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Solvent Extraction of Alkali Metal Cations from Aqueous Solutions by Crown Ether Carboxylic Acids

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Abstract

Competitive solvent extractions of alkali metal cations from aqueous solutions by the crown ether carboxylic acids *sym*-dibenzo-13-crown-4-oxyacetic acid, *2*; *sym*-dibenzo-19-crown-6-oxyacetic acid, *3*, and *sym*-dibenzo-14-crown-4-oxyacetic acid, *4*, in chloroform have been conducted. Influences of aqueous phase pH and metal ion concentrations upon the concentrations of metals and complexing agent in the organic phase are assessed and compared with those reported for *sym*-dibenzo-16-crown-5-oxyacetic acid, *1*. Extraction selectivity orders of $K > Rb > Na \approx Cs > Li$, $K > Rb \geq Na \approx Cs > Li$, and $K > Na > Rb > Cs \approx Li$ were found for extractions using *2*, *3*, and *4*, respectively. In terms of selectivity and metal extractability, *3* surpasses *1*, *2*, and *4*.

INTRODUCTION

Potential practical applications of crown ethers (macrocyclic polyethers) for the selective removal of metal ions from natural and industrial water sources are strongly affected by the influence of the aqueous phase anion upon the ability of the macrocyclic compounds to extract metal ions from water into organic solvents. The anions normally encountered in process solvent extraction are chloride, nitrate, and sulfate. Distribution coefficients between an aqueous phase and a hydrocarbon or chlorocarbon phase which

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contains a crown ether are too low to be useful for metal chlorides, nitrates, or sulfates (*1–4*).

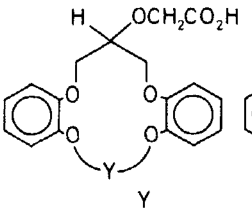
Recent efforts to conntrol these unfavorable distribution coefficients involve the addition of compounds such as tributylphosphate, di(2-ethylhexyl)phosphoric acid, nonylphenol, and 2-ethylhexanol to the organic phase to hydrogen bond with the anion and make it more lipophilic (*1–3*). For extraction of Cs and Sr nitrates into organic media, substantial synergistic effects are noted when both a crown ether and an anion lipophilizing agent are employed (*3*).

An alternative solution to this problem is the use of macrocylic complexing agents for which metal extraction does not involve concomitant transfer of the aqueous phase anion into the organic phase. Such compounds might resemble acyclic carboxylic acid ionophores, such as monensin and nigericin, which, when ionized, effectively transport mono- and divalent cations across membranes (5).

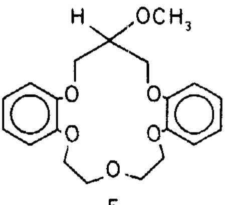
We recently reported the results of an investigation in which the crown ether carboxylic acid *1* was utilized to extract alkali metals from aqueous solutions of metal chlorides or sulfates into chloroform (*6*). It was demonstrated that metal extraction did not involve the transfer of the aqueous phase anion into the organic medium. The extraction efficiency and selectivity observed with *1* surpassed those of the closely related, nonionizable crown ether 5 and of phenoxyacetic acid.

In a second study (*7*) the extraction of the alkaline earth metals Mg, Ca, Sr, and Ba from aqueous solutions of the metal chlorides into chloroform by the crown ether carboxylic acids *1–3* was explored. All of the crown ether carboxylic acids were found to be more efficient agents for alkaline earth metal extraction than was the neutral crown ether 5. However, variation of the polyether ring size changed both the extraction efficiencies and selectivities of the crown ether carboxylic acids.

In view of these findings, it seemed reasonable to expect that variation of



	Y
1	$CH_2CH_2OCH_2CH_2$
2	CH_2CH_2
3	$CH_2CH_2OCH_2CH_2OCH_2CH_2$
4	$CH_2CH_2CH_2$



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the ring size might also influence the efficiencies, selectivity, and selectivity orders for extraction of alkali metals by crown ether carboxylic acids. We now report results for the competitive solvent extractions of alkali metals using crown ether carboxylic acids *2–4* and compare these results with those obtained previously with *1*.

EXPERIMENTAL

Apparatus

Alkali metal cation concentrations in aqueous phases were determined with a Dionex Model 10 ion chromatograph. Concentrations of the organic complexing agent in the chloroform phases were measured using a Cary 17 ultraviolet-visible spectrophotometer. A Fisher Scientific Accumet Model 620 pH meter with a Fisher Scientific E-5A glass body combination electrode was used for the pH measurements.

Reagents

Synthetic routes to *sym*-dibenzo-13-crown-4-oxyacetic acid, *2*; *sym*-dibenzo-19-crown-6-oxyacetic acid, *3*; and *sym*-dibenzo-16-crown-5 methyl ether, 5, have been reported previously (*6, 7*). *sym*-Dibenzo-14-crown-4-oxyacetic acid, *4*, was prepared by the reaction of *sym*-hydroxydibenzo-14-crown-4 (*8*) with sodium hydride in tetrahydrofuran followed by the addition of bromoacetic acid. Sources of inorganic chemicals include: Aldrich (Milwaukee, Wisconsin): LiCl, NaCl, RbCl, RbOH, CsCl, CsOH; MC & B (Norwood, Ohio): LiOH, NaOH; Baker (Phillipsburg, New Jersey): KCl; Merck (Rahway, New Jersey): KOH. Demineralized water was prepared by passing distilled water through three Barnstead D8922 combination cartridges in series. Reagent grade chloroform (MCB, Cincinnati, Ohio, Omnisolve) was treated by shaking four times with demineralized water to remove the stabilizing ethanol and saturate the chloroform with water.

Procedure

A chloroform solution (5.0 mL) of the complexing agent and the aqueous alkali metal chloride and hydroxide solution (5.0 mL) were shaken for 15 min in a 30-mL separatory funnel at room temperature (20–23°C). The 5.0 mL phases were separated and the equilibrium pH of the aqueous phase was measured. A small sample (0.025 mL) of the organic phase was removed and diluted with chloroform in a 10-mL volumetric flask. Measurement of the adsorption at 273–274 nm determined the concentration of all forms of the complexing agent in the chloroform phase. Compounds *2–4* in chloroform exhibited maxima at 273–274 nm with $\varepsilon = 3600$ (*7*), 4170 (*7*), and 5040, respectively. Neither the position nor the intensity of the maxima varied significantly when the crown ether carboxylic acids were converted into their carboxylate forms. The remainder of the chloroform phase was shaken with 5.0 mL of 0.1 *N* HCl for 20 min to strip the metals from the organic phase into aqueous solution for analysis by ion chromatography.

RESULTS AND DISCUSSION

In our previous studies of metal extraction by crown ether carboxylic acids (*6, 7*) it was observed that the efficiencies and selectivity orders for competitive extractions may be quite different from expectations based upon the results of single ion extractions. Therefore, competitive extractions were utilized throughout this study.

Extraction of Alkali Metals by *sym*-Dibenzo-13-crown-4-oxyacetic Acid, *2*

Results from competitive extractions of aqueous solutions of Li, Na, K, Rb, and Cs chlorides and hydroxides in which each initial cationic concentration was 0.060 and 0.250 *N* by chloroform solutions of *2* (initial concentration = 0.050 *N*) are recorded in Fig. 1.

The general curve shapes for alkali metal concentrations in the chloroform phase vs the equilibrium pH of the aqueous phase are similar to those found for alkaline earth metal extractions using this crown ether carboxylic acid (*7*). In acidic regions with $\mathrm{pH} < 4$, low extractability of all alkali metals is observed. As the equilibrium pH of the aqueous phase increases above 4, the concentration of metals in the chloroform phase rises sharply and reaches a maximum value when $\mathrm{pH} = 6$. Further pH enhancements cause an abrupt decrease in the concentration of metals in the organic phase. Above a pH of approximately 7.5 the chloroform phase metals concentration remains essentially constant at a low value.

An important factor in determining the curve shapes for the chloroform phase metals concentrations vs the pH of the aqueous phase is the concentration of all forms of the complexing agent (both the carboxylate and carboxylic acid forms) in the organic phase (in Fig. 1). As the pH increase from 4 to 5, this concentration decreases by 15–25%. Marked decreases of complexing agent concentration in the chloroform phase attend further pH increases with minimal values (approximately 2% of the initial concentration) being noted above $\mathrm{pH} = 8$.

A dependence of the metals concentrations in the chloroform phase upon

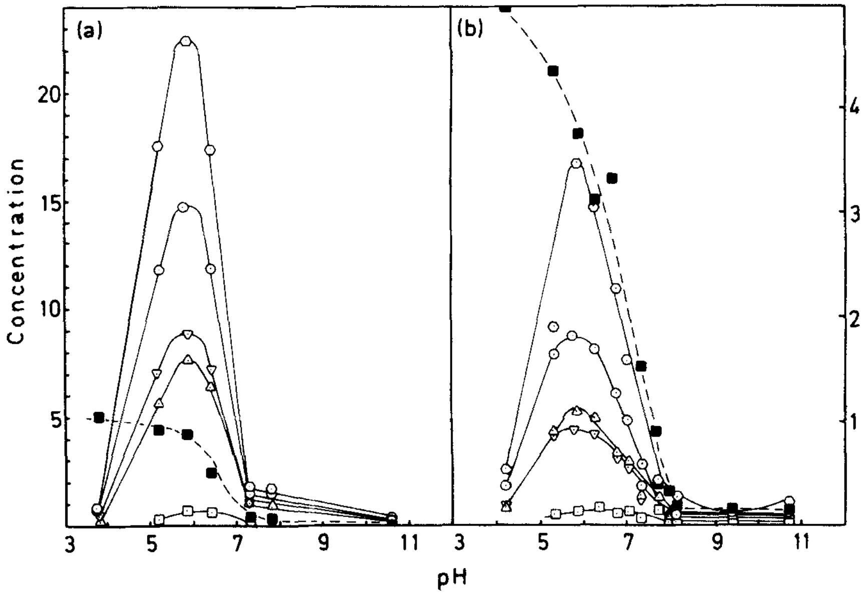

FIG. 1. Concentrations of metals and of complexing agent (× 10^2) in the chloroform phase vs the pH of the aqueous phase for competitive extractions of alkali metal cations by 0.05 *N* *2*. (a) [Metals] × 10^4. Initial concentrations: Each alkali metal cation = 0.060 *N*. (b) [Metals] × 10^3. Initial concentrations: Each alkali metal cation = 0.25 *N* (■ = complexing agent, □ = Li, △ = Na, ⬡ = K, ○ = Ra, ▽ = Cs).

the initial salt concentrations in the aqueous phase is also evident. Increasing the salt concentration raises the organic phase metals concentrations. This observation is quite different from that made for alkaline earth metal extractions using this crown ether carboxylic acid in which salt concentration increases in the aqueous phase lowered the chloroform phase metals concentrations (*7*).

The selectivity order noted at pH = 6 for extractions using *2* is K > Rb > Na ≈ Cs > Li. From an examination of Corey-Pauling-Kortun (CPK) space-filling models, the polyether cavity diameter is estimated to be < 1.2 Å which is smaller than the 1.36 Å diameter of Li (*9*). Therefore the observed selectivity order probably reflects only interactions of the alkali metal cations with the carboxylate portion of the complexing agent.

The selectivity in alkali metal extractions using *2* is rather poor. Under the best conditions (pH = 6 and 0.25 *N* salt concentations) the concentration ratio of K to the other alkali metals is 1.9, 3.1, 3.8, and 87 for Rb, Na, Cs, and Li, respectively.

Extraction of Alkali Metals by *sym*-Dibenzo-14-crown-4-oxyacetic Acid, *4*

Complexing agents derived from *4* and *2* have identical numbers and types of oxygen atom binding sites. However, the larger polyether cavity (estimated to be 1.2–1.5 Å from CPK models) may allow for stronger interactions of small alkali metal cations with the crown ether protion of the complexing agent.

The influence of the aqueous phase equilibrium pH upon the concentrations of metals and all forms of the complexing agent in the chloroform phase is recorded in Fig. 2 for extractions of aqueous alkali chloride and hydroxide solutions which were 0.060 or 0.25 *N* in each cationic species with 0.050 *N* chloroform solutions of *4*.

With the exception of improved extractability of K with *4* at low pH, the general curve shapes for the metals and complexing agent (all forms) concentrations in the organic phase as a function of the aqueous phase equilibrium pH are quite similar for extractions using *4* and *2*. However, the maximum chloroform phase metals concentrations obtained with *4* are approximately double those found with *2*. At alkaline pH's the concentration

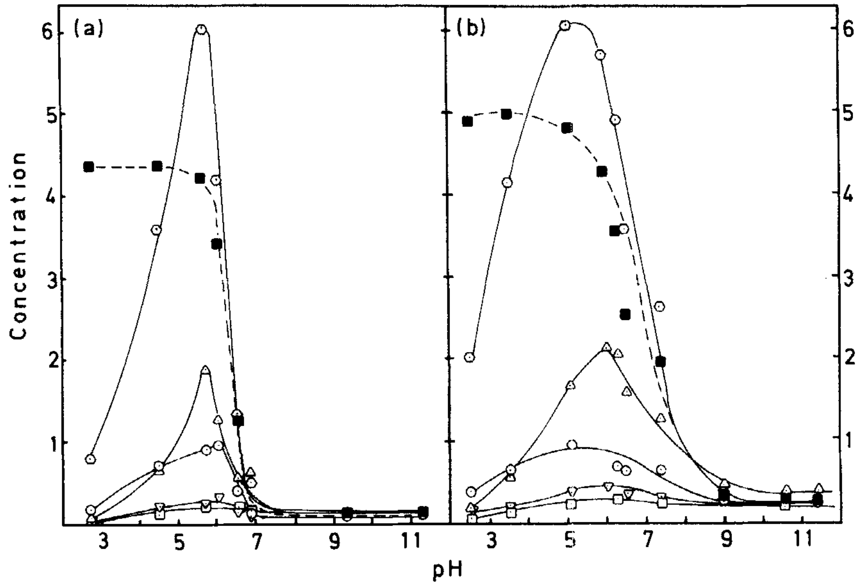

FIG. 2. Concentrations of metals (× 10^3) and complexing agent (× 10^2) in the chloroform phase vs the pH of the aqueous phase for competitive extractions of (a) 0.060 *N* and (b) 0.25 *N* alkali metal cations by 0.050 *N* *4* (■ = complexing agent, □ = Li, △ = Na, ○ = K, ○ = Rb, ▽ = Cs).

of complexing agent in the chloroform phase is only 3–4% of the initial concentration of *4*. In contrast to the results obtained for *2* (*vide supra*) and previously reported for *1* (*6*), the maximum metals concentrations in the chloroform phase are apparently insensitive to changes in the aqueous phase salt concentration for extractions involving *4*.

The selectivity order for extractions with *4* at the pH for maximum extractability is K > Na > Rb ≈ Cs > Li. This is similar to the selectivity order noted for *2* with the exception of a better competitive extraction of Na. Presumably this change arises from the interaction of sodium cations with both the polyether and carboxylate portions of the complexing agent derived from *4*.

The selectivity observed for extractions with *4* is somewhat better than that noted with *2*. For the higher initial aqueous phase salt concentration and pH = 5.4, the concentration ratio of K to the other alkali metals is 3.2, 6.4, 14.5, and 29 for Na, Rb, Cs, and Li, respectively.

Extraction of Alkali Metals by *sym*-Dibenzo-19-crown-6-oxyacetic Acid, *3*

Crown ether carboxylic acid *2* and the previously reported *1* differ by the inclusion of an additional ethyleneoxy bridge in the latter. Addition of another ethyleneoxy bridge to *1* gives *3*.

Data for competitive extractions of aqueous alkali chloride and hydroxide solutions in which each cation was initially 0.060 or 0.25 *N* with 0.050 *N* chloroform solutions of *3* are presented in Fig. 3.

The curve shapes for the metals and complexing agent (all forms) concentrations in the organic phase as a function of the aqueous phase pH more nearly resemble those obtained earlier for extractions with *1* (*6*) rather than those found for *2* or *4*. Thus the metals concentration in the chloroform phase is very low when pH < 4. From pH = 4 the metals concentration rises sharply with increasing pH and reaches a maximum at pH = 7. Increasing the pH from 7 to 10 causes a gradual decrease in the chloroform phase metals concentration which is followed by constant, but very significant concentration levels in the region pH = 9–11. The much higher metals levels in the chloroform phase for extractions at alkaline pH which utilize *3* rather than *2* or *4* is attributable to concomitant higher complexing agent concentrations. In the region of the basic plateau (pH = 9–11), 24 and 43% of the initial concentration of *3* remains in the chloroform layer after extracting aqueous solutions in which each alkali metal cation is 0.060 and 0.25 *N*, respectively.

The selectivity order at the pH of maximum metal extractability using *3* is K > Rb ≥ Na ≈ Cs > Li and differs from the order of K > Na > Rb ≈ Cs > Li reported for *1* (*6*). The selectivity observed with *3* surpasses that

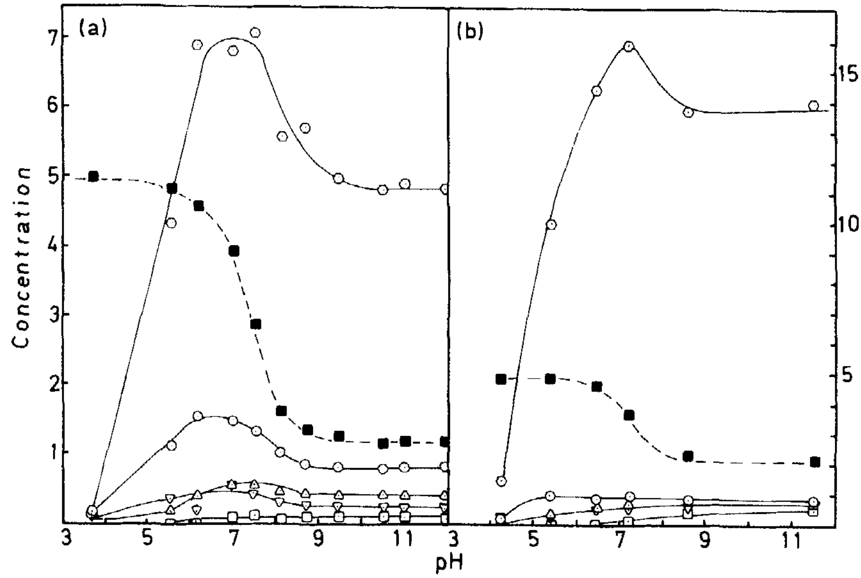

FIG. 3. Concentrations of metals (× 10^3) and complexing agent (× 10^2) in the chloroform phase vs the pH of the aqueous phase for competition extractions of (a) 0.060 *N* and (b) 0.25 *N* alkali metal cations by 0.050 *N* *3* (■ = complexing agent, □ = Li, △ = Na, ⬡ = K, ○ = Rb, ▽ = Cs).

found for *1*, *2*, and *4*. For the 0.25 *N* initial cations concentration and pH = 7.2, the ratio of K concentration to that of the other individual alkali metals is 16, 23, 34, and 87 for Rb, Na, Cs, and Li, respectively.

Comparison of Alkali Metal Extractions by Crown Ether Carboxylic Acids, *1–4*

In terms of extraction efficiency and selectivity, *4* is the best of the four crown ether carboxylic acids examined and *2* is the worst.

The polyether cavity diameters of *2*, *4*, *1*, and *3* are estimated from CPK models to be <1.2 Å, 1.2–1.5 Å, 2.0–2.4 Å, and 3.0–3.5 Å, respectively. Ionic diamers of the alkali metal cations are Li, 1.36 Å; Na, 1.96 Å; K, 2.66 Å; Rb, 2.98 Å; and Cs, 3.30 Å (*9*). The selectivity orders at the pH for maximum extractabilities vary with increasing polyether cavity size as follows: $K > Rb > Na \approx Cs > Li$ for *2*; $K > Na > Rb > Cs \approx Li$ for *4*; $K > Na > Rb \approx Cs > Li$ for *1* (*6*); and $K > Rb > Na \approx Cs > Li$ for *3*. These selectivity orders may be rationalized by considering the relative complexing abilities of the polyether cavities and carboxylate portions of the complexing agents.

Due to the very small polyether cavity size in the carboxylate form of *2*, interactions with alkali metals should be confined largely or soley to the carboxylate group. Therefore, the selectivity order K > Rb > Na ≈ Cs > Li is assumed to be that for the ionic group of a crown ether carboxylate species in competitive alkali metal extractions. The change to selectivity orders of K > Na > Rb > Cs ≈ Li for *4* and K > Na > Rb ≈ Cs > Li for *1* indicates strengthened interactions of Na with the complexing agent. Presumably this arises by interactions of Na with the polyether cavities. For *4*, Na is too large to insert completely into the polyether cavity which suggests that the cation may be "sandwiched" between the carboxylate and polyether portions of the complexing agent. For *1*, the polyether cavity may accommodate Na. As the polyether cavity size is increased further in *3*, the selectivity order becomes K > Rb > Na ≈ Cs > Li. The relative increase in Rb extractability is explainable in terms of interactions with the polyether cavity which is of the appropriate size for Rb.

The predominant extraction of K by all of the complexing agents suggests strong interactions of the cations with the carboxylate portions of the complexing agents. However, the changes in selectivity orders and the enhanced total metals extractability which result from increasing the polyether cavity size indicates the presence of supplemental metal–polyether interactions within the extraction complex.

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