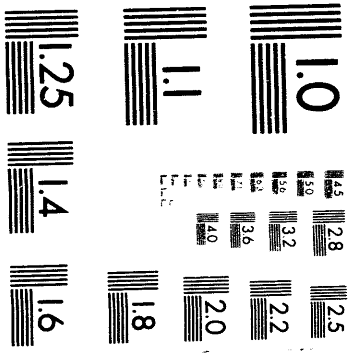
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METAL ION COMPLEXATION BY IONIZABLE CROWN ETHERS

Progress Report

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I. ABSTRACT

During the report period a variety of new cyclic and acyclic polyether compounds with pendent carboxylic acid, phosphonic acid monoethyl ester, sulfonic acid, phosphinic acid and hydroxamic acid groups have been synthesized. In some cases, the proton-ionizable polyether compounds possess lipophilic groups which allow them to be utilized as extractants in solvent extraction of metal ions or as carriers in metal ion transport across liquid membranes. In other cases, proton-ionizable polyether compounds without lipophilic groups were prepared to study how structural variations within the ligand influence metal ion complexation in homogeneous media as assessed by titration calorimetry and NMR spectroscopy.

Two types of lipophilic di-ionizable lariat ethers for complexation of divalent metal ions have been prepared. The first type has a single, pendent, di-ionizable group. The second variety contains two pendent, mono-ionizable groups.

Conformations of proton-ionizable lariat ethers have been probed by solid state structure determinations using X-ray diffraction and in solution by NMR spectroscopy. Dissociation constants in water as determined by a new micro method have also been utilized to probe the conformational relationship between the pendent proton-ionizable group and the crown ether ring in solution.

A detailed investigation of the influence of experimental variables upon competitive alkali metal cation transport by <u>sym</u>-(decyl)dibenzo-16-crown-5-oxyacetic acid in polymer-supported liquid membranes was conducted. In addition the influence of structural variation upon the selectivity and efficiency of competitive alkali metal cation transport across polymer-supported liquid membranes by a series of lipophilic proton-ionizable, dibenzo lariat ethers under standardized experimental conditions were

assessed.

Thermodynamic parameters for complexation of alkali-metal cations with ionized lariat ethers have been determined in 90% methanol-10% water by titration calorimetry. The influence of structural variation within the ionophore upon log K, ΔH and $T\Delta S$ values in homogeneous solution provides insight into the selectivity and efficiency of metal ion separations using the proton-ionizable lariat ethers in multi-phase systems.

Condensation polymerization of cyclic and acyclic dibenzo polyethers containing pendent mono-ionizable groups with formaldehyde produces novel ion-exchange resins which possess not only ion-exchange sites for metal ion complexation, but also polyether binding sites for metal ion recognition. Rapid alkali metal cation sorption and stripping with these new crown ether polymers allow them to be utilized in batch sorption and concentrator column separations. The influence of structural variation within the proton-ionizable dibenzo polyether monomer units upon the selectivity and efficiency of competitive alkali metal cation sorption selectivity and efficiency has been probed. Resins prepared from lariat ether dibenzo phosphonic acid monoethyl esters also exhibit strong sorption of divalent heavy metal cations with selectivity for Pb^{2+}.

II. RESULTS AND DISCUSSION

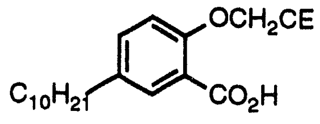
A. Synthesis of Proton-Ionizable Cyclic and Acyclic Polyether Ligands

To probe the effects of structural variation within the complexing agent upon metal ion complexation by proton-ionizable polyethers, a variety of new cyclic and acyclic ligands has been prepared. The common features of these ligands include the presence of one or more ionizable group (carboxylic acid, phosphonic acid monoethyl ester, phosphonic acid) and at least two ethereal oxygen atoms. Ligands which are to be utilized in multiphase separations, such as solvent extraction or liquid membrane transport of metal ions, often have a lipophilic alkyl group attached to retain the complexing agent in the organic phase. On the other hand, for ligands whose metal ion complexation behavior is to be assessed in homogeneous media by titration calorimetry and by NMR spectroscopy, such lipophilic groups are not necessary.

1. Mono-Ionizable Cyclic and Acyclic Polyethers with Pendent Carboxylic Acid Groups

Previously we have investigated competitive solvent extractions of alkali-metal cations into chloroform by lipophilic lariat ether carboxylic acids 1 (with CE = 12C4, 13C4, 14C4, 15C4, 15C5, 16C5, 18C6, 19C6, 21C7, 24C8, 27C9 and 30C10)[1] and by lipophilic acyclic polyether carboxylic acids 2 (with n = 0-4)[2]. To allow for comparison of the solvent extraction results with association constants for interactions of the alkali metal cations by analogous ionized lariat ethers in homogeneous media (90% methanol-10% water), the non-lipophilic analogues 3 (with CE = 12C4, 13C4, 14C4, 15C5, 18C6 and 21C7) and 4 (with n = 0-2) have been prepared.

In earlier work, we synthesized lariat ether phosphonic acid monoethyl esters 5 (CE = 12C4, 15C5 and 18C6) for examination of ligand conformations in homogeneous solution by ^{1}H NMR spectroscopy.[3] The benzylic protons in 5 are diastereotopic. When the ionized side arm is conformationally restricted by interaction with a crown ether complexed metal ion, the benzylic protons become magnetically non-equivalent and give an AB pattern in the ^{1}H NMR spectrum. We are probing the potential for use of the weighted average chemical shift difference[4] for the benzylic protons as a measure of side arm restriction in the ionized crown ether metal ion complex. To expand this NMR study and include a different proton-ionizable group, lariat ether carboxylic



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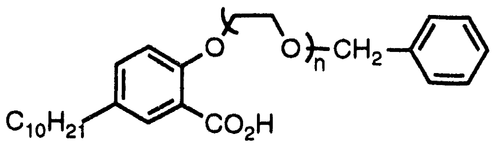

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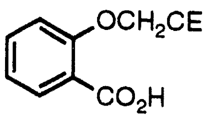

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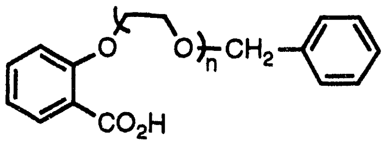

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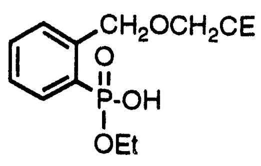

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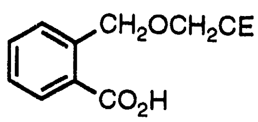

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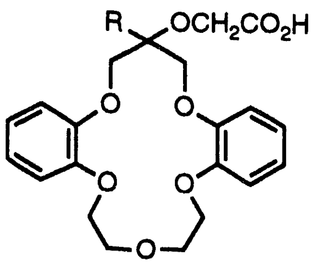

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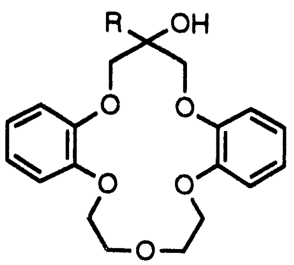

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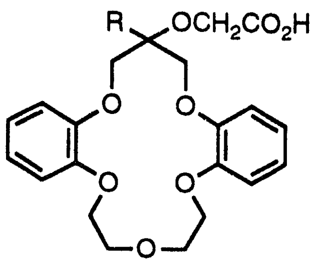
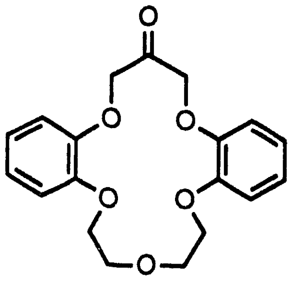


	R
9	$CH_2C(CH_3)_3$
10	$CH(CH_3)_2$
11	$CH=C(CH_3)_2$
12	C_6H_5
13	$C\equiv CC_4H_9$
14	$C\equiv CC_6H_{13}$
15	$C\equiv CC_8H_{17}$



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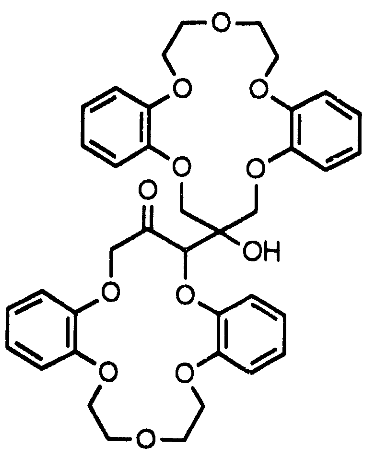


17

acids **6** (with CE = 12C4, 15C5 and 18C6) have been prepared. Also comparison of association constants for ionized **6** (with CE = 12C4, 15C5 and 18C6) determined by titration calorimetry in aqueous methanol with values for ionized **3** will allow the influence of side arm length on the strength of metal ion complexation to be assessed for this type of lariat ether carboxylic acid.

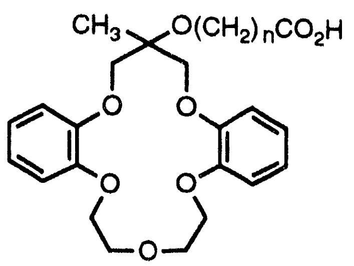
In earlier investigations, we have utilized sym-(R)dibenzo-16-crown-5-oxyacetic acids (**7** with R = normal alkyl, normal perfluoroalkyl and 2-ethylhexyl) to study the influence of this structural variation upon the selectivity and efficiency of alkali-metal cation solvent extraction[5] and transport across liquid membranes.[6] Lariat ether carboxylic acids **7** had been prepared by reaction of the analogous alcohols **8** with sodium hydride in tetrahydrofuran followed by addition of bromoacetic acid. During the current grant period, we have found that the use of potassium hydride instead of sodium hydride significantly enhanced the yield for this coupling reaction to 82-93%. It is postulated that the crown ether alkoxide ion is less nucleophilic when the counterion is sodium ion which is well-accommodated within the crown ether cavity and interacts with the alkoxide oxygen atom to diminish its electron density. On the other hand, potassium ion is too large to fit within the polyether cavity and the electron density on the alkoxide oxygen is higher which provides greater nucleophilicity.

In the lariat ether carboxylic acids **7** examined to date, the geminal alkyl group has always been attached with a primary carbon atom. To further probe the influence of structural variation of the geminal group to i) a sterically hindered primary alkyl group, ii) a secondary alkyl group, iii) alkenyl and phenyl groups with sp^2-hybridized first atoms, and iv) alkynyl groups with sp-hybridized first atoms, a new series of lariat ethers **9-15** was prepared. For the synthesis of **9-12**, appropriate alkyl, alkenyl and phenyl bromides were converted into the corresponding Grignard reagents by reaction with magnesium in tetrahydrofuran followed by the addition of sym-keto-dibenzo-16-crown-5 (**16**) to produce the corresponding lariat ether alcohols **8**. The alcohols **8** were then converted into lariat ether carboxylic acids by reaction with potassium hydride and bromoacetic acid in tetrahydrofuran. Interestingly the reaction of crown ether ketone **16** with tert-butylmagnesium bromide did not provide the desired lariat ether alcohol **8** with R = tert-butyl. Instead the dimeric product **17** was isolated. Apparently nucleophilic attack by the sterically hindered Grignard reagent on the carboxyl carbon of the crown ether ketone was retarded resulting in removal of an α-hydrogen to form an enolate anion which coupled with another molecule of the crown ether ketone. For attachment of geminal alkynyl groups, terminal alkynes were added to solutions of ethylmagnesium bromide in tetrahydrofuran to form the 1-alkynyl-magnesium bromides.

To probe the influence of varying the side arm which joins the proton-ionizable group and the macrocyclic polyether ring, lariat ether carboxylic acids **18** with n = 1-3 were synthesized.

To investigate the effect of crown ether ring size variation upon metal ion complexation selectivity, a series of dibenzo-19-crown-6-oxyacetic acids (**19** with R = H, methyl, ethyl, propyl and butyl) was prepared from the corresponding lariat ether alcohols **20** with sodium hydride and bromoacetic acid in tetrahydrofuran. Once again a mismatch of the alkali-metal cation of the metal hydride and the crown ether ring size gave higher yields in the coupling reaction. Thus sodium hydride rather than potassium hydride gave higher yields for alkylation of the dibenzo-19-crown-6 alcohols **20**. (Recall that a change from sodium hydride to potassium hydride in the alkylation of dibenzo-16-crown-5 alcohols **8** enhanced the coupling yield.)

For use as model compounds the series of dibenzo acyclic polyether carboxylic acids **21-30** was prepared.



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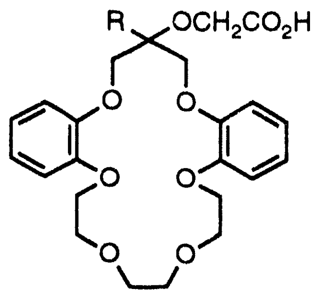

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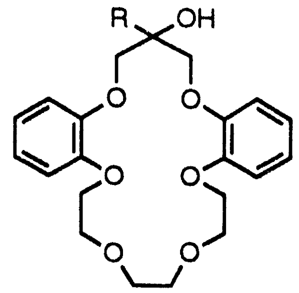

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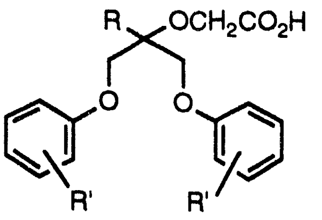
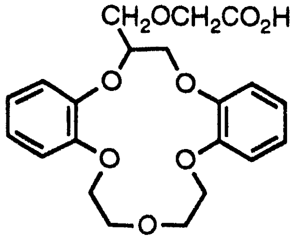


	R	R'
21	H	H
22	C_3H_7	H
23	H	*o*-CH_3
24	C_3H_7	*o*-CH_3
25	H	*o*-OCH_3
26	C_3H_7	*o*-OCH_3
27	$C_{10}H_{21}$	*o*-OCH_3
28	H	*p*-OCH_3
29	C_3H_7	*p*-OCH_3
30	$C_{10}H_{21}$	*p*-OCH_3



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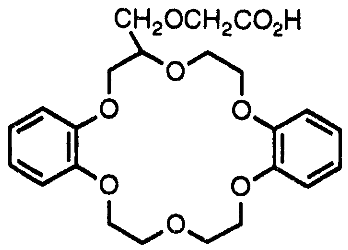

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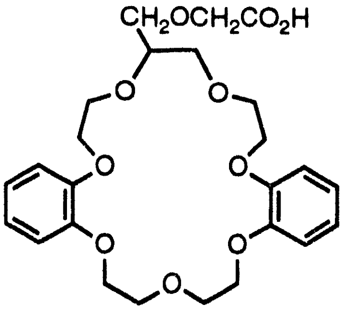

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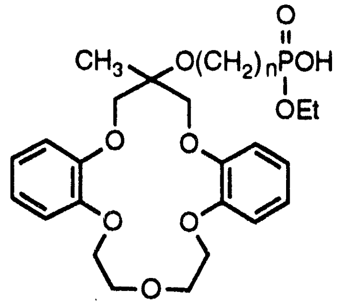

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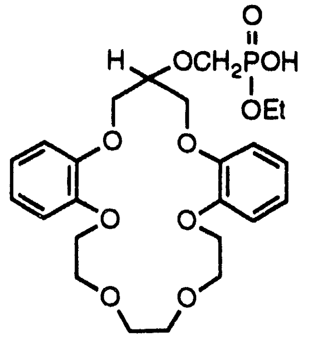

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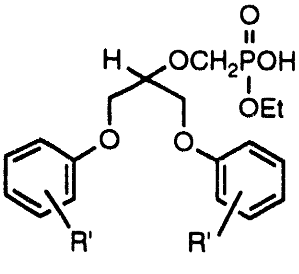
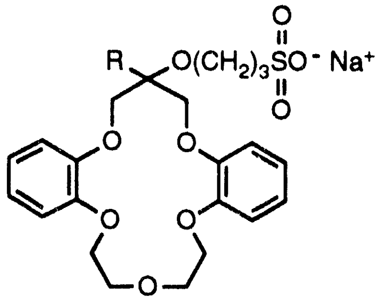


	R'
36	*o*-OCH_3
37	*p*-OCH_3



	R
38	H
39	C_3H_7

Lariat ether carboxylic acids **7** and **19** contain a three-carbon bridge in the polyether ring. For comparison of metal ion recognition by dibenzo lariat ether carboxylic acids which contain only two carbon bridges in the macrocyclic polyether units, the dibenzo-15-crown-5, -18-crown-6 and -21-crown-7 carboxylic acids **30-32**, respectively, have been synthesized.

2. Mono-Ionizable Cyclic and Acyclic Polyethers with Pendent Phosphonic Acid Monoethyl Ester Groups

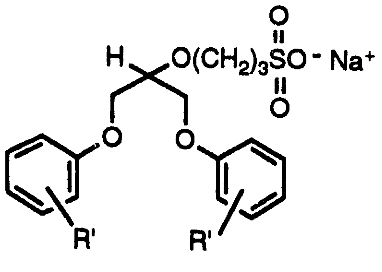
Phosphonic acid monoethyl ester functions are mono-ionizable groups with higher acidity than carboxylic acid groups. For comparison with analogous lariat ether carboxylic acids, the new lariat ether phosphonic acid monoethyl esters **34** with n = 0-3 and **35** were prepared. Also acyclic polyether phosphonic acid monoethyl esters **36** and **37** were synthesized.

3. Mono-Ionizable Cyclic and Acyclic Polyethers with Pendent Sulfonic Acid Groups

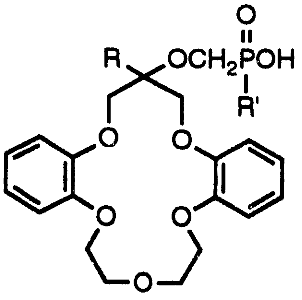
Even more acidic mono-ionizable functions are sulfonic acid groups. Lariat ether sulfonates **38** and **39** and acyclic polyether sulfonates **40** and **41** were prepared by reaction of the appropriate alcohol with sodium hydride and 1,3-propanesultone in tetrahydrofuran.

4. Mono-Ionizable Lariat Ethers with Pendent Phophinic Acid and Hydroxamic Acid Groups

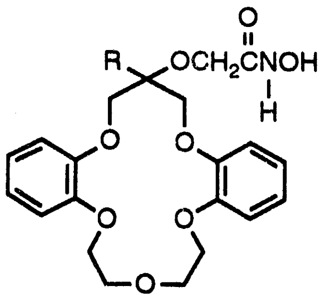
To better understand the effect of varying the acidic function in lariat ethers with mono-ionizable groups, lariat ethers phosphinic acids **42** and **43** were prepared. Use of the route which provided good yields of **42** was unsuccessful for the synthesis of **44**, a structural analogue with a geminal alkyl group. Lariat ether hydroxamic acids **45** and **46** were also prepared. These compounds share a common ring structure and side arm length with lariat ether carboxylic acids **7** and analogous phosphonic acid monoethyl esters.



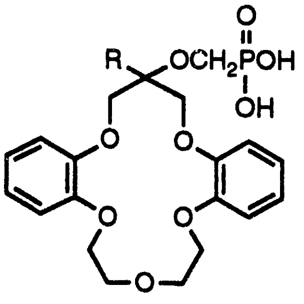
	R'
40	o-OCH_3
41	p-OCH_3



	R	R'
42	H	CH_3
43	H	C_4H_9
44	C_3H_7	alkyl



	R
45	H
46	C_3H_7



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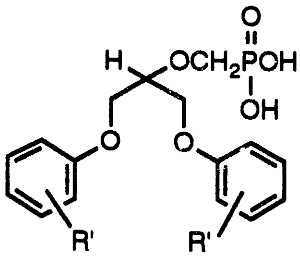
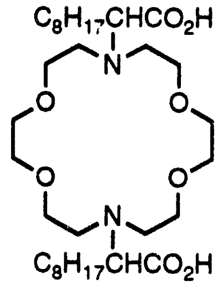


	R'
48	o-OCH_3
49	p-OCH_3



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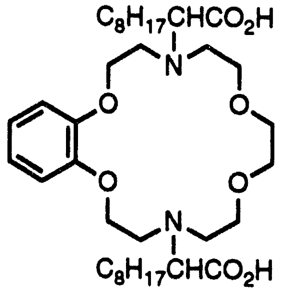

	n
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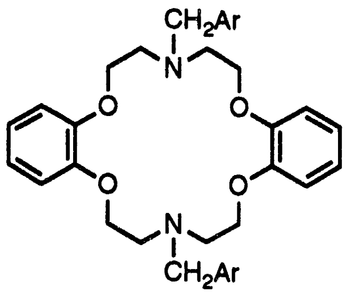
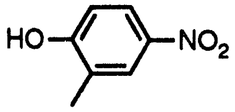


Ar

53



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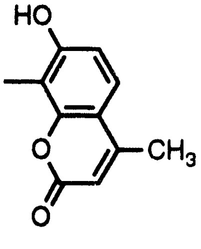

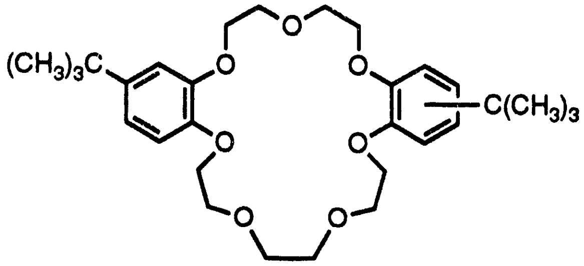

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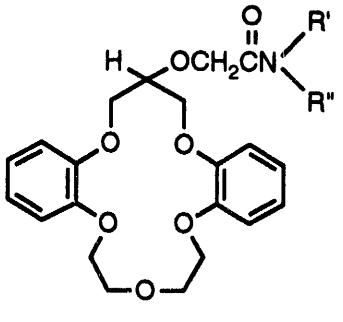

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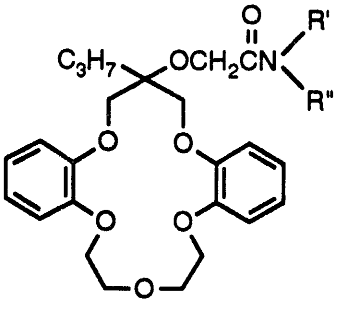

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5. Di-Ionizable Cyclic and Acyclic Polyethers with Pendent Phosphonic Acid Groups

Cyclic or acyclic polyethers with pendent phosphonic acid groups possess di-ionizable functionality for formation of electroneutral complexes with divalent metal ions. New lariat ether phosphonic acids **47** with R = H, methyl, ethyl and propyl were synthesized. Also the acyclic polyether phosphonic acids **48** and **49** were prepared.

6. Diazacrown Ethers with Two Pendent Mono-Ionizable Groups

For studies of divalent metal ion extraction and transport across liquid membranes, diazacrown ethers substituted on both nitrogens with lipophilic, carboxylic acid containing sidearms were realized. For lipophilic macrocyclic diamino acids **50** and **52**, the structural variation is the presence or absence of a benzo groups substituent on the 1,10-diaza-18-crown-6 ring. For **51** and **52** the diazacrown ether ring size is varied from 15-crown-5 to 18-crown-6.

In earlier work, we discovered that chromogenic di-ionizable macrocyclic ligand **53** possesses extremely high Hg^{2+} selectivity for solvent extraction into 1,2-dichloroethane.[7] To determine if a structurally related compound with proton-ionizable fluorogenic groups would also exhibit high selectivity for Hg^{2+}, compound **54** was designed and synthesized.

B. Synthesis of Non-Ionizable Crown Ethers and Lariat Ethers

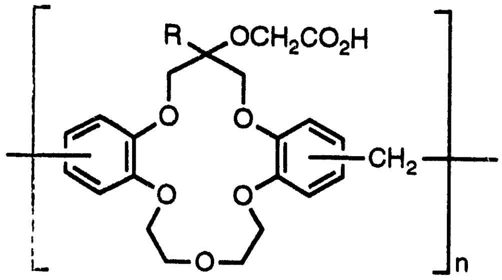
For application in the solvent extraction of cesium ions, a viable synthetic route to bis(tert-butylbenzo)-21-crown-7 (**55**) was developed.[8]

Through research conducted in the current and previous funding period considerable insight has been gained into the influence of structural variation within proton-ionizable dibenzo-16-crown-5 lariat ethers upon the selectivity and efficiency of alkali-metal cation complexation. To compare these alkali metal cation complexation propensities with those for analogous lariat ethers which have non-ionizable chelating groups on the side arm, two series of N-substituted dibenzo-16-crown-5-oxyacetamides **56** and **57** with R' = H, alkyl and R" = H, alkyl have been prepared.[9] For both series of compounds there was systematic structural variation in the R' and R" groups to alter the electron density at the carboxyl oxygen and the steric properties of the amide groups. The compounds of series **57** possess a geminal propyl group to orient the amide group containing side arm over the polyether cavity and preorganize the binding site.

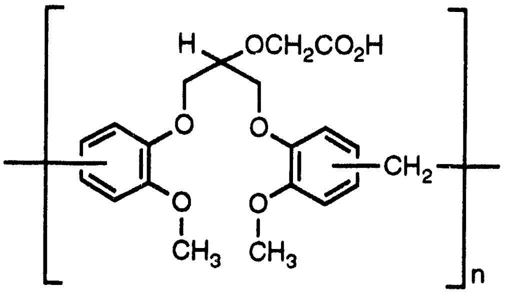
C. Synthesis of Proton-Ionizable Cyclic and Acyclic Polyether Resins

As we have reported previously,[10] condensation polymerization of dibenzo-16-crown-5-oxyacetic acid and sym-(propyl)dibenzo-16-crown-5-oxyacetic acid with formaldehyde in formic acid produces polymers **58** and **59**, respectively.[10] These polymers are a new type of ion-exchange resin with both ion-exchange and cyclic polyether binding sites for metal ion complexation. Since some degree of crosslinking is anticipated in such polymers, the structural representations shown in **58** and **59** are oversimplifications.

It was demonstrated that alkali-metal cation sorption by cyclic polyether carboxylic acid resins **58** and **59** and acyclic polyether carboxylic acid resin **60** and stripping by treatment with aqueous hydrochloric acid were rapid.[10] Furthermore it was found that the selectivity for Na^+ in competitive alkali-metal cation sorption increases in the order **60** < **58** < 59. Thus the presence of a dibenzo-16-crown-5 ring in resins **58** and **59** enhanced sorption of Na^+ over that observed with the structurally related acyclic polyether carboxylic acid resin **60**. The greater Na^+ sorption selectivity of



	R
58	H
59	C_3H_7



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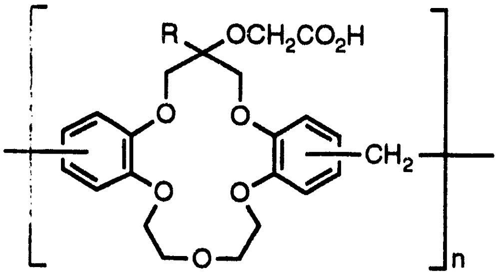
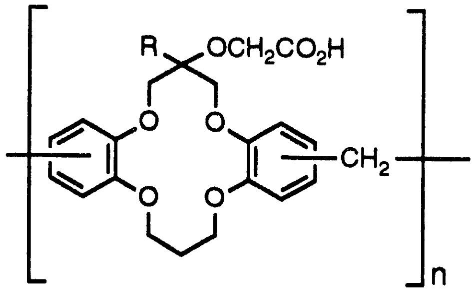
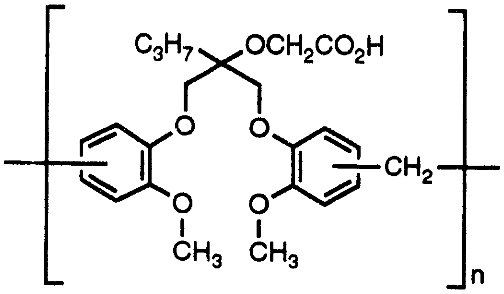


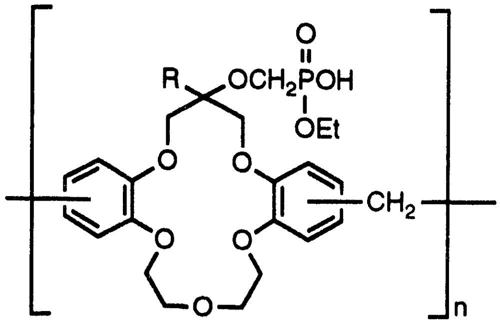
	R
61	CH_3
62	C_2H_5
63	C_4H_9
64	C_6H_{13}
65	$C_{10}H_{21}$



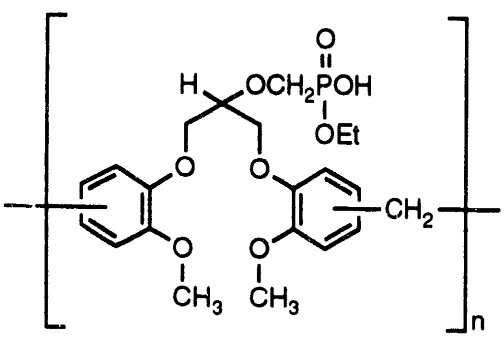
	R
66	H
67	C_3H_7



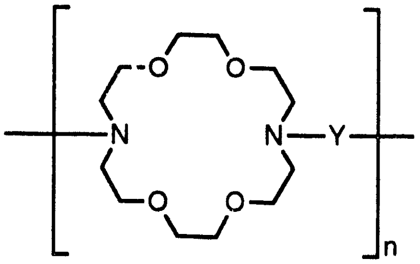
68



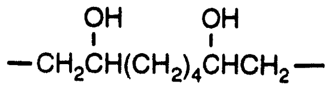
	R
69	H
70	CH_3



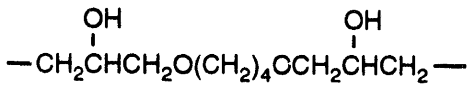
71



Y

72 

$-CH_2\overset{OH}{C}H(CH_2)_4\overset{OH}{C}HCH_2-$

73 

$-CH_2\overset{OH}{C}HCH_2O(CH_2)_4OCH_2\overset{OH}{C}HCH_2-$

resin **59** than **58** is attributed to the geminal propyl group in the former which orients the proton-ionizable group over the crown ether cavity to pre-organize the binding site.

To further probe the influence of structural modification within the dibenzo polyether carboxylic acid monomer upon the selectivity and efficiency of competitive metal ion sorption, additional proton-ionizable dibenzo polyether resins have been synthesized. To examine the effect of varying the geminal alkyl group, the series of lariat ether carboxylic acid resins **61-65** was prepared.[11] For the series of polymers **58**, **61**, **62**, **59**, **63-65**, there is systematic structural variation of the geminal group from hydrogen to methyl to ethyl to propyl to butyl to hexyl to decyl.

In lariat ether carboxylic acid resins **66** and **67**, the crown ether ring has been changed to dibenzo-14-crown-4. The resin pairs of **66** and **60** and of **67** and **68** are very similar in structure except for the variation from a cyclic polyether unit to an acyclic polyether linkage with the same number of oxygens.

Another important structural variation is the identity of the pendent proton-ionizable group. Lariat ether resins **69** and **70** are identical with **58** and **61** with the exception that the proton-ionizable group is a phosphonic acid monoethyl ester in the former pair and a carboxylic acid in the latter pair. Proton-ionizable acyclic polyether resins **71** and **60** are related similarly.

D. Synthesis of Water-Soluble Polymers with Diazacrown Ether Units in the Backbone

For evaluation of their performance in homogeneous, aqueous-phase separation of metal ions by liquid-phase, polymer-based retention (LPR), polymers **72** and **73** were prepared by condensation polymerization of 1,10-diaza-18-crown-6 with 1,2,7,8-diepoxyoctane and 1,4-butanediol diglycidyl ether. In water-soluble polymers **72** and **73**, the metal ion chelating diazacrown ether unit is incorporated into the polymer backbone.

E. Proton-Ionizable Lariat Ethers in Homogeneous Media

1. Acidity in Aqueous Solution

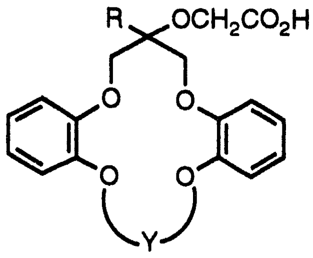
For the application of proton-ionizable lariat ethers in separation processes, the acidity of the ionizable group is a very important factor. Previously we have determined dissociation constants for proton-ionizable lariat ethers in aqueous dioxane.[12,13] A mixed aqueous-organic solvent system was utilized due to the very low solubilities of lipophilic proton-ionizable lariat ethers in water.

Recently Dasgupta and Nara reported a novel micro method for determination of acid dissociation constants of weak acids in water by cation exchange and conductance.[14] A distinct advantage of this method is that only a very small quantity (ca. 10 milligrams) of the sodium salt of the acid is required.

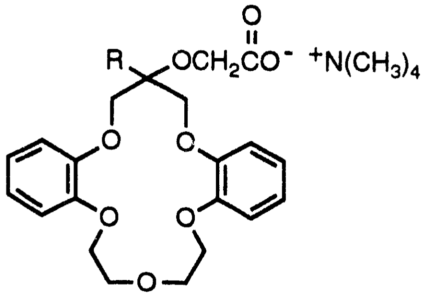
Using this method, the determination of acidity constants for non-lipophilic lariat ether carboxylic acids in water has been undertaken. Some of the initial results are presented in Table 1.

Table 1. Acidity Constants for Dibenzo Lariat Ether Carboxylic Acids in Water at 25.0 °C.

Compound	Ring Size	pK_a
74	13-crown-4	3.949 ± 0.002
75	14-crown-4	4.018 ± 0.004
76	16-crown-5	4.585 ± 0.007
77	19-crown-6	4.268 ± 0.003
78	16-crown-5	4.761 ± 0.005



	R	Y
74	H	CH_2CH_2
75	H	$CH_2CH_2CH_2$
76	H	$CH_2CH_2OCH_2CH_2$
77	H	$CH_2(CH_2OCH_2)_2CH_2$
78	CH_3	$CH_2CH_2OCH_2CH_2$



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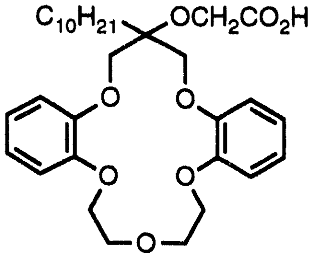

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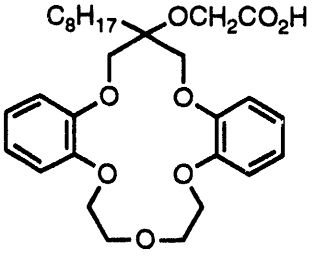

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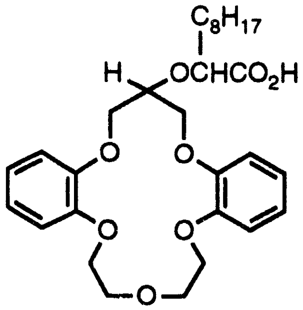
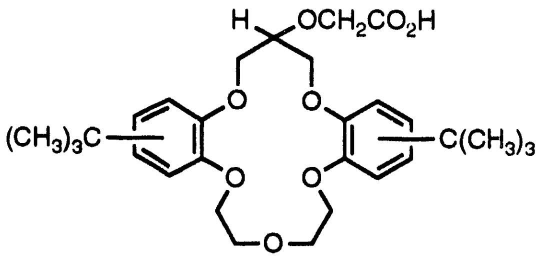
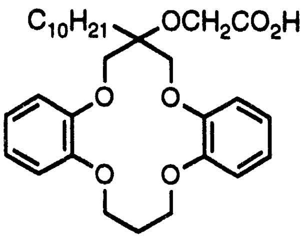


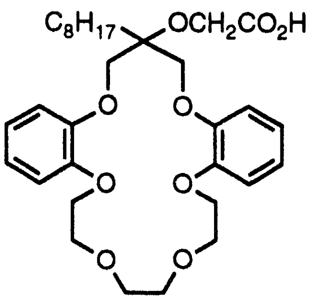
82



83



84



85

Thus for the series of dibenzocrown ether oxyacetic acids **74-77** which differ only by variation of ring size from 13-crown-4 to 14-crown-4 to 16-crown-5 to 19-crown-6, the acidity is found to first decrease then increase. From examination of CPK space-filling models, its appears that intramolecular hydrogen bonding of the pendent carboxylic acid group with the dialkyl ether oxygen of the crown ether ring in dibenzo-16-crown-5 compound **76** is responsible for the lowest acidity within the series. Attachment of a geminal methyl group in **78**, which is postulated to orient the carboxylic acid group containing side arm over the macrocyclic cavity, should accentuate the acid-weakening, intramolecular hydrogen bonding. In agreement, sym-(methyl)-dibenzo-16-crown-5-oxyacetic acid (**78**) is found to be less acidic than sym-dibenzo-16-crown-5-oxyacetic acid (**76**). These results demonstrate that the precise acidity constants determined by this method can provide valuable insight into conformations of proton-ionizable lariat ethers in solution.

2. Alkali-Metal Cation Complexation Assessed by Titration Calorimetry

To provide information about metal ion complexation by ionized crown ethers in homogeneous solution, the thermodynamics of alkali metal cation complexation by anionic forms of proton-ionizable lariat ethers are being determined by titration calorimetry. Preliminary studies revealed that a mixed solvent of 90% methanol-10% water (v/v) is appropriate for the measurements. The experimental procedure consists of titrating at 25.00 ± 0.02 °C an aqueous methanolic solution which is 4.0 mM in the proton-ionizable crown ether and 5.0 mM in tetramethylammonium hydroxide with an aqueous methanolic solution which is 4.0 mM in an alkali metal chloride and 5.0 mM in tetramethylammonium hydroxide. Heats of dilution are determined by titrating the aqueous methanolic solution of the alkali metal chloride (4.0 mM) and the tetramethylammonium hydroxide (5.0 mM) into a 5.0 mM solution of tetramethylammonium hydroxide in 90% methanol-10% water in the absence of the ligand. When this titration was repeated but with no alkali metal chloride in the titrant, the heat of dilution was negligible.

The resulting titration curves from addition of the aqueous methanolic solution of alkali metal chloride and tetramethylammonium hydroxide to the aqueous methanolic solution of the proton-ionizable lariat ether and tetramethylammonium hydroxide are analyzed by a least squares method to obtain log K, ΔH and TΔS.[15] The values of log K and ΔH are corrected to their thermodynamic values using the Debye-Hückel relationship with 4.5 Å as the distance of closest approach in 90% methanol-10% water.[16]

By this method, values of log K, ΔH and ΔS have been and continue to be determined for complexation of Li^+, Na^+, K^+, Rb^+ and Cs^+ by the ionized forms of proton-ionizable lariat ethers. An example of the type of data which has been obtained appears in Table 2. In this investigation, the effect of geminal alkyl groups on the complexation of alkali-metal cations by *sym*-(R)-dibenzo-16-crown-5-oxyacetates is assessed.[17]

For **79** with R = hydrogen, the association constant for Na^+ is largest, as would be predicted for the 16-crown-5 ring size. When a methyl group is introduced on the ring carbon geminal to the carboxylate containing side arm, the association constants for Na^+, K^+ and Rb^+ increase, while that for Cs^+ remains unchanged. The increase in log K is much larger for Na^+ than for K^+ and Rb^+. Thus the methyl group not only gives overall binding enhancement for appropriately sized alkali-metal cations, but also increases the Na^+ selectivity. Replacement of R = methyl with ethyl causes only minor alteration in the association constants and for the series of **79** with R = ethyl, butyl, hexyl, octyl, and decyl, the association constants are essentially the same. Thus the enhanced Na^+ selectivity of *sym*-(alkyl)-dibenzo-16-crown-5-oxyacetic acids relative to *sym*-dibenzo-16-crown-5-

Table 2. Association Constants for Complexation of Alakli Metal Cations by Tetramethylammonium sym-(R)dibenzo-16-crown-5-oxyacetates (79) in 90% methanol-10% water.[a]

R	log K Na+	K+	Rb+	Cs+
hydrogen	3.69 ± 0.15	3.27 ± 0.14	2.63 ± 0.07	2.43 ± 0.09
methyl	4.69 ± 0.07	3.56 ± 0.07	3.22 ± 0.24	2.35 ± 0.08
ethyl	4.47 ± 0.08	3.60 ± 0.10	2.92 ± 0.12	2.18 ± 0.10
butyl	4.46 ± 0.06	3.43 ± 0.06	2.85 ± 0.14	2.11 ± 0.12
hexyl	4.50 ± 0.01	3.47 ± 0.06	2.73 ± 0.08	2.01 ± 0.03
octyl	4.40 ± 0.06	3.42 ± 0.04	2.87 ± 0.15	2.34 ± 0.21
decyl	4.41 ± 0.01	3.31 ± 0.03	2.90 ± 0.25	2.32 ± 0.01

[a] In all cases insufficient heat was generated with lithium ion for calculation of the association constant.

oxyacetic acid occurs for both small and extended normal alkyl groups.

In similar fashion the influence of crown ether ring size and lipophilic group attachment site upon the complexation of alkali-metal cations by dibenzo lariat crown carboxylic acids has been probed.

3. Conformational Studies by Proton NMR Spectroscopy

In the ^1H NMR spectrum of sym-dibenzo-16-crown-5-oxyacetic acid (76) the absorption for the methylene protons on the three-carbon bridge appears as a singlet at 4.29 ppm in deuteriochloroform. For sym-(methyl)dibenzo-16-crown-5-oxyacetic acid (78), the absorption for the methylene protons on the three-carbon bridge is changed to a widely spaced AB pattern with a chemical shift difference (calculated as the weighted average chemical shift difference[4]) of 197 Hz and a geminal coupling constant of 10 Hz.[17] Such non-equivalence of the diastereotopic methylene protons in the ^1H NMR spectrum of **78** demonstrates that their interconversion by flipping of the three-carbon bridge is slow on the NMR time scale. Thus the introduction of a geminal methyl group causes a marked change in conformational flexibility. (It should be recalled that Na^+ selectivity as assessed by titration calorimetry in 90% methanol-10% water is substantially enhanced by the introduction of a geminal methyl group.)

The effect of solvent upon the chemical shift difference was assessed for sym-(decyl)-dibenzo-16-crown-5-oxyacetic acid (**80**). The results which are recorded in Table 3 reveal a very substantial influence of the NMR solvent upon the chemical shift difference for the diastercotopic methylene group hydrogens. This result is rationalized on the basis of intramolecular versus intramolecular hydrogen bonding for the lariat ether carboxylic acid. Benzene is neither a hydrogen bond donor nor a hydrogen bond acceptor.

Table 3. Influence of Solvent upon the Chemical Shift Difference for the Methylene Hydrogens of the Three-Carbon Bridge of sym-(Decyl)-dibenzo-16-crown-5-oxyacetic Acid (**80**)

Solvent	Chemical Shift Difference, Hz
Benzene-d_6	244
Deuteriochloroform	205
Acetone-d_6	134
Acetonitrile-d_3	127
Dimethyl Sulfoxide-d_6	87

Therefore in benzene intramolecular hydrogen bonding of the pendent carboxylic acid group with a crown ether oxygen is maximized which provides the greatest restriction to flipping of the three-carbon bridge and the largest chemical shift difference. On the other hand, dimethyl sulfoxide is a hydrogen bond acceptor which should markedly reduce the level of intramolecular hydrogen bonding. In agreement, the chemical shift difference is diminished to approximately one third of the value observed in benzene.

Thus it appears that the chemical shift difference for the diasteriotopic methylene protons in the three-carbon bridge of sym-(alkyl)-dibenzo-16-crown-5 oxyacetic acids may be a useful probe of conformational rigidity in solution.

4. Solid State Structures

To provide further insight into the conformational changes produced by attachment of a geminal alkyl group in sym-dibenzo-16-crown-5-oxyacetic acid (**76**), solid state structures for **76** and the analogous compound with a geminal decyl group **80** have been determined in collaboration with Professor N. K. Dalley of Brigham Young University.[17] In the crystal structure of **76**, the carboxylic acid containing side arm is directed away from the crown ether ring; whereas in **80**, the oxyacetic acid side arm is oriented over the polyether cavity.

F. Proton-Ionizable Lariat Ethers and Their Polymers in Heterogeneous Metal Ion Complexation Systems

Lariat ether carboxylic acids were utilized as carriers for transport of alkali-metal and alkaline-earth cations across polymer-supported liquid membranes. Novel proton-ionizable lariat ether resins were employed in separations of alkali-metal cations and of heavy metal cations.

1. Alkali-Metal and Alkaline-Earth Cation Transport across Polymer-Supported Liquid Membranes by Proton-Ionizable Lariat Ethers

Considerable effort was expended in the investigation of competitive, proton-coupled transport of alkali-metal cations across polymer-supported liquid membranes by sym-(decyl)dibenzo-16-crown-5-oxyacetic acid (80). In this system, the source phase was an aqueous solution of lithium, sodium, potassium, and rubidium chlorides. (Contact with cesium chloride was found to degrade the membrane.) The receiving phase was aqueous hydrochloric acid. The liquid membrane was supported by Accurel 0.2 porous polypropylene sheet. Within the vacant spaces in this porous material (70% voids) was absorbed a solution of 80 in an alkyl 2-nitrophenyl ether. This type of liquid membrane solvent was chosen due to the combination of good polarity and low water solubility. In earlier work, we established that among a number of alkyl 2-nitrophenyl ethers evaluated pentyl 2-nitrophenyl ether gave the best combination of flux and Na^+ selectivity.[18] It should be noted that this membrane system exhibits very high selectivity for Na^+ transport. The Na^+/Li^+ and Na^+/K^+ transport selectivities are near 50. Since no Rb^+ could be detected in the receiving phase, the Na^+/Rb^+ transport selectivity is even higher.

A variety of experimental variables were investigated to determine their influence upon the metal ion flux and Na^+ selectivity. These included:

a) The technique for loading the solution of 80 in pentyl 2-nitrophenyl ether into the porous polypropylene sheet;

b) The influence of the carrier concentration in the pentyl 2-nitrophenyl ether membrane solvent;

c) The effect of temperature;

d) The effect of pH of the aqueous source phase;

e) The effect of the hydrochloric acid concentration in the aqueous receiving phase;

f) The effect of the alkali-metal cation concentrations in the aqueous source phase; and

g) The ability of the system to selectively remove Na^+ from an aqueous source phase in which the K^+ concentration is several times larger than Na^+.

In another experiment, competitive transport from an aqueous source phase containing four alkali-metal cation species and the four alkaline-earth cations was performed. At the final sampling, no Li^+, Rb^+ or Sr^{2+} were detected in the receiving phase and the Na^+/K^+, Na^+/Mg^{2+}, Na^+/Ca^{2+} and Na^+/Ba^{2+} transport selectivity ratios were 30, 87, 28 and 47, respectively. Thus this polymer-supported liquid membrane system provides highly selective separation of Na^+ from alkaline-earth cations as well as other alkali metal cations.

The study was then expanded to examine the effectiveness and selectivities of other lipophilic lariat ether carboxylic acid carriers for alkali metal cations. Under standardized conditions, the lipophilic dibenzo-16-crown-5-oxyacetic acid series of **81-83** was examined. These compounds are structural isomers which differ in the attachment sites for the lipophilic groups(s). Of the three, the Na^+ flux was the highest with **81**, as well as the Na^+/Li^+ and Na^+/K^+ transport selectivities. In **81** presence of the geminal octyl group is postulated to orient the carboxylic acid group over the crown ether cavity and pre-organize the binding site which enhances the Na^+ selectivity.

It was determined that the fit of the alkali-metal cation within the crown ether cavity determines the predominant cation transported. Thus sym-(decyl)dibenzo-14-crown-4-oxyacetic acid (**84**) and sym-(octyl)dibenzo-19-crown-6-oxyacetic acid (**85**) exhibited transport selectivities for Li^+ and K^+, respectively.

2. Metal Ion Sorption by Proton-Ionizable Lariat Ether Polymers

In earlier work,[10] condensation polymerization of dibenzo polyether carboxylic acids with formaldehyde in formic acid provided novel ion-exchange resins **58-60**. These resins possess both ion-exchange and polyether binding sites for metal ion complexation. Therefore this new class of ion-exchange resins is expected to exhibit metal ion sorption selectivities which are unavailable with common, commercially available ion-exchange resins.

It was demonstrated that alkali-metal cation sorption from aqueous solutions by resin **58** was rapid (> 85% complete after shaking for five minutes).[10] This contrasts sharply with the slow sorption of alkali-metal salts from aqueous solutions by condensation polymers of dibenzocrown ethers and formic acid as reported by Blasius et al.[19] Furthermore, sorbed alkali-metal cations can be readily stripped from resin **2** by shaking with aqueous hydrochloric acid.[10]

The enhanced Na^+ sorption selectivity for resin **59** compared with **58** was attributed to the presence of the geminal propyl group in the former which positions the carboxylic acid group over the crown ether cavity and pre-organizes the binding site.[10] To more thoroughly explore the influence of the geminal alkyl group, resins **61-65** were prepared and their behavior in competitive alkali-metal cation sorption examined.[11] In these resins the geminal alkyl group was varied to include methyl, ethyl, butyl, hexyl and decyl. The highest efficiency (loading) and Na^+ sorption selectivity were obtained when the geminal alkyl group was methyl, ethyl or propyl. The longer alkyl groups were found to be detrimental to both sorption efficiency and selectivity.[11]

The influence of medium polarity upon competitive sorption of alkali-metal cations from aqueous and aqueous methanolic solutions by lariat ether carboxylic acid resins **58**, **61**, **62**, **59**, **64** and **65** and acyclic polyether carboxylic acid resin **60** was assessed.[20] Enhancement of metal ion-crown ether interactions as the percentage of methanol in the medium was increased accentuates the Na^+ sorption selectivity for the lariat ether carboxylic acid resins. The highest Na^+ sorption selectivity was obtained when the geminal alkyl group was ethyl or propyl in 80% methanol-20% water.

Column concentration of alkali-metal cations from dilute aqueous solutions by lariat ether carboxylic acid resins **58** and **59** was investigated.[21] Selective column concentration of alkali-metal cations was attained with resin **59**. Due to the strong interaction of Na^+ with resin **59**, the elution peak for Na^+ in the stripping solution was retarded with respect to the other alkali-metal cations. With gradient stripping, the maximum concentration factor for Na^+ from aqueous sample solution which was 6.0×10^{-5} M in each of the five alkali-metal cations reached 1030 with an 84% purity.

Selective sorption and column concentration of alkali-metal cations by carboxylic acid resins **66** and **67** with dibenzo-14-crown-4 units and their acyclic analogues **60** and **68** were also studied.[22] The lariat ether carboxylic acids exhibited enhanced sorption selectivity over the acyclic polyether resins. Good sorption selectivity for Li^+ and Na^+ was obtained with resin **67** which has a geminal propyl group. For column concentration of alkali metal cations from dilute aqueous solutions, gradient elution of the sorbed metal ions from resin **67** gave selective column concentration of Li^+ and Na^+.

Competition sorption of alkali-metal cations by lariat ether phosphonic acid monoethyl ester resins **69** and **70** and the acyclic analogue **71** was also examined.

Assessment of potential applications from proton-ionizable lariat ether resins in the separations of heavy metal ions has been initiated. It has been found that lariat ether phosphonic acid monoethyl ester resins are much more effective at sorbing Pb^{2+} and Zn^{2+} from acidic aqueous solutions than are lariat ether carboxylic acid resins or acyclic polyether phosphonic acid monoethyl ester or carboxylic acid resins. Lariat ether phosphonic acid monoethyl resins **69** exhibits good selectivity for sorption of Pb^{2+} over Cd^{2+},

Co^{2+}, Cu^{2+}, Hg^{2+}, Ni^{2+} and Zn^{2+}.

G. Non-Ionizable Crown Ethers and Lariat Ethers and Their Polymers in Heterogeneous Metal Ion Complexation Systems

Although most of the research conducted during the report period involved proton-ionizable lariat ethers and acyclic analogues and their polymers, some very interesting results were also obtained with non-ionizable lariat ethers and crown ethers and their polymers.

1. Alkali-Metal Cation Extraction by a Lipophilic Crown Ether and by Lariat Ether Amides

In a collaborative project with W. J. McDowell at Oak Ridge National Laboratory,[8] the selective extraction of Cs^+ from acidic nitrate solutions by didodecylnaphthalenesulfonic acid (HDDNS) synergized with bis-(tert-butylbenzo)-21-crown-7 (**55**) was achieved. Under non-loading condition, the distribution coefficient for Cs^+ between a toluene solution 0.025 M in HDDNS and crown ether **55** and an aqueous solution 0.1 M in nitric acid is 100 with separation factors of 1.2 from Rb^+, 5.6 from K^+ and 294 from Na^+. Under loading and competitive extraction conditions, the distribution coefficients were lower (5 for Cs^+), but the separation factors remained in the same order and of useful magnitude, 1.5 from Rb^+, 6.4 from K^+ and 192 from Na^+.

The alkali-metal cation extracting ability of lariat ether amides **56** and **57** with R' and R" = H and alkyl was examined by the picrate extraction method using chloroform as the organic solvent. For **56** the Na^+ extraction selectivity and efficiency were found to be higher for dialkyl (ethyl, propyl, butyl, pentyl, hexyl) tertiary amides than for the unsubstituted amide (R' = R" = H) or a monoalkyl substituted amide (R' = H, R" = pentyl). For **57**, the presence of the geminal propyl group enhanced both the Na^+ extraction efficiency and selectivity compared with **56**. The highest Na^+

extraction selectivity was obtained for **57** and R' = R" = pentyl.

2. Alkali-Metal Complexation by Lariat Ether Amides in Polymeric Membrane Electrodes

Alkali-metal cation selectivities of the lariat ether amides **56** and **57** have been determined in solvent polymeric membrane electrodes. Using the fixed interference method in membrane electrodes composed of poly(vinyl chloride), *o*-nitrophenyl octyl ether and **57** with R' = R" = pentyl as the ionophore, excellent Na^+/K^+ and Na^+/Li^+ selectivities of 145 and 810, respectively, have been obtained.

3. Heavy Metal Complexation by Water-Soluble Diazacrown Ether Polymers

Polymers **72** and **73** possess 1,10-diaza-18-crown-6 ether units in the polymer backbone. These polymers are water-soluble and were designed and synthesized for use in homogeneous, aqueous phase separation of toxic, heavy metal ions from dilute aqueous solutions. The objective is to complex the heavy metal ion species on the chelating polymer and thereby prevent its passage through an ultrafiltration membrane which is permeable to uncomplexed metal ion species. In this liquid-phase, polymer-based retention (LPR) method, polymers **72** and **73** exhibited high propensity (>90%) from complexation of Hg^{2+} and Pb^{2+} in dilute aqueous solutions. Unfortunately, it has been found that the higher molecular weight components of the polymers are absorbed on the hydrophobic surface of the ultrafiltration membrane.

H. References

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III. RESEARCH PUBLICATIONS FROM THIS PROJECT WHICH HAVE APPEARED SINCE SUBMISSION OF THE LAST PROGRESS REPORT IN JUNE OF 1990.

1. "Effect of Structural Variations within Lipophilic Dibenzocrown Ether Carboxylic Acids on the Selectivity and Efficiency of Competitive Alkali-Metal Cation Solvent Extraction into Chloroform," W. Walkowiak, W. A. Charewicz, S. I. Kang, I.-W. Yang, M. J. Pugia, and R. A. Bartsch, Analytical Chemistry, **1990**, 62, 2018-2021.

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3. "Selective Sorption of Alkali-Metal Cations by Carboxylic Acid Resins Containing Acyclic or Cyclic Polyether Units," T. Hayashita, M.-J. Goo, J. C. Lee, J. S. Kim, J. Krzykawski and R. A. Bartsch, Analytical Chemistry, **1990**, 62, 2283-2287.

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Polymer-Supported Liquid Membranes Containing sym-(Decyl)-dibenzo-16-crown-5-oxyacetic Acid: Variation of the Alkyl 2-Nitrophenyl Ether Membrane Solvent," P. R. Brown, J. L. Hallman, L. H. Whaley, D. H. Desai, M. J. Pugia and R. A. Bartsch, Journal of Membrane Science, **1991**, 56, 195-206.

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9. "A Lipophilic Lariat Ether with Different Intraannular and Pendent Acidic Functions: Synthesis and Metal Ion Extraction," Journal of Organic Chemistry, **1992**, 57, 725-728.
10. "Separation of Alkali Metal Cations by Polymer-Supported Liquid Membranes Using Ionizable Crown Ethers," J. Strzelbicki, B. Strzelbicka, E. Luboch and R. A. Bartsch, in "Solvent Extraction 1990," J. Sekine, Ed., Elsevier, Amsterdam, 1992, pp. 1517-1522.
11. "Crown Ethers in Separation of Alkali Metal Cations," J. Strzelbicki, B. Strzelbicka, K. Schügerl and R. A. Bartsch, in "Solvent Extraction 1990," T. Sekine, Ed., Elsevier, Amsterdam, 1992, pp. 1523-1528.
12. "Selective Sorption and Column Concentration of Alkali-Metal Cations by Carboxylic Acid Resins with Dibenzo-14-crown-4 Subunits and Their

Acyclic Analogues," T. Hayashita, J. H. Lee, M. G. Hankins, J. C. Lee, J. S. Kim, J. M. Knobeloch and R. A. Bartsch, Analytical Chemistry, **1992**, 64, 815-819.

13. "Effect of Solvent upon Competitive Liquid-Liquid Extraction of Alkali Metal Cations by Isomeric Dibenzo-16-crown-5-oxyacetic Acids," W. Walkowiak, E.-G. Jeon, H. Huh and R. A. Bartsch, Journal of Inclusion Phenomena and Molecular Recognition in Chemistry, **1992**, 12, 213-222.
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15. "Competitive Solvent Extraction of Alkali Metal Cations into Chloroform by Lipophilic Acyclic Proton-Ionizable Polyethers," W. Walkowiak, G. M. Ndip, D. H. Desai, H. K. Lee, and R. A. Bartsch, Analytical Chemistry, **1992**, 64, 1685-1690.
16. "Synthesis of Lipophilic Crown Ethers with Pendant Phosphonic Acid or Phosphonic Acid Monoethyl Ester Groups," B. P. Czech, D. H. Desai, J. Koszuk, A. Czech, D. A. Babb, T. W. Robison, and R. A. Bartsch, Journal of Heterocyclic Chemistry, **1992**, 29, 867-875.
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19. "Synthesis of Dibenzocrown Ethers with Pendent Amide Groups," S. Kasprzyk and R. A. Bartsch, Journal of Heterocyclic Chemistry, **1993**,

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20. "Anion Effect on Selectivity in Crown Ether Extraction of Alkali Metal Cations," U. Olsher, M. G. Hankins, Y. D. Kim and R. A. Bartsch, Journal of American Chemical Society, **1993**, 115, 3370-3371.

21. "Ionic Recognition by Proton-Ionizable Lariat Ethers and Their Polymers," R. A. Bartsch, J. S. Kim, U. Olsher, D. W. Purkiss, V. Ramesh, N. K. Dalley, and T. Hayashita, Pure and Applied Chemistry, **1993**, 65, 399-402.

22. "Metal Ion Separations with Proton-Ionizable Crown Ethers and Their Polymers," R. A. Bartsch, T. Hayashita, J. H. Lee, J. S. Kim and M. G. Hankins, Supramolecular Chemistry, **1993**, 1, 305-311.

IV. PROJECT SUPPORTED PRESENTATIONS SINCE SUBMISSION OF THE LAST PROGRESS REPORT IN JUNE OF 1990.

1. "Proton-Coupled Transport of Alkali-Metal Cations across Polymer-Supported Liquid Membranes by Lipophilic Crown Ether Carboxylic Acids," R. A. Bartsch and J. Strzelbicki, 201st National Meeting of the American Chemical Society, Atlanta, Georgia, April, 1991. (Invited paper in the Symposium on Macrocycles in Separation Science sponsored by the Separation Science and Technology Subdivision of the Division of Industrial and Engineering Chemistry.)

2. "Synthesis and Alkali-Metal Cation Sorption of Ion Exchange Resins Formed from Proton-Ionizable Crown Ethers," T. Hayashita and R. A. Bartsch, 201st National Meeting of the American Chemical Society, Atlanta, Georgia, April 1991. (Invited paper in the Symposium on Macrocycles in Separation Science sponsored by the Separation Science and Technology Subdivision of the Division of Industrial and Engineering Chemistry.)

3. "Influence of Structural Variation within Lipophilic, Proton-Ionizable Crown Ether Carriers upon Proton-Coupled Transport of Alkali-Metal Cations across Polymer-Supported Liquid Membranes," R. A. Bartsch, J. Strzelbicki and B. Strzelbicka, 201st National Meeting of the American Chemical Society, Atlanta, Georgia, April, 1991. (Invited paper in the Symposium on Membrane Technology for New Applications sponsored by the Separation Science and Technology Subdivision of the Division of Industrial and Engineering Chemistry.)
4. Effect of Structural Variation within sym-(R)dibenzo-16-crown-5-oxycetic Acid Resins upon the Selectivity and Efficiency of Alkali-Metal Cation Sorption," T. Hayashita, M.-J. Goo, J. S. Kim and R. A. Bartsch, 46th Northwest Regional Meeting of the American Chemical Society, La Grande, Oregon, June 1991.
5. "Metal Ion Separations with Proton-Ionizable Lariat Ethers and Their Polymers," R. A. Bartsch, First Hanford Separation Science Workshop, Richland, Washington, July 1991. (Invited paper.)
6. "Synthesis and Alkali-Metal Separation by Proton-Ionizable Crown Ether Resins," T. Hayashita and R. A. Bartsch, 63rd Spring Meeting of the Chemical Society of Japan, Osaka, Japan, March 1992.
7. "Metal Ion Separations with Crown Ether Carboxylic Acid Resins," R. A. Bartsch, T. Hayashita, J. H. Lee and M. G. Hankins, 203rd National Meeting of the American Chemical Society, San Francisco, California, April 1992. (Invited paper in the Symposium on Polymeric Complexing Agents Applied to Environmental Separation Problems sponsored by the Separation Science and Technology Subdivision of the Division of Industrial and Engineering Chemistry.)
8. "Solvent Extraction of Heavy Metal Nitrates with Polythiacrown Ethers," R. A. Bartsch and J. P. Shukla, 203rd Meeting of the American Chemical

Society, San Francisco, California, April 1992. (Invited paper in the Symposium on Complexing Agents for Ions and Molecules Applied to Environmental Separations sponsored by the Separation Science and Technology Subdivision of the Division of Industrial and Engineering Chemistry.)

9. "Ionic Recognition by Proton-Ionizable Lariat Ethers," R. A. Bartsch, J. S. Kim, V. Ramesh and N. K. Dalley, 203rd National Meeting of the American Chemical Society, San Francisco, California, April 1992. (Invited paper in the James Flack Norris Award Symposium of the Division of Organic Chemistry.)
10. "Metal Ion Separations with Proton-Ionizable Crown Ethers and Their Polymers," R. A. Bartsch, T. Hayashita, J. H. Lee, J. S. Kim and M. G. Hankins, 7th International Symposium on Molecular Recognition and Inclusion, Kyoto, Japan, July 1992. (Invited paper.)
11. "Ionic Recognition by Proton-Ionizable Lariat Ethers and Their Polymers," R. A. Bartsch, J. S. Kim, T. Hayashita, D. W. Purkiss, and N. K. Dalley, XVII International Symposium on Macrocyclic Chemistry, Provo, Utah, August 1992. (Invited paper.)
12. "Synthesis of Crown Ethers with Pendent Carboxylic Acid Groups," D. E. McGowen, J. S. Kim and R. A. Bartsch, 48th Southwest Regional Meeting of the American Chemical Society, Lubbock, Texas, October 1993.
13. "Ion-Pair Sorption of Alkali Metal Chlorides by Resins Prepared from Substituted Dibenzocrown Ethers and Correspond Acyclic Polyethers," J. C. White, T. Hayashita and R. A. Bartsch, 48th Southwest Regional Meeting of the American Chemical Society, Lubbock, Texas, October 1993.
14. "Selective Sorption of Heavy Metal Cations by Condensation Polymers Prepared from Proton-Ionizable Dibenzo-16-crown-5 Monomers," E. E. Laney, T. Hayashita, J. S. Kim and R. A. Bartsch, 48th Southwest

Regional Meeting of the American Chemical Society, Lubbock, Texas, October 1993.

15. "Synthesis of New sym-(R)Dibenzo-16-crown-5-oxyacetic Acids," J. S. Kim and R. A. Bartsch, 48th Southwest Regional Meeting of the American Chemical Society, Lubbock, Texas, October 1993.
16. "Synthesis of Crown Ether Carboxylic Acids Based on Dibenzo-15-crown-5, -18-crown-6, and -21-crown-7," J. S. Kim and R. A. Bartsch, 48th Southwest Regional Meeting of the American Chemical Society, Lubbock, Texas, October 1993.
17. "The Anion Effect in Solvent Extraction of Alkali Metal Cations by Dicyclohexano-18-crown-6 Isomers," M. G. Hankins, U. Olsher, S. Kasprzyk and R. A. Bartsch, 48th Southwest Regional Meeting of the American Chemical Society, Lubbock, Texas, October 1993.
18. "Picrate Extraction of Alkali Metal Cations by Lariat Ethers with Pendent Amide Groups," M. D. Eley, S. Kasprzyk and R. A. Bartsch, 48th Southwest Regional Meeting of the American Chemical Society, Lubbock, Texas, October 1993.
19. "Amide-Armed Crown Ethers: Side Arm Effects in Cooperative Binding," V. Ramesh, S. Kasprzyk and R. A. Bartsch, 48th Southwest Regional Meeting of the American Chemical Society, Lubbock, Texas, October 1993.
20. "Thermodynamics of Alkali Metal Cation Complexation by Crown Ethers with Intraannular Groups," V. Ramesh, J. Krzykawski, J. C. Lee, B. P. Czech and R. A. Bartsch, 48th Southwest Regional Meeting of the American Chemical Society, Lubbock, Texas, October 1993.
21. "Molecular Design of Novel Crown Ether Resins and Their Function for Metal Ion Separation," T. Hayashita, K. Yamasaki, J. C. White and R. A. Bartsch, Kyushu and Chubu-Shikoku Regional Meeting of the Chemical Society of Japan, Saga, Japan, October 1993.

22. "Metal Ion Separations by Proton-Ionizable Crown Ether Resins," R. A. Bartsch, T. Hayashita, M. G. Hankins and E. E. Laney, 205th National Meeting of the American Chemical Society, Denver, Colorado, April 1993, (Invited paper in Symposium on Chemically Specific Separations sponsored by the Separation Science and Technology Subdivision of the Division of Industrial and Engineering Chemistry.)

V. GRANT COMPLIANCE

It is estimated that by the termination of the present grant period on December 31, 1993, all funds allocated by the U. S. Department of Energy will be expended or encumbered. During the grant period, Dr. Richard A. Bartsch, the Principal Investigator, has devoted 15 percent of his time and effort during the calendar year and 35 percent of his time during the summer to the project. All items of the Agreement and Supplemental Agreements have met compliance.

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