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METAL ION COMPLEXATION
BY IONIZABLE CROWN ETHERS

Progress Report
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I. ABSTRACT

Research conducted since the last progress report includes the synthesis and characterization of twenty three novel proton-ionizable crown ether compounds. Metal ion complexation behavior of new and previously-synthesized proton-ionizable crown ether compounds has been probed by solvent extraction and transport across polymer-supported liquid membranes. The behavior of neutral polyether and proton-ionizable polyether ligands in polymeric membrane electrodes has been assessed. Studies of the use of proton-ionizable crown ethers for separation of lithium isotopes were initiated. Also, the thermodynamics of interactions between alkali metal cations and ionized crown ethers have been probed by titration calorimetry.

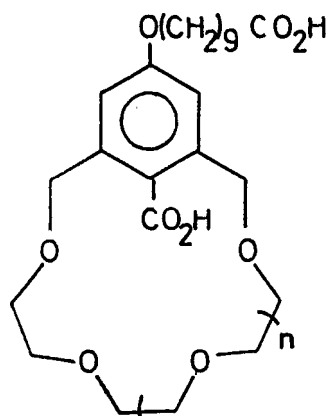
II. ACCOMPLISHMENTS

A. Synthesis

For continuing investigations of the influence of structural variation within proton-ionizable crown ethers upon their efficiency and selectivity in metal ion separation processes, twenty three novel mono- or di-ionizable crown ether compounds have been synthesized.

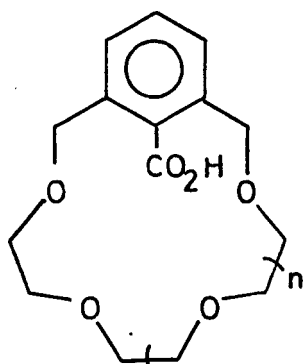
1. Mono-ionizable Crown Ethers

Our earlier studies have involved proton-ionizable crown ethers in which the acidic functional group was attached to the polyether framework with a flexible arm. To examine the structural variation of fixing the acidic group position so it points directly into the polyether ring, the series of lipophilic proton-ionizable crown ethers 1-4 was prepared. The non-lipophilic analogs 5-7 were previously reported by Cram and coworkers¹ and 5-8 by Reinhoudt and coworkers.^{2,3} By adaptation of the procedure of Reinhoudt and coworkers, the series of lipophilic crown carboxylic acids 1-4 was realized.



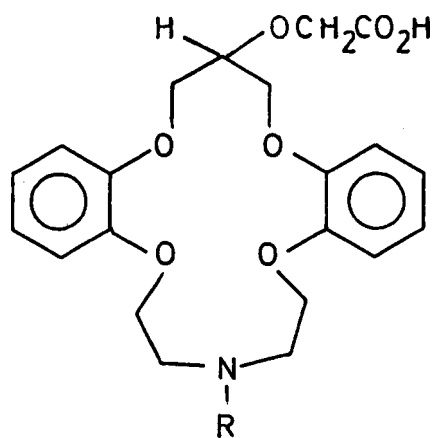
1
2
3
4

n
1
2
3
4



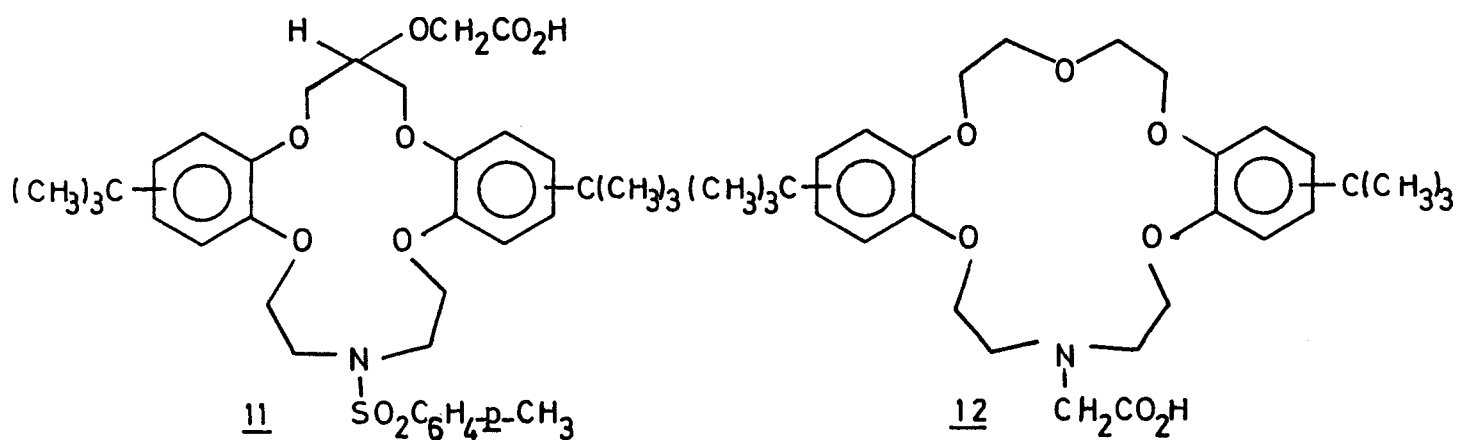
5
6
7
8

n
1
2
3
4



9
10

R
-(CH₂)₉CH₃
-SO₂C₆H₄-p-CH₃

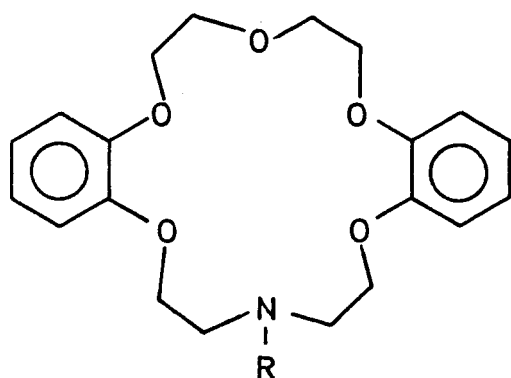


11

-SO₂C₆H₄-p-CH₃

12

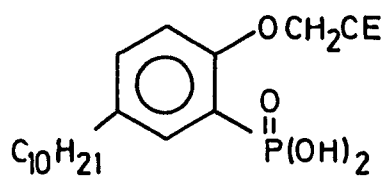
-CH₂CO₂H



13

14

R
-CH(CO₂H)C₈H₁₇
-C₆H₄(NO₂)(OH)



15

16

17

18

19

CE

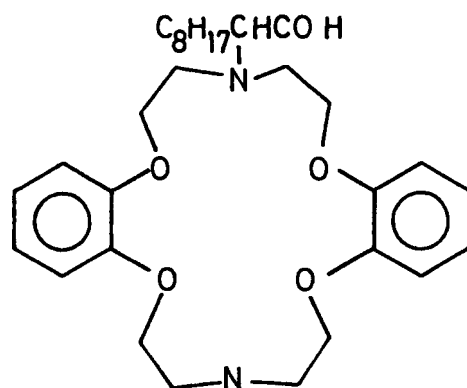
14C4

15C5

18C6

21C7

24C8



20

In addition, the non-lipophilic crown carboxylic acids 5-8 were prepared for investigations of the thermodynamics of alkali metal cation complexation by the corresponding crown carboxylates using titration calorimetry.

To investigate the structural effect of substituting a nitrogen atom for one of the oxygens in the polyether ring, several proton-ionizable crown compounds 9-14 derived from monoaza crown ethers were synthesized. Of this series, compounds 9-13 are lipophilic crown carboxylic acids. Compound 14 has a pendant *p*-nitrophenol unit which gives a chromogenic response when ionized.

2. Di-ionizable Crown Ethers

To provide proton-ionizable crown ethers capable of forming one-to-one complexes with divalent metal ions, two different type of di-ionizable crown ethers have been prepared.

The first type is a series of crown phosphonic acids 15-19. These compounds possess a single, di-ionizable functional group.

The second type of di-ionizable crown ethers is derived from a diaza crown ether possessing two mono-ionizable groups attached to a common polyether framework. Compounds of this type which were synthesized include the crown dicarboxylic acid 20 and crown ethers 21 and 22 which bear two pendant chromogenic groups. The latter two compounds are structural variations of chromogenic crown compound 23 whose synthesis and extremely high extraction selectivity for Hg(II) were described in the last progress report.⁴ Synthetic attempts to prepare crown dicarboxylic acid 24, a structural isomer of 20, were unsuccessful.

B. Metal Ion Complexation by Proton-Ionizable Crown Ethers

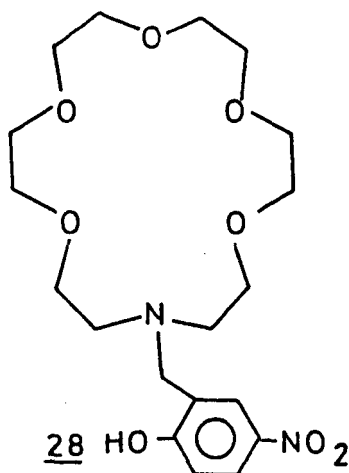
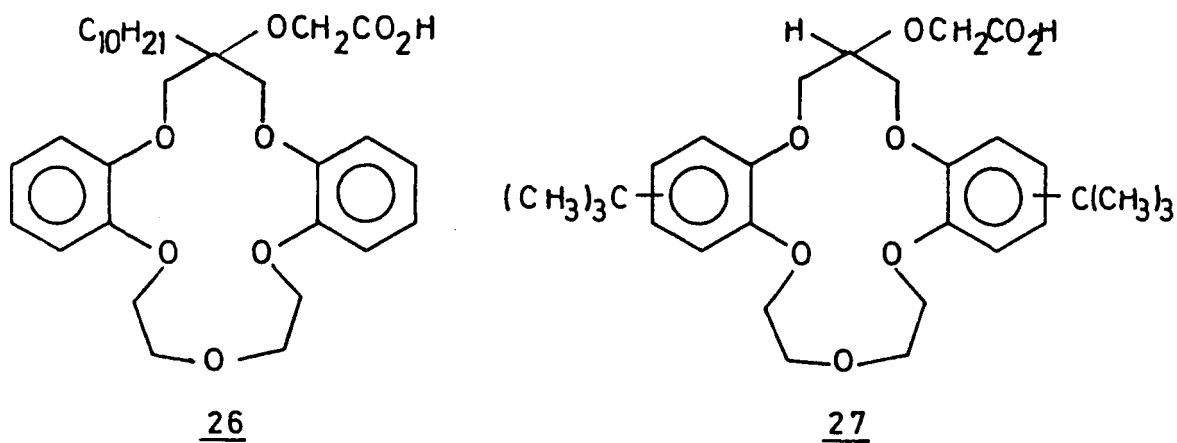
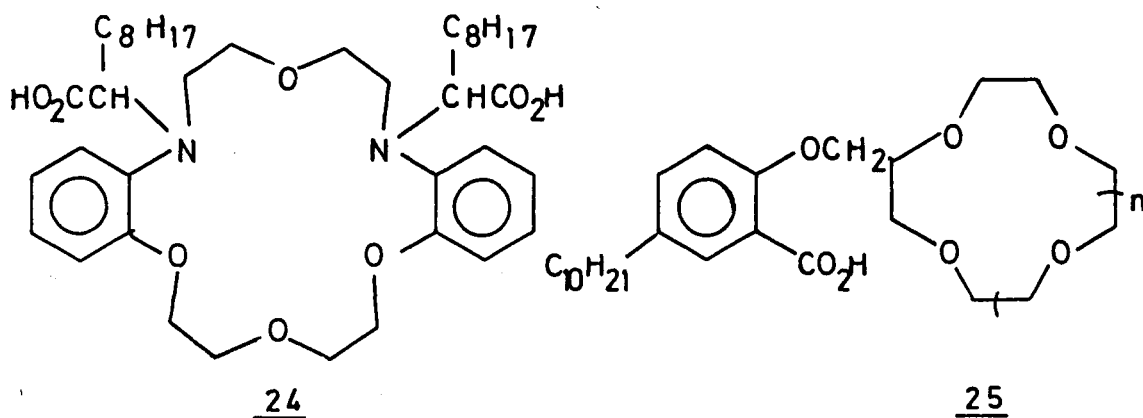
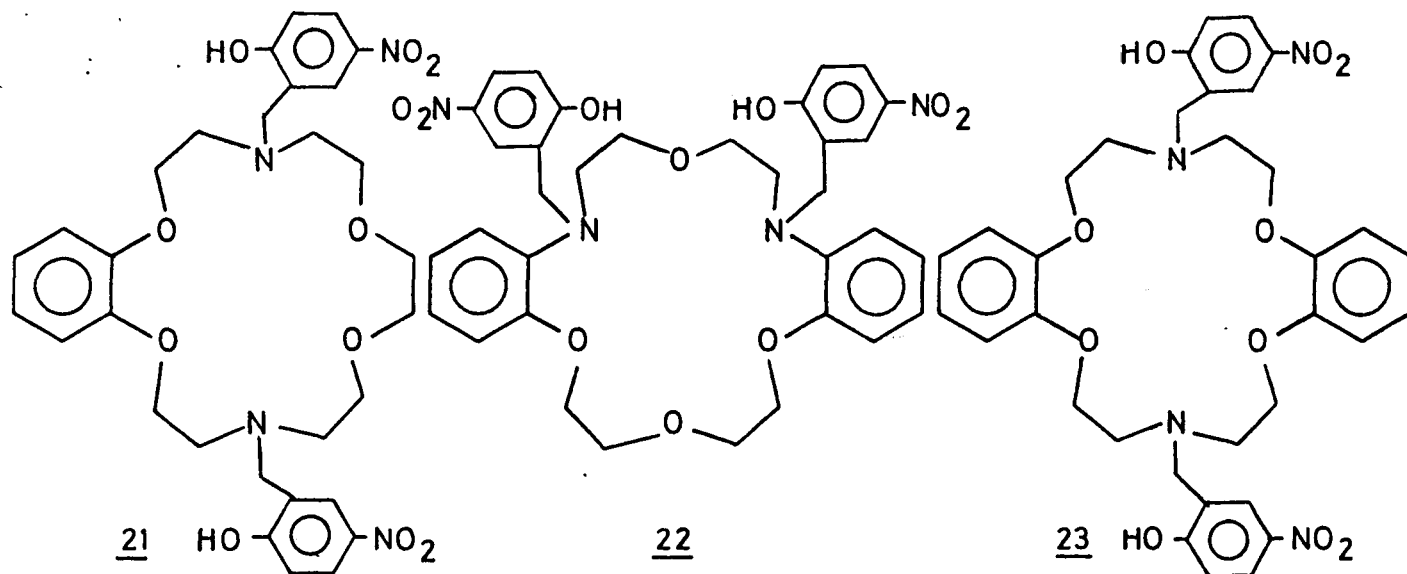
1. Solvent Extraction

a. Mono-ionizable Crown Ethers

For the lipophilic crown carboxylic acid series 1-4, the crown ether ring size is systematically increased from 15-crown-4 to 18-crown-5 to 21-crown-6

to 24-crown-8. For competitive solvent extraction of alkali metal cations into chloroform the extraction selectivities were: $\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Rb}^+ \sim \text{Cs}^+$ for 1; $\text{Li}^+ > \text{K}^+ > \text{Na}^+ > \text{Rb}^+ > \text{Cs}^+$ for 2; $\text{Cs}^+ > \text{Rb}^+ > \text{K}^+ > \text{Na}^+ > \text{Li}^+$ for 3; and $\text{Cs}^+ > \text{Rb}^+ \sim \text{K}^+ > \text{Li}^+ \sim \text{Na}^+$ for 4. Even though these results demonstrate that the extraction selectivity is influenced by ring size variation, the relationship is more complicated than that reported earlier for crown carboxylic acids with pendant ionizable groups, such as 25.⁵ Clearly the inward-facing carboxyl groups in 1-4 are a complicating factor.

Crown carboxylic acids 9-11 bear a close structural relationship to previously-investigated dibenzo-16-crown-5 crown carboxylic acids such as 26 and 27, which possess only oxygen heteroatoms in the macrocyclic ring. Hence for 9, the structural variation is that an oxygen atom of the polyether ring has been replaced with a nitrogen atom. Also the requisite lipophilic group for retention of the extractant in the organic phase during solvent extraction is now attached to nitrogen rather than carbon. For competitive solvent extraction of alkali metal cations into chloroform, crown carboxylic acid 9 provides outstanding selectivity for Na^+ which surpasses even the very high Na^+ extraction selectivity ($\text{Na}^+ \gg \text{Li}^+, \text{K}^+, \text{Rb}^+, \text{Cs}^+$) exhibited by the all-oxygen crown carboxylic acid 26. In contrast, for 10 and 11 the extraction selectivity was much poorer and the selectivity order was $\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Rb}^+, \text{Cs}^+$ for both compounds. This marked change in extraction selectivity when the group attached to the ring nitrogen is changed from decyl to tosyl can be readily understood by considering the strong electron-withdrawing properties of the latter. Hence in 10 and 11, sufficient electron density is removed from the ring nitrogen that it is no longer a metal ion coordination site. The four oxygens form a distorted crown-4 structure which prefers complexation of Li^+ .



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Lipophilic crown carboxylic acids 12 and 13 are derived from monoazadibenzo-18-crown-6. For competitive solvent extraction of alkali metal cations into chloroform, both 12 and 13 exhibited extraction selectivity orders of $\text{Na}^+ > \text{K}^+ > \text{Li}^+, \text{Rb}^+, \text{Cs}^+$. The extraction selectivity for Na^+ is surprising since selectivity for K^+ would be predicted for this ring size.

In chromogenic crown ether 14, a pendant *p*-nitrophenol unit has been attached to monoazadibenzo-18-crown-6. From single species solvent extractions of Li^+ , Na^+ and K^+ into 1,2-dichloroethane by the closely-related chromogenic crown ether 28, Takagi, Ueno and coworkers⁶ estimated slight selectivity in the order $\text{Li}^+ > \text{Na}^+ > \text{K}^+$. On the other hand, for 14 the alkali metal extraction selectivity is found to be higher and the selectivity order was $\text{Na}^+ > \text{K}^+ > \text{Rb}^+ > \text{Li}^+, \text{Cs}^+$. These results are similar to those noted for competitive solvent extraction of alkali metal cations into chloroform by crown carboxylic acid 13. Although the new chromogenic crown ether 14 gave precipitates when its 1,2-dichloroethane solutions were contacted with aqueous solutions of Ag(I) or Hg(I) , this ligand gave highly efficient extraction of Tl(I) . Based upon results from single species extractions, the selectivity for extraction of Tl(I) over the alkali metal cations would be 380-1,100:1.

Separation efficiencies and selectivities in solvent extraction of Co(II) and Ni(II) ammine cations from aqueous solution into chloroform and toluene have been determined for six proton-ionizable crown ethers with differing lipophilicities, polyether cavity sizes and ionizable groups.⁷ Good extraction selectivity for Co(II) over Ni(II) was obtained. Apparently the ionized crown ether acts as a second sphere ligand and is hydrogen bonded to the first sphere ammine ligands.

b. Di-ionizable Crown Ethers

Competitive solvent extractions of alkaline earth cations into chloroform by crown phosphonic acids 15-19, in which the crown ether ring size is

systematically varied from 14-crown-4 to 15-crown-5 to 18-crown-6 to 21-crown-7 to 24-crown-8, were conducted. For 15 in which the crown ether ring size is 14-crown-4, the extraction selectivity order was $\text{Ca}^{2+} > \text{Mg}^{2+}$, $\text{Ba}^{2+} > \text{Sr}^{2+}$. However, the extraction selectivity orders for 16-19 exhibited biphasic behavior with different orders when the aqueous solutions were acidic and alkaline (Table I).

Table I. Selectivity Orders for Competitive Solvent Extraction of Alkaline Earth Cations from Aqueous Solutions into Chloroform by Crown Phosphonic Acids 15-19.

Extractant	Ring Size	Selectivity Order	
		pH 3-6	pH 8-10
15	14C4	$\text{Ca}^{2+} > \text{Mg}^{2+}, \text{Ba}^{2+} > \text{Sr}^{2+}$	$\text{Ca}^{2+} > \text{Mg}^{2+}, \text{Ba}^{2+} > \text{Sr}^{2+}$
16	15C5	$\text{Ba}^{2+} \gg \text{Ca}^{2+}, \text{Sr}^{2+} > \text{Mg}^{2+}$	$\text{Ca}^{2+} > \text{Sr}^{2+} > \text{Ba}^{2+} > \text{Mg}^{2+}$
17	18C6	$\text{Ba}^{2+} > \text{Sr}^{2+} > \text{Ca}^{2+} > \text{Mg}^{2+}$	$\text{Ca}^{2+} > \text{Ba}^{2+} > \text{Sr}^{2+} > \text{Mg}^{2+}$
18	21C7	$\text{Ba}^{2+} > \text{Ca}^{2+} > \text{Sr}^{2+} > \text{Mg}^{2+}$	$\text{Ca}^{2+} > \text{Ba}^{2+} > \text{Sr}^{2+} > \text{Mg}^{2+}$
19	24C8	$\text{Ba}^{2+} > \text{Ca}^{2+} > \text{Sr}^{2+} > \text{Mg}^{2+}$	$\text{Ca}^{2+} > \text{Ba}^{2+} > \text{Sr}^{2+} > \text{Mg}^{2+}$

Crown phosphonic acid 15 exhibits selectivity for Ca^{2+} which is too large to be accommodated within the crown ether cavity. For 16-18, greater or lesser selectivity for Ba^{2+} is noted at acidic pH and greater or lesser selectivity for Ca^{2+} at basic pH. Presumably, the Ba^{2+} selectivity at acidic pH arises from ionization of only one proton from the phosphonic acid groups which requires formation of a two-to-one extraction complex. On the other hand, the Ca^{2+} selectivity at alkaline pH for all five crown phosphonic acids strongly suggest primary coordination of the metal ion outside the polyether ring.

Competitive solvent extractions of alkali metal cations into chloroform by crown dicarboxylic acid 20 also gave biphasic extraction selectivity orders of $\text{Na}^+ > \text{K}^+ > \text{Li}^+ > \text{Rb}^+ > \text{Cs}^+$ at pH 6-8 and $\text{Li}^+ > \text{K}^+ > \text{Na}^+ > \text{Rb}^+ > \text{Cs}^+$ at pH

9-12. The high extractability of Li^+ by 20 at alkali pH suggests cooperative complexation of Li^+ by the two carboxylate anions outside the polyether cavity.

Due to the extremely high extraction selectivity for Hg(II) exhibited by chromogenic di-ionizable crown ether 23, single species extractions into chloroform were also conducted with the structural isomer 22 and the closely-related compound 21. In sharp contrast to 23, structural isomer 22 distributed badly into the aqueous layer during attempted extraction. On the other hand, 21 was much better behaved and exhibited high extractability of Hg(II) into 1,2-dichloroethane compared to other divalent metal ions.

2. Ion Selective Electrodes

In a collaborative research project with Professor Gary D. Christian and his coworkers, the behavior of several of our neutral and proton-ionizable crown ethers in polymeric membrane electrodes has been examined⁸⁻¹¹. Of particular interest was the behavior of crown ether compounds with four ring oxygen atoms and different pendant groups in potential ion selective electrodes for Li^+ .^{9,11} When compared with solvent extraction data, the electrode selectivities exhibited a general correlation which demonstrates that solvent extraction selectivity data can aid in the design and performance prediction of electrode ionophores.

3. Transport through Liquid Membranes

For competitive transport of Co(II) and Ni(II) transport through bulk toluene membranes, it was found that lipophilic crown carboxylic acids provide efficient and selective transport of Co(II) .⁷

Considerable attention continued to be focused upon competitive transport of alkali metal cations across polymer-supported liquid membranes by crown carboxylic acid 26. Following the preliminary studies in which various parameters for membrane constitution and preparation and operational factors

were optimized with flat membrane configurations⁴, this metal ion separation technology has now been transferred to hollow fiber membranes. Due to their much higher surface areas, hollow fiber membranes possess a much higher potential for commercial development than do flat membranes. Once again a variety of operational parameters (e.g. flow rates and concentrations of the source and receiving solutions which flow through the hollow fiber membrane module) had to be evaluated and optimized. An efficient system for the separation of Na^+ from aqueous alkali metal cation solutions has been developed.

4. Separation of Lithium Isotopes by Solvent Extraction with Proton-Ionizable Crown Ethers

Results obtained for the separation of lithium isotopes by a solvent extraction method using a proton-ionizable crown ether have been limited. Lengthy delays in the analysis of lithium samples by the Finnegan MAT 261 Isotope Ratioing Mass Spectrometer at Mound Laboratories allowed only one complete set of experiments to be conducted.

5. Thermodynamics of Metal Ion Complexation by Ionized Crown Ethers

To provide quantitative information concerning metal ion complexation by proton-ionizable crown ethers, the thermodynamics of alkali metal cation complexation by the carboxylate forms of crown carboxylic acids in 90% methanol-10% water (v/v) have been determined by titration calorimetry. Log K, ΔG , ΔH and $T\Delta S$ values have been determined for complexation of Li^+ , Na^+ , K^+ , Rb^+ and Cs^+ by the ionized forms of a variety of crown carboxylic acids. To determine the influence of structural variation within the crown carboxylate upon the strength of metal ion binding, several series of crown carboxylic acids have been examined. The structural variations include: crown ether ring size, lipophilic group attachment site, and structure and length of the lipophilic group. This information provides important insight into the

results of solvent extraction and liquid membrane transport experiments in which these crown carboxylic acids are used as extractants or metal ion carriers.

C. References

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III. PROJECT-SUPPORTED PUBLICATIONS SINCE LAST PROGRESS REPORT

- (1) "Thermodynamic Acid Dissociation Constants for Proton-Ionizable Crown Compounds in Aqueous Dioxane," J. P. Shukla, E.-G. Jeon, B. E. Knudsen, M. J. Pugia, J. S. Bradshaw and R. A. Bartsch, Thermochim. Acta, 130, 103 (1988).
- (2) "Flow Injection Analysis Potentiometric Selectivity Study of Alkali Metal and Alkaline Earth Cation Complexation by 1,3-Bis(tropone-2'-oxy)-propane," A. S. Attiyat, G. D. Christian, M. J. Pugia and R. A. Bartsch, Microchem. J., 38, 246 (1988).
- (3) "Comparative Evaluation of Neutral and Proton-Ionizable Crown Ether Compounds as Lithium Ionophores in Ion-Selective Electrodes and in Solvent Extraction," A. S. Attiyat, G. D. Christian, R. Y. Xie, X. Wen and R. A. Bartsch, Anal. Chem., 60, 2561 (1988).
- (4) "A Comparative Study of the Effect of o-Nitrophenyl Octyl Ether and o-Nitrophenyl Pentyl Ether as Plasticizers on the Response and Selectivity of Carrier-Based Liquid Membrane Ion-Selective Electrodes," A. S. Attiyat, G. D. Christian, J. L. Hallman and R. A. Bartsch, Talanta, 35, 789 (1988).
- (5) "Potentiometric Selectivity Study of Crown Ethers Containing Four Ring Oxygen Atoms and Benzoxyethyl or Carboxylic Acid Side Chains as Ionophores for Lithium and Potassium," A. S. Attiyat, G. D. Christian and R. A. Bartsch, Electroanalysis, 1, 63 (1989).
- (6) "Solvent Extraction and Bulk Liquid Membrane Transport of Co(II) and Ni(II) Ammine Cations by Proton-Ionizable Crown Ethers," J. Strzelbicki, W. A. Charewicz and R. A. Bartsch, J. Inclusion Phenom. Mol. Recogn. Chem., 7, 349 (1989).

IV. PROJECT-SUPPORTED PRESENTATIONS SINCE LAST PROGRESS REPORT

- (1) "A New Chromogenic Crown Ether with Very High Selectivity for Mercury (II)," J. L. Hallman, B. Strzelbicka and R. A. Bartsch, Fifth International Symposium on Inclusion Phenomena and Molecular Recognition, Orange Beach, Alabama, September 1988.
- (2) "Influence of Lipophilic Group Attachment Site and Polyether Ring Size on Complexation of Alkali Metal Cations By Lipophilic Crown Carboxylates in Aqueous Methanol," J. Strzelbicki and R. A. Bartsch, Fifth International Symposium on Inclusion Phenomena and Molecular Recognition, Orange Beach, Alabama, September 1988.
- (3) "Thermodynamics of Alkali Metal Cation Complexation by Dibenzo-16-crown-5 Compounds in Aqueous Methanol," J. Strzelbicki and R. A. Bartsch, Fifth International Symposium on Inclusion Phenomena and Molecular Recognition, Orange Beach, Alabama, September 1988.
- (4) "Synthesis of Di(tert-butyldibenzo-21-crown-7 and Its Alkali Metal Cation Complexation," J. A. McDonough, B. Strzelbicka and R. A. Bartsch, Fifth International Symposium on Inclusion Phenomena and Molecular Recognition, Orange Beach, Alabama, September 1988.
- (5) "Effects of Structural Variation within Proton-Ionizable Crown Ethers upon the Selectivity and Efficiency of Solvent Extraction of Alkali Metal and Alkaline Earth Cations," R. A. Bartsch, Invited lecture in Symposium on Recent Initiatives in the Synthesis of Organic Extractants, 197th National Meeting of the American Chemical Society, Dallas, Texas, April 1989.