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Selectivity in Stripping of Alkali-Metal Cations from Crown Ether Carboxylate Complexes

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NOTE

Selectivity in Stripping of Alkali-Metal Cations from Crown Ether Carboxylate Complexes

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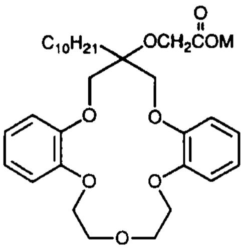
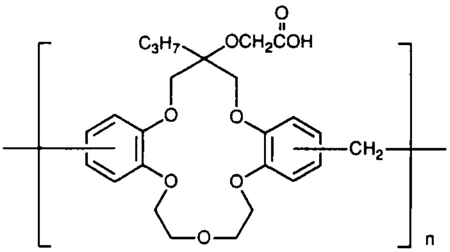
INTRODUCTION

The potential of crown ethers (macrocyclic polyethers) 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 (*1–5*). It has been shown that metal ion extraction does not require concomitant transfer of an aqueous phase anion into the organic medium (*6*). For potential practical applications of these proton-ionizable crown ethers in which hard aqueous phase anions (chloride, nitrate, sulfate) would be involved, this factor is of immense importance. In addition, the combination of ion binding cavities possessing fixed dimensions with proton-ionizable groups creates novel bifunctional chelating agents. A final factor is the ease with which extracted metal ions may be stripped from the organic phase by shaking with aqueous mineral acid.

To probe the effect of structural variations within the ionophore upon the efficiency and selectivity of solvent extraction, a variety of crown ether carboxylic acids and phosphonic acid monoesters have been synthesized (*7*). For example, the dibenzocrown ether carboxylic acid **1** has been found to provide high Na^+ selectivity for competitive solvent extraction of the five alkali-metal cation species from aqueous solution into chloroform (*8*). With an overall 82% extraction efficiency, the extraction selectivity order for **1** was $Na^+ >> K^+ > Li^+ > Rb^+, Cs^+$ with $Na^+/K^+ = 32$, $Na^+/Li^+ = 66$, and no detectable Rb^+ or Cs^+ in the chloroform phase (*8*). In other studies the influence of the organic diluent upon extraction



	M
1	H
2	Alkali metal cation



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efficiency and selectivity has been probed for such proton-ionizable crown ethers (*9*, *10*).

In the present investigation, attention is focused upon selectivity in the stripping step. Although the efficiency of metal ion stripping is often examined in solvent extraction studies, the selectivity of competitive metal ion release under different conditions is much less frequently considered. In this study, competitive stripping of metal ions from chloroform solutions of five alkali-metal crown ether carboxylates **2** by varying concentrations of aqueous hydrochloric acid is examined.

EXPERIMENTAL

Reagents and Solutions

sym-(Decyl)dibenzo-16-crown-5-oxyacetic acid (**1**) was prepared by the reported method (*8*). *n*-Butyllithium in tetrahydrofuran and sodium, potassium, rubidium, and cesium carbonates were purchased from Aldrich. Deionized water was prepared by passing distilled water through three Barnstead D8922 combination cartridges in series. Tetrahydrofuran (Fisher Scientific) was dried by distillation from benzophenone ketyl. Reagent grade chloroform (Fisher Scientific) was treated by shaking it four times with demineralized water to remove the stabilizing ethanol and saturate the chloroform with water. Standardized hydrochloric acid solutions and reagent grade dichloromethane were obtained from Fisher Scientific.

The lithium crown ether carboxylate was prepared by dissolving crown ether carboxylic acid **1** in dry tetrahydrofuran and cooling the solution to

−78°C. One equivalent of *n*-butyllithium in tetrahydrofuran was added and the solution was stirred for 30 min at −78°C. A few drops of water were added, the solvent was removed *in vacuo*, and the solid residue was dissolved in dichloromethane. The dichloromethane solution was dried over magnesium sulfate, filtered, and evaporated *in vacuo* to give **2** (M = Li).

A different procedure was utilized for the preparation of the sodium, potassium, rubidium, and cesium crown ether carboxylates **2**. A mixture of crown ether carboxylic acid **1** and 1.5 equivalents of the appropriate alkali-metal carbonate was stirred in dichloromethane for 30 min at room temperature. The mixture was filtered and the filtrate was evaporated *in vacuo* to give **2** with M = Na, K, Rb, and Cs.

Procedure and Apparatus

A chloroform solution (5.00 mL) of all five alkali-metal crown ether carboxylates **2** (0.010 *M* in each) was shaken with 5.0 mL of the aqueous hydrochloric acid solution (0.010–1.00 *M*) in a 30-mL separatory funnel for 30 min with a Burrell Model 25 wrist action shaker. The aqueous solution was separated and diluted with deionized water for determination of the alkali-metal cation concentrations with a Dionex Model 2000i ion chromatograph.

RESULTS AND DISCUSSION

Data for the alkali-metal cation concentration in the aqueous phases after competitive stripping of the chloroform solutions containing 0.050 *M* crown ether carboxylates **2** (0.010 *M* in each of the five alkali-metal carboxylates) with 0.010–1.00 *M* hydrochloric acid are shown in Fig. 1. In addition, the stripping efficiency as a function of the initial hydrochloric acid concentration is summarized in Table 1.

When the hydrochloric acid concentration was 0.010–0.050 *M* (pH 2.0–1.3), the competitive stripping selectivity ordering is $Cs^+ > Rb^+ > Li^+ > K^+ > Na^+$ (Fig. 1). This is the reverse of the selectivity order for competitive solvent extraction of alkali-metal cations into chloroform by **1** (*8*). Thus, under these conditions in which the relative initial concentrations of hydrochloric acid in the aqueous phase and crown ether carboxylates in the chloroform phase vary from 1:5 to 1:1, Na^+, the alkali-metal cation which is best extracted into chloroform by **1**, is stripped the poorest.

Even when the hydrochloric acid solution has pH 1 and the ratio of hydrochloric acid to crown ether carboxylate concentrations is 2:1, Na^+ is not stripped completely and 8% of this alkali-metal cation remained in the chloroform phase. Only when the initial hydrochloric acid concentra-

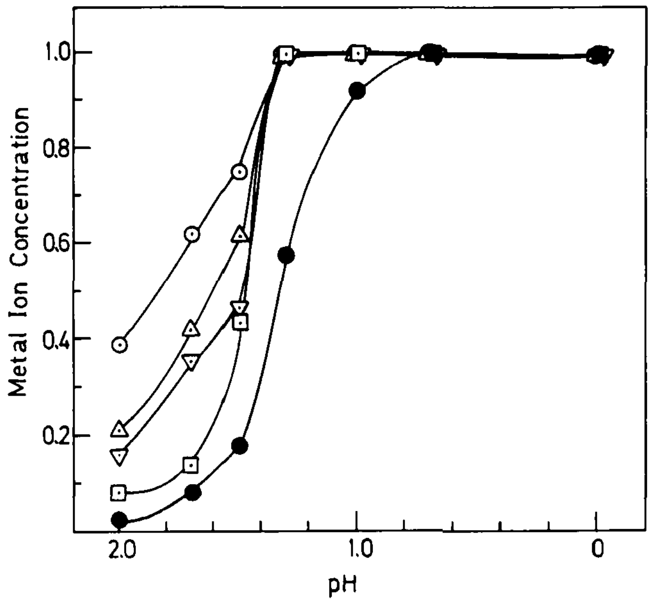

FIG. 1. Molar concentrations of alkali metal cations (× 10^2) in the aqueous phase after stripping of a 0.050-*M* solution of **2** in chloroform vs the initial pH of the aqueous hydrochloric acid stripping solution. Li^+ (▽), Na^+ (●), K^+ (□), Rb^+ (△), Cs^+ (○).

TABLE 1

Effect of Initial Hydrochloric Acid Concentration upon the Stripping Efficiency of Alkali-Metal Cations from Alkali-Metal Crown Ether Carboxylates **2**

Initial HCl concentration (*M*)	Stripped alkali-metal cations (%)	
	Theoretical	Observed[a]
0.010	20	17
0.020	40	32
0.030	60	50
0.050	100	88
0.10	100	98
0.20	100	100
1.00	100	99

[a] Estimated uncertainty is ±2%.

tion ≥ 0.20 *M* (Fig. 1 and Table 1) is Na^+, as well as the other four alkali-metal cations, completely stripped from the organic phase.

The selective release of complexed metal ions from proton-ionized crown ether complexes possesses the potential for application in metal ion separation processes. Very recently we have explored the use of crown ether carboylic acid resin **3** in the selective column concentration of the five alkali-metal cations from dilute aqueous solutions (*11*). By gradient elution of the sorbed alkali-metal cations with a small portion of 0.050 *M* hydrochloric acid, then water, and then 0.50 *M* hydrochloric acid, a fraction was obtained which contained Na^+ in 84% purity.

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