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Chromatographic Behavior of Cryptand[2,2] Modified Resin on Metal Cations

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Cryptand[2,2] was grafted to low crosslinked styrene-divinylbenzene copolymer by substitution reaction with chloromethylated styrene-divinylbenzene copolymer. This resin was stable in concentrated acid and base, and showed a good resistance to heat. The pH, time, and concentration dependence of the adsorption of metal ions by this resin were studied. Studies on the chromatographic separation of lanthanides, Cu^{2+}, and UO_2^{2+} were also carried out with various eluents. These studies demonstrate that this resin has the applicability to the preconcentration and separation of metal ions.

Introduction

Many investigations have been devoted to the synthesis of macrocyclic compounds, their complexing properties, characterization of the solid complexes, and selective complex formation of the compounds with metals[1-4]. Recently, these compounds were used in the field of analytical chemistry such as solvent extraction, chromogenic reagent, ion-selective electrode, and liquid chromatography[3,5-8].

In liquid chromatography, macrocyclic compounds were used as a coating material on silica gel or as a modifier of an eluent to separate various cations, anions, organic compounds, and optically active compounds[3,7-10]. Polymers modified with macrocyclic compounds were also used rather frequently as a stationary phase due to their excellent properties in chromatography[3,11-13]. Many kinds of these polymeric compounds which can selectively adsorb inorganics and organic compounds have been prepared by condensation, by substitution, and by copolymerization with various crown ethers or cryptands. Although several attempts have been made to separate alkali and alkaline earth cations by the pioneering works of Blasius *et al.*[11-13], the study of the applications to the heavy metals containing the lanthanides and actinides was not found, so far.

In a previous paper[14], we reported that cryptand[2,2] forms a stable complex with UO_2^{2+} but not with lanthanide cations of +3 valence state in aqueous solution. It is of interest to extend these particular properties of cryptand[2.2] to analytical work. In this study, we describe the synthesis of styrene-divinyl benzene(DVB) resins modified with cryptand[2,2] as a functional group, their adsorption characteristics for various metal cations, and their application to the chromatographic separation of rare earth cations, UO_2^{2+}, and Cu^{2+}.

Experimental

Reagents. Cryptand[2,2] was the reagent grade chemical obtained from Merck and other chemicals used for the preparation of resin carried a certified purity. All other reagents were in analytical grade and used without further purifications. $N(Me)_4OH$ was prepared from $N(Me)_4Cl$ using the method of G. Anderegg *et al*[15]. $N(Me)_4NO_3$ stock solution was prepared by neutralizing the $N(Me)_4OH$ solution with conc-HNO_3.

Synthesis of Resin. The styrene-DVB copolymer(II) modified with cryptand[2,2] (I) was synthesized as illustrated in Figure 1. The fine bead of styrene-DVB was prepared by suspension copolymerization of styrene and DVB at 90°C as described elsewhere[16-18]. The crosslinkages of copolymers were adjusted to 1% and 4% by varying the amount of DVB added in the reaction mixture.

Chloromethylation of dried styrene-DVB copolymer was carried out by refluxing with chloromethylmethylether for 5 hours. A catalytic amount of $ZnCl_2$ was added to the mixture. After the reaction was completed, the solution was removed by decantation and the product was washed successively with dioxane-water, water and methanol, and was dried at 50°C for 3 days in an oven.

The substitution reaction of chloromethylated copolymer (III) with cryptand[2,2] proceeded as follows. Five grams of chloromethylated copolymer was added to 200m*l* of benzene

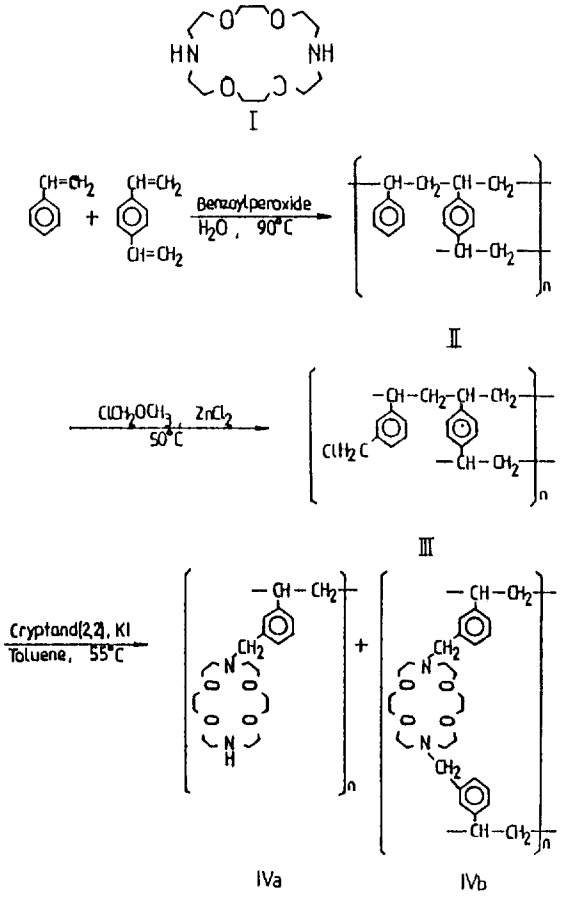

Figure 1. Synthesis of the resin modified with cryptand[2,2].

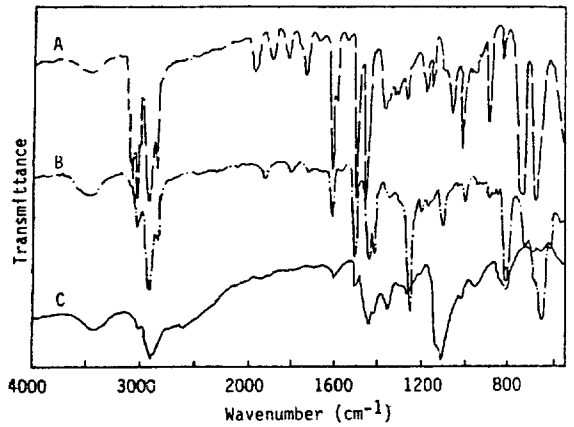

Figure 2. IR spectra of styrene-DVB copolymer(A), chloromethylated styrene-DVB copolymer(B), and the resin modified with cryptand[2,2] (C).

and the mixture was refluxed for 1 hour. The mixture was then cooled to room temperature, and benzene was removed by decantation. To this copolymer, 250m*l* of toluene, 10g of cryptand[2,2], and 6g of KI were added, and the mixture was stirred at 55°C for 30 hours under N_2 atmosphere. The product was washed successively with dil-HCl, water, dil-NaOH, and water. Hereafter cryptand[2,2] modified resin will be denoted as P1C and P4C, the numbers referring to the degree of crosslinkage of the resins.

The IR spectra of compound II, III and IVa/b are presented in Figure 2. A strong absorption band near 650cm^{-1} in

Table 1. Chlorine Contents in Compound III

Crosslinkage(%)	Chlorine Content(%)	
	Calculated	Found
1	23.2	24
4	23.1	21

Table 2. Elemental Analysis of Resins

Resin	Crosslinkage (%)	Element Found(%)		
		C	H	N
P1C	1	63.8	7.8	5.2
P4C	4	71.8	8.2	4.9

Figure 2B indicates a chloromethyl substituted copolymer. The Cl contents of compound III were determined by pyrohydrolysis followed by potentiometry with ion-selective electrode and the results are give in Table 1.

The strong and broad absorption band at 1100cm^{-1} in Figure 2C is believed to result from the C-O-C stretching vibrations of the cryptand [2,2] moiety in the resin. Table 2 summarizes the results of elemental analysis of cryptand [2,2,] modified resins.

Batch Test. The adsorption of UO_2^{2+} on the resin P1C was measured at various pH values. Amounts of HNO_3 or NH_4OH solution were added to 20m*l* of 1.15×10^{-3}M $UO_2(NO_3)_2$ soluton so that the final pH of the solution with resin in equilibrium remained in the range of 1 to 5. A quantity (0.1g) of resin was added to this solution and the mixture was gently stirred for 18 hours at room temperature. The mixture was then filtered with a fine glass filter, and the uranium content in the filtrate was determined by Arsenazo-III colorimetry. The quantity of uranium adsorbed on the resin was calculated from the difference between quantities in the starting solution and in the filtrate.

The adsorption of Cu^{2+}, Nd^{3+}, Ca^{2+}, and Na^+ on the resin P1C was measured following the same procedure as described above. The concentrations of Cu^{2+}, Ca^{2+}, and Na^+ in the filtrate were determined by atomic absorption spectrophotometry, and that of Nd^{3+} was determined by the Arsenazo-III colorimetry.

To measure the equilibrium time, the identical mixtures of the resin and UO_2^{2+} solution were prepared following the same procedure as used in the experiment of UO_2^{2+} adsorption as a function of pH, and the content of uranium in solution was determined in the same manner as described earlier at an interval of 0.5, 1, 2, 4, 6, 8, and 10 hours.

The adsorption of UO_2^{2+}, Cu^{2+}, Nd^{3+}, K^+, and Na^+ on the resin P1C was measured at pH between 4 and 5 as a function of metal ion concentration.

To investigate the adsorption dependence on crosslinkage of the resins, similar experiments were carried out with $UO_2(NO_3)_2$ solutions in the concentration range of 1×10^{-4}M to 2×10^{-2}M.

To study the adsorption of metal ion depending on NO_3^- concentration, 0.1g of the resin was equilibrated with a volume of 20m*l* of the metal ion solution (1×10^{-3}M) prepared by adding metal nitrate salt to a diluted $N(Me)_4NO_3$ stock solution followed by adjusting pH to 2 with conc-HNO_3.

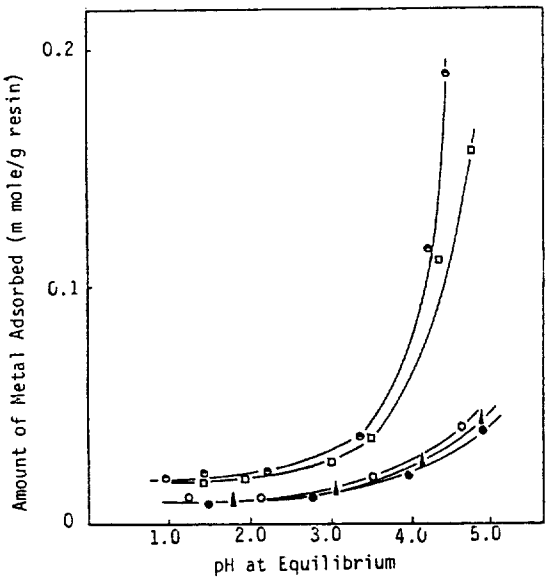

Figure 3. pH dependence of adsorption of metal ions by the resin P1C in aqueous solution. UO_2^{2+}(●): Cu^{2+}(□): Nd^{3+}(○): Ca^{2+}(▲): Na^+(●).

The adsorption of the metal ions on the resin was also measured at various HNO_3 concentrations. One tenth gram of the resin was added to a volume of 20m*l* of the HNO_3 solution containing metal ion. After equilibration, the resin was removed by filtration and the content of metal ion in the filtrate was determined by the same methods as described previously.

Chromatography. The slurry of the resin P1C (200-400 mesh) with water was poured into a glass column 0.6cm in diameter. The height of resin bed was adjusted to 5cm. One-tenth molar HCl, H_2O, 0.1M NaOH, and H_2O were passed successively through the column. Two-tenth milliliter of the synthetic solution (pH 4.2) containing 110μg of Nd, 50μg of Cu, and 190μg of U was loaded on the column. Dilute HNO_3 solution (pH 2.3 or 2.5) was used as an eluent. The eluate was collected fractionally, and the cation concentration in each of the fraction was measured by the methods described above.

Another column was prepared by the same procedure as described above, and followed by conditioning with 100m*l* of 0.02M $NaNO_3$ solution. The Nd^{3+}, Cu^{2+}, and UO_2^{2+} were separated from the mixture on this column using 0.02M $NaNO_3$ solution (pH 2.6) as an eluent.

A third column was conditioned with 0.02M NH_4NO_3 solution and 0.02M NH_4NO_3 solution of pH 2.6 was used as an eluent for the separation of Cu^{2+}, Nd^{3+}, and UO_2^{2+}.

A fourth column was conditioned with 6M HNO_3, followed by loading 3m*l* of the synthetic solution containing 286mg of U, 70μg of Cu, 100μg of Nd, and 6M HNO_3, and the metal ions were eluted with 6M HNO_3.

Results and Discussion

Adsorption Characteristics. The concentrations of UO_2^{2+}, Cu^{2+}, Nd^{3+}, Ca^{2+}, and Na^+ adsorbed on the resin P1C as a function of pH are shown in Figure 3. It can be seen from Figure 3 that the metal ions are hardly adsorbed at low pH. This may be caused by that the protonation to the nitrogen atoms of cryptand[2,2] might prevent the resin from adsorbing the metal ions. Also, Figure 3 shows that the adsorptivity of the resin for UO_2^{2+} and Cu^{2+} increases slowly from pH 2 and rapidly increases above pH 4. Such a pH dependence of adsorptivity could explain the stable complex formation of UO_2^{2+}, Cu^{2+} and/or their hydrolyzed species with an unprotonated cryptand[2,2] above pH 4[14, 19]. From Figure 3, it can be understood that the resin phase concentrations of Nd^{3+}, Ca^{2+}, and Na^+ do not increase remarkably as the pH of solution increased. Such low adsorptions of Ca^{2+} and Na^+ on the resin are caused by that amine has little affinity for alkali or alkaline earth ions[20]. As Nd^{3+} is strongly hydrated due to the high charge density, the complex formation of Nd^{3+} with cryptand[2,2] could be hindered[14].

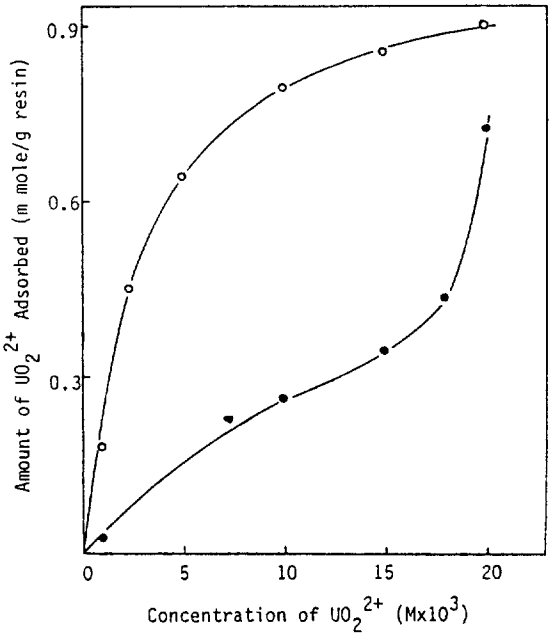

Figure 4. Adsorption of UO_2^{2+} on the resin P1C(○) and P4C(●) at various concentrations in aqueous solution.

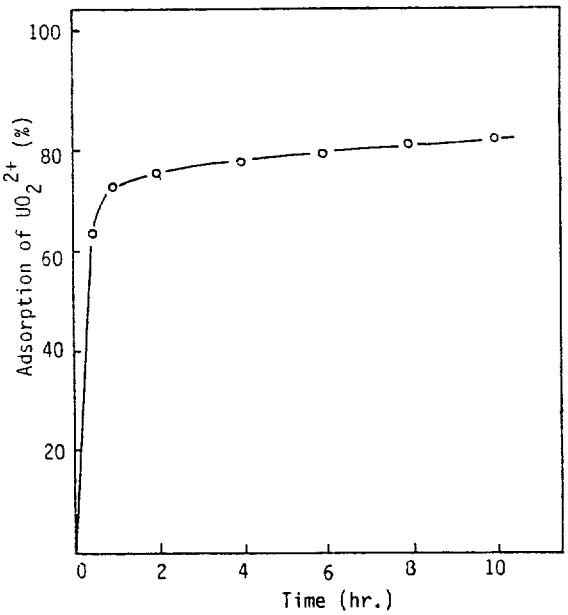

Figure 5. Adsorption rate of UO_2^{2+} on the resin P1C in aqueous solution(pH 4-5).

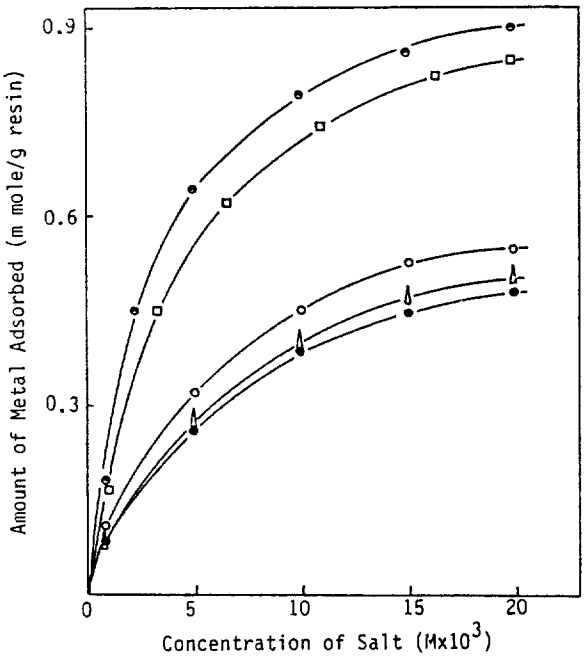

Figure 6. Adsorption of metal cations on the resin P1C at various concentrations in aqueous solution. UO_2^{2+}(●): Cu^{2+}(□): Nd^{3+}(○): K^+(△): Na^+(●).

Table 3. Distribution Coefficients and Separation Factors of Metal Cations for Resin P1C in Aqueous Solution

	K(m*l*/g)	α
UO_2^{2+}	130	2.7
Cu^{2+}	110	2.3
Nd^{3+}	55	1.2
K^+	53	1.1
Na^+	48	1.0

The concentration of UO_2^{2+} adsorbed on the resins P1C and P4C as a function of UO_2^{2+} concentration between pH 4 and 5 is shown in Figure 4. The adsorptivity of P1C for UO_2^{2+} is higher than that of P4C, and from this result, it seems that the adsorption kinetics of UO_2^{2+} is limited by its diffusion process into the resin.

For the study of the rate of metal ion uptake by the resin, UO_2^{2+} among the metal ions examined in this study was selected since UO_2^{2+} has the highest affinity to the resin. The results obtained from the experiment are presented in Figure 5. As shown in Figure 5, the adsorption rate of UO_2^{2+} on the resin is sufficient enough for the application of this resin to liquid chromatography and for extracting uranium from solution.

Plots of the adsorptivity for the metal ions such as UO_2^{2+}, Cu^{2+}, Nd^{3+}, Na^+ and K^+ at various concentrations are in Figure 6. Based on these results, distribution coefficients and relative separation factors for the metal cations are calculated using the following equations. The results are given in Table 3.

$$K_M = \frac{\text{Concentration of metal in resin(m mole/g)}}{\text{Concentration of metal in solution(m mole/m}l\text{)}}$$

$$\alpha_M^{M'} = K_{M'}/K_M$$

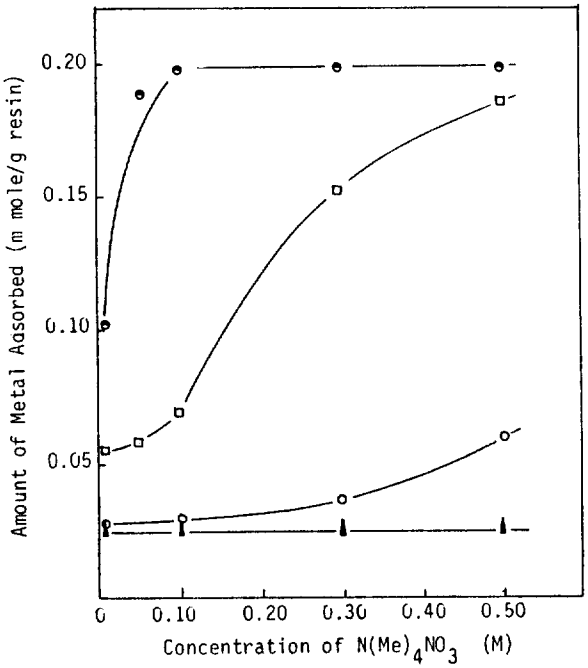

Figure 7. Adsorption of metal ions on the resin P1C as a function of nitrate concentration. UO_2^{2+}(●): Cu^{2+}(□): Nd^{3+}(○): Ca^{2+}(▲).

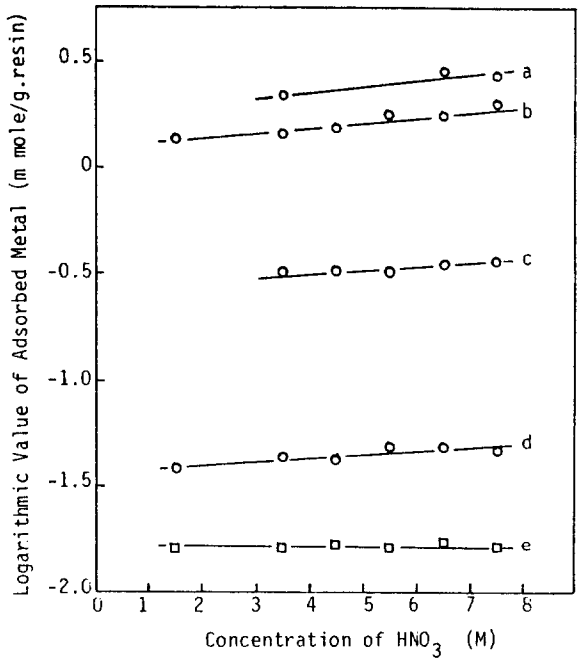

Figure 8. Adsorption of metal ions on the resin P1C as a function of HNO_3 concentration. a,b,c, and d: Adsorbed amount of UO_2^{2+} in 1.0×10^{-1}, 5.0×10^{-2}, 1.0×10^{-2}, and 1.0×10^{-3}M of UO_2^{2+}, respectively; e: Adsorbed amount of Cu^{2+}, Nd^{3+}, Ca^{2+}, and Na^+ in 1.0×10^{-3}M of each ion.

Where K_M and $K_{M'}$ denote distribution coefficients for the cation M and M′, and $\alpha_M^{M'}$ is the separation factor for cation M′ referred to M. Considering the separation factor for P1C, the selectivity sequence is $UO_2^{2+} > Cu^{2+} \gg Nd^{3+} > Ca^{2+}$, $K^+ > Na^+$. This resin shows excellent selectivity for UO_2^{2+} and Cu^{2+} over other cations used in this experiment.

To examine the adsorption of the cations on the resin

Table 4. Capacities of Resins (m mole / g.resin)

		P1C	P4C
Cryptand content (m mole/g.resin)		1.86	1.75
Cal'd	pH 4-5	1.86	1.75
	conc-HNO_3	3.7	
Obs.	pH 4-5	1.0	0.8
	conc-HNO_3	2.8	

depending on the nitrate concentration, tetramethylammonium salt of which cation size is larger than that of the cavity of cryptand[2,2] was selected. The data obtained from the solutions with the resin in pH 4 are presented in Figure 7. The adsorptivity for UO_2^{2+} and Cu^{2+} having a great affinity to the resin improves abruptly increasing the nitrate concentration. The result seems to indicate that these cations are adsorbed on the resin as an ion pair (cryptand·M^{n+}·nNO_3^-). Frensdorff discussed more in detail the ion pair extraction of cation with crown compounds[21]. On the other hand, even at the higher concentration of NO_3^- no significant adsorption of Nd^{3+} and Ca^{2+} has occurred.

The adsorption of the metal ions on the resin depending on the concentration of nitric acid is illustrated in Figure 8. The adsorptivity for uranium increases slightly with the HNO_3 concentration increased, but increases remarkably with the uranium concentration increased. The resin slightly adsorbs Cu^{2+}, Nd^{3+}, Ca^{2+}, and Na^+, and their adsorptions do not change due to the change of HNO_3 concentration used in this study. The cryptand[2,2] is a diamine and has one unshared pair of electrons on each nitrogen atom. The protonation occurs on these lone pairs in conc-HNO_3, then the resin could behave like an anion-exchange resin, which can adsorb the anionic complex of UO_2^{2+}.

The ion exchange capacity of the resin containing cryptand[2,2] varies with the acidity of solutions due to the amine nitrogens easily protonated. Theoretical and apparent capacities of the resins are tabulated in Table 4. Theoretical capacities (Cal'd) are calculated on the content of nitrogen in the resins, and the apparent capacities (Obs.) correspond to the maximum adsorption amount of uranium found in Figure 4 and 8. The apparent capacity of the resin P1C in conc-HNO_3 increases about three times the value in the mild acidic solution. This result (2.8 m mole/g.resin) in conc-HNO_3 was also ascertained by a column method. Differences between two capacity data (Cal'd and Obs. at pH 4-5) may result from the fact that, in the mild acidic medium, protonation on the amine groups in the cryptand[2,2] has occurred. If the anion-exchangable species is $UO_2(NO_3)_3^-$ in conc-HNO_3, one mole of the protonated cryptand[2,2] which gives two anion-exchangable sites may uptake two moles of uranium. But the apparent capacity of the resin P1C does not agree with the theoretical capacity (3.7 m mole/g.resin). This seems to be caused by the presence of a large amount of NO_3^- ions in conc-HNO_3 which could affect the adsorption of anionic uranium complex.

Though these capacities are not as high as those of many commercially available ion-exchangers, this resin may be adequately used for the preconcentration and separation of heavy metal cations. This is true when one considers that cryptand[2,2] has little affinity for alkali, alkaline earth, and lanthanide cations, but forms stable complexes with heavy

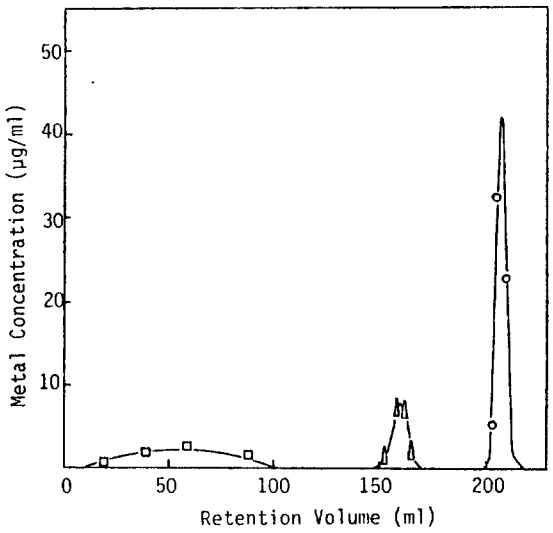

Figure 9. Elution curves for Nd^{3+}(□), Cu^{2+}(△), and UO_2^{2+}(○). Column: 0.6 × 4.5cm P1C, Eluent: Nitric acid (pH 2.3), Elution rate: 9ml/hr.

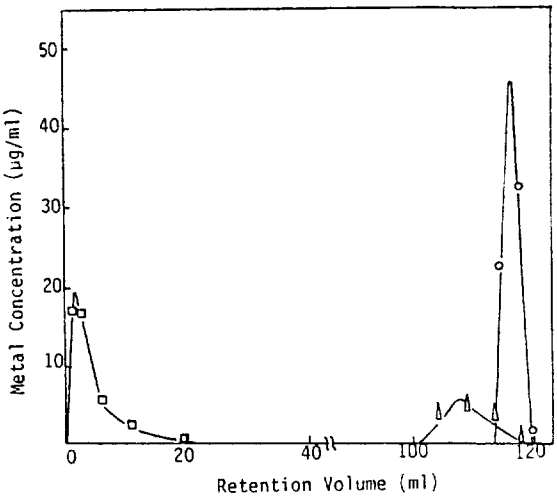

Figure 10. Elution curves for Nd^{3+}, Cu^{2+}, and UO_2^{2+}. Eluent: 0.02M $NaNO_3$ (pH 2.6). Other conditions for elution and symbols used are identical with those in Figure 9.

metal ions such as Hg^{2+}, Pb^{2+}, Cd^{2+}, and Ag^{+}[19]. Moreover, we found that this resin was very stable in the concentrated acidic and basic solutions (8M HNO_3, 8M HCl, and 5M HaOH) and had a good resistance to heat (110°C). These properties are different from those of chelate immobilized silica gel and cellulose exchangers which have limited application in acidic or basic solution[20].

Chromatographic Separation of Lanthanides, Cu^{2+}, and UO_2^{2+} In general, the cation uptake of macrocyclic resin containing nitrogen atom as a functional group is dependent of pH. Considering the above adsorption characteristics of cryptand[2,2] resin, Cu^{2+} and UO_2^{2+} could not be eluted with pure H_2O or organic solvent because of the high adsorptivity of this resin above pH 4. Thus, we chose dilute HNO_3, $NaNO_3$, and NH_4NO_3 solutions for the eluent. The pH of $NaNO_3$ and NH_4NO_3 was adjusted with HNO_3.

Figure 9 gives the result of chromatographic separation on P1C with dilute HNO_3 at pH 2.3. The elution sequence in the order of Nd^{3+}, Cu^{2+}, and UO_2^{2+} shows a good agreement

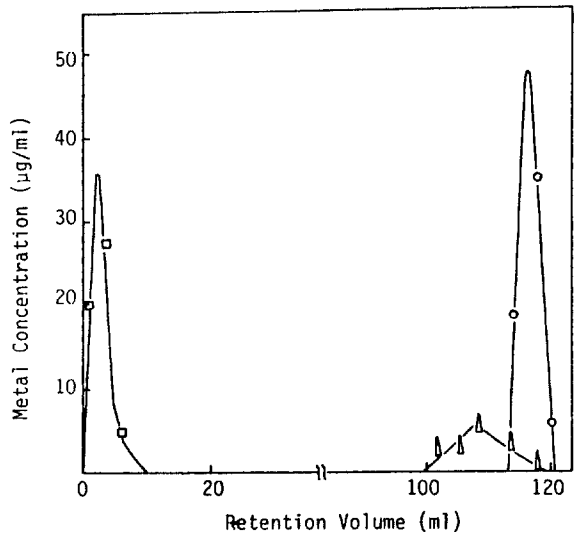

Figure 11. Elution curves for Nd^{3+}, Cu^{2+}, and UO_2^{2+}. Eluent: 0.02M NH_4NO_3 (pH 2.6). Other conditions for elution and symbols used are identical with those in Figure 9.

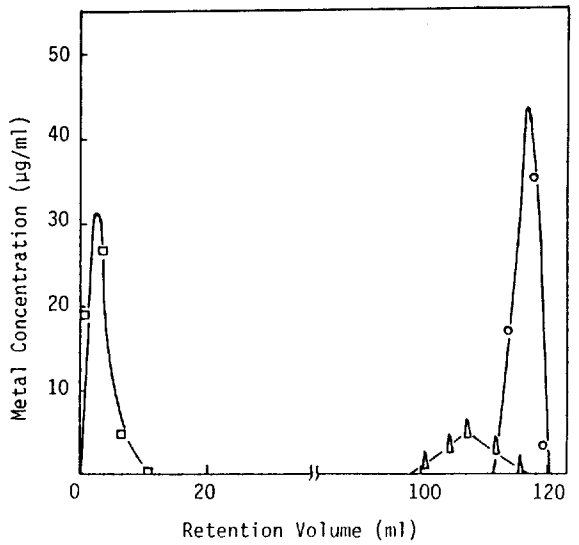

Figure 12. Elution curves for Gd^{3+}(□), Cu^{2+}, and UO_2^{2+}. Other conditions for elution and symbols used are identical with those in Figure 11.

with the selectivity observed with cryptand[2,2]. Above pH 2.5, it took twice as long to elute all the cations due to high adsorptivity of the resin. In addition, below pH 2.3, the metal cations were all eluted together, namely they could not be separately eluted.

Using 0.02M $NaNO_3$ solution (pH 2.6) Nd^{3+} is eluted more rapidly than in dilute HNO_3 solution and the peak has a better shape(Figure 10). This result suggests that both Na^+ and Nd^{3+} interact with cryptand[2,2] through very weak ion-dipole force. Therefore Nd^{3+} could hardly displace Na^+ pre-adsorbed on the resin.

Changing the eluent to 0.02M NH_4NO_3 solution(pH 2.6) gave similar results (Figure 11). In order to investigate the applicability of this resin to a group separation of lanthanides from uranium, Gd^{3+}, Dy^{3+}, Cu^{2+}, and UO_2^{2+} were also tested on the same column using 0.02M NH_4NO_3 solution (pH 2.6) as an eluent. There appears to be no difference in the retention data for Gd^{3+} and Nd^{3+} as shown in Figure 11

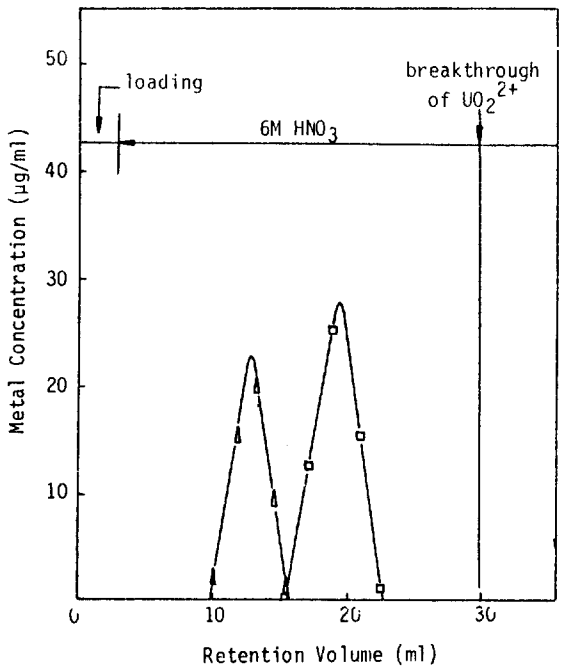

Figure 13. Elution curves for Cu^{2+}(△), Nd^{3+}(□), and UO_2^{2+}. Column: 1.15 × 12cm P1C, Eluent: 6M HNO_3, Elution rate: 30ml/hr.

and Figure 12. The elution behavior showed exactly the same as for Dy^{3+} for the identical system. This agrees well with the results that +3 valence lanthanides do not form complexes with cryptand[2,2] in aqueous solution as in a previous study[14].

The above chromatographic systems can be applied to the preconcentration or separation of trace amount of heavy metals. But in the case of a sample containing large amount of metal ions, the adjustment of pH suitable to loading may cause the metal hydroxide precipitation.

For this reason we considered conc-HNO_3 system for the group separation of lanthanides from nuclear grade uranium compounds. The separation profile of Nd^{3+} and Cu^{2+} from large amount of uranium using 6M HNO_3 as an eluent suggests that group separation of lanthanides from uranium will be achievable on the resin P1C chromatographic system (Figure 13).

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The $[M(cod)(PPh_3)_2]PF_6$ (M = Rh, Ir; cod = 1,5-cyclooctadiene) Mediated Activation of Aldehyde C-H Bond

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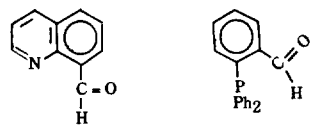
Acetone solution of quinoline-8-carbaldehyde reacts with $[Rh(cod)(PPh_3)_2]PF_6$ and $[Ir(cod)(PPh_3)_2]PF_6$ to yield $[Rh(NC_9H_6CO)(H)(PPh_3)_2(CH_3COCH_3)]PF_6$ (1) and $[Ir(NC_9H_6CO)(H)(PPh_3)_2(CH_3COCH_3)]PF_6$ (2), respectively. The compound $[Ir(cod)(PPh_3)_2]PF_6$ also reacts with $Ph_2PC_6H_4$-o-CHO in the acetone/H_2O mixture to give $[Ir(Ph_2PC_6H_4\text{-}o\text{-}CO)(H)(PPh_3)_2(CH_3COCH_3)]PF_6$ (3). Compounds 1, 2, and 3 were characterized by infrared, ^1H NMR, ^{31}P NMR spectra and conductivity measurement. The ^1H NMR spectra of 1, 2, and 3 support the presence of a terminal hydride that is cis to the phosphine. The IR band of 3 at 2185 cm^{-1}, which is assigned to ν(Ir-H), and the hydride cleavage reaction of 3 with CCl_4, provide evidence for the Ir-H bond.

Introduction

Transition metal acyl hydride compounds are known or postulated to be key intermediates in catalyzed hydroformylation reaction[1] and metal-catalyzed carbonylation processes[2]. In addition, formation of coordinatively unsaturated acyl metal hydride intermediates through the oxidative addition of aldehydes to metal centers is thought to be involved in metal catalyzed decarbonylations of aldehydes.

Recently, we reported the Pt $PCy_3(C_2H_4)$[3] and $Ir(PPh_3)_2(CO)OClO_3$[4] mediated activation of aldehyde C-H bonds, which led to transition metal acyl hydride compounds. The stable transition metal acyl hydrides have been obtained through reactions involving the scission of C-H bonds in cases where a coordinating group on the metal is available to form a five-membered chelate and where the transition metal precusor is strongly nucleophilic. In an extension of these works, $[M(cod)(PPh_3)_2]PF_6$ (M = Rh, Ir; cod = 1,5-cyclooctadiene) were selected as candidates, because they are coordinatively unsaturated, and provide a nucleophilic metal center. The complexes $[M(cod)(PPh_3)_2]PF_6$ also show different features from those of previously used iridium (1) and platinum (0) compounds due to the bidentate character of the cod group. Readily available aldehydes able to form a chelate are quinoline-8-carbaldehyde (A) and o-diphenylphosphinobenzaldehyde (B), which stabilize intermediates in the reactions of the aldehyde group with metal ions.



A B

We describe here the reactions between $[M(cod)(PPh_3)_2]PF_6$ and A, B, which lead to C-H activation through formation of stable five-coordinate rhodium(III) and iridium acyl hydride compounds.

Experimental

All synthetic procedures were carried out with use of standard Schlenk tube under a dry and oxygen free atmosphere of N_2. The $[Ir(cod)(PPh_3)_2]PF_6$[5], $[Rh(cod)(PPh_3)_2]PF_6$[6], quinoline-8-carbaldehyde[7], and $Ph_2PC_6H_4$-o-CHO[8] were prepared according to literature methods. Solvents were reagent grade and were distilled from the appropriate drying agents. Infrared spectra were recorded on a Shimazu IR-440 spectrophotometer from KBr pellet. ^1H NMR spectra were recorded on a Bruker WP 80 spectrometer. ^{31}P NMR spectra