

COMPLEXING AGENTS FOR METAL CATIONS  
AND FOR ANIONS

by

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# CHAPTER I

## INTRODUCTION

In recent years, the selective complexation of some organic compounds with specific metal cations and anions have drawn the interest of many chemists. These compounds have been found useful in analytical, environmental and other industrial fields. For the purpose of developing new complexing agents and probing their complexation behaviors, a series of novel macrocyclic polyether compounds has been synthesized by members of the Bartsch Research Group. The complexation of crown ethers for alkali and alkaline earth metal cations will be determined by the metal picrate extraction method. Chromatographic columns will be used to probe the anion selectivity of some new anion exchange resins. An ultrafiltration approach will be used to evaluate the complexation of heavy metals by a water-soluble polymer. A brief review of the literature for these methods follows.

## Metal Ion Complexation by Crown Ethers

In 1967, Charles J. Pedersen [1, 2] reported that cyclic polyether compounds possess specific cation complexation capabilities. This inspired an avalanche of synthetic efforts to prepare new polyether compounds. The field progressed to include not only cyclic polyether compounds, but also bicyclic, tricyclic and other related three-dimensional structures. In 1987, the Nobel prize was jointly awarded to D. J. Cram, J.-M. Lehn, and C. J. Pedersen for their achievements in the area of host-guest chemistry.

Since the IUPAC names for crown ethers are complicated and cumbersome, trivial names are used more often in the nomenclature of these compounds. These trivial names consist of naming in order: (1) the number and kind of substituents on the polyether ring; (2) the total number of atoms in the polyether ring; (3) the class name, crown; and (4) the number of oxygen atoms in the polyether ring [2]. For example, the compound shown in Figure 1-1 is given the trivial name of dibenzo-18-crown-6.

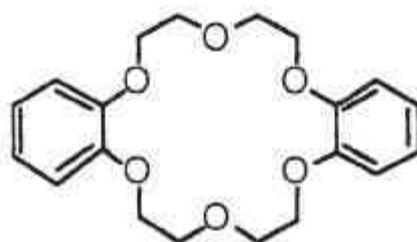


Figure 1-1. Structure of Dibenzo-18-crown-6

Pedersen described the complexation of inorganic and organic cations by a variety of crown ethers in several publications [1, 2, 7]. In these papers, he determined the factors which most affect the relative stabilities of crown ether-cation complexes. Of greatest importance was the relationship between the diameter of the crown ether cavity and the ionic diameter of the cation. It has been found [3] that alkali-metal cations fit best in molecules with cavities slightly larger than the ionic radius. For example, of the alkali metal cations  $\text{Na}^+$  (1.90 Å) best fits the cavity of a 15-crown-5 compound (1.7 - 2.2 Å).

The placement of oxygen donor atoms in the ring is also important. Such donor atoms should be relatively coplanar and evenly spaced around the ring in a symmetric fashion. Good complexation may also be possible if the donor sites are not coplanar in the uncomplexed ligand, if they can adopt coplanarity

in the complex. However, the need to change from one conformation to another for complexation decreases the complexation rate and the overall efficiency of complexation. Therefore ligands with conformational rigidity which enforces coplanarity of the donor atoms form stronger complexes than more flexible ones, other things being held constant.

The donating ability of the ether oxygen atoms is also affected by alkyl and aryl substituents. Generally better complexation is obtained when electron-releasing groups are connected to the oxygen atom. Hence attached alkyl groups are better than aryl groups. The presence of electronegative groups gives ligands with poorer complexing abilities.

The identity of the donor atoms also determines whether “hard” or “soft” cations will form complexes [4]. Hard oxygen donor atoms are selective for the hard alkali-metal and alkaline earth metal cations. Replacing oxygen donor atoms with sulfur increases selectivity for the softer cations, such as transition metal cations. Nitrogen, which is intermediate in donor hardness, is able to efficiently coordinate with either hard or soft cations [5, 6].

Bulky alkyl or aryl groups located close to the cavity of a crown ether may provide steric hindrance to the approach of a cation and its counterion, thus decreasing the complexation ability. Hard cations, such as  $\text{Li}^+$ , which strongly associate with solvent molecules must shed the molecules of solvation during complexation [4]. Bulky alkyl or aryl groups force the cations to shed the associated solvent molecules as the cation approaches the cavity, making complexation more difficult [8].

Another factor which helps to determine the selectivity and binding ability of a ligand is the formation of “sandwich” complexes which involve more than one ligand molecule. Whereas most of the early complexes studied by Pedersen formed 1:1 (ligand:metal cation) complexes, it is possible for two small ligands to “share” a large metal cation. Preventing sandwich-type complexation of a large cation by small crown ethers can greatly enhance the selectivity of that ligand for the small cation with which it forms a 1:1 complex.

In recent years, a variety of analytical methods which incorporate crown ether ligands have been developed. These methods can be divided into three classifications.

## Chromogenic Methods

In this method, the function of the crown ether ligand is a color change that occurs upon complexation with the metal ion. Molecules of this type generally have a side arm that interacts with the bound metal ion and perturbs molecular conjugation. This method is usually used to determine alkali and alkaline earth metal ions. It has potential for applications in environmental analysis and clinical laboratories [18, 35].

## Chromatography Method

Cation and anion separations may be performed with water, methanol or aqueous methanol eluents on columns packed with polystyrene or silica gel-bound neutral polyether ligands [9]. These separations are unique since conductivity detection may be used without the requirement for background suppression. Good resolution of alkali metal salts has been demonstrated by silica gel-bound benzo-15-crown-5 [5].

## Liquid-liquid Extraction Method

In this method, polyether chelating agents are used for the separation, enrichment and recovery of metal ions from aqueous solutions.

Picrate extraction is a frequently utilized method for assessing the efficiency with which a crown ether complexes metal ions. In this method, the extraction of an alkali-metal picrate salt from an aqueous solution into a solution of the crown ether compound in a water-immiscible organic solvent is measured [10]. In Pedersen's procedure [7], the aqueous solution contained picric acid and an excess of an alkali-metal hydroxide and a dichloromethane layer contained the crown ether compound. Before the two solutions were mixed, all of the picrate ion was in the aqueous phase, as evidenced by a strong yellow color. After equilibration of the two solutions, the crown compound had complexed a certain amount of the metal cation and transferred it into the organic phase, along with an equivalent amount of picrate anion for charge neutrality. The organic phase acquired the yellow color of the picrate anion.

Frensdorf extended this method by elucidating the basis for calculating the stability constant,  $K_s$ , for a given metal cation-crown ether complex from the UV spectra of both the aqueous and organic solutions after extraction [9]. Although more precise methods for determining  $K_s$  values have been developed, Pedersen's picrate extraction, as extended by Frensdorf, remains the most convenient way to determine the relative complexing abilities of crown ether compounds.

Even though the extent of extraction depends not only on the complexation equilibria but also on the solubilities and partition coefficients of the various uncomplexed and complexed species, the picrate extraction method has proven to be very convenient for rapid screening and has led to conclusions with regard to the effects of such factors as ring size and cation size on complexation [6].

### Selective Column Separation

Polyvinyl resins with positively charged sites can be packed into columns for selective separation of anions. Selectivity can be regarded as a competition between the resin phase and the

aqueous phase for stabilizing the charge of the counterions [19]. Clifford and Weber [20] reported that the distance of fixed charge separation in the resin is the primary determinant of divalent-monovalent selectivity. Matrix hydrophobicity is another important determinant of selectivity in monovalent-divalent anion systems. The selectivity of an anion exchange resin is also influenced by the equilibrium, kinetics and mechanism of the anion-exchange process [21].

Utilization of polyvinyl resins in ion chromatography has been reported by several authors [11-17]. Polyvinyl resins have also been used for selective concentration of anions [18]. When a solution containing multiple anion species is passed through a column packed with an anion-selective polyvinyl resin, anions which are bound strongly to the polymer remain on the column whereas anions which are weakly bound tend to pass through the column. After loading the column, a stripping solution is utilized to release the sorbed anions. This results in concentration of specific anionic species.

## Liquid-phase Polymer-based Retention

Preconcentration techniques are often required in inorganic analysis, especially in trace analysis to separate elements to be determined from interfering constituents [25]. Although many such methods have been developed and successfully used, their application may encounter problems, such as heterogeneous reactions and interphase transfer [22]. Two-phase systems can be avoided by application of separation methods based on membrane processes. One of these methods is liquid-phase, polymer-based retention (LPR) which is used for selective ion separation and enrichment in a homogeneous aqueous phase [23]. By application of polychelators, polymeric ion associates are formed which are separated from other ionic species and low-molecular compounds by membrane filtration. Thus, inorganic ions which are not bound to the chelating polymer pass through the membrane, whereas the water-soluble macromolecules with bound ions can not traverse the membrane. This method allows for the selective enrichment and separation of various ions in the presence of large excesses of other ionic species [22, 24]. Ultrafiltration, in which the different

chemical compounds are separated exclusively according to their molecular dimensions, is used in the LPR method.

The principle of this process was first suggested by Michaels [27]. The solution containing the metal ion to be removed in a mixture with other salts is fed into a vessel which contains a solution of a macromolecular complexing or chelating agent that selectively binds the desired metal ion species. The solution is filtered through an ultrafiltration unit which retains the macromolecular complex completely, but passes unbound salts or other low molecular weight components. The rejected macromolecular complex is either fed back into the contacting vessel or collected for further treatment when completely loaded.

For this process to be effective, certain requirements have to be fulfilled by the complex. In general, these chelating polymers should have: (a) the desired selectivity for a certain metal ion or groups of metal ions; (b) sufficient solubilizing power of the constitutional repeating unit which provides water-solubility of the polymer complexes; (c) a high concentration of complexing agent units on the polymer for high capacity; and (d) a high molecular

weight to allow for easy separation by usual methods from metals not bound to the polymer.

The selectivity of a polychelatogen for inorganic ions depends on both the reactivity of the functional group and the chemical nature of the polymer backbone. In most cases, the influence of the functional group is stronger than that of the repeating unit in the polymer chain [24]. Water solubility is provided by a high content of hydrophilic groups, e.g., amino, hydroxyl, carboxyl, amide and sulfonic acid groups, or hydrophilic units in the polymer backbone. A number of soluble polymers have been found to be suitable for the complexation of metal ions [26], such as poly(vinylamine), poly(ethylenimine) [29-30], poly(acrylic acid), poly(vinylalcohol), and poly(ethylene-oxide) [31-32].

The membranes used in ultrafiltration can be made of the usual materials, e.g., polysulfone, polyamide cellulose, etc.. Also commercially available membranes are suitable for LPR ( Amicon PM 10, Millipore PTGC, or their equivalents) [33].

It is advantageous to combine modern analytical instrument with such a preconcentration and separation method. For

example, flame atomic absorption determination of metals in conjunction with LPR has proved to be very useful [34].

### Statement of Research Objectives

The first portion of this thesis research will involve the determination of the complexation efficiency of different crown ethers for alkali and alkaline earth-metal cations by the picrate extraction method. Several series of crown ethers with systematic structural variations are to be investigated in this manner.

A second study probes the merits of a column separation method which incorporates novel poly(4-vinylpyridinium) resins. To evaluate the selectivity of the resins for some common anions, packed columns will be loaded with multi-anion solutions and eluted.

The potential of an emerging metal ion separation technique is evaluated in the third study. Soluble polymeric chelating resins are employed in combination with ultrafiltration for removal of heavy metals from dilute aqueous solutions. The objective is to ascertain the potential for selective separation and concentration of heavy metal ions by liquid-phase, polymer-based retention.

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CHAPTER II  
ASSESSMENT OF METAL ION COMPLEXING  
ABILITIES OF CROWN ETHERS BY  
PICRATE EXTRACTION

Chapter Introduction

When an aqueous solution of an alkali metal picrate is mixed with an equal volume of an immiscible liquid like dichloromethane or toluene, nearly all of the picrate is present in the yellow aqueous phase and the organic phase remains essentially colorless. If a crown ether is added to the system, the complexed metal picrate transfers to the organic phase which imparts a yellow color. The intensity of the color, as monitored by ultraviolet-visible spectroscopy, is taken to be a measure of the extent to which the salt is extracted into the organic phase and thereby a measure of the complexing ability of the crown ether [1-9].

The use of metal picrate salts as guest cations to provide a spectrometric method for determining the stoichiometry of the crown ether-cation complex was reported by Smid and co-workers

[11]. The position of the absorption maximum of the picrate anion in THF was noted to be sensitive to the ion pairing of the metal salt. For crown-cation complexes of 1:1 stoichiometry, the salt forms a tight ion pair which has an absorption maximum between 350 and 362 nm, depending on the alkali metal cation used. When the stoichiometry of the complex is two crown ethers to one cation, the salt forms a "crown separated" ion pair and the absorption maximum shifts to 375-390 nm. "Crown-separated" ion pairs for a 1:1 complex are also possible [5, 10, 12].

Iwachido and co-workers later reported the distribution of alkali metal picrate complexes between an aqueous phase and a benzene solution of dibenzo-18-crown-6 [3]. The extraction constant ( $K_{ex}$ ) was defined by the equilibrium between free metal and picrate in the aqueous phase ( $[M^+]_a$  and  $[A^-]_a$ ), free crown ether in the organic phase ( $[Cr]_o$ ), and the complex ion pair in the organic phase ( $[MCrA]_o$ ) (Equation 2-2).



$$K_{ex} = [MCrA]_o / [M^+]_a [Cr]_o [A^-]_a \quad (2-2)$$

The extraction constant defined by Iwachido and co-workers represents only the concentration equilibrium constant of the crown ether with a particular metal picrate and does not include ionic activity coefficients or any compensation for the increased lipophilicity of the picrate salts as the ionic diameter increases. Thus, the extraction constant is only a measure of the activity of the crown ether in single ion solvent extraction systems and has no thermodynamic significance.

Even though the extent of extraction depends not only on the complexing equilibria but also on the solubilities and partition coefficients of the various uncomplexed and complexed species, the picrate extraction method has proven to be very convenient for rapid screening [3].

In the following study, several sets of crown ethers were analysed for their metal ion complexation abilities by picrate extraction.

## Experimental

### Reagents, Apparatus and Instrumentation

The crown ethers were synthesized by other co-workers in the Bartsch Research Group. Acetonitrile (99.5%) was obtained from EM Science. Chloroform (stabilized, 99.9%) was obtained from Mallinckrodt. Before use, the chloroform was washed with deionized water to remove the ethanol stabilizer. Deionized water was used to make aqueous solutions and rinse the glassware. Deionized water was prepared by passage of distilled water through three Barnstead combination ion-exchange cartridges in series. Extractions were performed by agitating samples in 15-ml, metal-free, conical polypropylene centrifuge tubes (Elkay) with a Fisher Vortex Genie 2 mixer. Phase separation following extraction was accomplished with a Clay Adams Safety-Head centrifuge. Extracted samples were analysed with a Shimadzu UV-260 spectrophotometer using a 1.0 cm optical cell. All extractions were conducted at room temperature

## Procedure for Picrate Extraction [6]

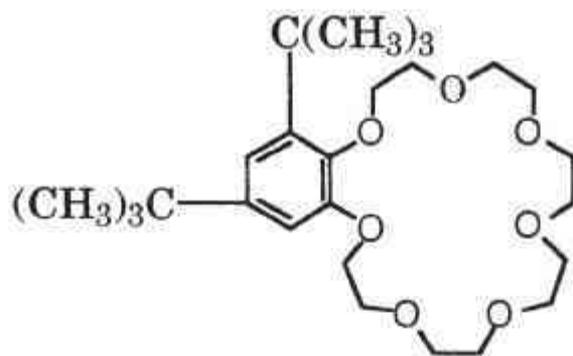
Crown ether solutions (5.0 mM) were prepared in ethanol-free chloroform. Extraction experiments were conducted by adding 0.50 mL of a 5.0 mM crown ether solution in chloroform to 0.50 mL of 5.0 mM picrate solution in a centrifuge tube and agitating the mixture with a vortex mixer for 3 min. Five identical samples were run concurrently. The mixtures were centrifuged for 10 min to assure complete separation of the layers. Precisely measured aliquots were removed from each layer with microsyringes and diluted in acetonitrile. UV-visible spectra of these solutions were measured in the region of 300-500 nm. The absorbance at the absorption maximum for picrate ion (375 nm) was measured and compared with that for a known concentration of the alkali metal picrate. From the absorbance values, the percent extraction was calculated. From the percent extraction values, the  $\log K_{\text{ex}}$  value was calculated using a computer program written by David A. Babb [8].

## Results and Discussion

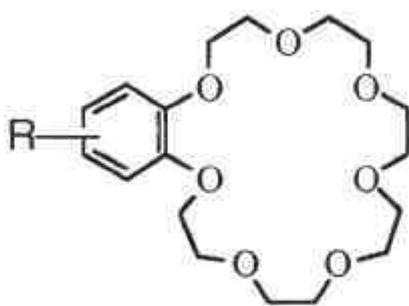
### Benzo-21-crown-7 and Dibenzo-21-crown-7 Compounds

A variety of benzo-21-crown-7 and dibenzo-21-crown-7 compounds (Figure 2-1) were tested for their efficiencies in complexation of alkali and alkaline earth metal picrates. For this ring size, these crown ethers would be expected to favor extraction of the larger alkali and alkaline earth-metal cations. Results of the extraction experiments (Table 2-1) show that the complexation selectivity for crown ethers **2-6** is  $\text{Cs}^+, \text{Rb}^+ \gg \text{K}^+ \gg \text{Na}^+, \text{Li}^+$  for the alkali-metal cations and  $\text{Ba}^{2+} > \text{Sr}^{2+} \gg \text{Ca}^{2+}, \text{Mg}^{2+}$  for the alkaline earth-metal cations. For crown ether **1**, the orderings are  $\text{Rb}^+ > \text{Cs}^+, \text{K}^+ \gg \text{Na}^+, \text{Li}^+$  and  $\text{Ba}^{2+} \gg \text{Sr}^{2+}, \text{Mg}^{2+} > \text{Ca}^{2+}$ . Selectivity for complexation of  $\text{Cs}^+$  relative to  $\text{Na}^+$  is important for the removal of radioactive  $\text{Cs}^+$  in the recycling of nuclear fuel rods [13].

It is interesting to note that for all of the compounds, extractions of  $\text{Cs}^+$  and  $\text{Rb}^+$  were almost equally efficient except with **1**, in which the presence of two bulky substituents on the benzene ring results in a diminished extraction on  $\text{Cs}^+$ .



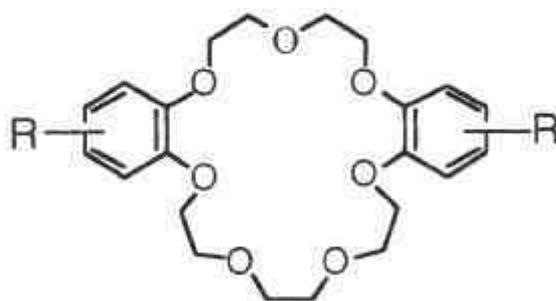
**1**



**R**

**2**      -CH(OH)CH(C<sub>2</sub>H<sub>5</sub>)C<sub>4</sub>H<sub>9</sub>

**3**      -CH(OCH<sub>2</sub>CH<sub>2</sub>OH)CH(C<sub>2</sub>H<sub>5</sub>)C<sub>4</sub>H<sub>9</sub>



**R**

**4**      -C(O)CH(C<sub>2</sub>H<sub>5</sub>)C<sub>4</sub>H<sub>9</sub>

**5**      -CH(OH)CH(C<sub>2</sub>H<sub>5</sub>)C<sub>4</sub>H<sub>9</sub>

**6**      -CH(OCH<sub>2</sub>CH<sub>2</sub>OH)CH(C<sub>2</sub>H<sub>5</sub>)C<sub>4</sub>H<sub>9</sub>

Figure 2-1. Structures of the Benzo-21-crown-7 and Dibenzo-21-crown-7 Compounds

The presence of a carbonyl group on the alkyl chain in compound **4** results in a reduced complexation ability. The stability of the complexes is related to the basicity of oxygen atoms of the crown ether [13]. Carbonyl groups reduce the oxygen basicity because of their electron-withdrawing effect.

It has been reported that the symmetry of the crown ether structure can be a factor affecting the host-guest complexation [9]. Compounds **2** and **3** have a side arm on only one side of the structure, while compounds **5** and **6** have identical arms on both sides. Comparing extraction abilities of **2** and **3** with **5** and **6**, it is noted that the unsymmetrical compounds **2** and **3** possess higher complexation capabilities.

It is interesting to note that compounds **2** and **3** are very similar in their complexation abilities. So are compounds **5** and **6**. Thus the elongated alcohol side arms in compounds **3** and **6** produced no enhancement in complexation above that found with crown ethers **2** and **5**.

Table 2-1. Extraction of Alkali and Alkaline Earth-Metal Picrates into Chloroform by 21-Crown-7 Compounds

Compound	M <sup>n+</sup>	% Ex	K <sub>ex</sub>
<b>1</b>	Li <sup>+</sup>	0.74 ± 0.27	2.46
	Na <sup>+</sup>	0.87 ± 0.34	2.53
	K <sup>+</sup>	16.2 ± 0.7	4.04
	Rb <sup>+</sup>	36.9 ± 0.6	4.77
	Cs <sup>+</sup>	15.6 ± 0.5	4.02
	Mg <sup>2+</sup>	2.96 ± 0.59	3.11
	Ca <sup>2+</sup>	0.69 ± 0.39	2.40
	Sr <sup>2+</sup>	2.99 ± 0.70	3.11
	Ba <sup>2+</sup>	72.7 ± 0.5	6.16
<b>2</b>	Li <sup>+</sup>	2.10 ± 0.70	2.93
	Na <sup>+</sup>	2.38 ± 0.52	3.00
	K <sup>+</sup>	26.2 ± 0.5	4.42
	Rb <sup>+</sup>	42.9 ± 0.8	4.97
	Cs <sup>+</sup>	44.7 ± 0.5	5.03
	Mg <sup>2+</sup>	1.15 ± 0.38	2.66
	Ca <sup>2+</sup>	0.52 ± 0.19	2.30
	Sr <sup>2+</sup>	15.1 ± 0.3	3.99
	Ba <sup>2+</sup>	65.7 ± 0.3	5.81

Table 2-1. (Continued)

Compound	M <sup>n+</sup>	% E <sub>x</sub>	K <sub>ex</sub>
<b>3</b>	Li <sup>+</sup>	2.42 ± 0.61	3.01
	Na <sup>+</sup>	2.88 ± 0.84	3.08
	K <sup>+</sup>	25.2 ± 0.9	4.38
	Rb <sup>+</sup>	43.3 ± 0.6	5.00
	Cs <sup>+</sup>	46.0 ± 0.7	5.07
	Mg <sup>2+</sup>	1.96 ± 0.32	2.92
	Ca <sup>2+</sup>	0.79 ± 0.37	2.47
	Sr <sup>2+</sup>	13.5 ± 0.3	3.92
	Ba <sup>2+</sup>	69.6 ± 0.3	6.00
<b>4</b>	Li <sup>+</sup>	2.37 ± 0.47	3.00
	Na <sup>+</sup>	1.46 ± 0.69	2.74
	K <sup>+</sup>	9.27 ± 0.64	3.70
	Rb <sup>+</sup>	23.4 ± 0.5	4.32
	Cs <sup>+</sup>	21.9 ± 0.7	4.27
	Mg <sup>2+</sup>	1.21 ± 0.56	2.65
	Ca <sup>2+</sup>	1.45 ± 0.49	2.76
	Sr <sup>2+</sup>	1.52 ± 0.71	2.74
	Ba <sup>2+</sup>	61.9 ± 0.3	5.65

Table 2-1. (Continued)

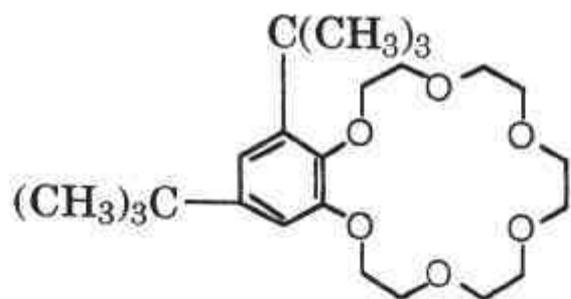
Compound	M <sup>n+</sup>	% Ex	K <sub>ex</sub>
<b>5</b>	Li <sup>+</sup>	1.14 ± 0.57	2.63
	Na <sup>+</sup>	0.86 ± 0.34	2.52
	K <sup>+</sup>	19.2 ± 0.5	4.16
	Rb <sup>+</sup>	32.9 ± 0.8	4.64
	Cs <sup>+</sup>	31.7 ± 0.3	4.60
	Mg <sup>2+</sup>	0.60 ± 0.21	2.37
	Ca <sup>2+</sup>	1.28 ± 0.43	2.71
	Sr <sup>2+</sup>	8.02 ± 0.43	3.61
	Ba <sup>2+</sup>	67.1 ± 0.5	5.88
<b>6</b>	Li <sup>+</sup>	0.70 ± 0.26	2.44
	Na <sup>+</sup>	0.74 ± 0.28	2.46
	K <sup>+</sup>	18.3 ± 0.4	4.13
	Rb <sup>+</sup>	32.0 ± 0.5	4.61
	Cs <sup>+</sup>	32.0 ± 0.3	4.61
	Mg <sup>2+</sup>	1.22 ± 0.56	2.65
	Ca <sup>2+</sup>	1.92 ± 0.96	2.84
	Sr <sup>2+</sup>	6.82 ± 0.33	3.53
	Ba <sup>2+</sup>	67.9 ± 0.7	5.92

## Benzo-18-crown-6 and Dibenzo-18-crown-6 Compounds

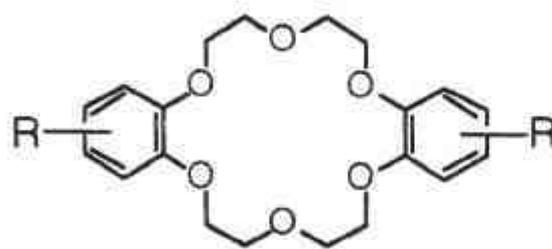
As part of a comprehensive study of the complexation of alkali and alkaline earth metal cations by 18-crown-6 ethers, several benzo-18-crown-6 and dibenzo-18-crown-6 compounds were evaluated by the picrate extraction methods. The compounds tested are shown in Figure 2-2. Since  $K^+$  should fit well into a 18-crown-6 cavity, selectivity for  $K^+$  complexation is expected. Results of the extraction experiments (Table 2-2) show that the complexation selectivity is  $K^+ > Rb^+ > Cs^+ > Na^+ > Li^+$  for the alkali metal cations. The percentages of alkaline earth metal picrates extracted into chloroform were all rather low.

In comparison with compounds **9**, **13** and **14**, the degree of complexation by **10** and **11** was reduced. The carbonyl groups on the side arms of compounds **10** and **11** reduce the basicity of the ether oxygens by an electron-withdrawing effect. This results in a decreased complexing ability.

The extraction results for compounds **9**, **13** and **14** are similar. They all show high extraction of  $K^+$ , good extraction of  $Rb^+$  and modest extraction of  $Cs^+$ . Comparing compounds **12**, **13**



**7**



R

- |           |  |
|-----------|--|
| <b>8</b>  | -H   |
| <b>9</b>  | -CH(OH)C <sub>6</sub> H <sub>13</sub>  |
| <b>10</b> | -C(O)C <sub>6</sub> H <sub>13</sub>  |
| <b>11</b> | -C(O)CH(C <sub>2</sub> H <sub>5</sub> )C <sub>4</sub> H <sub>9</sub>   |
| <b>12</b> | -CH(OH)CH(C <sub>2</sub> H <sub>5</sub> )C <sub>4</sub> H <sub>9</sub>   |
| <b>13</b> | -CH(OCH <sub>2</sub> CH <sub>2</sub> OH)CH(C <sub>2</sub> H <sub>5</sub> )C <sub>4</sub> H <sub>9</sub>                                  |
| <b>14</b> | -CH(OCH <sub>2</sub> CH <sub>2</sub> OCH <sub>2</sub> CH <sub>2</sub> OH)CH(C <sub>2</sub> H <sub>5</sub> )C <sub>4</sub> H <sub>9</sub> |

Figure 2-2. Structures of the Benzo-18-crown-6 and Dibenzo-18-crown-6 Compounds

Table 2-2. Extraction of Alkali and Alkaline Earth-Metal Picrates into Chloroform by 18-Crown-6 Compounds

Compound	M <sup>n+</sup>	% Ex	K <sub>ex</sub>
7	Li <sup>+</sup>	0.72 ± 0.27	2.45
	Na <sup>+</sup>	1.24 ± 0.44	2.69
	K <sup>+</sup>	7.73 ± 0.65	3.59
	Rb <sup>+</sup>	5.28 ± 0.64	3.39
	Cs <sup>+</sup>	3.41 ± 0.40	3.18
	Mg <sup>2+</sup>	1.14 ± 0.60	2.61
	Ca <sup>2+</sup>	1.12 ± 0.65	2.61
	Sr <sup>2+</sup>	1.42 ± 0.72	2.70
	Ba <sup>2+</sup>	10.1 ± 0.3	3.14
8	Li <sup>+</sup>	0.89 ± 0.56	2.51
	Na <sup>+</sup>	5.09 ± 1.20	3.37
	K <sup>+</sup>	64.6 ± 1.0	5.76
	Rb <sup>+</sup>	52.1 ± 0.6	5.28
	Cs <sup>+</sup>	19.3 ± 1.5	4.17
	Mg <sup>2+</sup>	0.61 ± 0.21	2.37
	Ca <sup>2+</sup>	10.3 ± 2.6	3.74
	Sr <sup>2+</sup>	11.5 ± 1.4	3.82
	Ba <sup>2+</sup>	Ppt <sup>a</sup>	

<sup>a</sup> Precipitation of the crown ether-barium picrate complex was observed.

Table. 2-2 (Continued)

Compound	M <sup>n+</sup>	% Ex	K <sub>ex</sub>
<b>9</b>	Li <sup>+</sup>	1.62 ± 0.71	2.79
	Na <sup>+</sup>	2.56 ± 0.80	3.03
	K <sup>+</sup>	49.6 ± 0.5	5.19
	Rb <sup>+</sup>	31.8 ± 1.1	4.61
	Cs <sup>+</sup>	15.5 ± 0.7	4.01
	Mg <sup>2+</sup>	0.96 ± 0.67	2.52
	Ca <sup>2+</sup>	3.49 ± 1.64	3.16
	Sr <sup>2+</sup>	3.39 ± 1.94	3.12
	Ba <sup>2+</sup>	9.62 ± 3.19	3.69
<b>10</b>	Li <sup>+</sup>	0.70 ± 0.26	2.44
	Na <sup>+</sup>	0.86 ± 0.56	2.51
	K <sup>+</sup>	25.7 ± 0.7	4.40
	Rb <sup>+</sup>	10.1 ± 0.4	3.74
	Cs <sup>+</sup>	4.23 ± 0.51	3.28
	Mg <sup>2+</sup>	1.04 ± 0.31	2.62
	Ca <sup>2+</sup>	1.70 ± 0.30	2.85
	Sr <sup>2+</sup>	0.84 ± 0.32	2.50
	Ba <sup>2+</sup>	1.34 ± 0.41	2.73

Table 2-2. (Continued)

Compound	M <sup>n+</sup>	% E <sub>x</sub>	K <sub>ex</sub>
<b>11</b>	Li <sup>+</sup>	1.54 ± 0.90	2.75
	Na <sup>+</sup>	0.96 ± 0.33	2.57
	K <sup>+</sup>	27.1 ± 0.5	4.45
	Rb <sup>+</sup>	10.6 ± 0.5	3.77
	Cs <sup>+</sup>	3.73 ± 0.64	3.22
	Mg <sup>2+</sup>	0.45 ± 0.42	2.04
	Ca <sup>2+</sup>	0.66 ± 0.47	2.86
	Sr <sup>2+</sup>	0.73 ± 0.53	2.55
<b>12</b>	Ba <sup>2+</sup>	4.57 ± 0.80	3.32
	Li <sup>+</sup>	0.74 ± 0.28	2.46
	Na <sup>+</sup>	0.85 ± 0.33	2.52
	K <sup>+</sup>	27.2 ± 1.0	4.45
	Rb <sup>+</sup>	11.6 ± 0.8	3.83
	Cs <sup>+</sup>	2.33 ± 0.58	2.99
	Mg <sup>2+</sup>	0.56 ± 0.22	2.33
	Ca <sup>2+</sup>	2.57 ± 1.13	3.00
	Sr <sup>2+</sup>	2.57 ± 1.64	2.95
Ba <sup>2+</sup>	2.37 ± 0.97	2.98	

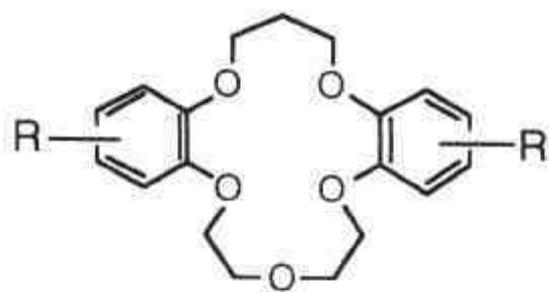
Table 2-2. (Continued)

Compound	M <sup>n+</sup>	% Ex	K <sub>ex</sub>
13	Li <sup>+</sup>	0.71 ± 0.26	2.44
	Na <sup>+</sup>	0.87 ± 0.34	2.53
	K <sup>+</sup>	47.0 ± 0.5	5.10
	Rb <sup>+</sup>	31.0 ± 1.0	4.58
	Cs <sup>+</sup>	12.1 ± 1.0	3.85
	Mg <sup>2+</sup>	0.61 ± 0.21	2.37
	Ca <sup>2+</sup>	1.05 ± 0.21	2.63
	Ba <sup>2+</sup>	8.27 ± 0.39	3.63
14	Li <sup>+</sup>	1.46 ± 0.33	2.78
	Na <sup>+</sup>	1.88 ± 0.97	2.84
	K <sup>+</sup>	46.0 ± 0.5	5.07
	Rb <sup>+</sup>	26.7 ± 0.4	4.43
	Cs <sup>+</sup>	17.1 ± 0.5	4.08
	Mg <sup>2+</sup>	0.63 ± 0.22	2.39
	Ca <sup>2+</sup>	2.00 ± 0.50	2.92
	Ba <sup>2+</sup>	26.8 ± 1.6	4.44

and **14**, it was observed that compounds **13** and **14**, having bulky side arms with both alcohol and ether groups in them, exhibit much higher complexing capacities than compound **12** which has only an alcohol group on its side arm. Among them, compound **14**, which has having the most electron-donating groups, showed the highest extraction efficiency. Compound **8** is dibenzo-18-crown-6. Its complexing ability is given here for comparison.

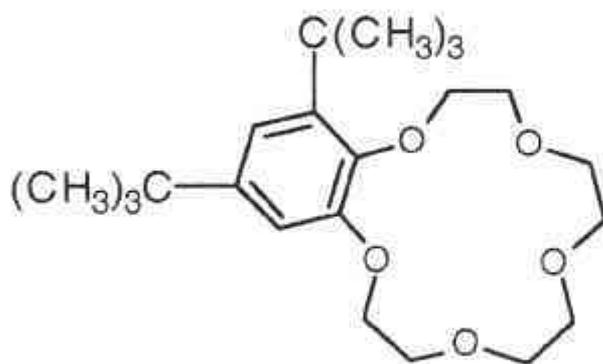
#### Benzo-16-crown-5, Benzo-15-crown-5 and Benzo-12-crown-4 Compounds

Several benzo-16-crown-5, benzo-15-crown-5 and benzo-12-crown-4 compounds (Figures 2-3 and 2-4) were tested for their abilities to extract alkali and alkaline earth-metal picrates into chloroform (Table 2-3). The percentages of alkali and alkaline earth-metal picrates extracted were found to be low in all cases. The  $K_{\text{ex}}$  values for all the cations and the dibenzo-16-crown-5 compounds **15** - **18** are similar and show only small changes with variation in the side arm.

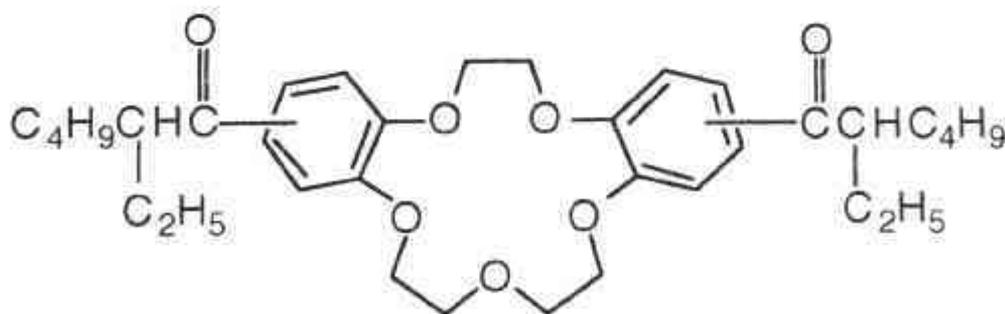


R

- 15**       $-\text{C}(\text{CH}_3)_3$
- 16**       $-\text{C}(\text{O})\text{CH}(\text{C}_2\text{H}_5)\text{C}_4\text{H}_9$
- 17**       $-\text{CH}(\text{OH})\text{CH}(\text{C}_2\text{H}_5)\text{C}_4\text{H}_9$
- 18**       $-\text{CH}(\text{OCH}_2\text{CH}_2\text{OH})\text{CH}(\text{C}_2\text{H}_5)\text{C}_4\text{H}_9$

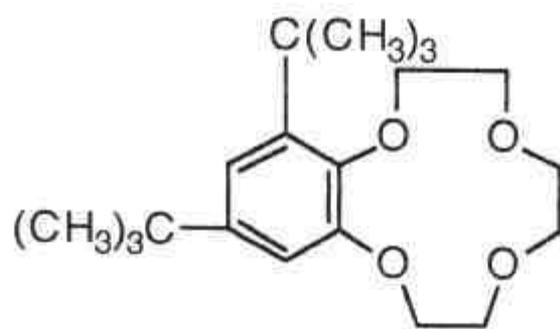


**19**



**20**

Figure 2-3. Structures of the Benzo-16-crown-5 and Benzo-15-crown-5 Compounds



**21**

Figure 2-4. Structures of Benzo-12-crown-4 Compound

Table 2-3. Extraction of Alkali and Alkaline Earth-Metal Picrates into Chloroform by 16-Crown-5, 15-Crown-5 and 12-Crown-4 Compounds

Compound	M <sup>n+</sup>	% Ex	K <sub>ex</sub>
<b>15</b>	Li <sup>+</sup>	1.21 ± 0.25	2.69
	Na <sup>+</sup>	2.53 ± 1.39	2.97
	K <sup>+</sup>	1.22 ± 0.61	2.66
	Rb <sup>+</sup>	0.86 ± 0.48	2.50
	Cs <sup>+</sup>	0.83 ± 0.33	2.51
	Mg <sup>2+</sup>	0.54 ± 0.21	2.32
	Ca <sup>2+</sup>	0.62 ± 0.52	2.18
	Sr <sup>2+</sup>	2.06 ± 1.79	2.84
Ba <sup>2+</sup>	2.04 ± 0.78	2.91	

Table 2-3. (Continued)

Compound	M <sup>n+</sup>	% E <sub>x</sub>	K <sub>ex</sub>
<b>16</b>	Li <sup>+</sup>	0.93 ± 0.52	2.53
	Na <sup>+</sup>	0.74 ± 0.28	2.46
	K <sup>+</sup>	0.81 ± 0.32	2.49
	Rb <sup>+</sup>	1.33 ± 0.30	2.73
	Cs <sup>+</sup>	0.91 ± 0.31	2.55
	Mg <sup>2+</sup>	0.49 ± 0.18	2.28
	Ca <sup>2+</sup>	0.44 ± 0.49	2.42
	Sr <sup>2+</sup>	0.82 ± 0.72	2.28
	Ba <sup>2+</sup>	0.52 ± 0.41	2.08
<b>17</b>	Li <sup>+</sup>	0.84 ± 0.33	2.51
	Na <sup>+</sup>	1.33 ± 0.47	2.72
	K <sup>+</sup>	0.78 ± 0.31	2.48
	Rb <sup>+</sup>	0.90 ± 0.31	2.55
	Cs <sup>+</sup>	0.71 ± 0.27	2.44
	Mg <sup>2+</sup>	0.50 ± 0.19	2.29
	Ca <sup>2+</sup>	0.42 ± 0.31	2.24
	Sr <sup>2+</sup>	1.50 ± 0.56	2.78
	Ba <sup>2+</sup>	2.55 ± 2.26	2.89

Table 2-3. (Continued)

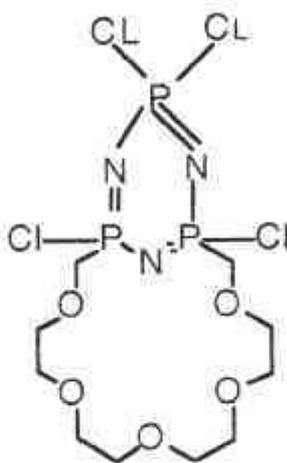
Compound	M <sup>n+</sup>	% Ex	K <sub>ex</sub>
<b>18</b>	Li <sup>+</sup>	0.71 ± 0.27	2.45
	Na <sup>+</sup>	0.75 ± 0.28	2.47
	K <sup>+</sup>	1.33 ± 1.22	2.62
	Rb <sup>+</sup>	1.20 ± 0.46	2.66
	Cs <sup>+</sup>	0.71 ± 0.27	2.45
	Mg <sup>2+</sup>	0.66 ± 0.55	2.35
	Ca <sup>2+</sup>	0.84 ± 0.41	2.62
	Sr <sup>2+</sup>	0.63 ± 0.32	2.45
	Ba <sup>2+</sup>	0.48 ± 0.71	2.32
<b>19</b>	Li <sup>+</sup>	0.98 ± 0.33	2.58
	Na <sup>+</sup>	1.49 ± 0.83	2.73
	K <sup>+</sup>	1.38 ± 0.51	2.73
	Rb <sup>+</sup>	1.91 ± 0.31	2.90
	Cs <sup>+</sup>	1.15 ± 0.41	2.65
	Mg <sup>2+</sup>	0.48 ± 0.18	2.27
	Ca <sup>2+</sup>	1.41 ± 0.53	2.75
	Sr <sup>2+</sup>	2.32 ± 1.88	2.89
	Ba <sup>2+</sup>	7.14 ± 1.09	3.55

Table 2-3. (Continued)

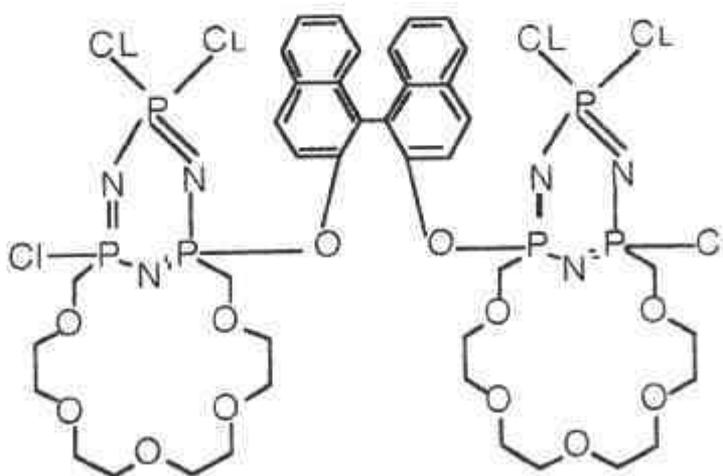
Compound	M <sup>n+</sup>	% Ex	K <sub>ex</sub>
<b>20</b>	Li <sup>+</sup>	1.08 ± 0.50	2.61
	Na <sup>+</sup>	0.72 ± 0.27	2.45
	K <sup>+</sup>	1.70 ± 0.40	2.84
	Rb <sup>+</sup>	2.42 ± 1.05	2.99
	Cs <sup>+</sup>	0.80 ± 0.31	2.49
	Mg <sup>2+</sup>	0.49 ± 0.18	2.28
	Ca <sup>2+</sup>	1.69 ± 0.66	2.83
	Sr <sup>2+</sup>	1.09 ± 0.41	2.64
	Ba <sup>2+</sup>	2.26 ± 0.84	2.95
<b>21</b>	Li <sup>+</sup>	1.21 ± 0.60	2.65
	Na <sup>+</sup>	0.74 ± 0.28	2.46
	K <sup>+</sup>	0.68 ± 0.25	2.42
	Rb <sup>+</sup>	1.88 ± 0.49	2.89
	Cs <sup>+</sup>	3.39 ± 0.89	3.17
	Mg <sup>2+</sup>	0.84 ± 0.41	2.25
	Ca <sup>2+</sup>	0.42 ± 0.27	2.07
	Sr <sup>2+</sup>	5.59 ± 1.40	3.41
	Ba <sup>2+</sup>	0.55 ± 0.31	2.42

## Phosphazene Ionophores

Ionophores **22** and **23** (Figure 2-5) were tested by the picrate extraction method to determine their abilities to complex alkali and alkaline earth metal cations. The extraction efficiencies were found to be generally poor (Table 2-4).



**22**



**23**

Figure 2-5. Phosphazene Ionophores **22** and **23**

Table 2-4. Extractions of Alkali and Alkaline Earth-Metal Picrates into Chloroform by Phosphazene Ionophores **22** and **23**

Compound	M <sup>n+</sup>	% Ex	K <sub>ex</sub>
<b>22</b>	Li <sup>+</sup>	1.43 ± 0.68	2.73
	Na <sup>+</sup>	3.79 ± 1.12	3.22
	K <sup>+</sup>	2.14 ± 0.47	2.95
	Rb <sup>+</sup>	0.86 ± 0.55	2.50
	Cs <sup>+</sup>	1.58 ± 0.47	2.81
	Mg <sup>2+</sup>	0.89 ± 0.43	2.51
	Ca <sup>2+</sup>	0.42 ± 0.52	2.02
	Sr <sup>2+</sup>	0.62 ± 0.71	2.11
	Ba <sup>2+</sup>	0.46 ± 0.32	2.01
<b>23</b>	Li <sup>+</sup>	0.72 ± 0.27	2.45
	Na <sup>+</sup>	0.73 ± 0.27	2.46
	K <sup>+</sup>	1.93 ± 0.31	2.91
	Rb <sup>+</sup>	2.09 ± 0.34	2.94
	Cs <sup>+</sup>	1.37 ± 0.87	2.70
	Mg <sup>2+</sup>	0.56 ± 0.22	2.33
	Ca <sup>2+</sup>	0.65 ± 0.24	2.21
	Sr <sup>2+</sup>	1.46 ± 0.93	2.73
	Ba <sup>2+</sup>	2.52 ± 0.75	3.02

## Monoazadibenzo-18-crown-6 Ionophores

Ionophores **24** and **25** (Figure 2-6) were also tested for their abilities to extract alkali and alkaline earth-metal picrates from water into chloroform. Ionophore **24** gave an extraction efficiency ordering of  $K^+ > Rb^+ > Cs^+ > Na^+ > Li^+$  for alkali metal cations and  $Ca^{2+} > Sr^{2+} > Ba^{2+} > Mg^{2+}$  for alkaline earth metal cations (Table 2-5). The levels of metal ion complexation for ionophore **25** are very low compared with those for **24** because of the strong electron-withdrawing effect of the tosyl group. In comparison with compound **8**, it was noted that ionophore **24** had a lower complexing ability with  $K^+$ ,  $Rb^+$  and  $Cs^+$  than dibenzo-18-crown-6, but had a higher complexing ability with the rest alkali and alkaline earth metal-cations.

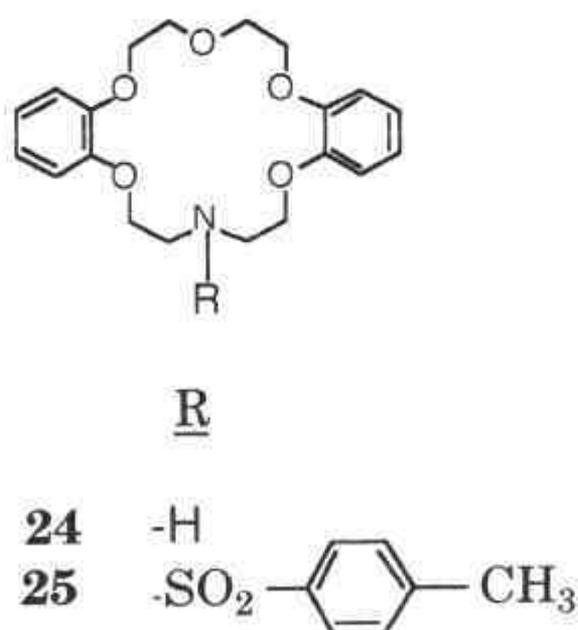


Figure 2-6. Monoazadibenzo-18-crown-6 Ionophores **24** and **25**

Table 2-5. Extraction of Alkali and Alkaline Earth-Metal Picrates into Chloroform by Monoazadibenzo-18-crown-6 Ionophores **24** and **25**

Compound	M <sup>n+</sup>	% Ex	K <sub>ex</sub>
<b>24</b>	Li <sup>+</sup>	12.2 ± 0.9	3.86
	Na <sup>+</sup>	13.1 ± 0.6	3.90
	K <sup>+</sup>	24.0 ± 0.6	4.34
	Rb <sup>+</sup>	16.1 ± 0.9	4.04
	Cs <sup>+</sup>	14.9 ± 0.7	3.98
	Mg <sup>2+</sup>	9.51 ± 0.98	3.71
	Ca <sup>2+</sup>	37.8 ± 0.6	4.80
	Sr <sup>2+</sup>	36.7 ± 0.4	4.76
	Ba <sup>2+</sup>	36.6 ± 0.5	4.76
<b>25</b>	Li <sup>+</sup>	1.15 ± 0.53	2.64
	Na <sup>+</sup>	1.46 ± 0.55	2.75
	K <sup>+</sup>	0.96 ± 0.54	2.55
	Rb <sup>+</sup>	1.29 ± 0.77	2.67
	Cs <sup>+</sup>	0.98 ± 0.55	2.56
	Mg <sup>2+</sup>	1.64 ± 0.42	2.83
	Ca <sup>2+</sup>	1.03 ± 0.23	2.62
	Sr <sup>2+</sup>	3.70 ± 0.69	3.21
	Ba <sup>2+</sup>	1.95 ± 0.28	2.91

## Chapter Summary

The effect of structural variation upon metal ion complexation has been determined for several series of crown ether compounds. The picrate extraction method was used to investigate their abilities to complex alkali and alkaline earth-metal ions. Benzo-21-crown-7 and dibenzo-21-crown-7 compounds were found to exhibit the strongest complexation of  $\text{Cs}^+$ ,  $\text{Rb}^+$  and  $\text{Ba}^{2+}$ . Benzo-18-crown-6 and dibenzo-18-crown-6 compounds showed the highest extraction of  $\text{K}^+$ . Series of benzo-16-crown-5, benzo-15-crown-5 and benzo-12-crown-4 compounds were also tested. Their extraction percentages were generally low.

The effects of various substituents attached to the side arms of the compounds upon their complexing abilities were evaluated. From these results, it is postulated that complexing ability of crown ethers can be enhanced by attaching electron donating substituents to the side arm.

Finally, two monoaza-18-crown-6 ionophores were tested. It was found that an electron-withdrawing substituent, such as a tosyl group, significantly decreases the complexing ability of ionophore.

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# CHAPTER III

## ANION SEPARATIONS WITH ANION-EXCHANGE RESINS HAVING TWO POSITIVE CHARGES PER SITE

### Chapter Introduction

Chromatographic separations by means of anion-exchange resins have been found to be superior to other analytical methods in certain instances, e.g., for the analysis of complicated mixtures of different phosphates. This method is extremely useful for the isolation of small amounts of anions from a dilute solution [1].

Lambert and Zitomer [2] reported separation of nitrate and nitrite by an anion-exchange resin in 1960. Later, the successful separation of the halogenides from each other by means of chromatographic elution from a strongly basic anion exchanger with nitrate solutions was demonstrated by Atteberry and Boyd [3-5]. A separation of halogenides by elution with sodium acetate was also obtained by DeGeiso and Rieman [6, 7]. In studies reported by Zipkin, Armstrong, and Singer [8] as little as 0.025 mg of fluoride ion was separated quantitatively from a 500-fold excess of phosphate with an anion-exchange resin. The separation of

fluoride from sulfate is also easily made by means of anion-exchange resins [9].

Chromatographic separations by anion-exchange resins are based upon differences in ion-exchange affinities. When a solution containing a mixture of anions with different affinity coefficients is passed through a column of anion-exchange resin, the mixture is adsorbed from the solution onto the resin until all the anion-exchange sites are occupied. If the passing of this solution continues, the most strongly adsorbed species in the solution will displace less strongly adsorbed ions. Each component in turn displaces less readily adsorbed species. As a result, the least adsorbed anion elutes from the column first. If a segment analysis is performed with the effluent, a stepwise diagram can be obtained in which each step as it emerges consists of one component [10].

Normally, the affinity of various anions for the same resin increases with the ionic charge. For anions of the same charge, the affinity is inversely proportional to the radius of the hydrated anions [11].

The first commercial anion-exchange resins were obtained by condensation of phenylenediamine and polyethyleneimine with formaldehyde. Similar condensation products are still produced commercially [12]. Most anion exchangers are now produced by the introduction of structurally bound exchange groups into polystyrene-divinylbenzene resins. The most important method for the preparation of strongly basic anion exchange resins is based upon the following principle. First, chloromethyl groups are introduced into the copolymer by treatment with chloromethyl ether in the presence of a swelling agent. Treatment of the chloromethylated resins with a tertiary amine, e.g., trimethylamine, produces a quaternary ammonium salt, i.e., the chloride form of a strongly basic anion exchange resin [1]. Weakly basic resins are made by amination with a mixture of aliphatic polyamines and contains a mixture of primary, secondary, and tertiary amine groups. Zerolit G and H are examples of monofunctional weakly basic resins which possess polystyrene networks [1]. The structures of representative, commercially available resins are shown in Figure 3-1.

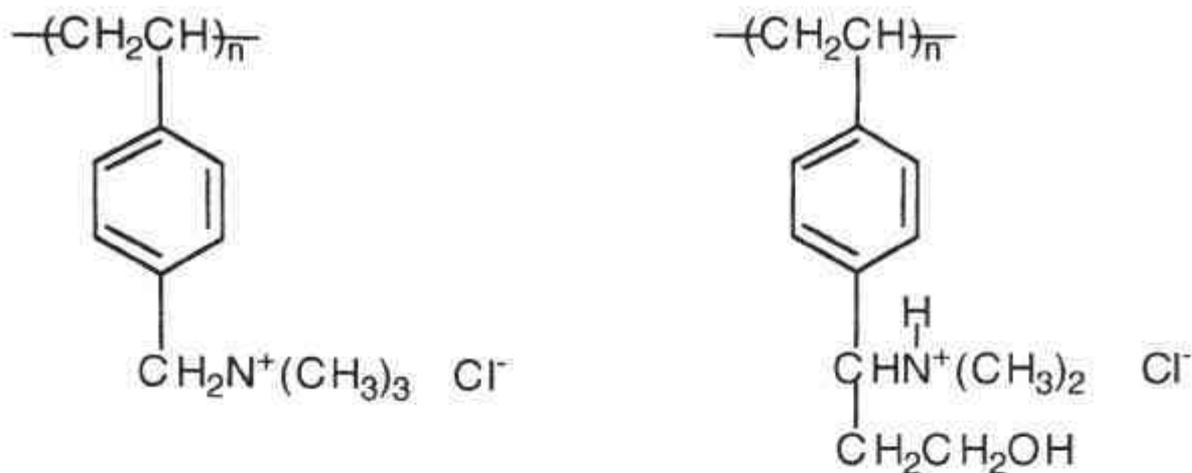
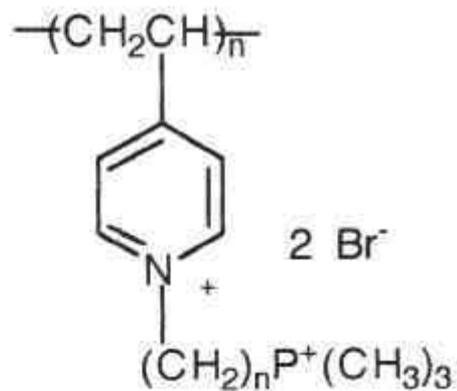
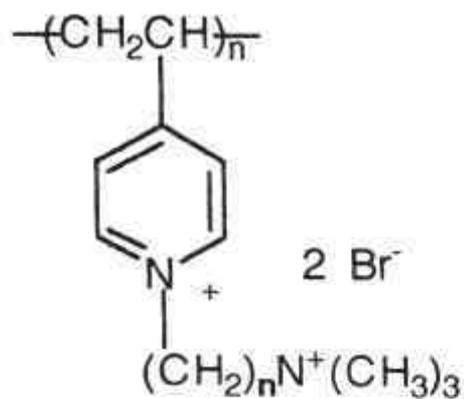


Figure 3-1. Structures of Commercial Anion-Exchange Resins

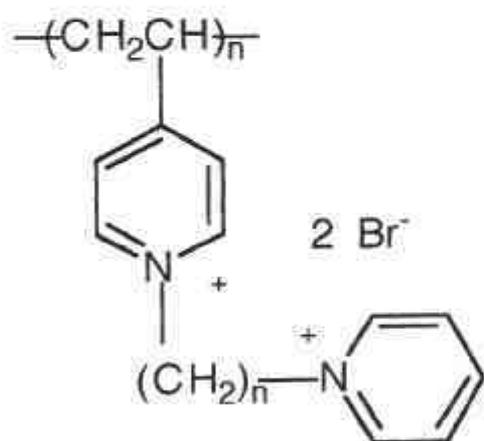
In recent years there has been considerable interest in anion-exchange resins which contain structurally bound pyridinium and phosphonium groups [13]. Quaternary pyridinium and phosphonium groups give strongly basic anion-exchange resins. A detailed study of the fundamental properties of the former type of resin has been published by Lindenbaum, Boyd, and Myers [14], but no analytical applications have appeared.

To determine the properties of anion-exchange resins with two positive charges per site, a series of new anion-exchange resins (Figure 3-2) has been synthesized by Jaewook Nam, another coworker in the Bartsch research group. These new resins will be analyzed for their abilities to separate some common anions by loading a mixture of such anions onto columns followed by



<u>Resin</u>	<u>n</u>
<b>26</b>	4
<b>27</b>	5
<b>28</b>	6

<u>Resin</u>	<u>n</u>
<b>29</b>	3
<b>30</b>	4
<b>31</b>	5



<u>Resin</u>	<u>n</u>
<b>32</b>	4
<b>33</b>	5
<b>34</b>	6

Figure 3-2. Structures of Anion-Exchange Resins with Two Positive Charges Per Site

chromatographic elution. The concentrations of each anionic species in the column effluent during both the loading and stripping steps will be determined by ion chromatography. In a separate analysis, resin columns will be preloaded with  $\text{Cl}^-$  followed by stripping with a solution of a single anion species. Segmental analysis of the effluent from the column will be performed during the stripping step. The amount of each anion used for stripping  $\text{Cl}^-$  from the column will be compared to determine their differences in affinity for the resin.

## Experimental

### Reagents, Apparatus and Instrumentation

Sodium bromide (99.9%), sodium nitrate (99.0%), sodium acetate (100%) and sodium phosphate dibasic (99.2%) were purchased from Baker. Sodium nitrite (99.0%) and monobasic sodium phosphate (99.9%) were obtained from Mallinckrodt. Sodium chloride (99.8%), sodium oxalate (99.9%) and sodium sulfate (99.9%) were products of Fisher.

Deionized, distilled water was utilized to prepare the aqueous solutions. Distilled water was deionized by passage

through three Barnstead combination ion exchange cartridges in series.

The column assembly incorporated four eluent reservoirs, a Rheodyne six position switch (Model 5012), a Milton Roy minipump (P/N 920148-03), with a flow rate from 4.6 to 460 mL per hour, a Dionex pressure gauge (0-4000 psi range), a Dionex air-operated, 4-way valve (P/N 35914), a 20 cm Dionex Tefzel column and a Bio-Rad Model 2100 fraction collector.

Resins were dry packed into Tefzel columns and held in place with 0.035-cm bed supports. Standard 1/4-28 Dionex plastic male nuts were used to attach the tubing and system components. Teflon tubing (1/8 inch ID) was employed to transport the sample, washing, and eluent solutions from the reservoirs to the pump. Tefzel tubing (1/16 inch ID) was used to carry solutions from the high pressure side of the pump to the column.

The column assembly was designed to allow for facile purging of a solution contained in the tubing with a second solution. The Rheodyne switching valve was installed to facilitate changing from one solution reservoir to another. When both the Dionex valve and the Rheodyne switch were switched

simultaneously, the tubing could be purged with the next solution to be used.

The anion concentrations in the effluent from the stripping step were determined with a Dionex Model 2000i ion chromatograph with conductivity detection, a Dionex AS4A anion exchange column and an anion membrane suppressor (Model AMMS-II). Peak areas were recorded with a Hewlett Packard Model 3394A integrator.

### Procedures

Each run involved several procedural steps including column preparation, column preconditioning, sample loading, elution, and effluent analysis.

#### Column Preparation

Columns were prepared from 0.10 gram of the anion-exchange resin. A 0.035-cm bed support was placed at the bottom of a 5-cm Dionex column to retain the powdery material. The bottom end of the empty column was attached to an aspirator assembly with a one-hole stopper so that air would be drawn

through the column when the aspirator pump was in operation. The dry resin was poured directly into the column using a piece of weighing paper shaped into a funnel to guide the powder into the column. Another 0.035-cm bed support was placed at the top of the column. The resin bed volume was approximately  $0.4 \text{ cm}^3$ .

### Column Preconditioning

The anion-exchange resin column was initially prewashed with approximately 20 ml of 0.10 M NaCl. The pre-wash was performed to insure the replacement of  $\text{Br}^-$  by  $\text{Cl}^-$  on all of the binding sites. The effluent was collected in 2.0-ml fractions with a Bio-Rad fraction collector. About 0.1 ml of concentrated  $\text{HNO}_3$  was added into each fraction. A yellow color was observed in the first three or four fractions which indicated that  $\text{Br}^-$  was still being eluted from the column packing resin. In subsequent fractions, no yellow color was observed. After this, 200 ml deionized water was used to wash any residual NaCl from the resin bed.

## Sample Loading

During the loading step, the flow rate was maintained at a pump setting of 10 (20 ml/hr). The sample solution was pumped through the column. Approximately 1.0-1.5 hours were required to complete this step. The column packing was washed with 200 ml of deionized water after the loading of the sample.

## Elution

With a flow rate of 20 ml/hr, 0.10 M NaCl solution was pumped through the column as eluent. Fractions of the effluent emerging from the column were collected with a Bio-Rad automatic fraction collector. The fraction collector was set to the approximate number of drops needed to produce 1.0 mL fractions. Between fifteen to twenty fractions were taken for anion analysis.

## Effluent Analysis

The effluent from the stripping step was diluted 200 times with deionized water. Ion chromatography was used to determine the concentration of each of the anionic species.

## Results and Discussion

The experiments may be separated into two types: (1) competitive anion system analysis; and (2) single anion system analysis.

### Competitive Anion System Analysis

#### Loading Analysis

A column was packed with anion-exchange resin **26**. After preconditioning the column with  $\text{Cl}^-$ , it was loaded with a mixed solution of  $\text{Br}^-$ ,  $\text{NO}_3^-$ ,  $\text{NO}_2^-$  and  $\text{SO}_4^{2-}$ . In this mixture, each anion species had a concentration of 0.10 M. The eluent from the column during this loading step was collected with a fraction collector with 1.0 ml fractions. The concentration of each of the anionic species in each fraction was determined by an ion chromatography. The concentrations of the various anions were plotted against the effluent volume to create a profile of compositions in the effluent (Figure 3-3).

Based on this profile, it took about 5 ml of the  $\text{Br}^-$ ,  $\text{NO}_3^-$ ,  $\text{NO}_2^-$  and  $\text{SO}_4^{2-}$  solution mixture to load the column. After 5 ml, the

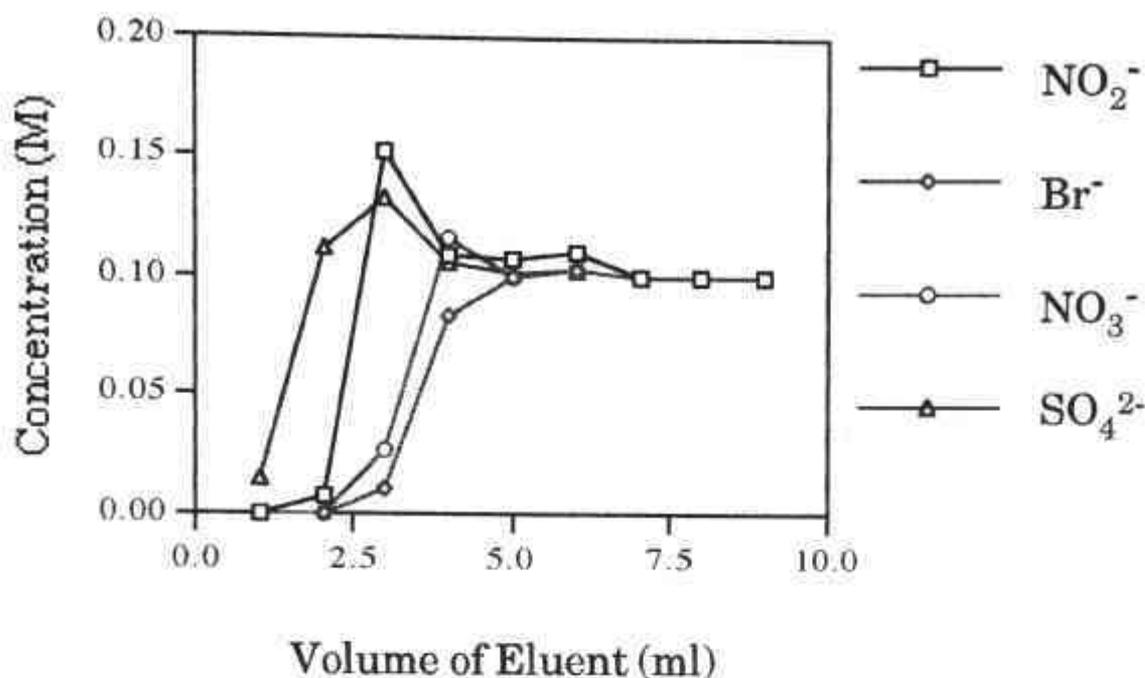


Figure 3-3 Loading Profile of NO<sub>2</sub><sup>-</sup>, Br<sup>-</sup>, NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> on a Column of Resin 26

concentration of each anion species returned to 0.10 M, which indicated that no more of the anion was being adsorbed. It was observed that at the beginning of the loading, concentrations of all the four anions were much lower than 0.1 M because of their adsorption onto the resin. At about 2.5 ml, the concentrations of Br<sup>-</sup> and NO<sub>3</sub><sup>-</sup> remained low, but the concentrations of SO<sub>4</sub><sup>2-</sup> and NO<sub>2</sub><sup>-</sup> were higher than 0.10 M. They fell back to 0.10 M after 5.0 ml. This shows that SO<sub>4</sub><sup>2-</sup> and NO<sub>2</sub><sup>-</sup> anions were adsorbed at the beginning, but were displaced by Br<sup>-</sup> and NO<sub>3</sub><sup>-</sup> because the affinities of SO<sub>4</sub><sup>2-</sup> and NO<sub>2</sub><sup>-</sup> for the resin were lower than those of Br<sup>-</sup> and NO<sub>3</sub><sup>-</sup>. When a solution containing a mixture of ions

having different affinity coefficients is passed through a column of ion-exchange resin in sufficient quantity to exceed the exchange capacity of the resin, the less strongly adsorbed ions will be adsorbed at first but displaced later by stronger bound ions. This method is commonly referred to as Frontal Analysis [10]. The results indicates that resin **26** has different selectivities toward these anions in the order:  $\text{Br}^-$ ,  $\text{NO}_3^- > \text{NO}_2^-$ ,  $\text{SO}_4^{2-}$ .

The same analysis was conducted with an anion mixture of  $\text{Br}^-$ ,  $\text{NO}_3^-$ , oxalate and acetate. The elution profile is shown in Figure 3-4. It was noted that acetate was adsorbed very little at

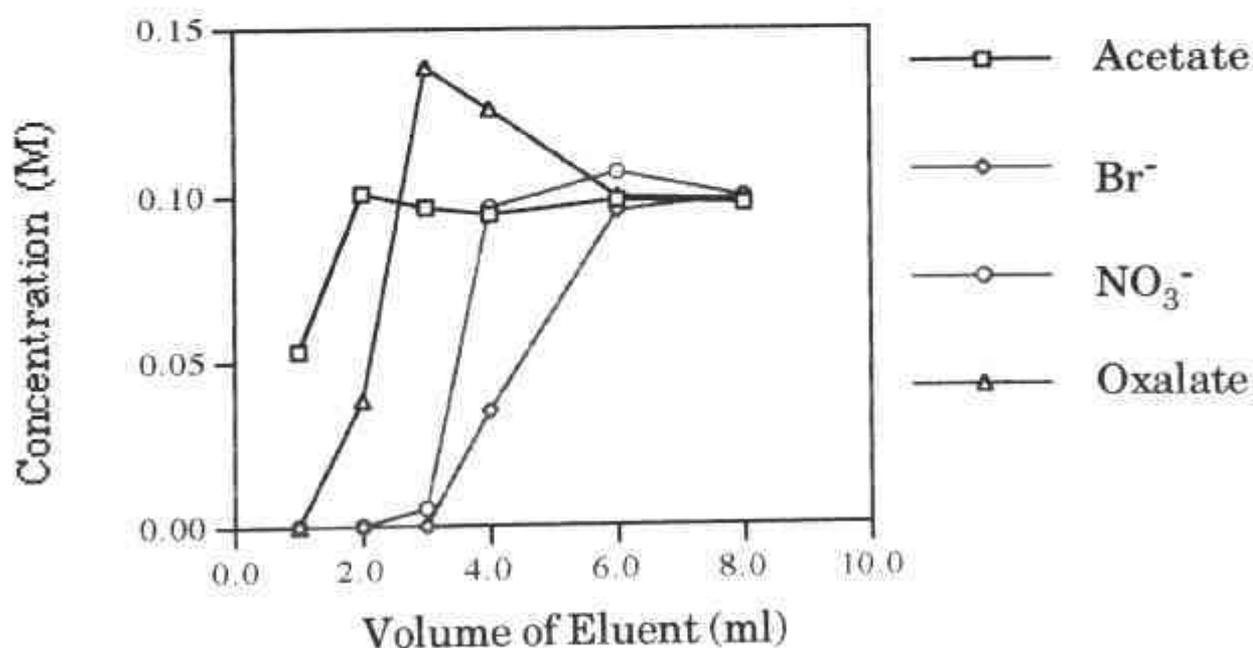


Figure 3-4 Loading Profile of Acetate,  $\text{Br}^-$ ,  $\text{NO}_3^-$  and Oxalate on a Column of Resin **26**

the beginning of the loading and was soon displaced by the other three anions. Acetate broke through the column first. Oxalate was adsorbed and was displaced by  $\text{Br}^-$  and  $\text{NO}_3^-$  after acetate. The affinities of these anions with resin **26** are in the order of  $\text{Br}^-$ ,  $\text{NO}_3^- > \text{oxalate} > \text{acetate}$ .

### Elution Analysis

A column packed with resin **26** was loaded with a mixed solution of  $\text{Br}^-$ ,  $\text{NO}_3^-$ ,  $\text{NO}_2^-$  and  $\text{SO}_4^{2-}$ . The concentration of each anionic species in the mixture was 0.10 M. After loading, a 0.10 M  $\text{Cl}^-$  solution was used as the eluent to strip the adsorbed anions from the column. The effluent was collected with a fraction collector in 1.0 ml fractions. The concentration of each of the anionic species was determined by ion chromatography and was plotted against the effluent volume. The elution profile is shown in Figure 3-5. It was observed that there was not much  $\text{SO}_4^{2-}$  in the effluent because most of this anion had broken through the column during the loading step. It took 5 ml of  $\text{Cl}^-$  eluent to elute  $\text{NO}_2^-$ , but took 10 ml to complete the elution of  $\text{Br}^-$  and  $\text{NO}_3^-$ . Due to the selective nature of the resin packing,

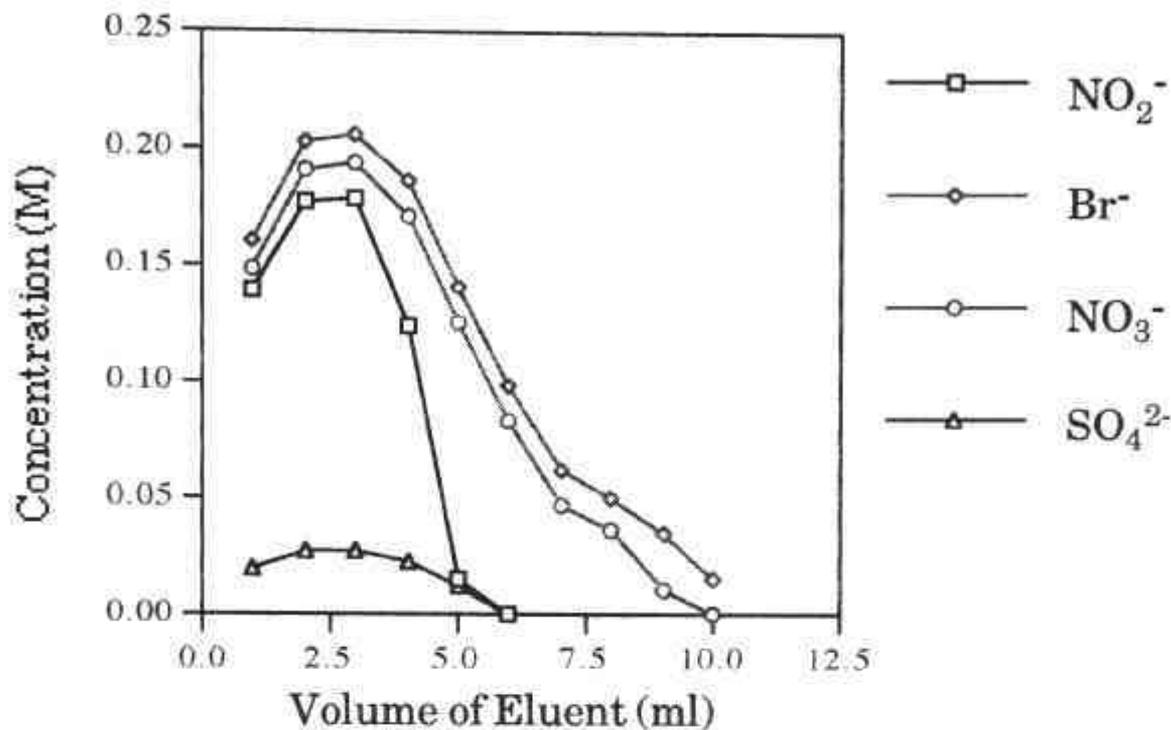


Figure 3-5. Elution Profile of NO<sub>2</sub><sup>-</sup>, Br<sup>-</sup>, NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> on a Column of Resin 26

different anions are adsorbed onto the column disproportionately. Anions which have better interaction with binding sites will be bound more firmly than others. When a relatively weak eluent solution is used to strip these anions from the column, the anions will undergo some chromatographic partitioning between the mobile and stationary phases. As a result, weakly bound anions emerge earlier while strongly bound anions elute from the column later and a separation is attained. According to the results of this

analysis, resin **26** has considerable potential for use in the separation of  $\text{Br}^-$  and  $\text{NO}_3^-$  from  $\text{SO}_4^{2-}$  and  $\text{NO}_2^-$ .

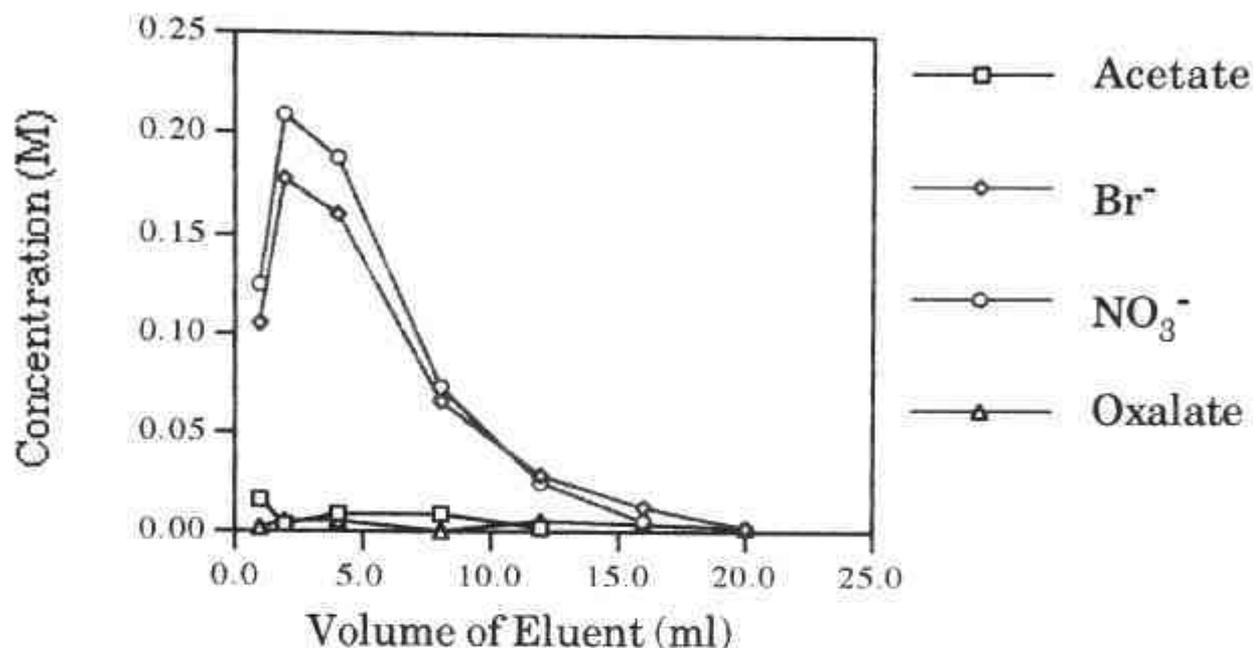


Figure 3-6 Elution Profile of Acetate,  $\text{Br}^-$ ,  $\text{NO}_3^-$  and Oxalate on a Column of Resin **26**

The same analysis was conducted with mixed anion solution of  $\text{Br}^-$ ,  $\text{NO}_3^-$ , oxalate and acetate. Results were shown in Figure 3-6. Very little oxalate and acetate were found in the effluent. They were displaced and broke through the column during the loading step because they were bound considerably more weakly than  $\text{Br}^-$  and  $\text{NO}_3^-$ . As a result, oxalate and acetate were separated from  $\text{Br}^-$  and  $\text{NO}_3^-$  by the selective adsorption with resin **26**.

In the same way, resins **27** and **28** were tested for their selectivity toward the anions  $\text{Br}^-$ ,  $\text{NO}_3^-$ ,  $\text{NO}_2^-$  and  $\text{SO}_4^{2-}$  (Figures 3-7 and 3-8, respectively). With both resins, less  $\text{SO}_4^{2-}$  and  $\text{NO}_2^-$  were found in the effluents and it took fewer mls of  $\text{Cl}^-$  eluent to strip  $\text{SO}_4^{2-}$  and  $\text{NO}_2^-$  from the column in comparison with  $\text{Br}^-$  and  $\text{NO}_3^-$ . Like resin **26**, these two resins have selectivities for  $\text{Br}^-$  and  $\text{NO}_3^-$  and therefore can be utilized for the separation of  $\text{Br}^-$  and  $\text{NO}_3^-$  from  $\text{NO}_2^-$  and  $\text{SO}_4^{2-}$ .

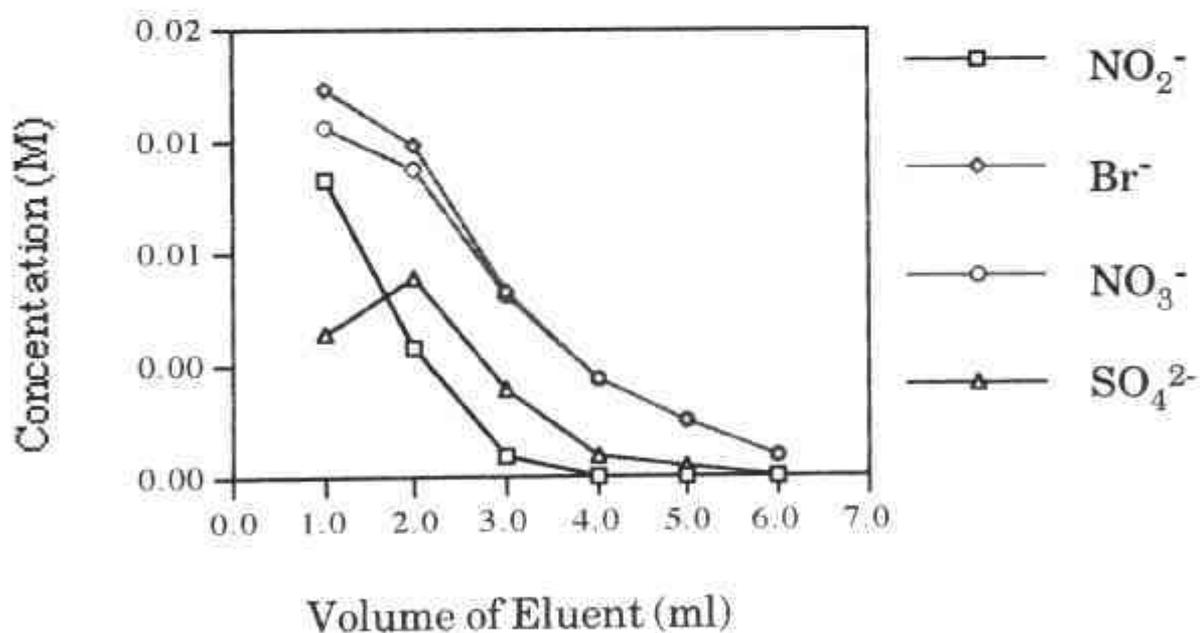


Figure 3-7 Elution Profile of  $\text{NO}_2^-$ ,  $\text{Br}^-$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  on a Column of Resin **27**

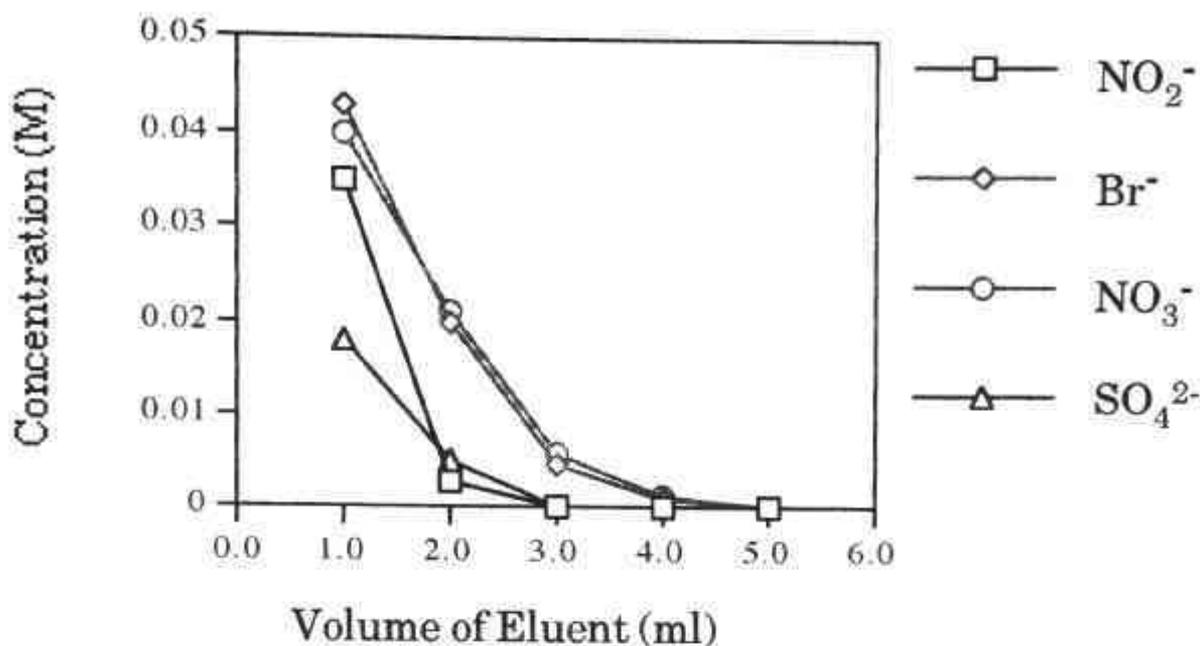


Figure 3-8 Elution Profile of  $\text{NO}_2^-$ ,  $\text{Br}^-$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  on a Column of Resin **28**

### Single Anion System Analysis

The column was packed with an anion-exchange resin and preconditioned with  $\text{Cl}^-$ . Then it was eluted with a solution containing one anionic species at a concentration of 0.10 M to strip the bound  $\text{Cl}^-$  from the column. Since the resin exhibits selectivity toward various anions, the anion which better interacts with the binding sites in the resin will displace  $\text{Cl}^-$  with higher efficiency and thus a lesser amount of solution will be needed. Comparison of the quantities used for various anions to complete the stripping process gives the order of their affinities with this resin. Based on

the results of these experiments (Tables 3-1, 3-2, 3-3), the following selectivity series have been found for each resin.

Resin **26**:  $\text{Br}^-$ ,  $\text{SO}_4^{2-}$ , oxalate  $>$   $\text{NO}_3^-$   $>$   $\text{NO}_2^-$ ,  $\text{HPO}_4^{2-}$   $>$   $\text{H}_2\text{PO}_4^-$   
 $>$  acetate

Resin **27**: oxalate  $>$   $\text{SO}_4^{2-}$   $>$   $\text{NO}_3^-$   $>$   $\text{NO}_2^-$ ,  $\text{HPO}_4^{2-}$   $>$   $\text{Br}^-$ ,  $\text{H}_2\text{PO}_4^-$   
 $>$  acetate

Resin **28**:  $\text{Br}^-$ ,  $\text{SO}_4^{2-}$ , oxalate  $>$   $\text{NO}_3^-$   $>$   $\text{NO}_2^-$   $>$   $\text{HPO}_4^{2-}$   $>$   $\text{H}_2\text{PO}_4^-$   
 $>$  acetate

Resin **29**: oxalate,  $\text{SO}_4^{2-}$   $>$   $\text{Br}^-$ ,  $\text{NO}_3^-$ ,  $\text{NO}_2^-$   $>$   $\text{HPO}_4^{2-}$   $>$   $\text{H}_2\text{PO}_4^-$   
 $>$  acetate

Resin **30**: oxalate  $>$   $\text{SO}_4^{2-}$   $>$   $\text{NO}_3^-$   $>$   $\text{Br}^-$   $>$   $\text{NO}_2^-$ ,  $\text{HPO}_4^{2-}$   $>$   $\text{H}_2\text{PO}_4^-$   
 $>$  acetate

Resin **31**: oxalate  $>$   $\text{SO}_4^{2-}$   $>$   $\text{Br}^-$   $>$   $\text{NO}_3^-$   $>$   $\text{NO}_2^-$ ,  $\text{HPO}_4^{2-}$   $>$   $\text{H}_2\text{PO}_4^-$   
 $>$  acetate

Resin **32**: oxalate,  $\text{NO}_3^-$   $>$   $\text{SO}_4^{2-}$   $>$   $\text{Br}^-$ ,  $\text{NO}_2^-$   $>$   $\text{H}_2\text{PO}_4^-$   $>$   $\text{HPO}_4^{2-}$   
 $>$  acetate

Resin **33**: oxalate,  $\text{SO}_4^{2-}$   $>$   $\text{NO}_3^-$ ,  $\text{NO}_2^-$   $>$   $\text{Br}^-$   $>$   $\text{HPO}_4^{2-}$ ,  $\text{H}_2\text{PO}_4^-$   
 $>$  acetate

Resin **34**: oxalate  $>$   $\text{NO}_3^-$   $>$   $\text{Br}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_2^-$   $>$   $\text{HPO}_4^{2-}$ ,  $\text{H}_2\text{PO}_4^-$   
 $>$  acetate

Table 3-1. Amounts of Anions Used to Strip Cl<sup>-</sup> from Columns Packed with Resins **26**, **27** and **28**

Resin	Amount of Anion (mole x 10 <sup>-4</sup> )							
	Oxalate	Br <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	NO <sub>3</sub> <sup>-</sup>	NO <sub>2</sub> <sup>-</sup>	HPO <sub>4</sub> <sup>2-</sup>	H <sub>2</sub> PO <sub>4</sub> <sup>-</sup>	Acetate
<b>26</b>	6	6	6	8	9	9	10	20
<b>27</b>	5	10	6	8	9	9	10	15
<b>28</b>	5	5	5	6	7	8	9	18

Table 3-2. Amounts of Anions Used to Strip Cl<sup>-</sup> from Columns Packed with Resins of **29**, **30** and **31**

Resin	Amount of Anion (mole x 10 <sup>-4</sup> )							
	Oxalate	Br <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	NO <sub>3</sub> <sup>-</sup>	NO <sub>2</sub> <sup>-</sup>	HPO <sub>4</sub> <sup>2-</sup>	H <sub>2</sub> PO <sub>4</sub> <sup>-</sup>	Acetate
<b>29</b>	5	7	5	7	7	9	10	14
<b>30</b>	5	9	6	8	10	10	12	14
<b>31</b>	4	7	6	8	9	9	10	14

Table 3-3. Amounts of Anions Used to Strip Cl<sup>-</sup> from Columns Packed with Resins **32**, **33** and **34**

Resin	Amount of Anion (mole x 10 <sup>-4</sup> )							
	Oxalate	Br <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	NO <sub>3</sub> <sup>-</sup>	NO <sub>2</sub> <sup>-</sup>	HPO <sub>4</sub> <sup>2-</sup>	H <sub>2</sub> PO <sub>4</sub> <sup>-</sup>	Acetate
<b>32</b>	6	8	7	6	8	10	9	12
<b>33</b>	5	7	5	6	6	10	10	12
<b>34</b>	6	8	8	7	8	9	9	12

According to Korkisch [11], the selectivity order for most traditional anion exchange resins (Figure 3-1) is: SO<sub>4</sub><sup>2-</sup> > NO<sub>3</sub><sup>-</sup>, Br<sup>-</sup> > NO<sub>2</sub><sup>-</sup> > H<sub>2</sub>PO<sub>4</sub><sup>-</sup> > acetate, which matches those of the resins tested in this experiment, except for Br<sup>-</sup>.

### Chapter Summary

A series of new anion-exchange resins with two positive charges per site was tested to determine their selectivities toward some common anions.

The results of competitive system analysis indicate that resins **26**, **27** and **28** will be useful for the separation of Br<sup>-</sup> and

$\text{NO}_3^-$  from  $\text{SO}_4^{2-}$  and  $\text{NO}_2^-$ . Resin **26** can be utilized to separate  $\text{Br}^-$  and  $\text{NO}_3^-$  from oxalate and acetate.

Separate tests with single anion species as eluents were conducted to compare the efficiency of various anions in the stripping of bound  $\text{Cl}^-$  from the column. Based on these results, selectivity orders of each tested resin for these anions were established.

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# CHAPTER IV

## REMOVAL OF HEAVY METALS FROM AQUEOUS SOLUTIONS BY LIQUID-PHASE, POLYMER-BASED RETENTION

### Chapter Introduction

In recent years, much research has been done with the goal of developing metal ion separation techniques which can be used for environmental protection and metal ion recovery. A new method that has emerged recently utilizes water-soluble polymeric chelates in combination with ultrafiltration. Soluble polymers such as polyethylenimine, polyvinylamine, poly(vinylsulfonic acid), poly(acrylic acid) and others have been functionalized with a variety of metal ion chelating agents [1-3] and employed in ultrafiltration systems for the removal of heavy metal ions from dilute aqueous solutions [4-11]. This combination of soluble polymeric chelating agents and ultrafiltration for the recovery of a specific ion, product or contaminant from an aqueous stream is referred to as liquid-phase, polymer-based retention (LPR). Aqueous solutions containing the water-soluble polymer and the

metal ion are combined prior to filtration and this solution is passed across an ultrafiltration membrane. Water and uncomplexed metal salts pass through the membrane, but larger species, such as polymer and polymer-complexed metal ions, are retained.

The removal of metal ions from aqueous streams by LPR requires that the water-soluble polymeric chelating agent function effectively in combination with the ultrafiltration membrane. In contrast to dual-phase separation techniques, such as extraction or sorption, LPR involves only a single aqueous phase in which both the chelating agent and sample are dissolved. Thus, the development of inexpensive, water-soluble, ion-selective polymers is of primary importance. Such polymers must have a sufficiently high molecular weight to prevent their passage through the ultrafiltration membrane. However, they must have a low enough molecular weight to maintain miscibility [12].

The present study was performed to investigate the effectiveness of a water-soluble polymer chelate (Figure 4-1) synthesized by Bartsch's group for the removal of mercury(II), copper(II), nickel(II), cobalt(II), zinc(II), cadmium(II) and lead(II)

from water samples using liquid-phase, polymer-based retention. The polymer was prepared by Jaewook Nam, another member of the Bartsch Research Group.

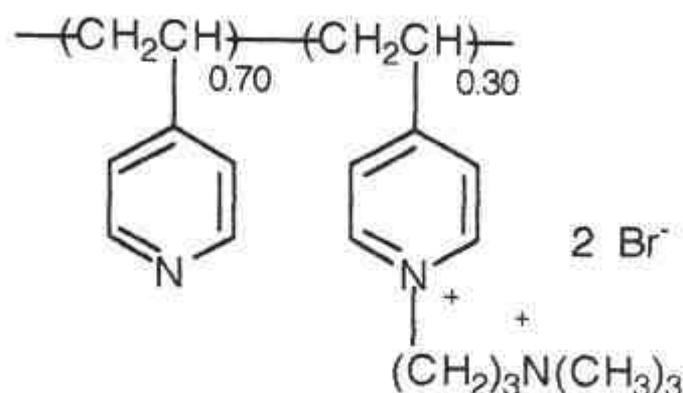


Figure 4-1 The Water-Soluble Polymer Chelate Used for Metal Ion Complexation

## Experimental

### Reagents, Apparatus and Instrumentation

The mercury(II) standard was prepared from mercury(II) oxide (99.9%) purchased from Aldrich using the standard method [12] and stabilized with potassium permanganate (99.9%) obtained from Fisher. Sodium borohydride (98%) which was employed as a reductant for the cold vapor mercury analysis was obtained from Aldrich. The lead standard solution (1015 ppm), copper standard solution (990 ppm), nickel standard solution

(1010 ppm), cobalt standard solution (1005 ppm), zinc standard solution (1010 ppm) and cadmium standard solution (1015 ppm) for atomic absorption analysis were purchased from Aldrich.

Sample solutions were prepared from mercury(II) chloride (99.9%), cupric(II) nitrate (99.7%) and lead(II) nitrate (99.9%) obtained from Fisher, zinc(II) nitrate (99.8%) purchased from Baker, cobalt(II) nitrate and nickel(II) nitrate obtained from Alfa and cadmium(II) nitrate (99.2%) purchased from Mallinckrodt. Acetic acid (99.7%) and sodium acetate (99.9%) obtained from Baker were used to make the buffer solutions.

Deionized, distilled water was used to prepare the aqueous solutions. Distilled water was deionized by passage through three Barnstead combination ion-exchange cartridges in series.

Lead(II), zinc(II), copper(II), nickel(II), cobalt(II) and cadmium(II) analyses were performed using conventional atomic absorption techniques on a Perkin Elmer Model 5000 atomic absorption spectrometer. Mercury(II) analysis was performed on the same spectrometer with a Perkin Elmer Model MHS-10 cold vapor mercury attachment.

The Model 7013 peristaltic pump used to pressurize the filter system was purchased from the Barnant Company (Barrington, IL). All filtration equipment and cartridges were supplied by A/G (Needham, MA). The filtration assembly was constructed from a hollow fiber membrane cartridge adapter kit and a hollow fiber membrane ultrafiltration cartridge (Model UFP-10-C-3). This specific filter cartridge had a 10,000 Dalton molecular weight cut-off. The filtration apparatus is shown in Figure 4-2.

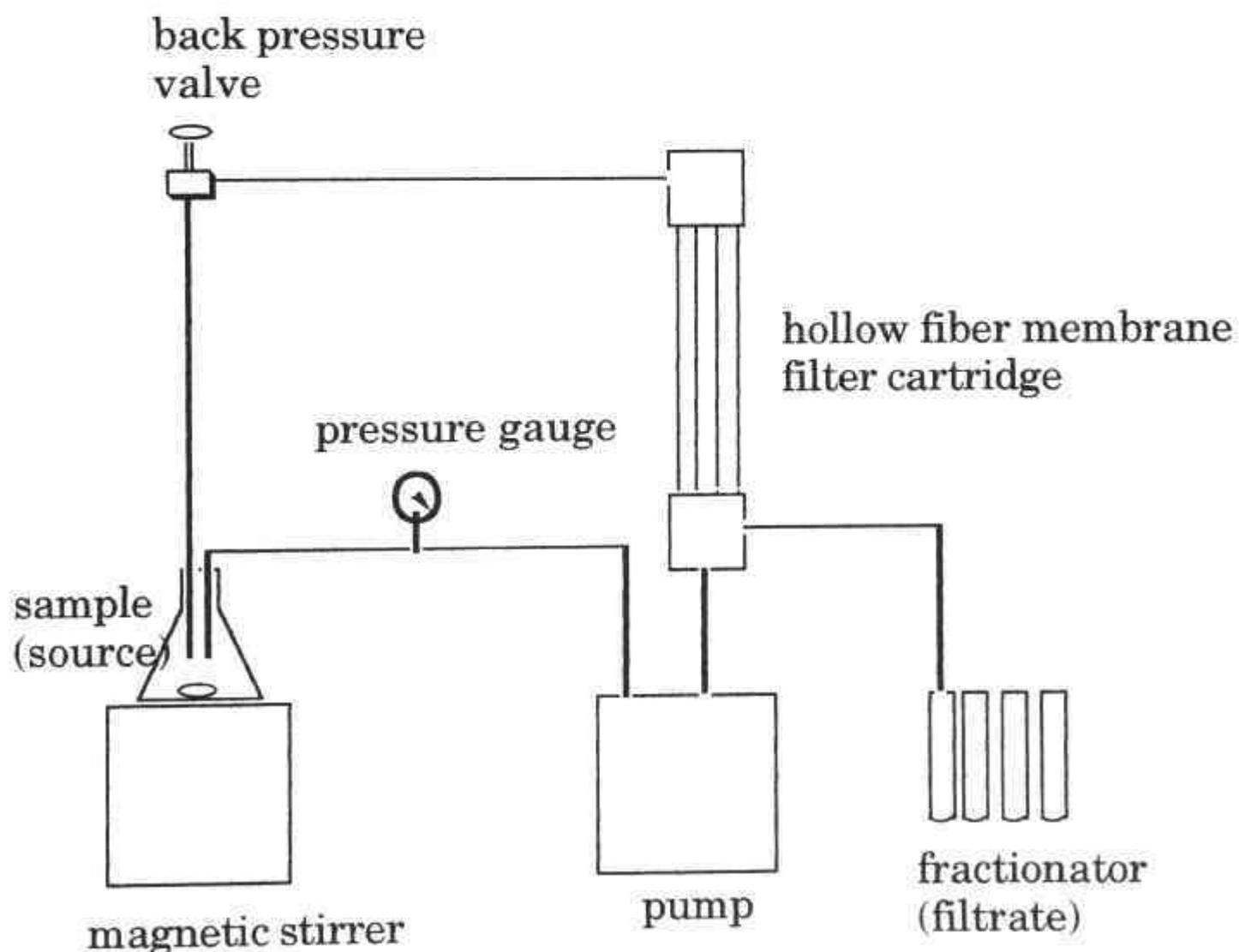


Figure 4-2 Ultrafiltration Apparatus for the Recovery of Metal Ions

## Procedures

For a given experiment, several procedural steps were needed which included sample preparation, cleaning of the ultrafiltration assembly, ultrafiltration, and filtrate analysis.

### Sample Preparation

Sample solutions were prepared from aqueous stock solution of the water-soluble polymer (0.10 M), mercury(II) chloride (0.050 M), cobalt(II) nitrate (0.085 M), nickel(II) nitrate (0.085 M), copper(II) nitrate (0.079 M), lead(II) nitrate (0.048 M), zinc(II) nitrate (0.076 M) and cadmium nitrate (0.044 M). Aliquots of the polymer solution were combined with aliquots of a metal ion solution and diluted in a 100-mL volumetric flask with acetic acid/sodium acetate buffer according to the formulations given in Table 4-1. It was assumed that the polymer/metal ion complex formed quickly with only mild mixing of the components. However, the solutions were agitated for 30 minutes before filtration.

**Table 4-1** Compositions of Sample Solutions for Complexation Studies of Lead(II), Zinc(II), Cadmium(II), Nickel(II), Copper(II), Cobalt(II) and Mercury(II) by the Water-Soluble Polymer

Metal Salt	Polymer (mL)	Metal Ion Solution (mL)	Buffer (mL)
Hg(Cl) <sub>2</sub>	1.00	1.00	98.0
Pb(NO <sub>3</sub> ) <sub>2</sub>	1.00	1.00	98.0
Cd(NO <sub>3</sub> ) <sub>2</sub>	1.00	2.00	97.0
Zn(NO <sub>3</sub> ) <sub>2</sub>	1.00	2.00	97.0
Cu(NO <sub>3</sub> ) <sub>2</sub>	1.00	2.00	97.0
Ni(NO <sub>3</sub> ) <sub>2</sub>	1.00	2.00	97.0
Co(NO <sub>3</sub> ) <sub>2</sub>	1.00	2.00	97.0

### Cleaning of the Ultrafiltration Assembly

The ultrafiltration assembly and filter were pre-washed by passage of 500 mL of 0.1 M HCL through the tubing and hollow filter membrane cartridge without noticeable back pressure. This was followed by rinsing with one liter of deionized water which was pumped through the system under slightly increased pressure (2 psi). The deionized water was then drained from the tubing and both the inside and outside of the hollow fibers of the

membrane cartridge. The water was removed from within the hollow fibers by forcing air through the tubing. This was accomplished by running the peristaltic pump for 10 minutes with the feed line open to the air. Water which accumulated on the outside of the hollow fibers was removed by passing nitrogen gas at 10 psi through the filtrate channel for ten minutes. In the final preparatory sequence, a 10-mL portion of the sample solution was pumped through the hollow fibers and tubing to remove the residual deionized water. This aliquot was discarded.

### Ultrafiltration

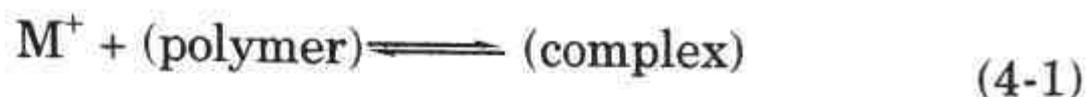
The sample solution was cycled through the filter cartridge and then back into the original volumetric flask at a relatively low flow rate of 40 mL/min for five minutes before beginning the ultrafiltration. Finally, to effectuate filtration, the back pressure valve at the top of the filter cartridge was adjusted to increase the pressure in order to obtain a flow rate of 75 mL/min. The filtrate was collected with a fraction collector in 2-3 mL portions.

## Filtrate Analysis

Conventional atomic absorption techniques were employed to determine the lead(II), zinc(II), nickel(II), copper(II), cobalt(II) and cadmium(II) concentrations in the filtrate fractions and cold vapor atomic absorption techniques were utilized for the mercury(II) analysis. The atomic absorption spectrometer was set to evaluate lead(II) and cobalt(II) concentrations in a linear range from 0 to 40 ppm, nickel(II) in a range from 0 to 20 ppm, and zinc(II), copper(II) and cadmium(II) in a range from 1 to 5 ppm. For the cold vapor mercury(II) analysis, the instrument was set to record the peak area. Standards for mercury analysis were prepared in a range from 0 to 500 nanograms. Filtrates were diluted such that the metal ion concentration could be evaluated within the ranges specified above.

## Results and Discussion

In the sample solution, metal ions are sorbed by the water-soluble polymer to form a complex. This metal ion/polymer complexation is represented by the following equations:



$$K = [\text{complex}]/[M^+][\text{polymer}] \quad (4-2)$$

The solution was cycled through the filter cartridge at a relatively high pressure. During filtration, the uncomplexed metal ions pass through the membrane with the filtrate while the complex and the host polymer are retained. Ten fractions of filtrate were collected. The metal ion content in these fractions was determined by atomic absorption spectrophotometry and compared with the metal ion concentration of the original unfiltered source solution to derive a retention value. This retention value represents the percentage of metal ions which was complexed by the polymer and retained by the filter membrane.

Data for the influence of pH upon the retention percentage are given in Table 4-2. Since the retention percentage varies as the ultrafiltration process proceeds and levels off after the first five fractions, the data recorded in Table 4-2 is the retention percentages of each metal ion in the 6th fraction. For each metal ion, the retention percentage was the highest at pH 6.0. At a lower pH, partial protonation of the pyridyne binding sites in the polymer is expected to diminish complexation.

Table 4-2 Retention Percentages of Mercury(II), Copper(II), Nickel(II), Cobalt(II), Lead(II), Zinc(II) and Cadmium(II) at Different pH

Metal Ion	pH			
	3.0	4.0	5.0	6.0
Hg <sup>2+</sup>	83.2	91.1	96.9	97.6
Cu <sup>2+</sup>	21.8	49.2	49.1	57.8
Ni <sup>2+</sup>	20.0	20.3	23.8	26.7
Co <sup>2+</sup>	10.0	10.0	10.4	26.3
Zn <sup>2+</sup>	16.3	25.8	25.8	26.2
Cd <sup>2+</sup>	8.6	12.4	14.0	20.0
Pb <sup>2+</sup>	8.1	14.0	15.7	16.5

From comparison of the results for the seven divalent transition metal ions tested, it is seen that this polymer is most effective in sorbing and removing mercury(II) ions. At pH values of 4.0, 5.0 and 6.0, Cu(II) ions are also absorbed well. Complexation of lead(II) and cadmium(II) is the weakest. The complexing capacities of this polymer for these metal ions at pH of 6 are in the order of: Hg<sup>2+</sup> > Cu<sup>2+</sup> > Ni<sup>2+</sup>, Co<sup>2+</sup>, Zn<sup>2+</sup> > Cd<sup>2+</sup> > Pb<sup>2+</sup>

(Figure 4-3). The reported complexing order of these metals with pyridine is:  $\text{Hg}^{2+} > \text{Cu}^{2+} > \text{Ni}^{2+} > \text{Cd}^{2+} > \text{Co}^{2+} > \text{Zn}^{2+}$  [13]. These orders are similar except for the position of  $\text{Cd}^{2+}$ .

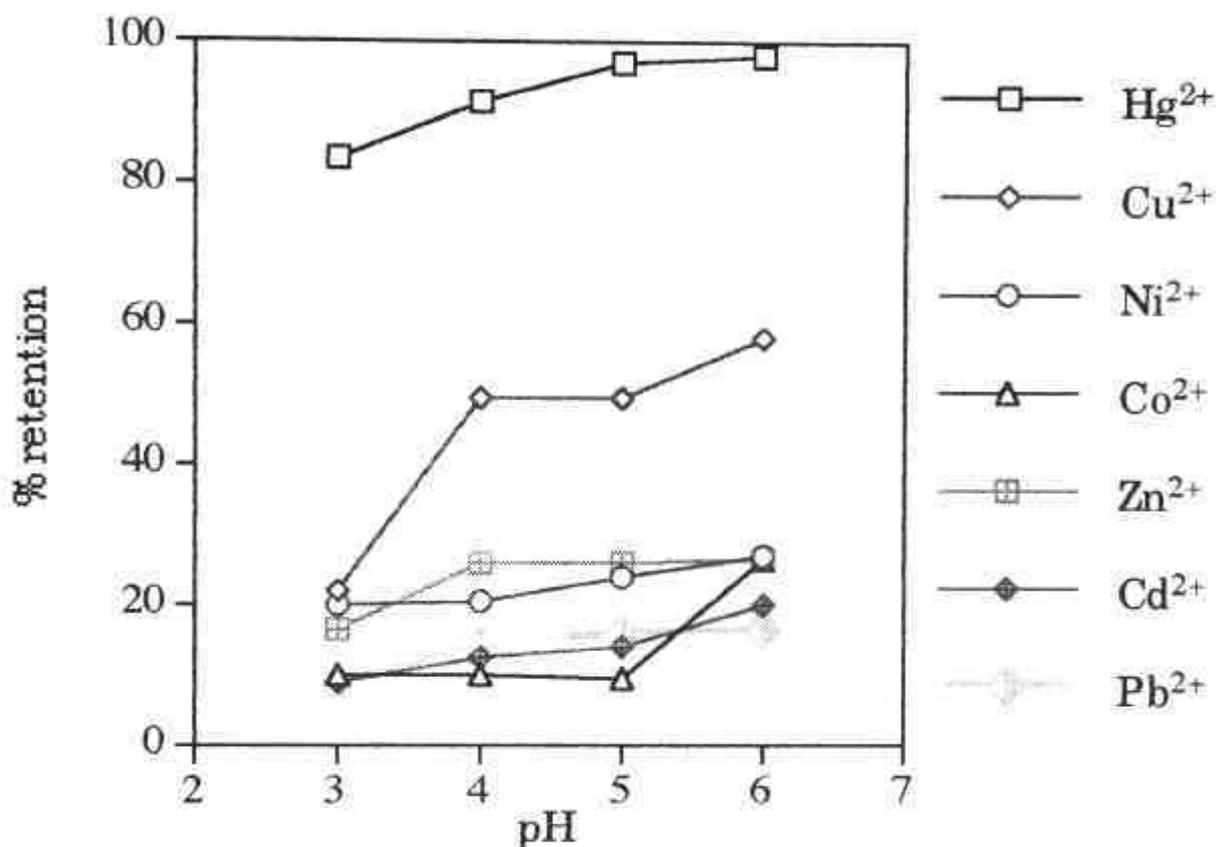


Figure 4-3 Retention Percentages of Mercury(II), Copper(II), Nickel(II), Cobalt(II), Zinc(II), Cadmium(II) and Lead(II) at Different pH Values

In all runs, the metal ion content in the permeate fractions progressively increased with increasing fraction number and leveled off somewhat after the first few fractions. A reasonable explanation for this observation is that as filtration occurred, the volume of liquid in the source solution gradually decreased. As a

result, according to Equation (4-2), a proportional increase in the concentrations of complex, the free host and the uncomplexed metal will occur. The increase of mercury(II) content during the ultrafiltration is shown in Table 4-3.

Table 4-3 Mercury(II) Content in Each Fraction of Filtrate  
( $10^{-3}$  mg)

pH	Fraction Number					
	1	2	3	4	5	6
3.0	0.245	0.278	0.360	0.413	0.390	0.420
4.0	0.134	0.135	0.173	0.192	0.189	0.223
5.0	0.057	0.057	0.058	0.064	0.075	0.076
6.0	0.031	0.033	0.033	0.042	0.042	0.059

### Chapter Summary

Removal of mercury(II), copper(II), nickel(II), cobalt(II), zinc(II), lead(II) and cadmium(II) from dilute aqueous solution was performed by complexation of the metal ions with a water-soluble polymeric chelating agent and subsequent filtration of the

complex by ultrafiltration. The effect of pH on the complexation of metal ions by polymer was assessed. It was found that the retention percentage was the highest for all metal ions at pH 6. This polymer was most effective in sorbing mercury(II) ions. Retention of lead(II), cadmium(II), zinc(II), cobalt(II), nickel(II), copper(II) and mercury(II) varies from 16.5 to 97.6% efficient.

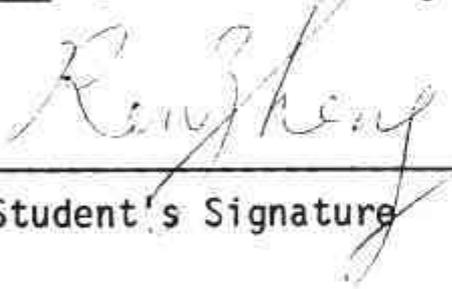
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