

CORRESPONDENCE

Removal and Separation of Metal Ions from Aqueous Solutions Using a Silica-Gel-Bonded Macrocycle System

Sir: The recent permanent attachment of macrocycles such as the crown ethers to silica gel via a hydrocarbon-type linkage (1, 2) has made possible the design of systems capable of the selective and quantitative removal of cations from aqueous solutions. These systems can be operated indefinitely without loss of the expensive macrocycle and maintain the selectivity shown toward metal ions in aqueous solution by the particular macrocycle in the free state (1). These systems are of potential value in concentrating cations present at the nanogram-per-milliliter level, making their analysis by conventional procedures possible, and in selectively removing either wanted or unwanted metal cations from solutions in which they are present in the milligram-per-milliliter to the nanogram-per-milliliter range. The latter application is treated in this correspondence using the alkaline-earth cations, Ag^+ , Hg^{2+} , Tl^+ , and Pb^{2+} .

Complexation of metal ions by macrocycles has been studied for many years (3). Macrocylic compounds have been used to selectively separate metal ions from mixtures of metal ions in bulk liquid membrane and/or solvent extraction systems (4-7). Those metal ions that form the complexes of greatest thermodynamic stability with the macrocycle are generally transported or extracted selectively. The same principle applies to the silica-gel-bound macrocycles. Metal ions that form the most stable complexes should be separated from those that form less stable complexes. Furthermore, the silica-gel-bound macrocycles have approximately the same affinity as the corresponding unbound macrocycles for metal ions in aqueous solutions (1). Thus, a knowledge of the equilibrium constants (K) for the interaction of metal ions with the free macrocycles (3) will enable one to prepare silica-gel-bound macrocycles capable of a particular separation. Silica-gel-bound macrocycles 1-4 (Figure 1) have been prepared (1), and some specific separations of metal ions are herein reported.

A known amount (2.3 g) of the macrocycle-silica gel material containing 10% by weight of the macrocycle compound was placed in a 19 mm diameter chromatography column yielding fixed bed heights between 15 and 20 mm. An aqueous solution containing the metal ions to be separated was passed through the column. The maximum amount of the aqueous solution that can be passed through the column before its cation-binding capacity is reached can be calculated on the basis of the K value and concentration of the cations vs the number of moles of macrocycle sites on the silica gel material (1). A small quantity of pH 10 ethylenediaminetetraacetate (EDTA) solution (for the alkaline-earth cations, Pb^{2+} , and Tl^+), pH 3.7 buffered acetic acid-sodium acetate (Ag^+ only), or basic EDTA and $\text{S}_2\text{O}_3^{2-}$ (for Hg^{2+} and Ag^+) was passed through the column to strip the metal ions from the macrocycle. Any effects of plain silica gel on the amount of any cation removed were determined from identical experiments using plain silica gel. The macrocycle-silica gel material can then be used again to remove metal ions. The amount of each metal ion in the stripping solution was determined by atomic absorption or inductively coupled plasma spectrophotometry. The process of metal ion removal from aqueous solutions and metal ion stripping from the column can be done repeatedly

Table I. Observed and Predicted Macrocycle-Mediated Selectivities of Alkaline-Earth Cations with Silica-Gel-Bound 18-Crown-6, 2

cation 1/cation 2	selectivity	
	observed ^a	predicted ^b
Ba^{2+} , Sr^{2+} , or $\text{Ca}^{2+}/\text{Mg}^{2+}$ ^c	∞	∞
$\text{Sr}^{2+}/\text{Ca}^{2+}$ ^d	54	7.2-72 ^e
$\text{Ba}^{2+}/\text{Ca}^{2+}$ ^d	339	102-1020 ^e
$\text{Ba}^{2+}/\text{Sr}^{2+}$ ^d	10	14

^aSelectivity measured as the ratio of the cation concentration ratios of the strip and loading solutions. ^bPredicted from the ratios of the cation-free macrocycle K values (3). Cation- NO_3^- interactions are minimal and were ignored. ^cSolutions were 0.001 M in the NO_3^- salt of both cations. The effect of silica gel on the selectivity has been subtracted out in the observed value. ^dNitrate salt solutions were 0.001 M in the first cation and 0.1 M in the second cation. The effects of silica gel on the observed selectivities were negligible. ^ePredictions given as a range; see text.

at 25 °C with no apparent loss of macrocycle activity, provided the pH values of the two solutions remain between the limits of -0.5 and 11.0 (1). The standard deviations in the values presented in this report are always less than 15% of the values.

With material 2, microgram-per-milliliter amounts of Ba^{2+} , Sr^{2+} , Pb^{2+} , and Tl^+ have been quantitatively removed and concentrated in the presence of other more concentrated cations such as Mg^{2+} and Ca^{2+} . Table I shows examples of selectivities obtained in the observed macrocycle-mediated separation of any two alkaline-earth cations from each other using 2. The separations observed are very close to those predicted by the log K values for the interaction of the cations with unbound 18-crown-6 (18C6) in water (3). The separations were performed by bringing the column to equilibrium with the aqueous solution containing the cations, stripping the column, and determining the cation concentration in the stripped solutions by spectrophotometric analysis. As predicted, all the larger alkaline-earth cations were quantitatively separated from Mg^{2+} , which does not interact with 18-crown-6 in aqueous solution. The separation of Ba^{2+} and Sr^{2+} is predicted accurately since K (H_2O) values for 18C6 interaction with these cations are known. The selectivities involving Ca^{2+} are difficult to predict, since K for 18C6- Ca^{2+} interaction has been determined accurately only in methanol (3). However, aqueous equilibrium constants for cation-macrocycle interaction have been shown to be ≈ 2 to 3 log K units lower than those in methanol (8, 9). Therefore, a range of predicted log K (H_2O) and selectivity values for Ca^{2+} can be calculated. The observed Ba^{2+} and Sr^{2+} over Ca^{2+} selectivities fall in the middle of these ranges (Table I).

The presence of nitrogen donor atoms in 3 and 4 affects cation separations in two ways. First, the greater affinity of nitrogen for several transition- and heavy-metal cations in comparison to that for alkali and alkaline-earth metal cations changes the selectivities observed. Second, the protonation chemistry of nitrogen allows pH effects to be used in making separations and in the stripping of metal cations from the column. These principles can be illustrated with separations

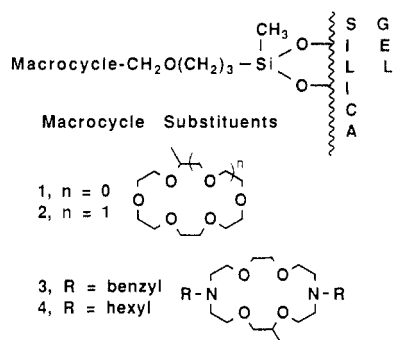


Figure 1. Silica-gel-bound macrocycles used in this study.

Table II. Experimental Concentrations and $\log K$ (H_2O) Interaction Values with Diaza-18-crown-6, 3, of Ag^+ , Hg^{2+} , and H^+

cation	[cation] ^a	$\log K$ (H_2O)
Ag^+	9.35×10^{-5}	7.8
Hg^{2+}	1.00×10^{-4}	17.85
H^+	1.00×10^{-2}	9.0
		7.8

^a Moles per liter.

involving Ag^+ and Hg^{2+} . Virtually quantitative removal (amount remaining below detection limits) of $1 \mu g/mL$ $AgNO_3$ from 5 L of solutions containing 100 times excess quantities of Mg^{2+} , Ca^{2+} , K^+ , and/or Na^+ was observed with both 3 and 4 at pH values ≥ 7.0 . The presence of excess quantities of the other cations prevents the binding of Ag^+ to the silica gel. However, the selectivity of 3 and 4 for Ag^+ over the other cations allows Ag^+ removal to occur. Less than 1% of any of the other cations were removed from the solution, and this removal is due to interactions with plain silica gel. The Ag^+ was then concentrated and recovered with use of an acetic acid-sodium acetate buffer solution of pH 3.7. A separation with 4 of Hg^{2+} ($20 \mu g/mL$) from Ag^+ ($10 \mu g/mL$) present in 100 mL of solution was performed by maintaining the solution at pH 2 with nitric acid. Under these conditions, 78% of the Hg^{2+} and 8% of the Ag^+ were removed from the solution. The column was regenerated by using a basic EDTA and $S_2O_3^{2-}$ solution. This degree of separation occurs because of the relative concentrations of Ag^+ , Hg^{2+} , and H^+ present and the relative magnitudes of the K values for the interaction of these cations with 4, which are given in Table II. Greater than 75% Ag^+ and Hg^{2+} removal with little separation of these cations occurs at pH values between 4.5 and 8 with the cations initially present at the levels given in Table II. Both Ag^+ and Hg^{2+} were found to be soluble to at least pH 8 at these low levels, as expected from equilibrium calculations (10). Identical experiments with plain silica gel showed that the Ag^+ removal observed in the pH 2 case was due almost entirely to interactions with silica gel, while Hg^{2+} removal is due primarily

to the presence of the macrocycle.

All of the experiments discussed have involved a single pass through the short columns to obtain full column equilibrium conditions. It is apparent that the appropriate number of multiple passes or theoretical plates would enable one to make effective separations despite the interactive properties of the column matrix. This is possible since the silica gel selectivity is based on electrostatic interactions and is relatively small compared to that which can be designed into macrocycles. In conclusion, these newly bonded macrocycles make possible (1) the use and reuse of immobilized macrocycles to perform cation separations and (2) the use of the large macrocycle interaction data base (5) and other chemistry to predict what columnar systems will be capable of a particular metal cation separation, recovery, removal, and/or concentration.

Registry No. Ba, 7440-39-3; Sr, 7440-24-6; Pb, 7439-92-1; Tl, 7440-28-0; Ca, 7440-70-2; Mg, 7439-95-4; Ag, 7440-22-4; Hg, 7439-97-6.

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Fused Silica Packed Microcolumns as Micropreparative Tools in Protein Analytical Studies

Sir: Increasingly smaller quantities of biological macromolecules have to be isolated and characterized in modern

biology and medicine. In the area of protein investigations, the traditional methods of amino acid analysis (1) limited