11**, and **12** form a series in which the size of the lipophilic group attached directly to the crown ether ring is varied from butyl to octyl and decyl to tetradecyl. Such systematic structural variation allows the effect of the size of the pendant lipophilic group on the selectivity and efficiency of alkali metal cation extraction to be probed. In Figure 5, results for competitive extraction of alkali metal cations into chloroform by ionophores **10**, **9**, **11**, and **12** are compared.

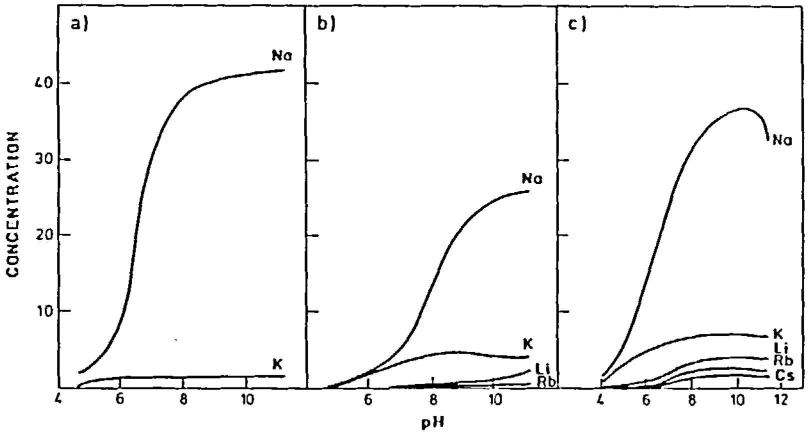

FIGURE 4 Molar concentrations of metal cations ($\times 10^3$) in the chloroform phase *vs* the equilibrium pH of the aqueous phase for competitive extractions of 0.25 M alkali metal cations by 0.050 M. (a) **9**, (b) **5**, and (c) **8**.

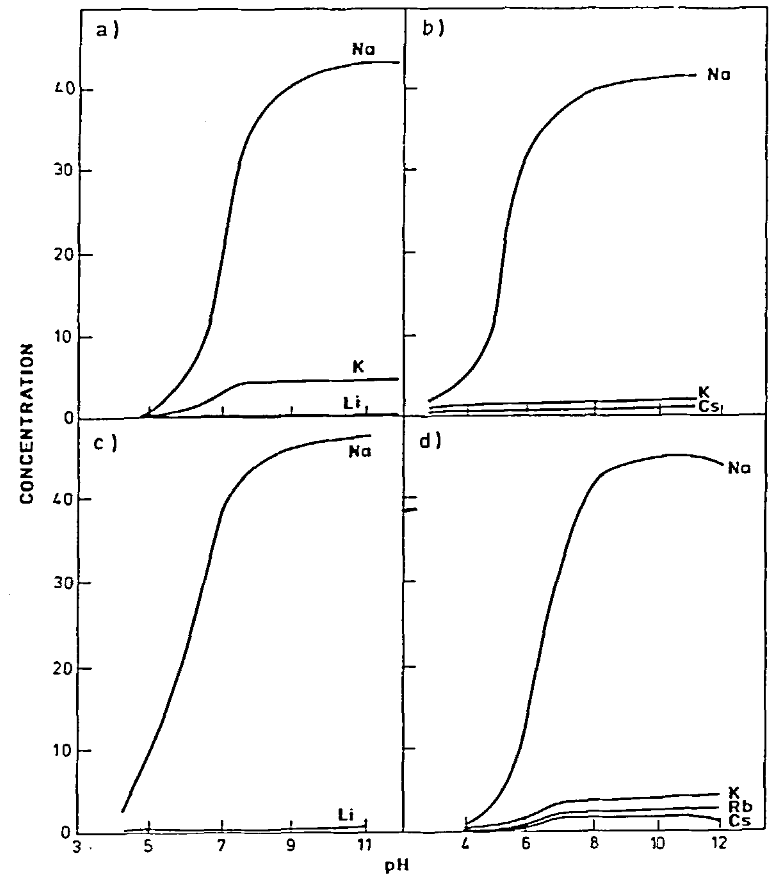

FIGURE 5 Molar concentrations of metal cations ( × $10^3$) in the chloroform phase *vs* the equilibrium pH of the aqueous phase for competitive extractions of 0.25 M alkali metal cations by 0.050 M. (a) **10**, (b) **9**, (c) **11**, and (d) **12**.

In addition, the selectivity orders and selectivity coefficients are shown in Table II. With respect to extraction efficiency, crown ether carboxylic acids **9–12** behave similarly with organic phase metal loadings of 93–97% at pH 10.0.

The differences in alkali metal extraction selectivity found for compounds **9–12** are appreciable. To interpret these data it should be recalled that the cavity size in ionophores **9–12** is that for dibenzo-16-crown-5 which is most appropriate for sodium complexation. As the alkyl group size is increased in going from **10** to **9** to **11**, the selectivity coefficient for sodium over potassium is enhanced. An explanation for this result is that a longer lipophilic group prefers to extend away from the hydrophilic polyether ring cavity which orients the carboxylate group directly over the crown ether cavity. Presumably such confinement of the ionizable group produces the enhanced selectivity. However, the selectivity diminishes in going from **11** to **12**. Perhaps the very long lipophilic tail in **12** imparts surfactant properties to the molecule which in some way diminishes the selectivity.

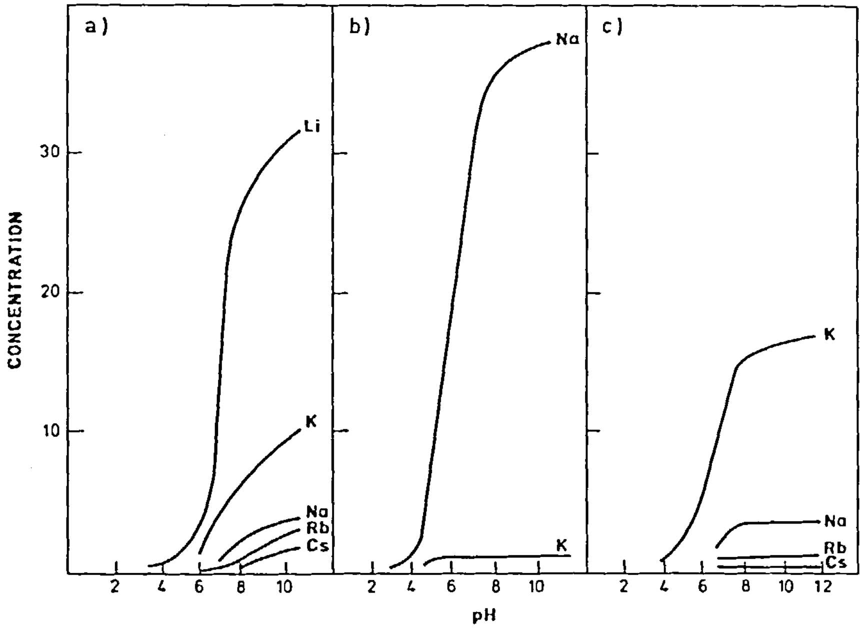

FIGURE 6 Molar concentrations of metal cations ($\times 10^3$) in the chloroform phase *vs* the equilibrium pH of the aqueous phase for competitive extractions of 0.25 M alkali metal cations by 0.050 M. (a) **13**, (b) **11**, and (c) **14**.

### *Effect of Ring Size Variation for Dibenzocrown Ether Carboxylic Acids with Decyl Lipophilic Groups*

Having established the best attachment site for the lipophilic group and size of this group, the effect of crown ether ring size variation is examined with crown ether carboxylic acids **13**, **11**, and **14**. Data for competitive solvent extraction of alkali metal cations from water into chloroform by these ionophores are shown in Figure 6. In addition, the selectivity orders, selectivity coefficients, and maximal loadings are presented in Table II.

In contrast to results obtained for compounds **4–7**, the extraction selectivity orders for **13**, **11**, and **14** change in accordance with the best fitting metal cation for that particular ring size. Thus with proper positioning of the lipophilic group, extraction selectivities for lithium, sodium and potassium are noted when the ring sizes are 14-crown-4, 16-crown-5, and 19-crown-6, respectively. The maximal loadings for **13**, **11**, and **14** are 100%, 82% and 48%, respectively. The very high sodium selectivity observed for **11** makes this compound a useful alkali metal cation extractant. Sodium is extracted with very high selectivity over potassium and lithium and no rubidium or cesium could be detected in the organic phase after extraction.

### *Effect of Ionizable Group*

Compounds **11** are **15** are structurally identical except for the ionizable group. For the former, the ionizable group is a carboxylic acid; whereas for the latter, it is a

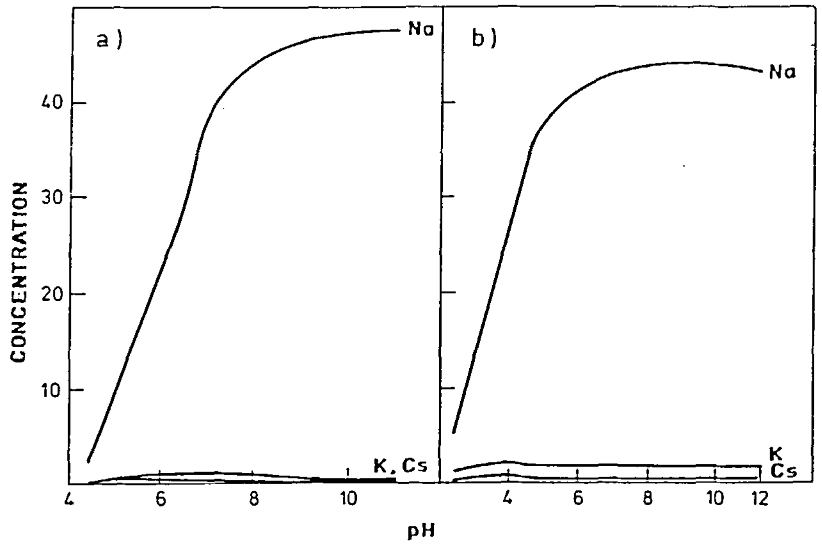

FIGURE 7 Molar concentrations of metal cations ( × $10^3$) in the chloroform phase *vs* the equilibrium pH of the aqueous phase for competitive extractions of 0.25 M alkali metal cations by 0.050 M. (a) **11** and (b) **15**.

phosphonic acid monoethyl ester. Comparison of the solvent extraction results for these two compounds (Figure 7) reveals a broader effective pH range for **15** than for **11** even though the shapes of the extraction curves are quite similar. The alkali metal cations are extracted into the organic phase by **15** even when the aqueous phase is acidic and the metal loading of the organic phase is approximately 75% at pH 5.0. Metal loading is less than 10% at pH 5.0 for **11**. This difference is readily interpretable in terms of the greater acidity of the phosphonic acid monoethyl ester group.

Although sodium is the dominant alkali metal cation extracted by both **11** and **15**, the selectivity order changes from $Na^+ \gg Li^+ > K^+ > Rb^+$, $Cs^+$ for **11** to $Na^+ \gg K^+ > Li^+ > Rb^+$, $Cs^+$ for **15**. The selectivity appears to be higher for crown ether carboxylic acid **11**. For extractions conducted with **11** and **15**, no rubidium or cesium was detected in the organic phase.

### *Effect of Sidearm Length*

Another potentially important structural variable is the length of the side arm that connects the polyether ring to the proton-ionizable group. The dibenzocrown phosphonic acid monoethyl esters **15–18** are a homologous series in which the number of methylene groups between the polyether ring and the ionizable group is varied from one to four. Such structural variation allows the effect of pendant arm length on the efficiency and selectivity of alkali metal extraction to be probed. In Figure 8 results for competitive extractions of alkali metal cations with ionophores **15–18** are shown. Selectivity orders, selectivity coefficients, and maximal metal loadings for these crown ethers are presented in Table II. The extraction efficiencies for ionophores **15** and **16** are similar with metal loadings of 99–100% at pH 10.0. For **17** and **18**

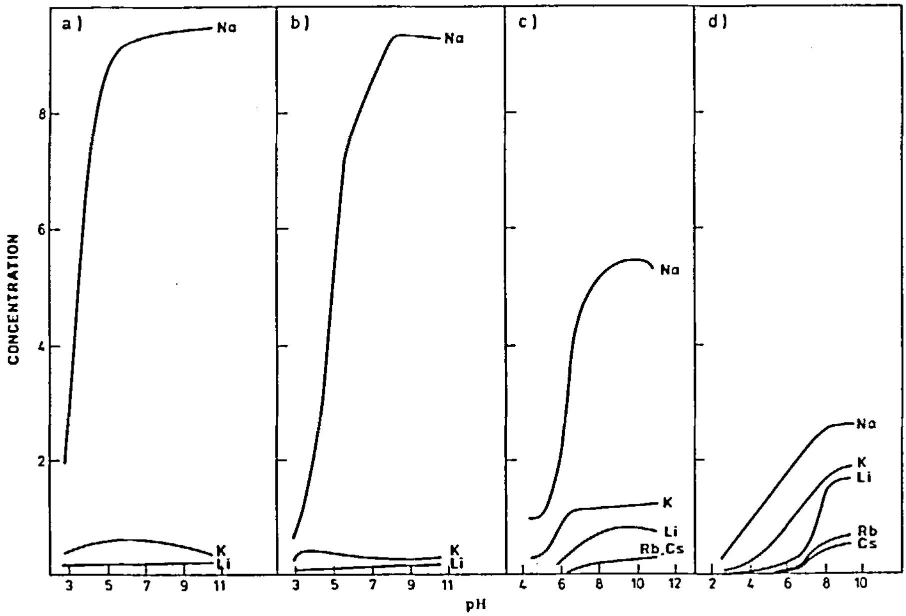

FIGURE 8 Molar concentrations of metal cations ($\times 10^3$) in the chloroform phase *vs* the equilibrium pH of the aqueous phase for competitive extractions of 0.10 M alkali metal cations by 0.010 M. (a) **15**, (b) **16**, (c) **17**, (d) **18**.

metal loading of the organic phase decreases to 74–75%. All four ionophores are selective for sodium. The extraction selectivity is high for **15** and **16** and no rubidium or cesium was detected in the organic phase. Crown ether **17** is considerably less selective. Ionophore **18** exhibits poor overall selectivity compared with the three other crown ethers of this series.

Examination of CPK models shows that in **15** and **16** the side arms is long enough to produce readily accessible conformations in which a metal cation complexed within the polyether ring can simultaneously coordinate with the pendant ionizable group. For **17** and **18**, the CPK models indicate that the ionizable group may not be easily oriented directly over crown ether cavity.

## 4. CONCLUSIONS

Based upon the results presented above several conclusions may be drawn for proton-ionizable dibenzocrown ether compounds **4–18**:

(1) The best extraction selectivity is achieved when the lipophilic group is attached to the central carbon of three-carbon bridge of the polyether ring.

(2) A longer lipophilic group prefers to extend away from the hydrophilic polyether cavity which orients the ionizable group directly over the crown ether cavity. However, a very long lipophilic tail appears to import surfactant properties to the molecule and causes a decrease of selectivity.

(3) With proper positioning of the lipophilic group, each crown ether exhibits selectivity for the alkali metal cation which should best fit within the crown ether cavity. Thus when the crown ether ring sizes are 14-crown-4, 16-crown-5 and 19-crown-6, extraction selectivity for lithium, sodium and potassium, respectively, is observed.

(4) Crown ether carboxylic acids extract alkali metal cations from neutral and basic solutions. On the other hand, crown ether phosphonic acid monoesters are effective extractants of alkali metal cations from acqueous solutions with pH > 5.

(5) The efficiency and selectivity of solvent extraction is influenced by the side arm length. When the number of methylene groups between the polyether ring and the ionizable group of 16-crown-5 is one or two, selectivity for sodium over the other alkali metal cations is the highest.

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