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NOVEL BIFUNCTIONAL RESINS IN METAL ION SEPARATIONS: ION EXCHANGE/COORDINATION RESINS AND ION EXCHANGE/PRECIPITATION RESINS

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ABSTRACT

Dual mechanism bifunctional polymers (DMBP's) as metal ion extractants are described within the context of two new examples. The carboxylic acid/pseudocrown resin is a new example of the DMBP class of resins described as ion exchange/coordination resins. The polyethylene glycol ligand within the resin functions as a coordinating site for metal ions which are brought into the resin via ion exchange with the acid ligand. Initial studies with alkali metal ions are presented. The third general class of DMBP's is also presented. In this case, precipitation is the reaction occurring along with ion exchange thus yielding the ion exchange/precipitation resins. Barium recovery from aqueous solution via barium sulfate precipitation is described.

INTRODUCTION

The selective separation and recovery of metal ions from the aqueous environment continues to be an important problem with respect to toxic metal removal and strategic metal recovery. The need for selectivity in the separation of one ion from a group of ions in solution has led to the development of a wide array of polymer-supported extractants (1) and an even wider array of liquid extractants (2). The liquid extractants, though versatile and readily prepared, are subject to entrainment and solubility losses (3). Extractant ligands covalently bound to polymer beads are clearly not subject to such losses, but these polymer-supported extractants can be more difficult to synthesize (4), especially on a large scale.

The focus of this research is the synthesis and characterization of a category of readily prepared polymeric extractants termed **dual mechanism bifunctional polymers** (DMBP's) (5). These polymers operate through two different mechanisms from two separate ligands on a given support structure. One of the two mechanisms is ion exchange via an acid ligand, while the other mechanism and corresponding ligand varies according to the desired metal ion specificity.

The first class of resins within the DMBP category is the ion exchange/redox resins (5). Ion exchange occurs through primary and secondary phosphinic acid ligands while redox occurs through the non-acidic P-H bonds on the primary acid ligands. The resin is capable of reducing metal ions with a reduction potential greater than 0.3 V, such as silver, mercury and gold, allowing for the isolation of pure metal from a solution of its ions.

The second class of resins superimpose a purely coordinative interaction upon the ion exchange mechanism. In the ion exchange/coordination resins (6) which have been reported to date, the ion exchange ligand is the phosphonic acid group while the coordinating ligand is, in one case, a phosphonate ester group and, in the other case, an amine group. Their ability to extract americium has been reported (6) and transition metal studies are currently underway (7).

In this report, initial studies of a new Class II resin are presented. The ion exchange ligand is a carboxylic acid group and the coordinating ligand is a pentaethylene glycol group in a pseudocrown arrangement. Continuing studies of these ion exchange/pseudocrown resins should show a size-selectivity for different cations. Additionally, initial studies with the third class of DMBP's are described. The **ion exchange/precipitation resins** employ a phosphonic acid group for the ion exchange reaction and a quaternary amine group with an ionically held anion for the subsequent precipitation reaction. Varying the anion to produce an insoluble salt with a targeted metal ion in solution leads to a resin with easily modified selectivity.

EXPERIMENTAL

The syntheses of the Class II ion exchange/pseudocrown resins and the Class III ion exchange/precipitation resins will be detailed elsewhere (v.i.).

Distribution Coefficients for the Group IA Ions with the Class II Resin

A Varian Series 1475 atomic absorption spectrophotometer in the emission mode was used in determining the equilibrated aqueous content of the Group IA ions. Five mL 0.001N solution of each metal ion (K, Rb, Cs) as the nitrate, sulfate or phosphate salt was placed in a vial containing enough resin to give 1 mequiv of ion exchange and/or coordination sites and the solution adjusted to pH 10. After shaking for 17h, the pH of the solution was measured and the absorbance of the samples determined (K at 766.5 nm, Rb at 780.0 nm, and Cs at 852.1 nm). The final solution concentration was calculated from a standard curve of known metal ion solutions.

Per Cent Group IIA Ions Absorbed with the Class III Resins

Barium nitrate and calcium nitrate absorption studies were set up at an initial ratio of 0.5 mequiv metal ions per mequiv phosphorus and/or amine sites on the resin. A given weight of resin was thus contacted with 50 mL 0.005N standard aqueous barium or calcium nitrate solution. The mixture was shaken for 3 h on a Burrell wrist-action shaker. The amount of barium or calcium remaining in solution was determined by EDTA titration.

RESULTS AND DISCUSSION

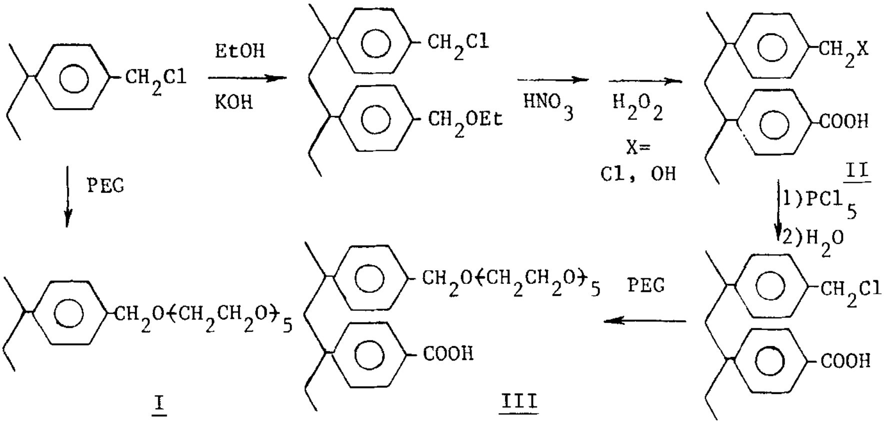
Class II: Ion Exchange/Coordination Resins with Pseudocrown Ligands as the Coordinating Sites

Crown ethers are among the most important coordinating groups due to their ability to distinguish metal ions, including the Group IA ions, on the basis of size (8). Their ability to strongly coordinate these ions has led to many applications as liquid extractants (9), phase transfer catalysts (10), and rate enhancers in anionic polymerizations (11). The polyethylene glycols, as linear analogues to the crown ethers, have found use as a low-cost alternative to the crowns, but they display a lower selectivity towards metal ions (12). Crown ethers have been modified in a number of ways such as with one or two polyethylene glycol side chains in order to study the effect on selectivity and metal ion binding constants (13). As purely coordinating molecules, the crown ethers alone and with glycol side chains extract not only the metal ion but also its counterion as required by charge neutrality. Size-selective metal ion extractions which are independent of the counterion are found with crown ethers substituted with an ionic ligand. This substituent is usually an alkyl acid (14). An alternate technique uses a non-ionic crown dissolved in an organic solution containing an organophilic acid; the acid obviates the need for the aqueous phase anion to follow the metal ion into the organic phase (15).

The difficulty of synthesizing large quantities of crown ethers makes it important that they are not subject to losses during any given process. As a result, crown ethers have been covalently bonded onto polymer supports for recovery and recycle (16). Polyethylene glycols have also been bound to polystyrene beads (17). Pseudocrown resins combine some of the selectivity of the crown ethers with the ease of supporting polyethylene glycols onto polymer beads (18): glycols terminating with alkoxy groups on both ends of the chain are reacted with poly (vinylbenzyl chloride) to yield cyclic structures of varying sizes. In each case, though, the polymer offers coordinating sites only and the metal ion extractions will necessarily be counterion - dependent. As an added disadvantage, the neutral coordinating polymers could display slower absorption rates due to the limited hydrophilicity of a polar but non-ionic ligand within a hydrophobic matrix.

The aim in this research is to prepare polymers which combine the coordinating ability of pseudocrown moieties with the exchange properties of ionic groups thus minimizing any dependency of extraction results on the solution counterion. A carboxylic acid/pseudocrown resin has been prepared with penta(ethylene glycol) [PEG] as the reacting glycol. This report presents the initial data. Synthesis of phosphonic acid/pseudocrown resins are currently underway.

The synthesis of the carboxylic acid/pseudocrown resin is summarized below. Full experimental details will be presented elsewhere (19). The poly(vinylbenzyl chloride) beads were prepared via suspension polymeriza-



tion with 2% divinylbenzene crosslinking. The fully functionalized pseudocrown resin I was prepared by reacting the poly(vinylbenzyl chloride) beads (-40+60 mesh) with penta(ethylene glycol) using dry dioxane as the solvent and sodium hydride to form the alkoxy groups. Resin I has a total capacity of 2.34 mequiv PEG groups per gram dry weight resin. Additionally, it was found to consist of 63% pseudocrown groups and 37% linear PEG by reacting the resin with phosphorus pentachloride and determining the increase in chlorine content (which could only be due to the presence of linear groups). The fully functionalized carboxylic acid resin (6.18 mequiv/g) II was prepared by first forming the ethyl ether of poly(vinylbenzyl alcohol) from poly(vinylbenzyl chloride) and ethanolic KOH, then oxidizing it to the acid through the alcohol/aldehyde by sequential reaction with 5% nitric acid and 20% hydrogen peroxide. A 48h reaction time with ethanolic KOH is important because it yields almost no unreacted $-CH_2Cl/-CH_2OH$ groups. The sequential oxidation provides for a cleaner reaction without the possibility of ring nitration as could occur when using the concentrated nitric acid conditions required for ether oxidation directly to the acid. Carboxylic acid resin with a much higher proportion of $-CH_2Cl$ groups (for reaction with PEG) is made by limiting the ethanolic KOH reaction to 8h. The peroxide oxidizes the aldehyde and most of the alcohol ligands to the carboxylic acid. This leaves the carboxylic resin with about 4 mequiv $-CH_2Cl$ groups/g. Reaction of this acid resin with phosphorus pentachloride converts the remaining alcohol to $-CH_2Cl$ groups and the acid to -COCl groups; the latter groups readily hydrolyze

TABLE 1

Distribution Ratios (log D) of Group IA Ions as a Function of Solution Counterion for PEG Pseudocrown, Carboxylic Acid, and Bifunctional PEG/acid Resins

	-PEG			-COONa			-PEG/COONa		
	K	Rb	Cs	K	Rb	Cs	K	Rb	Cs
NO_3^-	2.02	2.22	2.35	2.83	3.20	3.31	2.85	2.85	2.89
$SO_4^=$	2.12	2.21	2.36	2.99	3.24	3.31	2.84	2.75	2.98
$PO_4^≡$	2.39	2.31	2.16	3.31	3.33	3.58	2.88	2.88	2.98

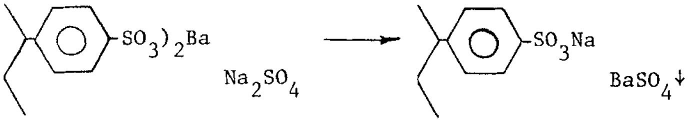
back to carboxylic acid groups. The final PEG/NaH reaction then leads to the bifunctional resin III which has a PEG capacity of 1.38 mequiv/g and an acid capacity of 2.06 mequiv/g. The PEG/acid ratio is thus varied by the ethanolic KOH reaction which controls the $-CH_2Cl$/ether ratio. Further analysis of the PEG capacity with chlorination of the resin, as noted above, leads to a determination of the ratio of linear to pseudocrown groups; resin III was found to consist of 61% linear and 39% pseudocrown moieties.

Initial results with resins I, II, and III in the extraction of Group IA ions from pH 9.6 solution are given in Table 1. Atomic absorption spectrophotometry was used; results were verified with radiotracers. At equilibrium, the carboxylic acid resin in the sodium form shows an affinity for Cs>Rb>K (20). An anion effect is seen, with higher levels of each metal being extracted from solutions in the order phosphate > sulfate > nitrate. (Note that the phosphate results are complicated by the fact that the monobasic form of the salt must also be present at the solution pH being studied.) The PEG resin shows a cation affinity series with a corresponding anion dependency: Cs>Rb>K from nitrate and sulfate solutions but K>Rb>Cs from phosphate solutions. The anion also plays a role in the extraction of a given cation: phosphate > sulfate > nitrate is seen with K and Rb but nitrate = sulfate > phosphate with Cs. In contrast to these results, the bifunctional PEG/acid resin shows only a small deviation from an average log D value. The bifunctional resin thus shows a negligible anion dependency on metal ion extractions. With a given anion, there is a less pronounced cation affinity series than found with the other two resins, though Cs is still somewhat preferred over Rb and K. Further studies will examine the generality of the bifunctional resin's anion independency in cation extractions. It is also important to note that extraction results obtained with a single ion in any given solution do not necessarily allow for the prediction of what will happen when two or more ions are combined in one solution (21). The extraction of K, Rb, and Cs will thus be studied against a background of other ions. Additionally, the bifunctional resin could display a unique selectivity series under conditions of kinetic control as would be true at very short resin - solution contact times; rapid metal ion extraction rates for bifunctional resins, relative to their monofunctional counterparts, have been observed with the ion exchange/precipitation resins (v.i.). Variables which will focus on the bifunctional resin itself include the linear/ pseudocrown ratio and the length of the poly(ethylene glycol) used in the pseudocrown formation reaction.

Class III: Ion Exchange/Precipitation Resins

When recovery of metal ions by reduction is not feasible due to a high reduction potential, and recovery by coordination is not feasible due to the unavailability of an appropriate coordinating agent, recovery by precipitation can be an important option due to the very high removal levels possible from aqueous solutions. Chemical precipitation has been found to be important, especially to electroplating facilities, for the removal of heavy metals from aqueous process streams (22). The hydroxide ion is the most often-used precipitant due primarily to its low cost, availability, and applicability to a wide range of metal ions (23). The sludge which is thus obtained, however, does not allow for further processing for metal ion recycle and must be landfilled. The technique, then, improves the water quality but leaves solid waste.

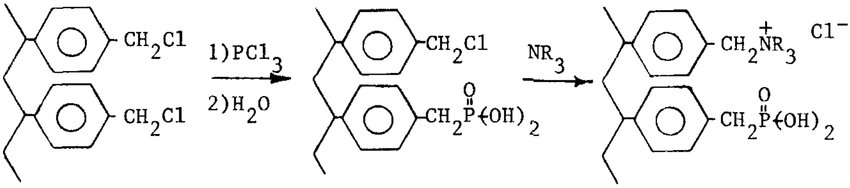
Research has been carried out into combining the specificity of the precipitation reaction with the ease of using monofunctional ion exchange resins by having the ion exchanger release ions into solution which produce a precipitate with ions already present in solution. For example, a cation exchanger in the barium form will remove sulfate ions from saline solutions via barium sulfate precipitation (24). Fixed bed operation, though,



is difficult, if not impossible, due to clogging of the resin's surface with the precipitate. Removal of the precipitate from the beads in order to prevent clogging may be accomplished in a continuous flow system by backwashing the resin with subsequent hydraulic classification of the precipitate from the resin (24). This technique requires that the solution - resin contact time be controlled so that the precipitate particles be of a much smaller size than the resin beads for their efficient removal by the solution upflow current.

The precipitation reaction can lead to the specific recovery of a targeted metal ion by proper choice of the counterion for metal salt formation and by adjusting the aqueous phase conditions (pH, ionic strength, etc.). Ion exchange resins allow for the immobilization of a metal ion within a confined space for its eventual recovery from a much more concentrated solution. The specificity of the former reaction is combined with the recoverability of the latter method within a single polymer backbone in the third class of dual mechanism bifunctional polymers, the ion exchange/ precipitation resins. The concept behind these resins is that reaction between a cation exchange site in the resin and the metal ion or ions in solution occurs first followed then by precipitation of a targeted cation with an anion already in the resin at an anion exchange site. Along the lines of earlier DMBP's, the ion exchange site draws the cation or cations into the resin while an additional reaction, in this case precipitation, introduces a high level of specificity to the recovery. Conditions are to be defined which would allow the precipitation reaction to occur within the resin thus simplifying the metal recovery. Resolubilization of the salt into a much more concentrated solution would be one method of recovery, but it is conceivable that the polymer support can be produced in such a manner that recovery of the salt itself would be possible. For example, a macroporous support allows for recovery of pure metal after reduction occurs within the Class I ion exchange/redox resins. A key advantage to the ion exchange/ precipitation resins would be their high selectivity combined with versatility since the anion leading to the insoluble salt could be varied according to the reactivity of the metal ion. A potential disadvantage to the resins would be clogging of the micropores by the precipitate; this will be monitored via the total per cent metal absorbed per gram of resin under batch, rather than continuous flow, conditions.

The cation exchange ligand for the Class III bifunctional resins is the phosphonic acid group. The ideal anion exchange ligand would be randomly placed among the cation exchange ligands, ionically bind the anion so that it would not be lost in solution yet allow it to react with the metal cation, and allow for anionic variation by column elution; such a ligand was found in the quaternary amine group. Synthesis of the phosphonic acid/quaternary trimethylamine resin is summarized below. Full experimental details will be presented elsewhere (25).



The poly(vinylbenzyl chloride) beads (2% divinylbenzene, -40+60 mesh cut) were contacted with phosphorus trichloride/aluminum trichloride at 40°C for 4h for partial functionalization to the phosphonic acid resin after hydrolysis. Subsequent reaction with a tertiary amine led directly to the phosphonic acid/ quaternary amine resin. With trimethylamine, the final resin has an amine capacity of 2.64 mequiv/g and a phosphorus capacity of 1.85 mequiv/g. Elution with an acid or salt leads to displacement of the chloride anion with any desired anion. The resin anion is one of three critical variables which have been studied. A second variable is the solution anion: if the anion in solution has a greater propensity for the resin than the resin anion, then anion exchange will occur first followed by precipitation with the cation in solution rather than in the resin. The third variable, the amine substituents, can be used to predispose the resin towards the precipitating anion by varying its polarity or organophilicity thus favoring precipitation within the resin rather than in solution. The resin anion and the amine substituents can, therefore, be tailored to the aqueous solution being considered and the metal ion targeted for recovery.

Barium recovery by ion exchange/precipitation

Barium recovery from aqueous solution involves precipitation of the insoluble barium sulfate salt (K_{sp} $1.08x10^{-10}$) (26). The bifunctional phosphonic acid/quaternary amine resin was eluted with 1L 1N sulfuric acid over a 1h period in order to convert the amine sites

TABLE 2

The Extraction (% absorbed) of Group IIA Ions for Bifunctional Amine/acid, Phosphonic Acid, and Amine Resins

	Amine/acid	acid	amine
%Ca abs	27.3	48.1	0
%Ba abs	92.8	45.3	85.4

to the sulfate form. The monofunctional phosphonic acid resin (3.57 mequiv P /g) (6) and quaternary amine resin (4.33 mequiv N /g) (25) were eluted in an identical manner as controls. Enough of each resin to yield 0.5 mequiv was then contacted with 50mL barium nitrate solution containing a total of 0.25 mequiv barium ions and with 50mL calcium nitrate containing 0.25 mequiv calcium ions. The six samples were shaken for 3h. The per cent metal absorbed from each solution is shown in Table 2 and was determined by EDTA titration.

Operating by pure cation exchange, the phosphonic acid resin is unable to distinguish calcium from barium ions, loading both to the same extent. The bifunctional resin, on the other hand, removes more than 90% of the barium from solution and less than 30% of the calcium. That the sole operative mechanism is not cation exchange followed by precipitation is clear from the amine resin results which show anion exchange followed by solution precipitation of barium sulfate. The amine resin is, of course, totally transparent to calcium. Less precipitate is evident with the bifunctional resin than with the amine resin though this could be due to some cation-exchanged barium remaining ionically bound to the phosphonic acid ligand. In any case, the trimethylamine/phosphonic acid resin displays cation exchange and anion exchange reactions followed by precipitation leading to the removal of barium ions from solution. The very high level of barium removal with both the bifunctional and monofunctional amine resin indicates that clogging of the resin by the precipitate is not a problem, at least with crosslinking at 2% divinylbenzene.

The synthesis of a resin with a dominant cation exchange/precipitation mechanism continues to be important so that metal recovery will be independent of the solution anion and so that all of the metal will be localized within the resin beads making quantitative recovery much simpler. An approach for carrying this out entails decreasing the resin anion hydrophilicity while increasing the amine substituent group organophilicity. Both effects decrease participation by the anion exchange mechanism. Progress in the synthesis of a resin with significant bifunctional group cooperativity leading to precipitate formation within the resin beads will be detailed elsewhere (25).

CONCLUSION

The second class of the dual mechanism bifunctional polymer category of specific metal ion complexing agents has been extended with the ion exchange/pseudocrown resins. Group IA and IIA metal ion extraction studies are currently in progress. The third class of the DMBP category, the ion exchange/precipitation resins, will be developed for the recovery of metal ions which would otherwise remain in solution by utilizing the specificity inherent to the precipitation reaction.

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