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Development of polymeric reagents with enhanced ionic accessibility

Stephanie Dawn Smith

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To the Graduate Council:

I am submitting herewith a dissertation written by Stephanie Dawn Smith entitled "Development of polymeric reagents with enhanced ionic accessibility." I have examined the final electronic copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Chemistry.

Spiro Alexandratos, Major Professor

We have read this dissertation and recommend its acceptance:

Mark Dadmun, Ben Xue, Gajanan Bhat

Accepted for the Council:

Carolyn R. Hodges

Vice Provost and Dean of the Graduate School

(Original signatures are on file with official student records.)

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And recommend its acceptance:

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Dr. Gajanan Bhat

Accepted for the council:

Associate Vice Chancellor and
Dean of The Graduate School

DEVELOPMENT OF POLYMERIC REAGENTS WITH ENHANCED IONIC ACCESSIBILITY

A Dissertation
Presented for the
Doctor of Philosophy
Degree
The University of Tennessee, Knoxville

Stephanie Dawn Smith
August 2000

DEDICATION

This dissertation is dedicated to my parents, Lauren and Ricky Smith, my brother Billy Smith and my boyfriend Mike for their unconditional love and support.

ACKNOWLEDGEMENTS

I would like to thank my major advisor Dr. Spiro Alexandratos for his encouragement, guidance, and support throughout this research. I would also like to thank my committee members: Professors Mark Dadmun, Ben Xue, and Gajanan Bhat. The foams used for part of this research were synthesized at Los Alamos National Laboratory. I would also like to express my appreciation and thanks to my co-workers who were like a second family to me, Christy, Cheryl, Subu, Kelly, Chris, Min, Marc, Latiff, Vijay, and Bob. I would also like to acknowledge Alicia, Tracie, Stacey, Erin, Sarah, Philip, Chris, Jeremy, Bryan, Terry, and Chris. Their friendship and support mean more to me than mere words can express. I am also grateful to my family for their encouragement and unconditional support. I would also like to acknowledge Mike for his unconditional love, understanding, and friendship. I would like to thank Dr. Dale Hutchens, Dr. Nancy McDonald, and Janice Kelley for giving me the strength to believe in myself to receive my dissertation. Finally, I would like to thank the University of Tennessee, Department of Chemistry, the Los Alamos National Laboratory, and the Department of Energy, Office of Basic Energy Sciences for financial support.

ABSTRACT

The focus of this research has been the design and development of polymeric reagents with enhanced ionic accessibility for application to separation science. Ion-complexing ligands were then coupled with polymeric foams, polystyrene beads, and high stability solvent impregnated resins (SIRs). The polymers were evaluated for their metal ion affinity.

Four ligands were supported onto the polymeric foams prepared with 8% and 15% crosslinking. The ligands studied were monophosphonic acid, diphosphonic acid, α-ketophosphonic acid, and β-ketophosphonic acid. The functionalized foams were studied for their ability to complex Cu(II), Fe(III), and Eu(III) in batch studies followed by column studies. The highly crosslinked foams were able to be functionalized as one solid piece. The foams demonstrated uniform functionalization throughout the polymer, making them applicable for a wide range of studies. Functionalized foams performed much better than beads in columns with the same type of ligands. This showed the increased porosity does increase the accessibility of the metal ion into the polymer matrix. Further research is needed to better understand reproducibility and regeneration of the functionalized foams.

Increased accessibility of metal ions into polymer beads was evaluated by three methods. The first method was to increase the surface area by studying the complexation of the metal ions at two different bead sizes. This did not increase the accessibility. Complexation of the four metals studied [Cu(II), Pb(II), Cd(II), and Eu(III)], was comparable. The second method was to increase the porosity by comparing microporous

beads to macroporous beads. The change in polymer support also did not increase the percent complexed of the metal ions for the ligands studied. The final method was the idea of dual-mechanism bifunctional polymers. The addition of a recognition ligand to the resins increased the percent complexed dramatically to >90% for all the metals studied.

High stability SIRs were synthesized and studied to evaluate the effect of complexation time and porosity of the polymer support on the percent complexed. SIRs were found to have rapid rates of complexation since decreasing the contact time from 24 hours to 15 min did not affect the percent complexed. Encapsulated SIRs complexed >90% over six contact/regeneration cycle. The SIR maintained a higher percent complexed at 15 min for longer contact periods in comparison to the 24 h study. Decreasing the porosity of the support matrix did not significantly affect the percent complexed for the encapsulated SIR.

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INTRODUCTION

In the past fifty years, the use of synthetic polymers have drastically increased.[1] Polymers are widely used due to the ability to produce polymers with specific chemical and physical properties that make them applicable to everyday life. Polymers can be found in products such as clothing made of polyester or nylon, adhesives such as epoxy glue, and false nails made of acrylic, just to name a few examples. In the chemical world, polymers are designed for specific applications according to the properties of the polymer, such as catalysis[2], chromatography[3], and the field of separation science.[4-6]

The development of efficient, cost-effective techniques for the complexation of metal ions from solutions is important for numerous applications, including environmental remediation and sensor technology. The cost of remediation of over three million hazardous waste sites in the United States is estimated to be 1 trillion dollars.[7] Additionally, the Hanford Reservation (Richland, WA) stores 65 million gallons of radioactive waste from nuclear weapons production in tanks, some of which are leaking.[8] Besides the removal of metals from waste sites, the recovery of precious metals and metal catalysts is important for economic as well as environmental reasons.[9-11] A challenging problem is the low concentration of the target metal (toxic or precious) found in solutions containing large amounts of benign ions such as sodium, potassium and calcium. The separation of metal ions from water is thus complicated by several variables including pH, competing ions, and the presence of organic substances.

The two most common methods for the removal of metal ions from solution are solvent extraction and solid-phase ion exchange. Solvent extraction[12,13] involves contacting an aqueous phase with an organic phase containing a hydrophobic complexant capable of forming chelates or ion exchanging with the metal ion. The organic phase becomes loaded with the metal ions upon mixing. After separating the phases, the organic phase is stripped of the metal ion with an appropriate solution. The metal ion solution recovered can then be purified or disposed. The main advantages of solvent extraction are fast kinetics, high capacities, and selectivity for targeted metal ions from the large number of available complexants.[14] Disadvantages include the finite aqueous solubilities of the extractants, solvents, and modifiers.[12] The loss of organics through evaporation and entrainment increases the cost of the procedure and the water becomes contaminated with toxic organics.[12] This method cannot be used for dilute metal ion solutions because of the large amount of extractants that would be needed.[15]

Ion-exchange resins are capable of complexing or exchanging with metal ions in the aqueous phase. After loading with the metal ions, they may be regenerated by eluting with a solution that removes the ions.[14] The advantage of ion exchange resins in comparison to solvent extraction is that there is no loss of extractant because the ligand is covalently bound to the polymer. This allows for the resin to be regenerated and reused in continuous processes.[16] A disadvantage can be slow complexation kinetics,[9] but this can be overcome in a number of ways. Traditionally, lowering the crosslink level or bead size would be used to increase ionic accessibility as would increasing the matrix porosity. Most recently, our research on bifunctional polymers has shown that introducing a sulfonic acid ligand into a polymer bearing a highly ion-selective ligand allows for complexation at a rapid rate of formation.

This review focuses on current research in the area of polymer-supported ion-selective reagents in order to summarize some of the chemistry that will have an important impact in the near future. This survey of the recent literature extends an earlier publication.[17] It describes a variety of immobilized ligands used in metal ion complexation chemistry, and is arranged according to the ligands most often used today.

Synthesis of Polymer Supports

Most polymer supports for ion-exchange resins are synthesized by suspension polymerization to yield spherical beads.[18] Some common monomers utilized for their ability to be modified with a variety of functional groups are styrene, vinylbenzyl chloride, (meth)acrylate esters, and glycidyl methacrylate.[19] A reactor equipped with an overhead stir paddle contains the organic solution which consists of monomers, crosslinking agents and initiator, and the aqueous solution which consists of stabilizers to prevent bead agglomeration. The aqueous solution suspends the spherical droplets formed from the monomer solution. The polymerization is thermally initiated. After polymerization, the beads are washed to remove the stabilizers and dried.[20] The bead size depends on the solution stir rate and the stabilizer concentration. The amount of crosslinking agent added determines the rigidity of the matrix while the addition of porogens in the organic solution leads to the formation of macropores in the final product[21] with pore sizes ranging from 50 Å (micropores) to more than 500 Å (macropores).

Polymer beads are not the only type of support used for ion-exchange. One type of support is a porous polyurethane foam that due to its enhanced kinetics and accessibility has been utilized in ion-exchange chromotography.[22-25] Another type of foam used for this type of research is poly(vinylbenzyl chloride)-based rigid foams with high porosities.[26] These types of foams were synthesized by water-in-oil emulsion polymerizations.[27] The crosslinking level of the foams, as with the beads, determines the rigidity of the polymer matrix.

Selective Polymer-Supported Reagents

The ability of the sulfonic acid ion-exchange resin to selectively complex metal ions from multi-component solutions is hindered by the small differences in free energy of reaction with many different ions.[28] This allows the resin to become saturated with ions other than the targeted ion. Ion-selective polymers, on the other hand, incorporate ligands capable of chelating or coordinating with a target metal ion. Such ligands include, amines, crown ethers, phenolics, and phosphonates, as detailed below.

Amine Ligands

A resin consisting of bis-picolylamine ligands covalently bound to a crosslinked polystyrene-divinylbenzene macroporous support with Cu(II) coordinated to the pyridyl nitrogens (Figure 1.1) selectively removed trace amounts of chromate in the presence of sulfate, chloride, bicarbonate, and nitrate anions.[29] The resin can be regenerated with brine. Phenylenediamine hydrochloride was covalently bound to macroporous chloromethylated polystyrene-divinylbenzene beads (Figure 1.2). The comparative metal ion affinities of the resin in aqueous acidic solutions show its selectivity for $AuCl_4^-$ over

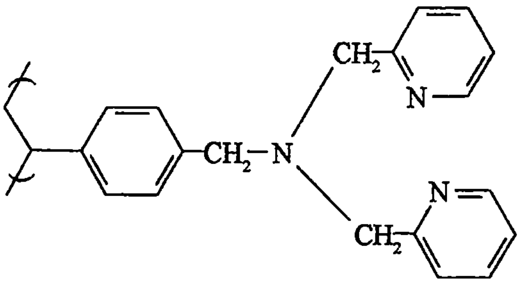


Figure 1.1. Polymer-supported bis-picolyamine

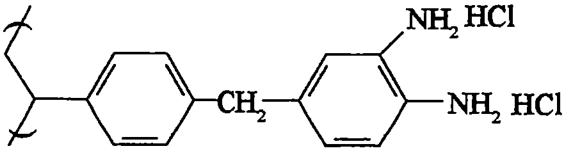


Figure 1.2. Polymer-supported phenylenediamine hydrochloride

other metals studied.[30] The affinity order for the remaining anionic metal chloride complexes is: Ru(III)>Pd(II)>Fe(III)>Rh(III)>Pt(II)>Cr(II)>Cu(II)>Ni(II)>Mn(II).

Bis(imidazol-2-yl)methylaminomethane was bound to crosslinked poly(glycidylmethacrylate) (Figure 1.3). In the presence of competing ligands (1,2-diaminoethane, 1,3-diaminopropane and 1,4-diaminobutane), the resin maintained a high uptake of copper ions.[31] The resin was selective for the chloride salts of Cu(II) over Ni(II), Co(II), Zn(II), and Cd(II) in the pH range of 1.1 - 6.0.[31] Poly(glycidyl methacrylate) modified with 3,3-dimethylpyrazole (Figure 1.4) was selective for Cu(II) at pH > 3.5 in the presence of competing divalent transition metal ions.[32] The same polymer support was also modified with three bis(imidazole) ligands: bis(1,1-imidazol-2-yl)(4-imidazol-4(5)-yl)-2-aza-butane, bis(1,1-imidazol-2-yl)(4-pyridine-2-yl)-2-aza-butane, and bis(1,1-imidazol-2-yl)(7-[3,5-dimethylpyrazol-1-yl])-2-aza-5-thia-heptane (Figure 1.5). The metal ion solutions consisted of Cu(II), Ni(II), Co(II), Cd(II), Zn(II), and Ca(II) as chlorides in buffered solutions within the pH range of 1.0 to 6.0.[33] The resins were selective for Cu(II) in competitive studies. The uptake for other metals was relatively low.

Poly(glycidyl methacrylate-co-trimethylolpropane trimethylacrylate) and the thiirane analogue of poly(glycidyl methacrylate-co-ethylene glycol dimethacrylate) were used as the polymer supports for 1,3-bis(benzimidazol-2-yl)propylamine (Figure 1.6).[34] Cu(II) was selectively removed from solutions with pH 0.9 to 6.0 by both resins under competitive conditions with Cd(II), Co(II), Ni(II) and Zn(II). At a pH > 4.5, the poly(glycidyl methacrylate) resin was also able to complex Zn(II). The thiirane resin was able to remove Cd(II) and Zn(II) under the same conditions. Poly(glycidyl methacrylate)

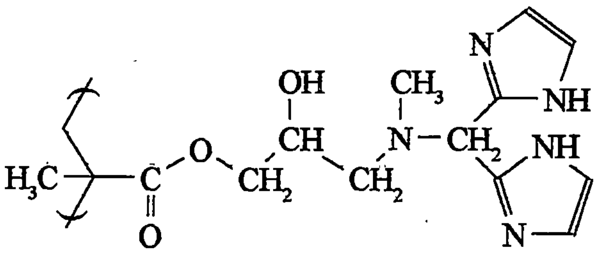


Figure 1.3. Polymer-supported bis(imidazol-2-yl)methylaminomethane

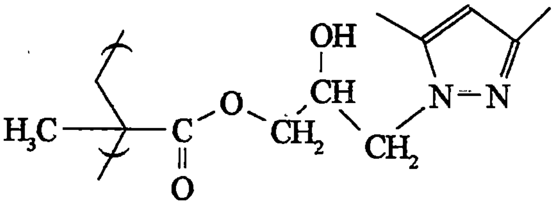


Figure 1.4. Polymer-supported 3,5-dimethylpyrazole

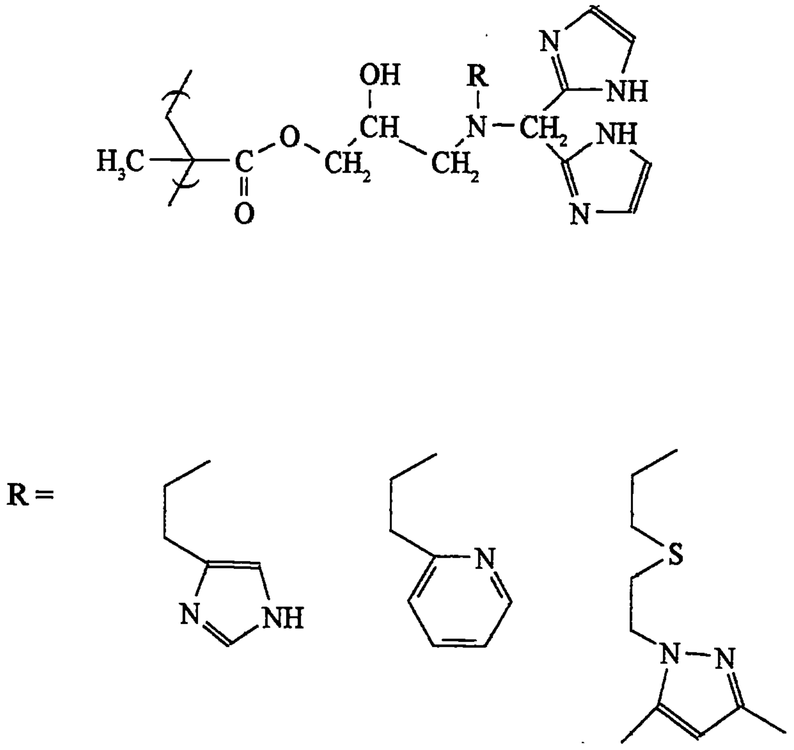


Figure 1.5. Polymer-supported bis(imidazole) ligands

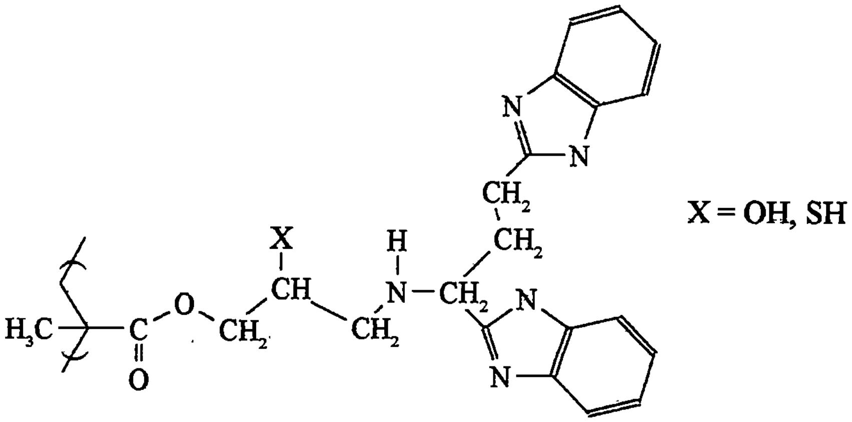


Figure 1.6. Polymer-supported bis(benzimidazole)

and its thiirane analogue were also modified with azole ligands (Figure 1.7). The ligands immobilized onto poly(glycidyl methacrylate) were pyrazole, imidazole, and 1,2,4-triazole.[35] The three resins selectively removed Cu(II) from a solution containing Cu(II), Ni(II), Co(II), Zn(II) and Cd(II) in a solution of pH > 2.5. The sulfur analogue was modified with the ligands pyrazole, imidazole, 1,2,4-triazole and tetrazole. Three of the modified resins (imidazole, triazole, and 1,2,4-tetrazole) were selective for Cu(II) in the presence of Ni(II), Co(II), Zn(II), and Cd(II) at pH > 2.5. The pyrazole resin was selective for Cu(II), Cd(II) and Zn(II) from solutions at pH > 5.

A reaction between poly(vinylbenzyl chloride) and 1-(2-aminoethyl)-piperazine yielded a resin (Figure 1.8), which was studied for its ability to complex precious metals.[36] The piperazine resin sorbed Au(III), Pt(IV), Ir(IV) and Os(IV) from 0.1 M HCl, and, from 0.5 M HCl, it sorbed Pd(III) and Ru(III). It also selectively complexed Au(III) and Pd(II) from a 0.1 M HCl solution containing Au(III), Pd(II), Cu(II), Ni(II), and Fe(III). A resin containing 1-(β-acrylamidoethyl)-3-hydroxy-2- methyl-4(1H)-pyridinone and N,N-dimethyl- acrylamide (Figure 1.9) was able to chelate Fe(III) from poisoned blood plasma.[37]

Azo and Amidoxime Ligands

Imidazolyl azo ligands were bonded to macroporous polystyrene beads (Figure 1.10) with the purpose of studying the ability of the resin to chelate Hg(II), Ag(I) and Pb(II) from solutions at varying pH.[38] The resin selectively removed Hg(II) and Ag(I) in the presence of an excess of Cu(II), Co(II), Ni(II), Fe(II), Mn(II), Ca(II), Ba(II), Mg(II) and Na(I). Polystyrene beads were also modified with the benzimidazolylazo ligand (Figure 1.11).[39] The resin selectively complexed Pd(II), Hg(II) and Ag(I) in the presence

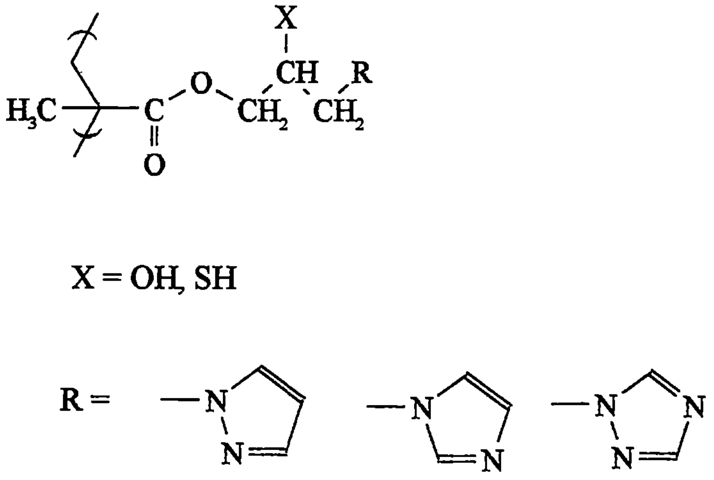


Figure 1.7. Polymer-supported azole ligands

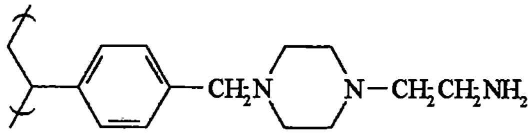


Figure 1.8. Polystyrene supported 1-(2-aminoethyl)piperazine

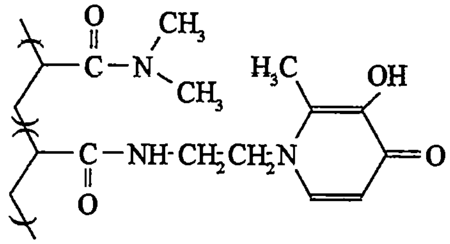


Figure 1.9. Copolymer of 1-(β-acrylamidoethyl)-3-hydroxy-2-methyl-4(1H)-pyridinone and N,N-dimethylacrylamide

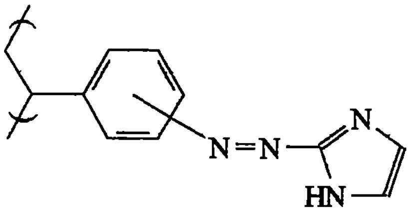


Figure 1.10. Polystyrene supported imidazolyl azo group

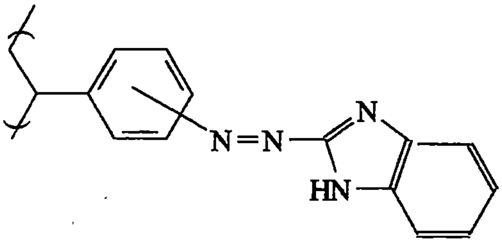


Figure 1.11. Polystyrene supported benzimidazole

of Cu(II), Co(II), Ni(II), Fe(III), Mn(II), Ca(II), Ba(II), Mg(II) and Na(I). The resin also selectively complexed Pd(II) in the presence of other platinum group metals. In studies using geological samples and metallic platinum, the resin selectively removed Ag(I) and Pd(II). Water samples spiked with mercury demonstrated that the resin could be effective in the removal of mercury from polluted water samples

Dithizone Ligands

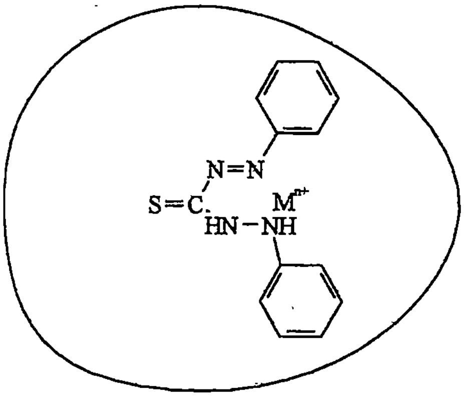
Polystyrene, poly(methyl methacrylate), poly(vinyl chloride) and polycarbonate were templated for Cu(II), Ni(II), Zn(II) and Co(II) by physically trapping (not chemically bonding) ion-complexed dithizone into the polymer supports (Figure 1. 12).[40] After removing the ions, the templated polymer demonstrated selectivity for the metal ion that was originally complexed to the ligand. Polystyrene was the most efficient polymer support.

Crown Ether Ligands

Copolymers of 6-(4'-vinylbenzyloxy)-1,4,8,11-tetrathia- cyclotetradecane with styrene or N-vinylpyrrolidone (Figure 1.13) were studied to determine whether they were selective for Hg(II) and Ag(I).[41] The styrene copolymer was selective for Ag(I) and Hg(II) over Cd(II), Cu(II) and Ni(II) in a 50/50 dichloromethane/water solution. The copolymer with N-vinyl-pyrrolidone was selective for Ag(I) over Cu(II) in aqueous solution.

Carboxylic Acid and Hydroxamic Acid Ligands

Polyacrylohydroxamic acids substituted with N-aryl groups were synthesized from polyacryloyl chloride and N-aryl hydroxylamines.[42] All resins made from this method demonstrated a high affinity for Cu(II), Pb(II) and Ni(II) from solutions with pH



$M^{n+} = Cu^{2+}; Ni^{2+}, Co^{2+}, Zn^{2+}$

Figure 1.12. Polymer template formed with dithizone

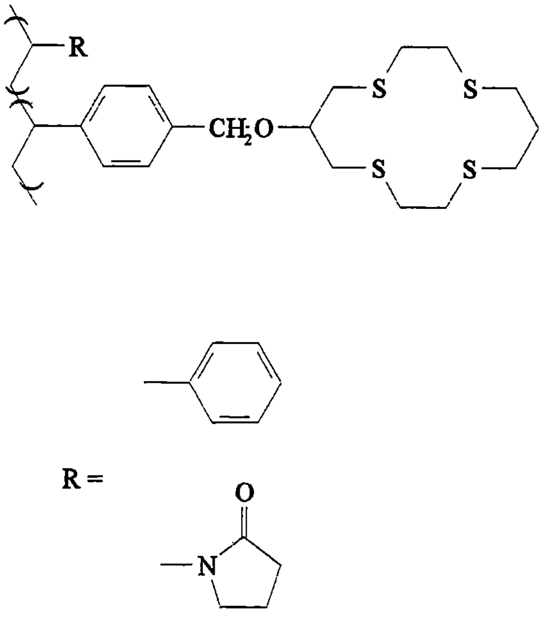


Figure 1.13. Thiacrown ether copolymers

2.5-5.0. When placed in a column, the metals can be separated from one another selectively by different eluents through the resin. Eluting with 0.5 M H_2SO_4 can separate Cu(II), Pb(II) can be eluted with 0.5 M HNO_3 and Ni(II) can be eluted with 1 M tartrate. Poly(methylacrylohydroxamic acid)s were synthesized by reacting poly(methacryloyl chloride) with several N-arylhydroxylamines and their affinity quantified for several divalent ions (Figure 1.14).[43] The order of affinity for the polymers at an optimal pH (between 3.5 and 5 for the various metal ions) was Cu(II)>Zn(II)>Ni(II)>Co(II)>Pb(II)~Fe(II). This work was continued with polystyrene-based resins prepared with various hydroxylamines including: N-phenyl, N-p-tolyl, N-p-chloro, and N-m-chlorophenyl (Figure 1.15).[44] The order of capacities for the substituted hydroxamic acids was: N-methyl>m-chlorophenyl>p-chlorophenyl>phenyl>p-tolyl. The unsubstituted poly(styrene-p-hydroxamic acid) had the highest capacity and was chosen for competitive column studies. From solutions at pH 6, the resin separated Ce(IV) from La(III) and Ce(IV) from Nd(III) and Y(III). At pH 2, La(III) was separated from Fe(III), Al(III), Cu(II) and Pb(II). At pH 4, La(III) was separated from a solution of Be(II), Mg(II) and Ca(II). A copolymer of 1-hydroxy-2-naphthaldoxime and formaldehyde was used to prepare a heterogeneous membrane with polyvinyl chloride (Figure 1.16).[45] The membrane selectively complexed Ni(II) in the presence of Zn(II), Cd(II), Co(II) and Pb(II) over a wide range of concentrations. A resin synthesized from the copolymerization of N-acryloyl diethyliminodiacetate with acrylic acid (Figure 1.17) complexed over 97% of the Eu(III) from a solution at pH 4.[46] A chelating poly(hydroxamic acid) resin was synthesized from crosslinked poly(methyl methacrylate) beads.[47] The resin had a high affinity for Cu(II), Pb(II) and Fe(II) at pH 5.

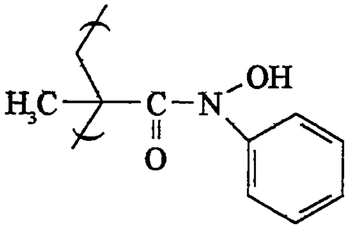
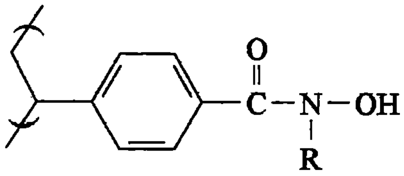


Figure 1.14. Poly(methacrylohydroxamic acid)



R = H, C_6H_5, CH_3, p-Cl-C_6H_4, m-Cl-C_6H_4, p-CH_3-C_6H_4

Figure 1.15. Poly(styrene-p-hydroxamic acids)

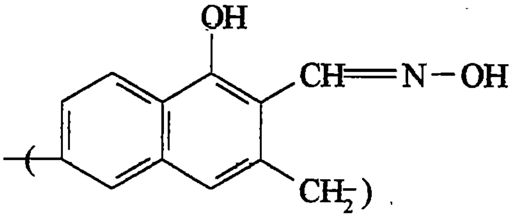


Figure 1.16. (1-Hydroxy-2-naphthalodoxime-formaldehyde polymer)

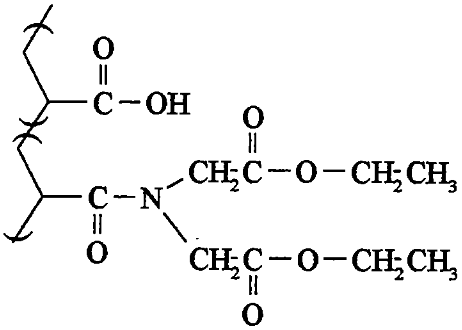


Figure 1.17. N-acryloyl diethyliminodiacetate copolymers

Co(II), Cu(II) and Fe(III) were selectively eluted from the resin by acetate buffer (pH 4), 0.1 M HCl and 0.1 M oxalic acid/1 M HCl, respectively. By eluting with acetate buffer at pH 3.5 and 4 M HNO_3, Pb(II) and Ni(II) were selectively eluted.

Oxy-Imines and Amide Ligands

A phenol-formaldehyde polymer, poly(salicylaldoxime-3,5-diylmeth-ylene), was prepared and studied for its chelating ability with various divalent ions (Figure 1.18).[48] The resin demonstrated a high affinity for Cu(II) and the order of selectivity for the remaining divalent ions from solutions at pH > 7 was Cd(II)>Zn(II)>Ni(II)>Ca(II)>Mg(II). The resin reached equilibrium rapidly with over 90% Cu(II) complexed at 1 hour.

A copolymer of acrylonitrile/vinyl acetate/divinylbenzene was modified with aminoguanidine bicarbonate (Figure 1.19).[49] The resin demonstrated good affinity for Cu(II) at pH 5. When the resin was modified with aminoguanidine bicarbonate in a solution of butanol/water, it demonstrated an affinity for gold cyanide.

Schiff Base Ligands

Reactions between salicylaldehyde and either o-phenylenediamine or ethylenediamine followed by condensation with formaldehyde resulted in Schiff base resins (Figure 1.20).[50] The resins were studied for their ability to complex Cu(II) and Ni(II) and found to have a maximum capacity for Cu(II) and Ni(II) at pH 6. The o-phenylenediamine-salicylaldehyde resin had the greater capacity of the two resins studied.

A condensation reaction between ethylenediamine, salicylaldehyde and 3-formylsalicylic acid gave a Schiff base that was then supported onto chloromethylated

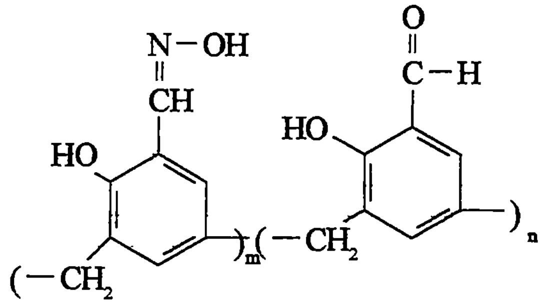


Figure 1.18. Poly(salicylaldoxime-3,5-diylmethylene)

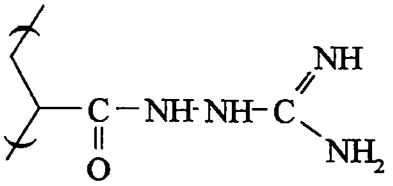


Figure 1.19. Polymer-supported aminoguanidine ligands

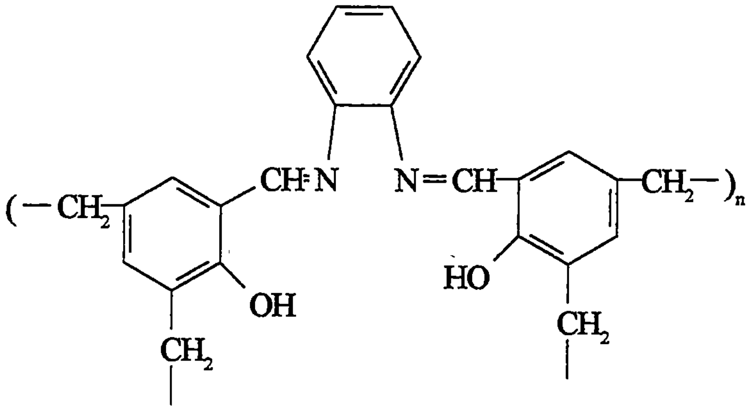


Figure 1.20. Polymeric o-phenylenediamine-salicylaldehyde-formaldehyde

polystyrene (Figure 1.21).[51] The resin formed complexes with Cu(II), Ni(II), Co(II), Fe(III), Zn(II), Cd(II), Mo(VI) and U(VI).

Phenol-Based Ligands

Poly[3,5-(1-propio-2,4-dihydroxyphenylene)butylene] was formed by the Friedel-Crafts polycondensation of 2,4-dihydroxypropiophenone with 1,4- butanediol (Figure 1.22).[52] The resin had a higher affinity for UO_2^{2+} compared to Fe(III), Cu(II) and Ni(II) with the order of selectivity being UO_2^{2+}>Fe(III) >Cu(II)>Ni(II). A copolymer from the polycondensation reaction of 2-hydroxy-4-ethoxypropiophenone with ethylene glycol (Figure 1.23) was studied for its exchange properties with divalent ions.[53] In the pH range of 2.5 to 5.0, the order of selectivity was UO_2^{2+}>Cu(II)>Ni(II). A higher affinity for the uranyl ion vs. Fe(III) was found in solutions of pH 1.0-2.5.

The acid catalyzed condensation of phenol with formaldehyde produced an ion-exchange resin that had higher affinities for Cs(I) and Rb(I) relative to the other alkali metals.[54] The resin had a higher selectivity for these ions compared to sulfonated phenol-formaldehyde resins. A quinol-crotonaldehyde resin (Figure 1.24) was selective for metal ions in the order Co(II)>Cd(II)>Cu(II)>Fe(II)>Mg(II) from a solution containing 1 M $NaNO_3$ at pH 10.[55]

Multi-Ligand Resins

A polymer with carboxyl, amino, phosphonic and hydrazide ligands was synthesized to study its chelating ability for various metal ions (Figure 1.25).[56] The selectivity order was Ag(I)>Pb(II)>Cu(II)>Ni(II)>Zn(II)>Cd(II)>Co(II) ~Hg(II)>Mn(II)>Cr(III). Even though it has a preference for certain metals, it still has high affinities for all metal ions studied. The polymer's ability to complex Cu(II) is

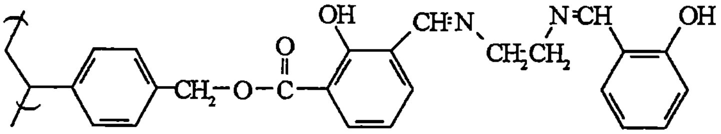


Figure 1.21. Polystyrene supported N,N'-ethylenemono(3-carbosalicylideneimine) mono(salicylideneimine)

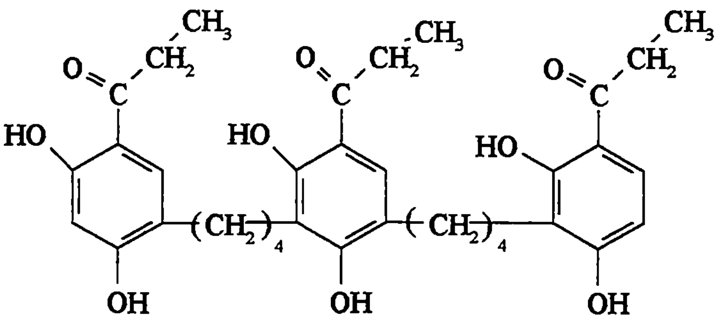


Figure 1.22. Poly[3,5-(1-propio-2,4-dihydroxy phenylene)butylene]

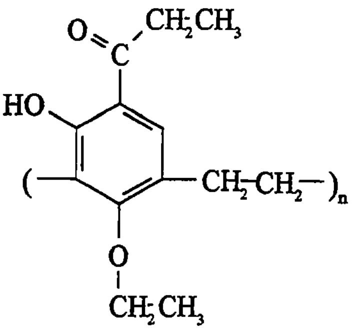


Figure 1.23. 2-Hydroxy-4-ethoxypropiophenone-ethylene glycol polymer

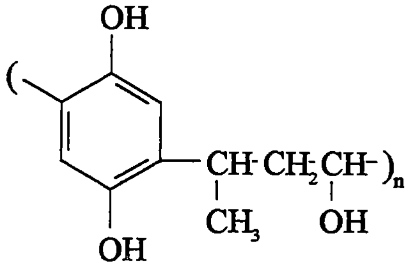


Figure 1.24. Quinol-crotonaldehyde resin

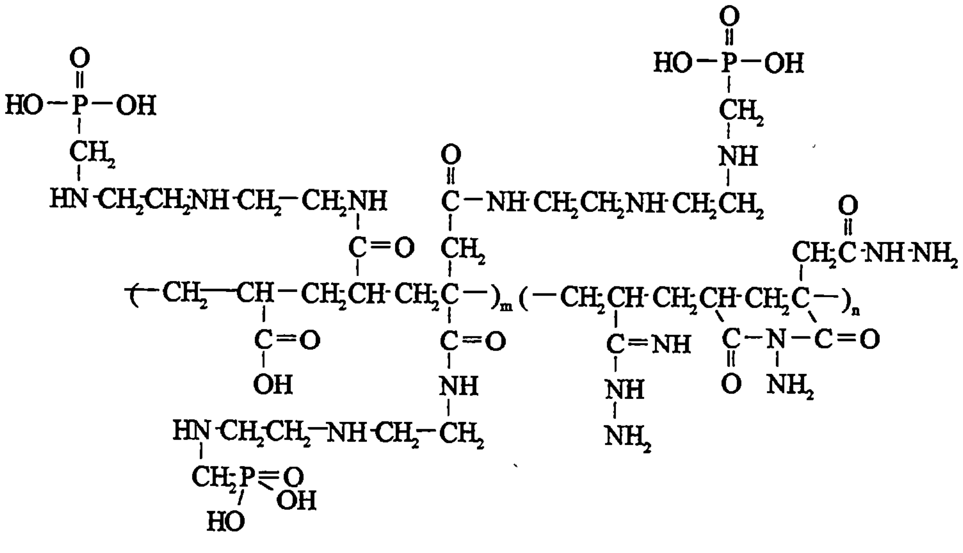


Figure 1.25. Poly(acrylaminophosphonic-carboxyl-hydrazide) fiber

affected by pH below 3 whereas the ability to complex Hg(II) is unaffected by pH over the range 1.5-7.5.

Aminothiophosphonate was supported onto copolymers of vinylbenzyl chloride divinylbenzene and acrylonitrile / ethyl acrylate / divinylbenzene (Figure 1.26).[57] The ligand demonstrated a selectivity for Cd(II) over Ni(II) from 0.2 M acetate buffer solution in the pH range 3.7-5.6.

Phosphorus Ligands

The aminomethylphosphonate ligand was immobilized onto crosslinked poly(methyl methacrylate) (Figure 1.27) and, after binding Al(III), complexed fluoride ions from tap water in the presence of chloride and sulfate ions.[58] Resins modified with α-aminoarylphosphonates (Figure 1.28) were analyzed for their chelating ability with Co(II) and Ca(II).[59] The resin modified with α-aminopyridylphosphonic acid had a high affinity for Co(II).

A phosphonic acid resin (Figure 1.29) complexed Mo(VI) from solutions within a pH range of 1-3.[60] The phosphoric acid group was bonded to the epoxy groups of poly(glycidyl methacrylate-co-divinylbenzene) (Figure 1.30) and resulted in a resin with a high affinity for Pb(II).[61] The resin was also selective for Fe(III), Ti(IV) and Mo(IV) from nitric acid media.

Resins with immobilized ketophosphonic acid ligands were prepared in order to determine whether the carbonyl and phosphoryl moieties can cooperate when binding metal ions and thus enhance the observed affinities; results were compared to the monofunctional phosphonic acid resin (Figure 1.31).[62] Experiments with Cu(II), Pb(II), and Eu(III) showed that the order of metal ion affinities for the four resins was

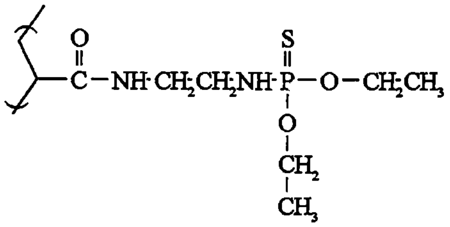


Figure 1.26. Polymer-supported aminothiophosphonate ligands

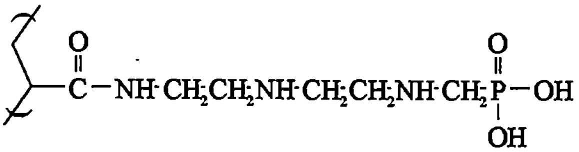


Figure 1.27. Aminomethyl phosphonic acid resin

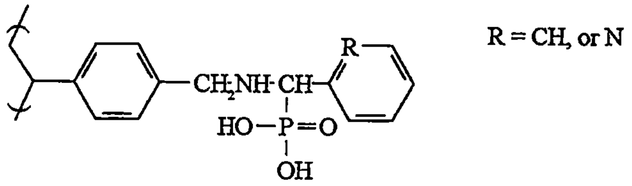


Figure 1.28. Polystyrene supported α-aminoalkylphosphonic acids

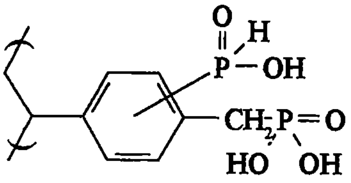


Figure 1.29. Polystyrene supported phosphonic acid

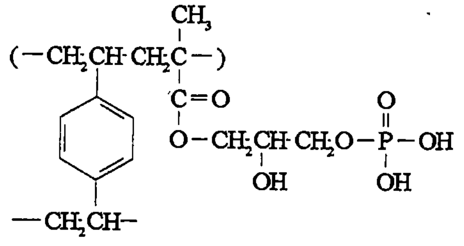


Figure 1.30. Phosphoric acid resin

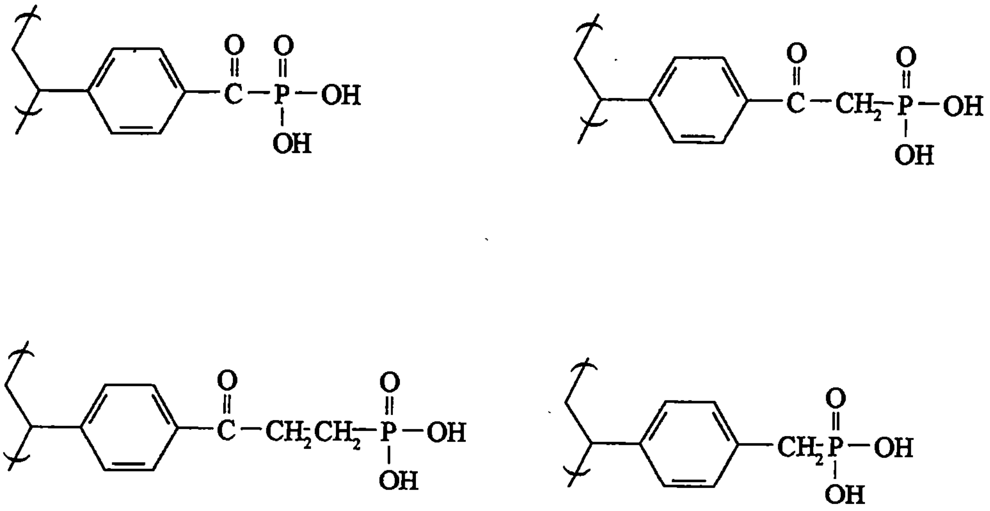


Figure 1.31. Immobilized ketophosphonic acid ligands:

α-ketophosphonic acid, β-ketophosphonic acid,

γ-ketophosphonic acid, monophosphonic acid α-ketophosphonate > β-ketophosphonate > γ-ketophosphonate > monophosphonate. This allows for the conclusion that intra-ligand cooperation occurs between the carbonyl and phosphoryl moieties when separated by no more than one methylene group.

The synthesis of bifunctional polymers demonstrated that it was possible to couple ion-selective ligands with rapid rates of complexation in a polymer support. In one example, a polymer with phosphinic acid ligands was modified by introducing sulfonic acid ligands (Figure 1.32).[63] The bifunctional polymer demonstrated a significant increase in complexation of Eu(III) from 1 M HNO_3: the monofunctional phosphinate polymer complexed only 53% Eu(III) whereas the bifunctional polymer complexed >99%. This study was extended by comparing the Eu(III) affinities of monofunctional phosphonic acid resins with bifunctional phosphonic / sulfonic acid resins crosslinked at various levels (Figure 1.33) from solutions of 0.10 M and 1.0 M HNO_3.[64] Complexation by the monofunctional polymer decreased from 91% to 3% as the crosslink level increased from 5% to 20% DVB at a contact time of 0.5 h whereas the bifunctional polymer complexed >99% Eu(III) regardless of the crosslink level at the same contact time.

Sulfonated phosphonic acid, phosphonoacetic acid (Figure 1.34) and β-ketophosphonic acid resins (Figure 1.35) were studied for their complexing ability with Cu(II), Pb(II), and Cd(II) in 0.10 M HNO_3 and Eu(III) in 1.0 M HNO_3.[65] The monofunctional polymers complexed from 22% to 91% of the metal ion depending on the ion and the ligand involved whereas the bifunctional polymer complexed >90% of all metals for all ligands studied. Bifunctionality, wherein an access

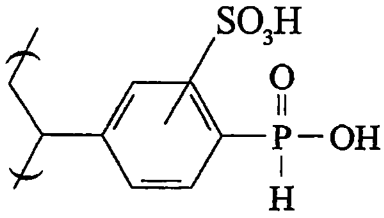


Figure 1.32. Polystyrene supported sulfonated phosphinic acid

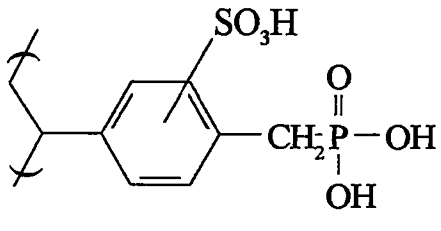


Figure 1.33. Polystyrene supported sulfonated phosphonic acid

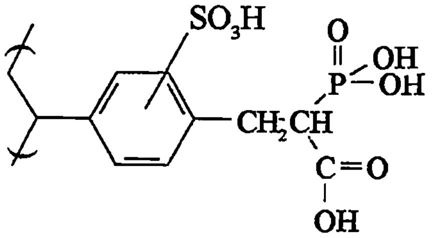


Figure 1.34. Polystyrene supported sulfonated phosphonoacetic acid

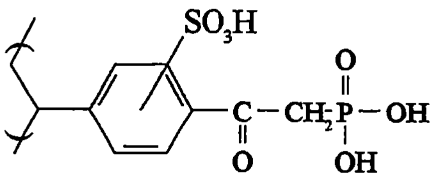


Figure 1.35. Polystyrene supported sulfonated β-ketophosphonic acid

ligand is coupled with a recognition ligand, is thus an important means of increasing the complexation kinetics of ion-selective resins and this has led to the commercial introduction of a new ion exchange resin, Diphonix^{TM}, based on coupling the ion-selective diphosphonate ligand with the hydrophilic sulfonic acid ligand.[66]

The use of functionilized foams is an important area of ion-exchange research in terms of increased accessibility into the polymer matrix. Vinylbenzyl chloride foams with crosslinking levels of 2.5% and 20% divinylbenzene were used for modification with trialkylphosphite and tetraalkylmethylene diphosphonate.[67] The foams were then further modified into the acid forms (Figure 1.36) of the ligands. The foams were then used in comparison studies with gel and MR beads with the same type of ligands and crosslinking levels.[67] At low acidity, the foams performed the same as the beads with the metals Eu(III), Fe(III), Cu(II) and Pb(II) but as the acidity of the solutions increased the foams in general had a higher uptake of the various metals than of the beads demonstrating a greater accessibility than present in the beads.[67]

The concept of solvent impregnated resins (SIRs) combines ideas of liquid-liquid separation and solid-liquid separations.[68] This is accomplished by sorbing a soluble extractant into a polymer support. The most common type of support used is highly crosslinked macroporous (MR) copolymer beads.[68] One problem with SIRs is the loss of extractant during complexation and regeneration.[69] To prevent this, the SIR was prepared with a semipermeable coating around the beads. A method was developed in which a copolymer consisting of poly(vinylbenzyl chloride-co-methyl methacrylate) was synthesized at 25% DVB crosslinked MR. The beads then underwent an Arbusov

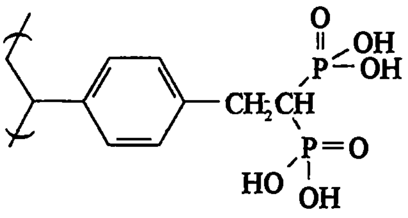


Figure 1.36. Polymer supported diphosphonic acid

Reaction on their surface and a subsequent Wadsworth-Emmons reaction to form double bonds on the surface which then served as anchors for the coating.[68] The beads were impregnated with 2M bis(2-ethylhexyl) hydrogen phosphate (DEHPA) (Figure 1.37) in toluene. The toluene was removed and the resin was tested to see if the extractant had become trapped in the pores of the beads. A portion of the beads then were coated with a 2% solution of glycidyl methacrylate and N,N'-methylenebisacrylamide in a 75/25 ratio. The coated beads were analyzed for nitrogen to ensure the coating had been placed onto the beads. Both the uncoated and coated resins were contacted with Cu(II) in pH 8.4 NH_3/NH_4NO_3 buffer solution over five complexation/regeneration cycles. Both resins complexed greater than 90% on the first contact, but the uncoated beads subsequently complexed significantly less whereas the coated resin remained constant throughout the five contacts at 96% Cu(II) complexed. The encapsulation of the SIR improved the ability of the SIR to be used continuously in contact and regeneration.[68]

This dissertation describes the synthesis and complexing ability of various ion-exchange resins. The resins were studied for the ability to increase accessibility into the polymer matrix by various methods. Polymeric foams were modified with various ligands to analyze the functionalized polymers ability to remove metal ions in a column compared to functionalized beads. Monofunctional and bifunctional polymers of various size and ligand type were synthesized to study the effect of surface area, bifunctionality, and type of ligand on accessibility into the polymer matrix. SIRs were encapsulated and studied for their complexing ability at various contact times and with various porosities of the polymer support.

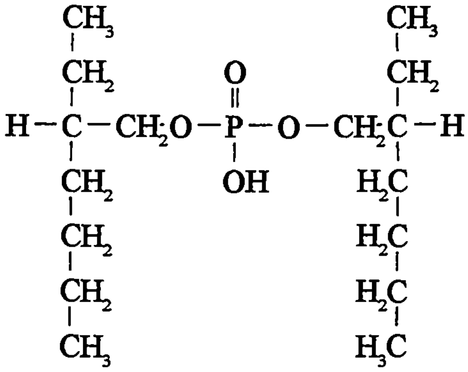


Figure 1.37. Bis(2-ethylhexyl)hydrogen phosphate

CHAPTER 2

POLYMERIC FOAMS MODIFIED FOR ION-EXCHANGE

Introduction

A new area of research for ion-exchange polymers is to vary the type of support. A common type of support used is the macroreticular (MR) beads which has a porosity of equal to or less than 50 %. The MR beads are made up of agglomerates of microspheres separated by pores.[70] The porosity of MR beads also includes the micropores present due to the unoccupied spaces between the polymer chains. This increased porosity in comparison to gel beads leads to greater accessibility into the polymer matrix, which in turn increases the kinetics of the resins.[71]

The synthesis of highly porous polymeric foams have also been reported.[72] Foams made from polyurethane has been used for ion-exchange of a variety of metal ions. The foams have been solvent impregnated with various extractants,[73,74] liquid ion exchangers,[75] and chelating agents.[76-78] The foams have also been functionalized in order to be used for ion-exchange.[79]

This research focuses on the use of a foam support with a porosity greater than 90%. The increased porosity of the foams theoretically should allow for greater accessibility of the metal ions. The disadvantage to this high porosity is the decrease in mechanical strength. In order to overcome the decrease in mechanical strength, the amount of crosslinking has to be increased. The increase in crosslinking should not greatly affect the resins ability to complex the metal ions. This would not be the case if the support was polymer beads.

Synthesis of Ion Exchange Polymers Supports

Los Alamos supplied the foams for the project. They were synthesized by water – in-oil emulsions.[27] The cylindrical foams used in the project were polystyrene crosslinked with 8% divinylbenzene (DVB), and of VBC/styrene copolymers at a 75:25 mole ratio crosslinked with either 8% or 15% DVB. The foams functionalized for metal ion studies. Before functionalization the foams were soxhlet extracted with methanol for 17 hours to remove any remaining surfactant from the polymerization process, then dried at 60°C for 17 hours. The four types of functionalized foams synthesized were monophosphonic acid, diphosphonic acid, α-ketophosphonic acid and β-ketophosphonic acid.

For comparison with the foams, 12% DVB crosslinked gel beads were made. The beads were then functionalized with monophosphonic acid, diphosphonic acid, and α-ketophosphonic acid ligands.

Synthesis of Monophosphonic Acid Foam

For every 1 gram of foam used, 100ml of triisopropyl phosphite was added to the reactor. A vacuum was applied for 10 minutes to remove all the air from the foam. The reaction was refluxed for 17 hours. The foam was then washed twice with acetone and twice with 0.1 N HCl for 15 minutes each. After washing, an excess of concentrated HCl was added and refluxed for 24 hours (Figure 2.1). The 8% and15% DVB 75/25 VBC/styrene foams were both functionalized.

Synthesis of Diphosphonic Acid Resin

To a 500 mL round bottom flask, 68.66 g of tetraisopropyl methylene diphosphonate(MDA) and 300 ml of dry toluene was added. Sodium metal (5.62 g) was

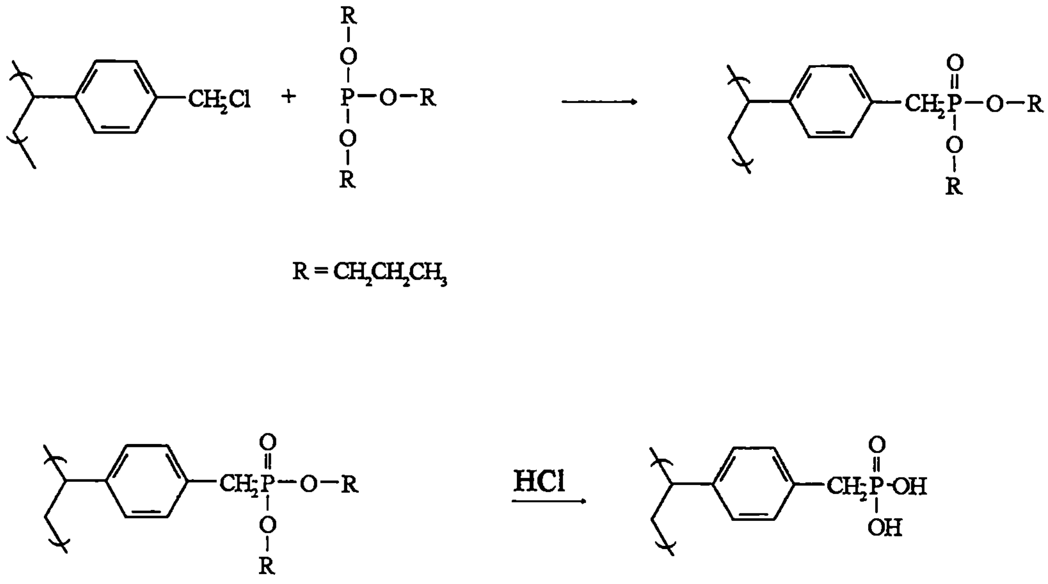


Figure 2.1. Synthesis of monophosphonic acid foam

added to the solution under a nitrogen sweep while stirring. This was left to stir overnight under nitrogen. The foam (3.2863 g) was placed in a reactor under a nitrogensweep and the deprotonated MDA solution was transferred on to it through a double tipped needle. The reaction was refluxed for 24 hours under nitrogen. The foam was then washed twice with ethanol and twice with distilled water for 15 minutes each. Hydrolysis was completed by adding an excess of HCl to the foam and refluxing for 24 hours (Figure 2.2). The 8% and15% DVB 75/25 VBC/styrene foams were both functionalized.

Synthesis of α-Ketophosphonic Acid Foam

To 5.1353g of the foam, 350 ml of dimethyl sulfoxide was added in a reactor. The reaction was refluxed for 8 hours after adding 34.57g of sodium bicarbonate. The washing cycle after the reaction was three times with ethanol and twice with hot distilled water for 15 minutes each. The foam was then contacted with 200 ml of dioxane for thirty minutes, followed by addition of 150 ml of 3N nitric acid and refluxing for 17 hours. The functionalized foam was washed twice with dioxane, then 100 ml of dioxane and 260 ml of 30% hydrogen peroxide was added and refluxed for 17 hours. The functionalized foam was washed four times with acetone and soxhlet extracted with dioxane for 17 hours to remove all the water. After soxhlet extraction, the foam was placed in the vacuum oven for 4 hours at 40°. The foam was placed back into a dry reactor and 300 ml of thionyl chloride was added under a nitrogen sweep. This was refluxed for 17 hours. The foam was then washed four times with toluene for 15 minutes each. Triethyl phosphite (300 mL) was added and refluxed for 17 hours, followed by washing twice with acetone and twice with dilute HCl (4 wt%) for 15 minutes each. The

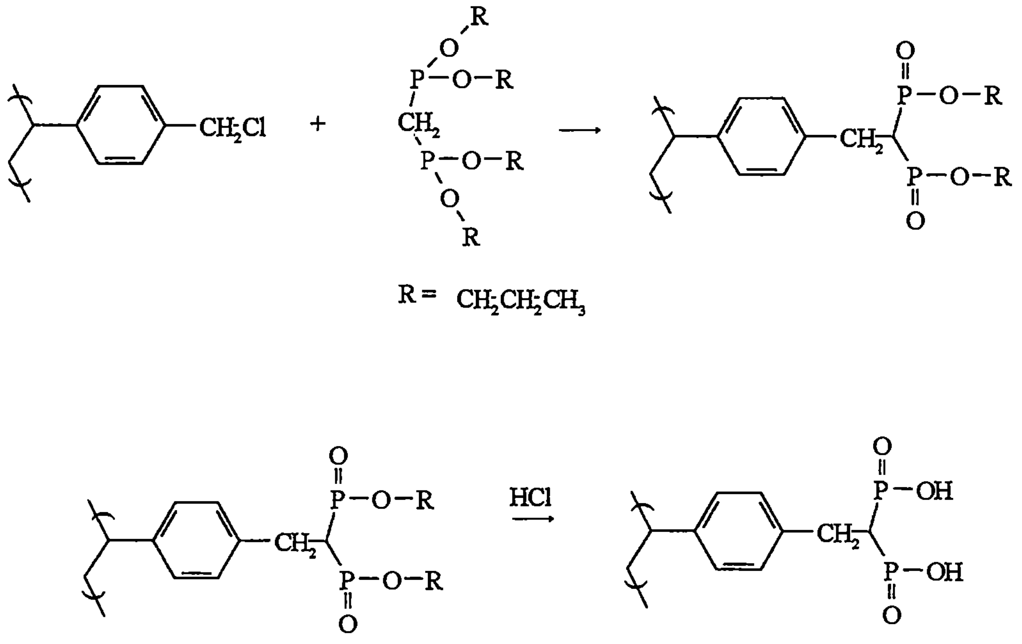


Figure 2.2. Synthesis of diphosphonic acid foam

hydrolysis of the foam was done by adding an excess of HCl and refluxing for 24 hours (Figure 2.3). The 8% and15% DVB 75/25 VBC/styrene foams were both functionalized

Synthesis of β-Ketophosphonic Acid Foam

Into a reactor was placed 2.9021 g of the 8% DVB polystyrene foam and swelled for 1 hour in 250 ml of carbon disulfide. The reactor was placed in an ice bath and 10.91g(81.75mmol) of $AlCl_3$, 4 ml(38.46mmol) of bromoacetyl bromide and 50 ml of carbon disulfide was added, then stirred for 48 hours. The ice bath was removed after the first hour to let the reaction stir at room temperature. The reaction was quenched by adding a mixture of ethanol and ice (40/60) twice to the foam followed by washing with 250 mL of water, 10% acetic acid, and ethanol. The foam was then placed in the vacuum oven overnight at 70°C. After removing the foam from the oven, it was placed back in the reactor with 300 ml of triethyl phosphite and refluxed for 24 hours. The washing afterwards included twice with acetone (250 mL) and twice with dilute HCl (250 mL of 4 wt. %) for 15 minutes each. Hydrolysis was completed by adding an excess of HCl and refluxed for 24 hours (figure 2.4).

Sulfonation of α-Ketophosphonic Acid Foam

The foam functionalized with the α-ketophosphonic acid ligands was washed 4 times with acetone before soxhlet extraction with dioxane for 17 hours. After soxhlet extraction, the foam was placed in the vacuum oven for 4 hours at 40°C. A weighed amount of foam (1.4630 g) was placed in a reactor with 200 ml of ethylene dichloride to swell for 1 hour. In an addition funnel, 16.5ml of chlorosulfonic acid and 66 ml of

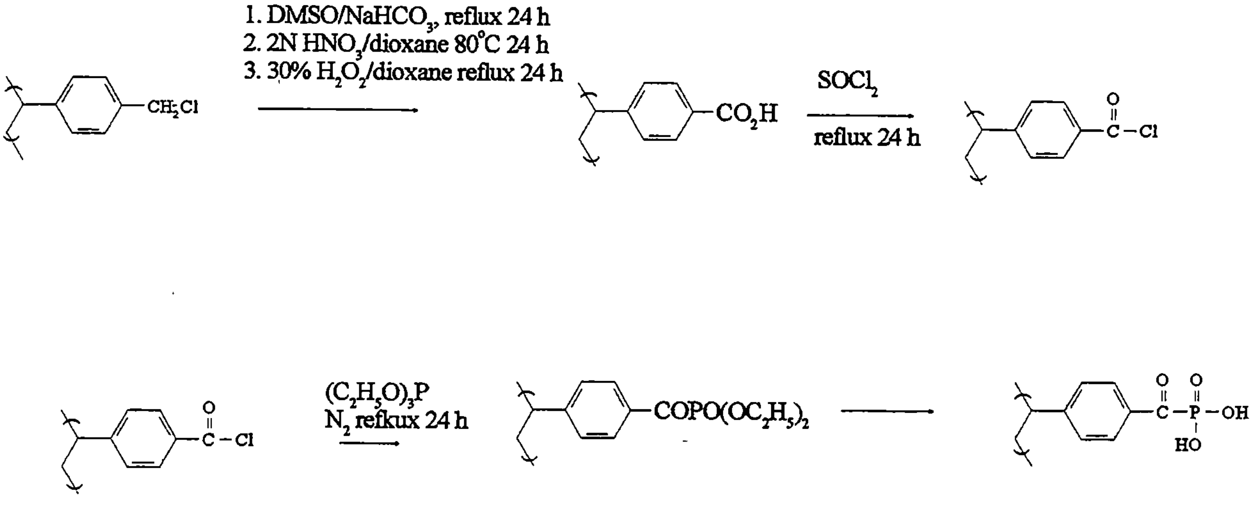


Figure 2.3. Synthesis of α-ketophosphonic acid foam

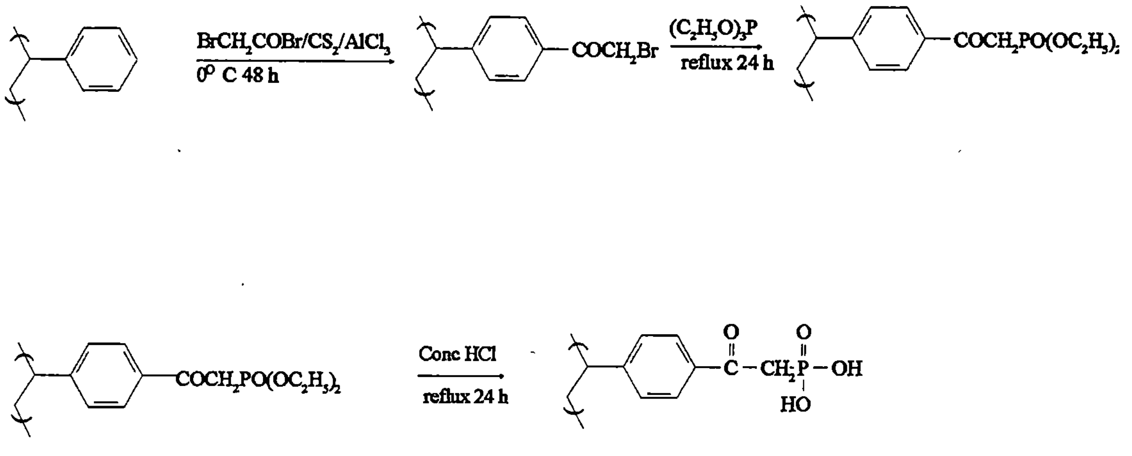


Figure 2.4. Synthesis of β-ketophosphonic acid foam

ethylene dichloride was placed. The mixture was dripped slowly into the reactor while stirring in an ice bath. The reaction was left stirring for 48 hours.

Characterization of Foams

The functionalized foams were conditioned with 1L each of water, 4 wt% NaOH, water, 4 wt % HCl, and water until neutral to pH paper at a rate of 1L per hour. This was followed by percent solid, acid capacity, phosphorus capacity, total anion exchange capacity (TAEC), and chlorine capacity characterization. With the exception of the acid capacity the other characterizations were by standard procedure as described in Chapter 5.

Total acid capacity

Büchner dried resin was accurately weighed (~ 1g) into a 250 mL Erlenmeyer flask using an analytical balance. To the Erlenmeyer flask 200 mL of standardized 0.1N NaOH containing 5 wt% NaCl was added by a pipette and the flask was stoppered with a ground glass stopper and gently stirred for 17 hours at 350 rpm. The solution is removed from the beads without transferring any of the beads and two 50 mL aliquots are titrated with a standardized 0.1N HCl to a phenolphthalein end point.

Modified Acid Capacity Procedure:

100 ml of 0.0659N NaOH(containing 5 wt% NaCl) was added to 1 g of Büchner dried resin in a stoppered 250 ml Erlenmeyer flask and stirred at 350 rpm. Two aliquots of 25 mL each were titrated to the end point with 0.0652 N HCl using phenolphthalein as an indicator.

Metal Ion Studies

Metal ion batch studies were performed with an amount of foam to give 1 milliequivalent (mequiv) of ligand capacity based on its phosphorus capacity. The functionalized foams were contacted at various times and various metals depending on the type of study being carried out. Batch studies were done first followed by column studies for certain functionalized foams.

Column Studies

A piece of solid foam about 1 to 1.5 inches in length was placed in a glass frit funnel. The sides of the column were then packed with alumina powder (Fischer 60-325 mesh). A vacuum was pulled on the foam by attaching a side arm to an aspirator then connecting the side arm to the frit. The solution was eluted through the top at varying rates depending on the study being done.

Results

Each of the four functionalized foams was synthesized numerous times in order to test for reproducibility in characterization and metal ion studies. The results from the analysis of the functionalized foams are given in Table 2.1. The first few attempts at each resin resulted in the foam breaking into fragments. This was overcome by carrying out the reactions in a 1000 ml reactor and conditioning in a large frit funnel in order to compensate for swelling of the foam. Some of the first resins attempted were sent to Los Alamos for further study. The resins made after that were kept at UT for metal ion studies.

The first metal ion studies were batch experiments. The foam was solvent exchanged 4 times with the appropriate background solution, then contacted with 10 ml

Table 2.1. Characterization of functionalized foams

RESIN	LIGAND	% SOLID	ACID CAPACITY (mmol/g)	PHOSPHORUS CAPACITY (COMBINED) (mmol/g)	PHOSPHORUS CAPACITY (INNER) (mmol/g)	PHOSPHORUS CAPACITY (OUTER) (mmol/g)
SS-01-213	Monophosphonic acid	6.97	Wet 11.96 Dry 6.43	3.26	3.35	3.10
SS-01-253	Monophosphonic acid	7.94	5.44	3.11	[A]	[A]
SS-02-028	Monophosphonic acid	6.30	8.57	3.02	3.05	3.03
SS-02-120	Monophosphonic acid	6.69	8.49	2.77	2.75	2.79
SS-01-181	Diphosphonic acid	9.20	5.43	2.90	[A]	[A]
SS-01-197	Diphosphonic acid	8.81	8.85	2.72	[A]	[A]
SS-02-091	Diphosphonic Acid	9.62	6.07	2.48	2.55	2.49
SS-02-110 beads	Diphosphonic acid	92.07	0.26	0.32	[B]	[B]
SS-01-285	α-ketophosphonic acid	8.67	9.66	2.50	[A]	[A]
SS-02-024	α-ketophosphonic acid	8.12	2.34	1.56	1.50	1.62
SS-02-068	α-ketophosphonic acid	8.27	6.41	2.07	2.30	2.36
SS-02-083 beads	α-ketophosphonic acid	75.70	5.35	0.19	[B]	[B]
SS-02-127	α-ketophosphonic acid	9.96	6.48	[C]	[C]	[C]
SS-01-261	β-ketophosphonic acid	11.60	9.71	3.21	[A]	[A]
SS-02-111	β-ketophosphonic acid	6.88	7.26	2.06	2.62	1.83

[A] This analysis was not possible because the foam was in fragments not solid pieces

[B] This analysis was not possible because the resin was supported on beads

[C] This analysis was not necessary since this was the sulfonated foam and the only change should have been the acid capacity of the ion-containing solution for 30 minutes while shaking. The samples were filtered and the filtered solution was read on the Atomic Absorption Spectrometer. The data from the batch experiments are given in Table 2.2.

The column studies were carried out as described in the experimental section. The functionalized foam was contacted with 500 ml of the metal solution with vacuum being applied, unless otherwise specified. The results from these experiments are given in Table 2.3.

Discussion

Characterization indicated that the foams were functionalized to 70% or greater. There were only a few minor problems that had to be addressed. The first dealt with the acid capacity which was clearly too high or negative. The acid capacity should theoretically be twice the phosphorus capacity of the four ligands studied. The procedure was modified to minimize the error in the acid capacity. The modified procedure was described in the experimental section. The acid capacity is still a little high but not as much as it was in the beginning. This is probably due to the low percent solids of the foams, which made it difficult to get an accurate wet weight. The other problem was with the phosphorus capacity. When the foam was functionalized as one solid piece, it was not clear if the phosphorus capacity was accurate for the foam all the way through. The problem was solved by three different phosphorus capacities for each piece of functionalized foam. The first type of phosphorus capacity was done with for a combined piece of foam. This was done by taking a cross-section of the foam. The second type of phosphorus capacity was done with an inner piece of functionalized foam. The inner

TABLE 2.2. Batch Studies of functionalized foams

RESIN	LIGAND	ACID CAPACITY (mmol/g)	P CAPACITY (mmol/g)	SOLUTION	TIME	% COMPLEXED	D
SS-01-213	Monophosphonic acid	6.43	3.26	$Cu(NO_3)_2$ in pH 5 buffer	30 min	98	1856
SS-01-253	Monophosphonic acid	5.44	3.11	$Eu(NO_3)_3$ in 1N HNO_3	30 min	24	10
SS-01-181	Diphosphonic acid	5.43	2.90	$Eu(NO_3)_3$ in 1N HNO_3	30 min	98	1181
SS-01-181	Diphosphonic acid	5.43	2.90	$Fe(NO_3)_3$ in 1N HNO_3	30 min	87	197
SS-02-091	Diphosphonic acid	6.07	2.48	$Fe(NO_3)_3$ in 1N HNO_3	23.5 h	66	47
SS-01-197	Diphosphonic acid	8.85	2.72	$Fe(NO_3)_3$ in 1N HCl	30 min	94	440
SS-01-197	Diphosphonic acid	8.85	2.72	$Cu(NO_3)_2$ in pH 5 buffer	30 min	99.7	7831
SS-02-024	α-ketophosphonic acid	2.34	1.56	$Eu(NO_3)_3$ in 1N HNO_3	30 min	64	159
SS-02-024	α-ketophosphonic acid	2.34	1.56	$Eu(NO_3)_3$ in 1N HNO_3	24 h	97	3136
SS-02-068	α-ketophosphonic acid	6.41	2.07	$Fe(NO_3)_3$ in 1N HNO_3	50 h	87	155
SS-01-261	β-ketophosphonic acid	9.71	3.21	$Eu(NO_3)_3$ in 1N HNO_3	30 min	100	∞
SS-01-261	β-ketophosphonic acid	9.71	3.21	$Fe(NO_3)_3$ in 1N HNO_3	30 min	92	350

D = (mequiv M^{n+} on polymer/$g_{polymer}$)/(mequiv M^{n+} in solution/$mL_{solution}$)

TABLE 2.3. Column studies of functionalized foams

RESIN	SOLUTION	TIME	% COMPLEXED	D
Monophosphonic acid (SS-02-028)	0.25N $Cu(NO_3)_2$ in pH 5 buffer[A]	30 min	52	43
Monophosphonic acid (SS-02-028)	$Cu(NO_3)_2$ in 0.01N HNO_3	1 h	27	569
Monophosphonic acid (SS-02-028)	$Cu(NO_3)_2$ in 0.01N HNO_3	3 h	45	1151
Monophosphonic acid Beads (SN-02-233A)	$Cu(NO_3)_2$ in 0.01N HNO_3	2 h	82	4458
Monophosphonic acid Beads (SN_02-233A)	$Cu(NO_3)_2$ in 0.01N HNO_3	1.5 h	79	1900
Monophosphonic acid (SS-02-028)	$Cu(NO_3)_2$ in 0.01N HNO_3	2.5 h	66	1747
Monophosphonic acid beads (SN-02-233A)	$Cu(NO_3)_2$ in 0.01N HNO_3	6 min under vacuum	38	236
Monophosphonic acid Regenerated beads (SN-02-2333A)	$Cu(NO_3)_2$ in 0.01N HNO_3	9 min under vacuum	42	272
Monophosphonic acid Regenerated beads (SN-02-233A)	$Cu(NO_3)_2$ in 0.01N HNO_3	8 min under vacuum	41	258
Monophosphonic acid (SS-02-028)	$Cu(NO_3)_2$ in 0.01N HNO_3	5 min under vacuum	80	2975
Monophosphonic acid regenerated (SS-02-028)	$Cu(NO_3)_2$ in 0.01N HNO_3	9 min under vacuum	65	1343
Monophosphonic acid Regenerated (SS-02-028)	$Cu(NO_3)_2$ in 0.01N HNO_3	5 min under vacuum	29	1390
Monophosphonic acid (SS-02-120)	$Fe(NO_3)_3$ in 1N HNO_3	36 min under vacuum	10	128
Monophosphonic acid (SS-02-120)	$Fe(NO_3)_3$ in 1N HNO_3	28 min under vacuum	10	140
Diphosphonic acid (SS-02-091)	$Cu(NO_3)_2$ in 0.01N HNO_3	24 min under vacuum	32	380
Diphosphonic acid (SS-02-091)	$Fe(NO_3)_3$ in 1N HNO_3	9 min under vacuum	3.3	26
Diphosphonic acid (SS-02-091)	$Fe(NO_3)_3$ in 1N HNO_3	30 min under vacuum	0.9	10
α-ketophosphonic acid (SS-02-068)	$Cu(NO_3)_2$ in 0.01N HNO_3	10 min under vacuum	23	231
α-ketophosphonic acid regenerated (SS-02-068)	$Cu(NO_3)_2$ in 0.01N HNO_3	5 min under vacuum	31	343
α-ketophosphonic acid (SS-02-068)	$Cu(NO_3)_2$ in 0.01N HNO_3	22 min under vacuum	77	2195
α-ketophosphonic acid regenerated (SS-02-068)	$Cu(NO_3)_2$ in 0.01N HNO_3	6 min under vacuum	6	59
α-ketophosphonic acid (SS-02-068)	$Fe(NO_3)_3$ in 1N HNO_3	7 min under vacuum	17	170
α-ketophosphonic acid (SS-02-068)	$Fe(NO_3)_3$ in 1N HNO_3	5 min under vacuum	19	189
β-ketophosphonic acid (SS-02-111)	$Cu(NO_3)_2$ in 0.01N HNO_3	27 min under vacuum	61	1407
β-ketophosphonic acid (SS-02-111)	$Fe(NO_3)_3$ in 1N HNO_3	33 min under vacuum	68	1791
β-ketophosphonic acid (SS-02-111)	$Fe(NO_3)_3$ in 1N HNO_3	25 min under vacuum	52	836

[A] Ran 30 mL through column instead of 1L piece was removed from a piece of functionalized foam by cutting the foam in half and removing a sample from the center to do a phosphorus capacity. The final type of phosphorus capacity was done with an outer piece. The outer piece was taken from the surface of the foam. This showed that almost always there was functionalization throughout the polymer.

The batch studies demonstrate that the resins synthesized had affinities for the three metals contacted: Cu^{2+}, Eu^{3+}, and Fe^{3+}. The diphosphonic acid had the highest affinity for Eu^{3+} in 1 N HNO_3 with a percent complexation of 98% after 30 minutes. Unfortunately the reproducibility run showed a great drop in the percent complexed. This could be credited to some error in one of the functionalized foams since they were synthesized at two separate occasions. Unfortunately, there was no more diphosphonic acid foam to do one more experiment with the Eu^{3+} in 1 N HNO_3 to determine which number was real and where the error had occurred.

The β-ketophosphonic acid also had a high affinity for the Eu^{3+} in 1 N HNO_3 over 30 minutes (percent absorbance of 100%). There was no reproducibility done on this batch study because there was not enough of the resin. The most surprising result was the percent absorbed by the α-ketophosphonic acid, which was only 64 % for the Eu^{3+} in 1 N HNO_3 over 30 minutes. This value should have been closer to the absorbance values for the β-ketophosphonic acid foam. The reason being the similarity in the structures of the α-ketophosphonic acid to the β-ketophosphonic acid. When the contact time was increased to 24 hours the percent absorbed increased to 97%. This shows that the resin has an affinity for the metal but that there can be diffusional limitations to complexation.

The higher porosity of the foams in comparison to the beads should allow for easier metal ion access to the binding sites within the resin. This should increase the absorbance over a shorter amount of time since diffusion is not as much of a factor as it is with the beads. However, we now find that the pore structure in foams can collapse at higher acidic concentrations of the medium as shown by the decreased complexation of the metal ions when the concentration of the acidic medium is increased. This is seen with the monophosphonic acid foam.

The monophosphonic acid showed very low absorbance for the Eu^{3+} in 1 N HNO_3. The monophosphonic acid supported on 5% DVB MR beads gives a similar value for the complexation for Eu^{3+} in 1 N HNO_3 over 30 min (20% complexed).[26] As the time increases the metal ion is able to get pass the collapsed chain to coordinate with the binding sites of the resin. There were no batch studies done for this resin at a longer contact time because the remaining resin was used for column studies.

The four ligands were not studied with all three of the metal ions. The only metal ion studied with all four was Eu^{3+} in 1 N HNO_3. Even though all the metals were not studied with all the ligands due to a limited amount of sample, the abilities of the ligands in comparison to one another can be seen. β-ketophosphonic acid foam is the only one studied that gave >90% percent complexed over the 30 min batch studies. The diphosphonic acid foam gave a percent complexed of >87% for the metals studied, whereas the α-ketophosphonic acid gave a percent complexed of 64% with the Eu^{3+} in 1 N HNO_3 possibly due to diffusional limitations. This theory may be explained by increasing the contact time and the ligand complexed >87%. The monophosphonic acid had the lowest percent complexed with the Eu^{3+} in 1 N HNO_3 but had a percent complexation of 98% with Cu^{2+} in pH 5 buffer. The reason for this was discussed previously in the chapter.

The monophosphonic acid resin was the first resin used for the column studies. The original studies were done without a vacuum and a liter of the $Cu(NO_3)_2$ in 0.01N HNO_3 was passed through the resin. These results were compared to the result found for the monophosphonic acid ligand supported on 12% DVB gel beads (250-425 μm). The first studies indicated a need for controlling the length of time it took the solution to pass through the resins. The column method was modified by applying a vacuum to the column in order to get a more reproducible time. The studies done under this method demonstrated that after contact of 500ml of Cu^{2+} in 0.01 N HNO_3 over 5 minutes under vacuum, the foam complexed (80%) twice as much as the beads (38%). This supported the theory that the foams would lead to an increase in complexation over a shorter time period relative to the beads.

The ability to regenerate the beads and foam in the columns was studied and compared for their ability to complex the desired metal consistently. Regeneration studies were done by eluting each of the resins with 1 L of 4 N HNO_3 over a 1 hour period. What this study showed was that the percent absorbed for the regenerated beads remained consistent at about 40% over 3 contact /regeneration cycles while the percent absorbed for the regenerated foam decreased from 80% to 29% over a 3 contact/regeneration cycle. The reason for the decrease in percent absorbed for the foam is unclear at this time. More extensive research into this area is needed to discover the cause of this phenomenon. One possible explanation can be the contact time under vacuum is insufficient to regenerate the foams for another contact. Comparison studies of the other resins to resins supported on 12% DVB beads was not possible. This was due to the inability to obtain functionalization of the diphosphonic acid and α-ketophosphonic acid onto the beads as seen by the phosphorus capacities shown in Table 2.1.

Several trends by the four resins used in the column studies were evident. $Cu(NO_3)_2$ in 0.01N HNO_3 showed the higher percent absorbed for the four resins. The α- and β-ketophosphonic acid functionalized foams showed the highest absorbance for the copper solutions. This is consistent with the results found with batch studies done with beads; α- and β-ketophosphonic acid resins both demonstrated 100% complexed.[80] The surprising result was that of the diphosphonic acid which showed a percent complexed of only 32%. This result is surprising due to the structure of the ligand and the results found with the batch studies whereas the foam complexed >87% for the metal ions studied. $Fe(NO_3)_3$ in 1 N HNO_3 showed lower absorbance's for the four resins. The absorption of iron was poor for all the resins with the exception of the β-ketophosphonic acid. The percent absorbed for the diphosphonic and α-ketophosphonic acid should have been much higher in comparison to the results obtained by batch studies. This result is surprising due to the structure of the ligands and the ability of the ligands during the batch studies. The diphosphonic had a lower percent absorbance than the monophosphonic acid resin. The absorbance of the α-ketophosphonic acid increased after 50 hours of shaking the resin (Table 2.2). This shows that it may be an accessibility problem, which possibly can be accounted for by the theory of chain collapse in highly acidic mediums. Even though the β-ketophosphonic acid gave the most consistent high percent absorbance, it demonstrated very poor reproducibility with the column studies. The cause for this is unclear. However, even the lowest percent absorbed of the β-ketophosphonic acid resin was higher than the percent absorbed for the other three resins.

Because of the low absorption for the Fe^{3+}, we attempted to improve absorption by sulfonating the resin. This did not work because of two problems that occurred. The characterization showed that the resin was not sulfonated because the acid capacity for the foam remained about the same when it should of increased by at least 1 mmol/g. Even if the resin would have been sulfonated, it would not be suitable for column studies because the foam broke apart during the reaction even though the 1000 mL reactor was used. The conditions appeared to be too harsh to keep the foam in one piece for column studies.

Conclusions

The increased porosity of the foams did increase the ability of the support to be functionalized. This was demonstrated by the inability to functionalize 12% DVB beads (Table 2.1). The foams also showed consistent functionalization throughout. In comparison with the beads, the foam had a higher percent complexed during the column studies as shown with the monophosphonic ligand. The major problem with this is the inability to maintain constant percent complexed for the foams after regeneration. The other major problem was reproducibility with the column studies. This could be better understood if a high number of column studies could be done at one time to better understand where the problem or possible error is occurring. The short flow rate also seems to be a factor. Results show that increasing the flow rate from 10 minutes under vacuum to 30 minutes under vacuum will increase the percent complexed of the metal.

Overall, the foams behave as expected and are a viable support for ion-exchange resins.

CHAPTER 3

BIFUNCTIONAL POLYMERS WITH ENHANCED IONIC ACCESSIBILITY

Introduction

The removal of metal ions from aqueous solutions is an important area of research. One common method of removal of metal ions from solution with immobilized ligands. Depending on the type of ligand supported on the polymer, the resin is capable of complexing or ion-exchanging with the metal ion in solution.[81] Some ligands that have been immobilized include amines,[82] carboxylic acids,[83] crown ethers,[84] and phosphorus-based ligands.[85] Phosphorus-based ligands are important for ion-exchange due to their selectivity depending on the precise structure of the ligand and their ability to coordinate various metal ions under highly acidic conditions.[86] One problem with polymer-supported reagents is the slow rates of complexation.[87] If the metal ion cannot get into the polymer matrix then the ligand cannot complex the metal ion.

One way to increase accessibility of the metal ion into the polymer matrix is to increase the porosity and surface area of the polymer support. The method that we have focused upon in our research is the concept of dual-mechanism bifunctional polymers. The idea of dual-mechanism bifunctional polymers[88] is that two different ligands operating through two different mechanisms (an access mechanism and a recognition mechanism) can increase ionic accessibility while maintaining high selectivity.

Synthesis of Polymer Supports

The polymer supports were synthesized by suspension polymerization. This method has been previously discussed in Chapter 2 and will be discussed in more detail in Chapter 5. The two types of supports utilized in this study were polystyrene and poly(vinylbenzyl chloride) cross linked with divinylbenzene. The crosslinking levels for the supports were set at 2% for microporous beads and 12% for macroporous beads. The beads were made with a particle size diameter of 250-425μm and 75-150μm.

Synthesis of Monophosphonic Acid Resins

The poly(vinylbenzyl chloride) beads at both porosities and particle sizes were funtionalized by refluxing 10g of beads with 300ml of triethyl phosphite for 24 hours.[9] The beads were washed twice with acetone and twice with dilute HCl. The reaction was followed by hydrolysis with 250ml of concentrated HCl (24 h reflux) (Figure 3.1).[9]

Synthesis of Phosphonoacetic Acid

Triethyl phosphonoacetate, 31.60g, was added to 150 ml of dry dioxane and 3.67g Na metal and left to stir overnight under a N_2 sweep. Poly(vinylbenzyl chloride) beads at both particle sizes (10.00g) were added to deprotonated triethyl phosphonoacetate and refluxed for 24 h. The beads were washed four times with toluene, dried *in vacuo* at 60°C for 17 h, swelled in $CHCl_3$ for 1 h under a N_2 sweep, refluxed with 27 ml of Me_3SiBr for 24 h, and washed twice with dioxane and twice with water. The beads were then refluxed with 150 ml of 3N NaOH for 24 h (Figure 3.2).

Synthesis of β-KetophosphonicAcid

The polystyrene beads of both porosities and particle sizes were functionalized by placing 10g of the polymer support with 200 ml of CS_2 to swell for 1 h while in an ice

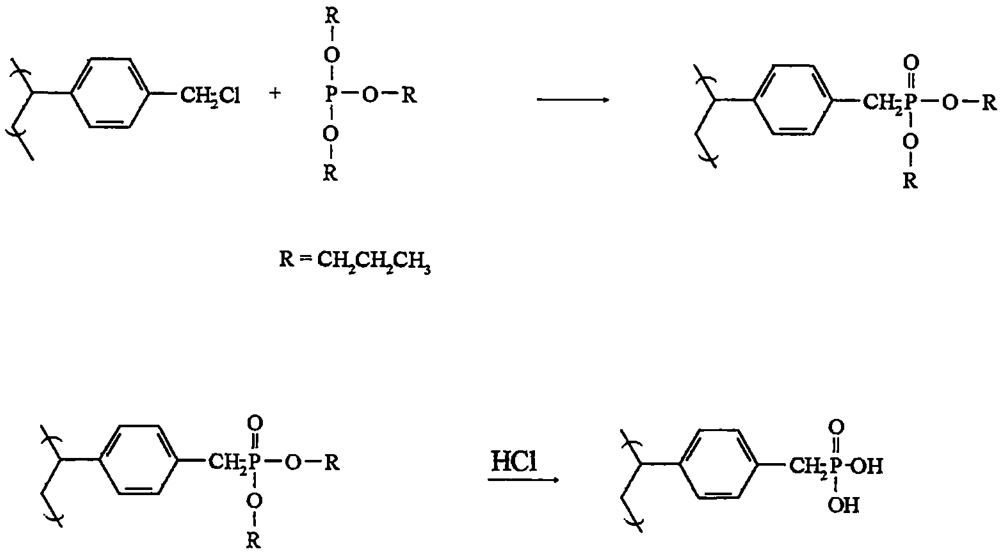


Figure 3.1. Synthesis of monophosphonic acid

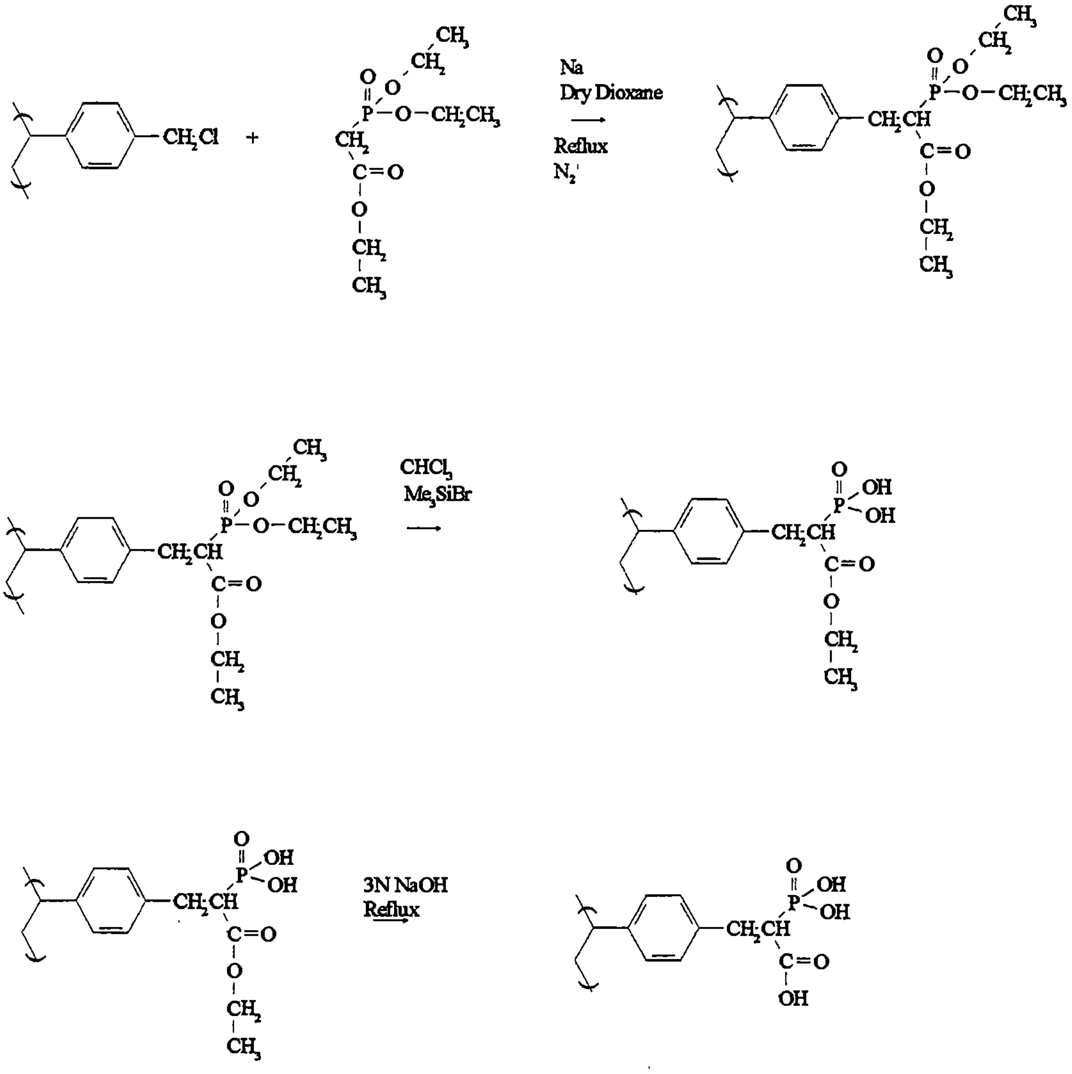


Figure 3.2. Synthesis of phosphonoacetic acid

water bath. In 65 ml of CS_2, 40g of $AlCl_3$ was dissolved, added to stirring beads and left to stir for 2 h. 40.4 g of bromoacetyl bromide was added to an addition funnel with 10 ml of CS_2. The solution was added drop wise to beads and allowed to stir for 48 h while under a N_2 sweep. After 48 h, the solution was removed with a fritted glass filter and the beads were washed with dioxane until the solution remained clear. Beads are then washed with a mixture of dioxane/water (100/0 – 0/100) changing the ratio of dioxane to water until the beads are just washed in water, twice with ethanol, and twice with acetone, then dried *in vacuo* at 70°C for 4 h. The beads are refluxed for 24 h with 100 ml of triethyl phosphite. After refluxing, the beads are washed twice with acetone and twice with dilute HCl. The reaction was followed by hydrolysis with 250ml of concentrated HCl (24 h reflux) (Figure 3.3).

Synthesis of Sulfonated Analogues of Functionalized Resins

Each resin (~10.0 g) at a particle size of 250-425μm after functionalization was dried by azeotropic distillation with heptane and then placed in 500 ml round bottom flask and stirred for 1 hr with ethylene dichloride (EDC; 200ml). In an addition funnel, 65 ml of EDC was added to 16.5 ml of chlorosulfonic acid and added drop wise slowly to the stirring beads. The mixture was stirred at room temperature for 48 h. The beads was then washed with a mixture of dioxane/water (100/0 – 0/100) changing the ratio of dioxane to water until the beads are just washed in water (Figure 3.4).

Characterization of Resins

Each resin was analyzed by its phosphorus capacity, acid capacity and percent solids. The procedures for these analyses are given in detail in Chapter 5. The results are given in Table 3.1 and Table 3.2.

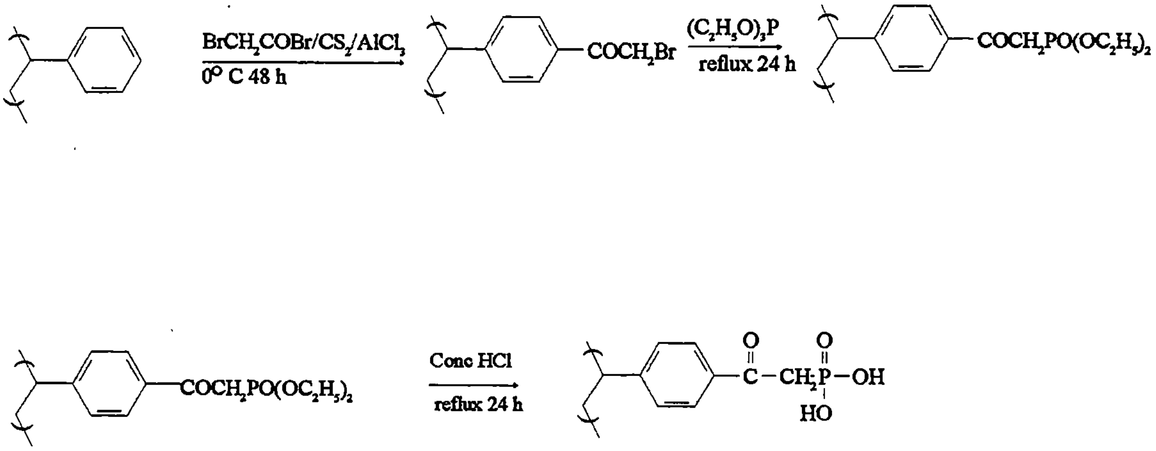
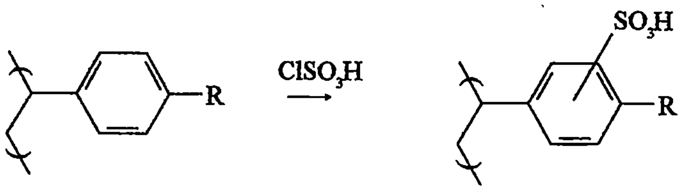


Figure 3.3. Synthesis of β-ketophosphonic acid



R = monophosphonic acid, phosphonoacetic acid, β -ketophosphonic acid

Figure 3.4. Sulfonated Analogues of resins

Table 3.1. Characterization of monofunctional resins

RESIN	LIGAND	TYPE	SIZE (μm)	PHOSPHORUS CAPACITY (mmol/g)	ACID CAPACITY (mmol/g)	% SOLIDS
SS-03-170	Monophosphonic acid	2% DVB gel	250-425	4.49 (5.08)[a]	10.07	54.3
SS-03-257	Monophosphonic acid	2% DVB gel	75-150	4.72	9.13	56.9
SS-04-252	Monophosphonic acid	12% DVB MR	250-425	3.66	8.33	26.5
SS-03-007B	Phosphonoacetic acid	2% DVB gel	250-425	2.09 (3.91)[B]	6.04	52.2
SS-03-085	Phosphonoacetic acid	2% DVB gel	250-425	2.14	5.02	57.8
SS-03-008B	Phosphonoacetic acid	2% DVB gel	75-150	2.47	5.88	49.0
SS-04-268	Phosphonoacetic acid	12% DVB MR	250-425	0.77	3.27	36.7
SS-03-040	β-ketophosphonic acid	2% DVB gel	250-425	1.78 (4.42)[C]	3.30	65.5
SS-04-023	β - ketophosphonic acid	2% DVB gel	250-425	3.51	6.85	53.0
SS-03-363	β - ketophosphonic acid	2% DVB gel	75-150	2.76	5.51	47.4
SS-04-095	β - ketophosphonic acid	2% DVB gel	75-150	2.92	6.06	50.0
SS-05-005	β - ketophosphonic acid	12% DVB MR	250-425	1.86	6.46	31.3

[A] Theoretical phosphorus capacity of monophosphonic acid
[B] Theoretical phosphorus capacity of phosphonoacetic acid
[C] Theoretical phosphorus capacity of β-ketophosphonic acid

Gel = microporous resin

MR = macroporous resin

Table 3.2. Characterization of bifunctional resins

RESIN	LIGAND	TYPE	SIZE (µm)	PHOSPHORUS CAPACITY (mmol/g)	ACID CAPACITY (mmol/g)	% SOLIDS
SS-03-182	Sulfonated Monophosphonic acid	2% DVB gel	250-425	4.03 (3.61)[A]	9.53	35.8
SS-04-266	Sulfonated Monophosphonic acid	12% DVB MR	250-425	2.87	10.12	28.1
SS-03-126	Sulfonated Phosphonoacetic acid	2% DVB gel	250-425	1.57 (2.98)[B]	6.93	53.9
SS-04-042	Sulfonated Phosphonoacetic acid	2% DVB gel	250-425	1.96	7.44	45.7
SS-04-267	Sulfonated Phosphonoacetic acid	12% DVB MR	250-425	0.64	4.79	31.3
SS-03-078	Sulfonated β-ketophosphonic acid	2% DVB gel	250-425	1.15 (3.27)[C]	7.20	20.0
SS-04-097	Sulfonated β-ketophosphonic acid	2% DVB gel	250-425	2.80	8.26	33.9
SS-05-006	Sulfonated β-ketophosphonic acid	12% DVB MR	250-425	1.26	6.38	26.3

[A] Theoretical phosphorus capacity of sulfonated monophosphonic acid
[B] Theoretical phosphorus capacity of sulfonated phosphonoacetic acid
[C] Theoretical phosphorus capacity of sulfonated β-ketophosphonic acid

Gel = microporous resin MR = macroporous resin

Metal Ion Studies

The resins are contacted with 10 ml 10^{-4} N of $Cu(NO_3)_2$, $Pb(NO_3)_2$, and $Cd(NO_3)_2$ solutions in 0.10 N HNO_3 and 0.10 N HNO_3/0.040 N $NaNO_3$ as well as 10^{-4} N $Eu(NO_3)_3$ in 1.00 N HNO_3. Enough of each resin is weighed to give 1 mequiv of phosphorus ligand, then shaken with 10 ml of solution for either 24 h or 15 min. The solutions are filtered and the amount of metal ion remaining in solution is determined via atomic absorption or atomic emission (depending on the metal being analyzed). The distribution coeffecient (D) is calculated by the following equation:

$$D = (\text{mequiv } M^{n+} \text{ on polymer}/g_{\text{polymer}})/(\text{mequiv } M^{n+} \text{ in solution}/mL_{\text{solution}})$$

The instrument used is a Perkin-Elmer model 3100 spectrophotometer.

Results

The six resins synthesized were monophosphonic acid, phosphonoacetic acid, β-ketophosphonic acid, sulfonated monophosphonic acid, sulfonated phosphonoacetic acid and sulfonated β-ketophosphonic acid. Each monofunctional resin was synthesized at two different particle sizes to determine the effect of surface area on ionic accessibility. The monofunctional and bifunctional resins were also synthesized at different porosities to determine the effect of porosity on ionic accessiblity of the metal ion into the polymer matrix.

The resins were contacted with various metal ions with and without the prescence of excess Na^+ in order to assess ligand selectivity. The results of the metal ion studies done with the monofunctional resins at a particle size of 250-425 μm are given in

Table 3.3. Results with the monofunctional resins at a particle size of 75-150 μm are given in Table 3.4. The effect on porosity of the monofunctional resins is shown in Table 3.5.

The bifunctional resins were studied at both porosities but only one particle size (250-425 μm). The results for the bifunctional gel resins are given in Table 3.6, while results with the MR resins are given in Table 3.7. The complexing ability of the monofunctional and bifunctional resins was also studied at a time of 15 min. The results from these studies are given in Table 3.8

Discussion

As seen in Table 3.1 the phosphonic acid resins give the highest amount of functionalization (>72%) (as determined by comparison to the theoretical values for each resin) whereas the phosphonoacetic acid resin (<65% functionalization) is the most difficult of the resins to synthesize as demonstrated by the inability to functionalize the 12% DVB crosslinked MR beads with the phosphonoacetic acid resin (phosphorus capacity = 0.77 mmol/g). Even with the increased porosity the higher crosslinking prevents the ligand from bonding to the polymer supports (functionalization was <20%). The phosphonoacetic acid was only functionalized onto the 2 % DVB gel beads at the two different particle sizes. The β-ketophosphonic acid resin has a percent of functionalization of<80%. The amount of functionalization for the β-ketophosphonic acid resin was sufficient to give a high percentage of complexation of metal ions in comparison to the other two ligands.

The results shown in Tables 3.3 and Table 3.4 show that the monofunctional

Table 3.3. Complexation by monofunctional gel resins with a particle size of 250-425μm after 24 h contact

RESIN	LIGAND	Cu^{2+}	Pb^{2+}	Cd^{2+}	Cu^{2+}/ Na^{+}	Pb^{2+}/ Na^{+}	Cd^{2+}/ Na^{+}	Eu^{3+}
SS-03-170	Monophosphonic acid	35.1 (24.3)‡	67.4 (91.6)	40.5 (30.5)	16.7 (8.95)	29.5 (18.8)	42.5 (43.9)	23.8 (13.7)
SS-03-007B[1] SS-03-085	Phosphonoacetic Acid	39.5[1] (14.0)	71.8 (54.4)	37.9 (13.0)	27.5 (2.25)	55.4 (26.6)	19.2 (5.07)	28.7[1] (8.60)
SS-03-040[2] SS-04-023	β-ketophosphonic acid	70.0[2] (41.4)	94.4[2] (297)	76.8 (114)	43.8[2] (13.6)	72.6[2] (46.9)	43.0 (26.4)	96.0 (841)

‡ Distribution Coefficient

[1] Resin SS-03-007B was used for the studies with Cu^{2+} and Eu^{3+}

[2] Resin SS-03-040 was used for the studies with Cu^{2+}, Cu^{2+}/Na^{+} and Pb^{2+}/Na^{+}

Table 3.4. Complexation by monofunctional gel resins with a particle size of 75-150μm after 24 h contact

RESIN	LIGAND	Cu^{2+}	Pb^{2+}	Cd^{2+}	Cu^{2+} /Na^{+}	Pb^{2+}/ Na^{+}	Cd^{2+}/ Na^{+}	Eu^{3+}
SS-03-257	Monophosphonic acid	30.7 (24.3)‡	56.8 (69.6)	34.3 (27.9)	14.6 (9.11)	26.2 (19.0)	17.7 (11.5)	23.0 (16.0)
SS-03-008B	Phosphonoacetic Acid	37.3 (15.0)	74.3 (71.2)	43.1 (18.6)	27.5 (2.71)	48.9 (23.4)	24.0 (7.74)	28.0 (10.0)
SS-03-263 SS-04-095[1]	β-ketophosphonic acid	67.6 (57.4)	92.9 (360)	71.7[1] (75.5)	44.1 (21.6)	68.4 (59.3)	42.0[1] (21.0)	87.5 (192)

‡ Distribution Coefficient

[1] Resin SS-04-095 was used for the studies with Cd^{2+} and Cd^{2+}/Na^{+}

Table 3.5. Complexation by monofunctional MR resins with a particle size of 250-425μm after 24 h contact

RESIN	LIGAND	Cu^{2+}	Pb^{2+}	Cd^{2+}	Cu^{2+}/ Na^{+}	Pb^{2+}/ Na^{+}	Cd^{2+}/ Na^{+}	Eu^{3+}
SS-04-252	Monophosphonic acid	32.3 (17.1)‡	80.0 (144)	36.6 (21.1)	21.9 (10.1)	43.4 (27.9)	22.0 (10.3)	1.8 (0.66)
SS-05-005	β-ketophosphonic acid	56.2 (23.8)	100 (∞)	54.7 (23.3)	39.3 (12.0)	71.3 (45.9)	40.1 (12.4)	83.2 (83.2)

‡ Distribution Coefficient

Table 3.6. Complexation by bifunctional gel resins with a particle size of 250-425μm after 24 h contact

RESIN	LIGAND	Cu^{2+}	Pb^{2+}	Cd^{2+}	Cu^{2+}/ Na^{+}	Pb^{2+}/ Na^{+}	Cd^{2+}/ Na^{+}	Eu^{3+}
SS-03-182	Sulfonated Monophosphonic acid	94.1 (633)‡	100 (∞)	96.2 (1002)	46.1 (34.4)	67.0 (81.8)	56.9 (52.1)	91.8 (448)
SS-03-126 SS-04-042[1]	Sulfonated Phosphonoacetic Acid	100 (∞)	100[1] (∞)	100 (∞)	82.5 (21.4)	94.1[1] (130)	72.3 (50.9)	97.7 (573)
SS-03-078 SS-04-097[2]	Sulfonated β-ketophosphonic acid	100 (∞)	100 (∞)	98.4[2] (1680)	83.2 (56.5)	100 (∞)	68.3[2] (60.2)	96.0[2] (677)

‡ Distribution Coefficient

[1] Resin SS-04-042 was used for the studies with Pb^{2+} and Pb^{2+}/Na^{+}

[2] Resin SS-04-097 was used for the studies with Cd^{2+}, Cd^{2+}/Na^{+} and Eu^{3+}

Table 3.7. Complexation by bifunctional MR resins with a particle size of 250-425μm after 24 h contact

RESIN	LIGAND	Cu^{2+}	Pb^{2+}	Cd^{2+}	Cu^{2+}/ Na^{+}	Pb^{2+}/ Na^{+}	Cd^{2+}/ Na^{+}	Eu^{3+}
SS-04-266	Sulfonated Monophosphonic acid	100 (∞)‡	100 (∞)	100 (∞)	74.5 (83.7)	100 (∞)	82.6 (135)	100 (∞)
SS-05-006	Sulfonated β-ketophosphonic acid	100 (∞)	100 (∞)	91.0 (126)	81.2 (54.4)	100 (∞)	81.1 (53.9)	100 (∞)

‡ Distribution Coefficient

Table 3.8. Complexation by monofunctional and bifunctional gel resins after 15 min contact

RESIN	**LIGAND**	**SIZE(μm)**	**Cu^{2+}**	**Cu^{2+}/Na^{+}**
SS-03-170	Monophosphonic acid	250-425	38.7 (28.3)[‡]	18.0 (9.83)
SS-03-257	Monophosphonic acid	75-150	34.6 (24.3)	10.7 (6.43)
SS-04-157	Phosphonoacetic Acid	250-425	43.8 (19.1)	20.1 (6.13)
SS-04-149	β-ketophosphonic acid	250-425	68.0 (56.5)	37.8 (16.3)
SS-04-095	β-ketophosphonic acid	75-150	72.1 (75.0)	44.0 (22.7)
SS-03-182	Sulfonated monophosphonic acid	250-425	94.4 (673)	50.3 (40.6)
SS-03-126	Sulfonated phosphonoacetic acid	250-425	100.0 (∞)	79.4 (53.0)
SS-04-097	Sulfonated β-ketophosphonic acid	250-425	98.4 (1739)	73.2 (76.0)

[‡] Distribution Coefficient

resins have low complexing ability for the metals studied. The percent complexed was within the range of 23%-75% depending on the metal and the type of ligand. All three ligands had a higher affinity for Pb^{2+} then the other three metals studied. The exception to the low complexing ability of the monofunctional resins was β-ketophosphonic acid resin for Pb^{2+} (94%) and Eu^{3+}(96%). The resins do exhibit selectivity for the metal studied, which is demonstrated by the comparison of the percent complexed of the metals without Na^+ to the percent complexed of the metals with Na^+. The three ligands had a loss of complexation of 12%-26%(Cu^{2+}), 16%-38%(Pb^{2+}), and 17%-34%(Cd^{2+}). In the presence of an excess of Na^+ the ligands could still selectively remove the target metal ion.

In comparing Table 3.3 to Table 3.4, it is seen that the increase in particle size does not increase accessibility of the resins: the percent complexed for the resins with the same ligands but at different particle sizes are comparable. For all three ligands the difference in particle size only changed the percent complexed by small amounts. The differences in percent complexed for each metal were 2%-4%(Cu^{2+}), 2%-11%(Pb^{2+}), and 5%-6%(Cd^{2+}) where there was no change with the percent complexed for Eu^{3+}. This shows that the increase in surface area does not affect accessiblity. The results in Table 3.5 demonstrate that making the polymer support macroporous does not greatly enhance the accessibility of the ligands. The two ligands supported on the 12% DVB MR beads, monophosphonic acid and β-ketophosphonic acid, did not demonstrate an increase in metal ion complexation. The monophosphonic acid demonstrated a complexation of <40% for Cu^{2+},Cd^{2+}, and Eu^{3+} whereas the percent complexed of Pb^{2+} was 80%. These numbers are comparable and lower in the case of the Pb^{2+} and Eu^{3+} than of the gel beads with the same ligand and particle size. The β-ketophosphonic acid had a loss in percent complexation for Cu^{2+} and Cd^{2+} of 14%-22%. The complexation of Pb^{2+}(100%) and Eu^{3+} (83%) remained high. The resins do not demonstrate an increase in accessibility even though the polymer supports are more porous than the gel beads. The trends with selectivity and complexing ability remain the same as seen in Tables 3.3 and 3.4. As stated earlier, the phosphonoacetic acid resin was not studied on the MR polymer supports due to a very low level of functionalization.

The β-ketophosphonic acid resin has the greatest affinity for the metals studied. In comparison to the monophosphonic acid and phosphonoacetic acid ligands the β-ketophosphonic acid has the greater complexing ability for all four metals. The difference in complexing ability of the β-ketophosphonic acid in comparison to the other two ligands for the four metals studied were 30%-35%(Cu^{2+}), 22%-27%(Pb^{2+}), 36%-39%(Cd^{2+}) and 67%-72%(Eu^{3+}). It outperforms the other ligands regardless of porosity or particle size. Even though β-ketophosphonic acid has a similar structure to phosphonoacetic acid, the β-ketophosphonic acid resin has the greater complexing ability. This is due to hydrogen bonding that can occur with the phosphonoacetic acid resin causing a lower amount of metal complexed in comparison to the β-ketophosphonic resin (Figure 3.5). All the ligands have a greater affinity for Pb(II) than the other metals studied.

The bifunctional resins give >90% complexed for all the metals studied (Table 3.6). By comparing the percent complexed of the metals without Na^+ to the percent complexed of the metals with Na^+ it can be determined that the recognition ligand is

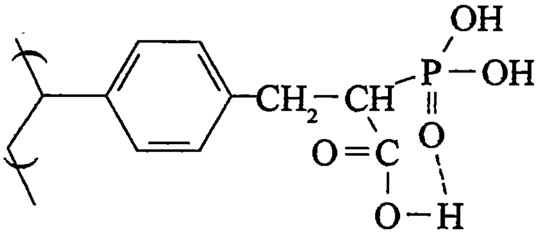


Figure 3.5. Hydrogen bonding of the phosphonoacetic acid resin

doing the complexing and not the sulfonic acid ligand. The three ligands had a loss of complexation of 17%-48%(Cu^{2+}), 5%-33%(Pb^{2+}), and 28%-39%(Cd^{2+}). In the presence of an excess of Na^+ the ligands could still selectively remove the target metal ion. The sulfonic acid ligand is attracting the metal ions into the matrix in order for the recognition ligand to complex with the metal ion. The trends seen in Table 3.7 remain the same even though the polymer supports have increased porosity. The bifunctional MR and gel resins give >90% complexed for all the metals studied regardless of porosity. The one difference is the decrease in the difference of the percent complexed of the metals without Na^+ to the percent complexed of the metals with Na^+. The ligands supported on the MR beads had a lower percent loss of complexation for three of the metals studied, 19%-26%(Cu^{2+}), 0%(Pb^{2+}), and 10%-17%(Cd^{2+}). Bifunctional resins supported on MR beads show no more increased accessibility then the bifunctional resins supported on the gel beads.

In comparing the monofunctional resin to the bifunctional resin, the percent complexed goes from <50% to >90% for the resins studied. Even the increase in porosity or surface area of the monofunctional resins does not increase the accessibility as demonstrated by the bifunctional resins. The presence of the sulfonic acid ligand is all that is needed to increase the accessibility of the resins. The sulfonic acid pulls the metal ions into the polymer matrix with very fast kinetics allowing the recognition ligand to complex the metal ion.

The decrease in time does not affect the complexing ability of the resins as shown in Table 3.8. The bifunctional resins still give a percent complexed of >90% whereas the monofunctional resins give a percent complexed of <75%. Even if the time of contact were increased over 24 hours the monofunctional resins would still remain significantly lower than the bifunctional resins.

Conclusions

Of the three ligands studied the β-ketophosphonic acid has the greatest complexing ability. The increase in surface area and porosity of the monofunctional resins does not increase the accessibility of the metal ion into the polymer matrix. The addition of an access ligand to the resins greatly increases the complexing ability of the resins studied. The access ligand does not complex the metal ions but serves to pull the metal ions into the polymer matrix in order for the recognition ligand to complex the metal ions. In order to increase the accessibility of a resin the addition of an access ligand is the best approach.

CHAPTER 4

DEVELOPMENT OF HIGH STABILITY SOLVENT IMPREGNATED RESINS (SIRs)

Introduction

The complexation of metal ions from aqueous solutions can be accomplished by two common methods. The first method is liquid-liquid separations[12,13] that is utilized widely in industrial applications. The second method is solid-liquid separations commonly known as ion-exchange. A third possibility focuses on solvent impregnated resins (SIRs) which, combine the advantages of both of these separations methods.[68] The SIR is synthesized by sorbing an extractant with a diluent into a support with a high internal surface (Figure 4.1).[89] The most common type of support is a highly crosslinked macroporous (MR) copolymer due to the fact that the macrochannels do not collapse in various solvents, which is an important property during the impregnation process.[89] SIRs have been prepared with various extractants, including phosphonic acids, phosphoric acids, phosphinic acids, thiophosphoric acids, phosphonates, hydroxyoximes, quaternary amines, and triphenylmethane or azo based chelating dyes.[89,90,91,92,93,94,95] Entrainment is obviated with SIRs, though extractant loss through solubility remains a problem.[96] The loss of extractant is significant enough that SIRs cannot be utilized on a large scale without modification. The modification that has been accomplished is the encapsulation of the SIR with a semi-permeable membrane (Figure 4.2).[68]

The encapsulation of the SIR allows for the metal ion to pass through the membrane by rapid diffusion while retaining the extractant and the extractant/metal

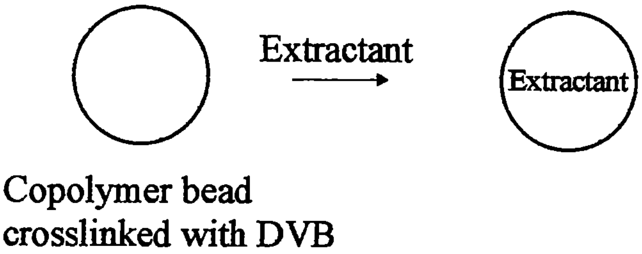


Figure 4.1. Preparation of SIR

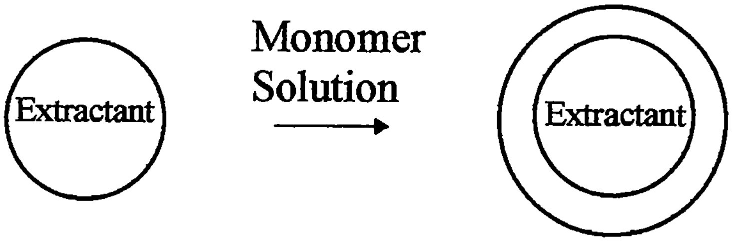


Figure 4.2. Preparation of encapsulated SIR

complex.[97] The encapsulated SIR exhibits an increased longevity and decrease in loss of extractant in comparison to the SIR not encapsulated.[97] The high stability SIR initially studied is a SIR impregnated with a 2N solution of bis(2-ethylhexyl) hydrogen phosphate (DEHPA) (Figure 4.3), then encapsulated with a 2% aqueous solution of glycidyl methacrylate (Figure 4.4) / N,N' methylene bisacrylamide (Figure 4.5) in a 75/25 ratio.[97]

The purpose of this research is to study the effect of polymer support porosity on high stability SIRs. Metal ion studies were done at 24 hour, 2 hour, and 15 minute for six contact/regeneration cycles. The results were graphed and compared. The polymer support was synthesized at 25%, 50%, 60%, and 75% porosity of the MR beads and as a microporous gel to determine the effect on the contact/regeneration cycles. Finally, the method was studied at 50% porosity with other extractants to see if the technique could be applied universally or if certain parameters were required for successful encapsulation.

Experimental

Synthesis of Copolymer Beads

The MR beads (bead size 75µm-150µm) were made by suspension polymerization with the desired porosity by altering the amount of porogen added in the process. The copolymer consists of the crosslinking agent divinylbenzene (DVB) to give a crosslinking level of 25%, the monomers vinylbenzyl chloride (VBC) (Figure 4.6) and methyl methacrylate (MMA) (Figure 4.7) in a 1:1 ratio and a free radical initiator. The high crosslinking level was chosen for the strong, rigid structure that provides an insignificant amount of swelling. The microporous (gel) beads were the same as the MR beads with the obvious exception of porosity.

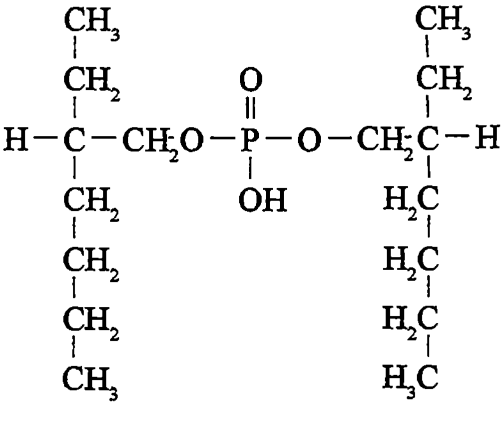


Figure 4.3. Bis(2-ethylhexyl)hydrogen phosphate (DEHPA)

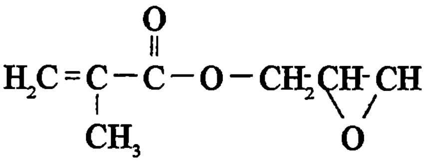
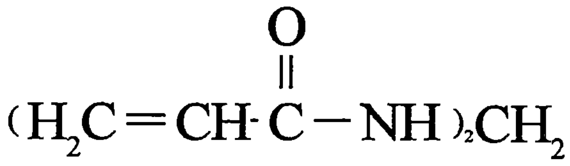


Figure 4.4. Glycidyl methacrylate



$$(H_2C=CH-\overset{O}{\overset{\|}{C}}-NH)_2CH_2$$

Figure 4.5. N,N'-methylene bisacrylamide

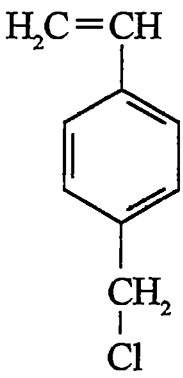
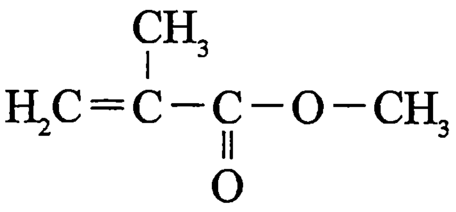


Figure 4.6. Vinylbenzyl chloride (VBC)



$$H_2C=\overset{\overset{\displaystyle CH_3}{|}}{C}-\underset{\underset{\displaystyle O}{\|}}{C}-O-CH_3$$

Figure 4.7. Methyl methacrylate (MMA)

Surface Modification of the Beads[97]

The beads (10g) are surface modified in preparation for the encapsulation via two reactions. The first reaction is a surface Arbusov (Figure 4.8). Triethyl phosphite in excess (100 mL) is brought to reflux in a 250 mL round bottom flask equipped with an overhead stirrer, condenser and stopper. The beads are added to the refluxing solution while stirring and allowed to react for 40 min. Removing the heat and placing the round bottom flask in an ice water bath stops the reaction. Once cooled, the triethyl phosphite is removed and the beads are washed twice with acetone, four times with toluene, and dried overnight in a 60°C oven. After drying, the beads are analyzed by phosphorus capacity to ensure the reaction has occurred. The values range from 0.3-0.7 mmol/g of phosphorus depending on the type of support being used.

The second reaction is a Wadsworth-Emmons reaction (Figure 4.9). The beads are placed in a 250 mL round bottom flask equipped with an overhead stirrer, gas inlet and addition funnel. The beads are swelled for 1 hour at room temperature with 100 mL N,N'-dimethylformamide (DMF). The round bottom flask is then placed in an ice water bath for 1 hour while under a nitrogen sweep. Phenyllithium (50 mL of 1.8 N solution in cyclohexane-ether) was added to the addition funnel via syringe and added dropwise slowly to the stirring beads. The reaction was allowed to go at room temperature for 24 hours. The beads were washed with 100 mL of dioxane, toluene, and water and then placed in a 60°C oven overnight. The beads are then analyzed for a drop in the phosphorus capacity (0.1-0.4 mmol/g) depending on the type of support being analyzed. The drop confirms the formation of double bonds on the surface, which acts as an anchor for the coating.[97]

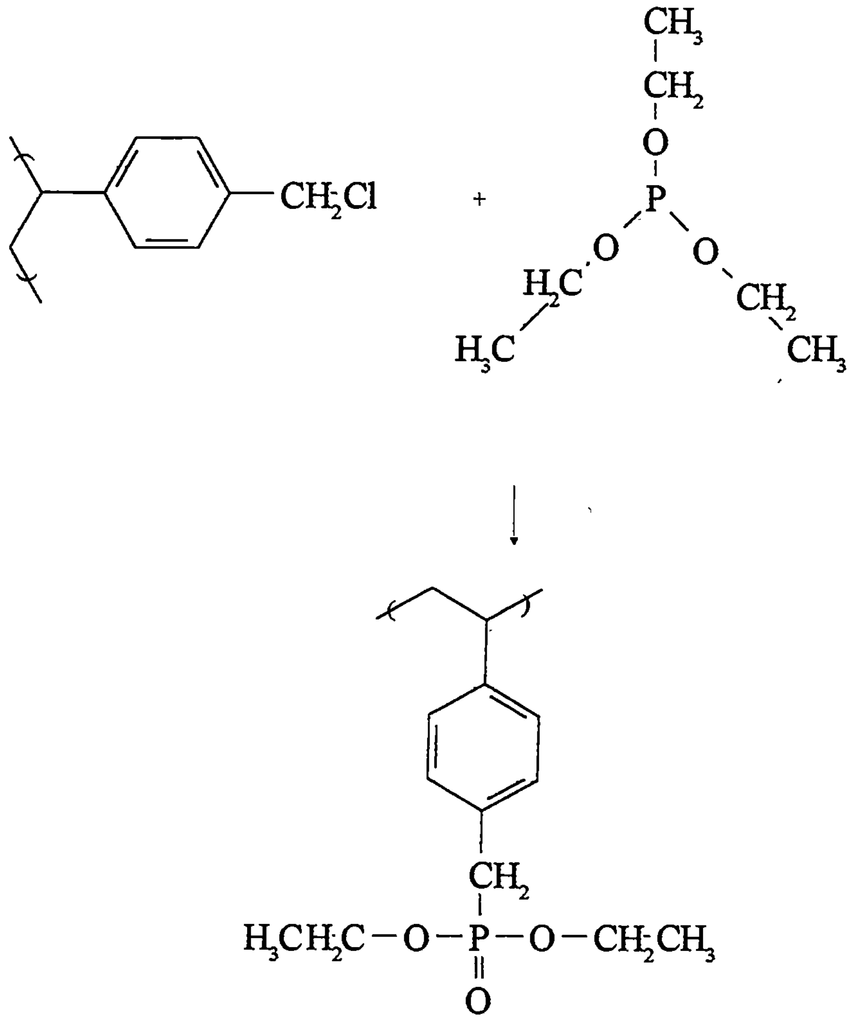


Figure 4.8. Arbusov reaction

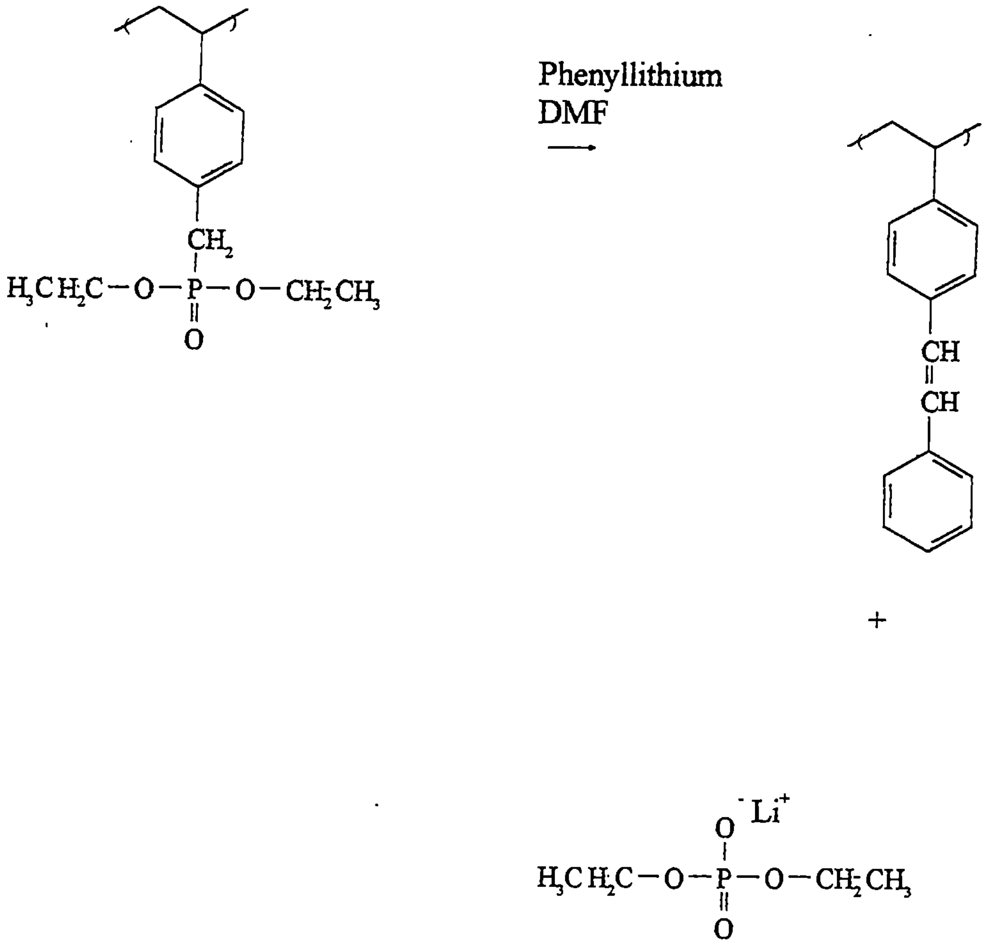


Figure 4.9. Wadsworth-Emmons reaction

Solvent Impregnation[97]

The modified beads (3.2g) are swelled in 25 mL of 2N extractant/solvent for 17 hours. The excess solution is removed from the beads and placed in a 50 mL one-neck round bottom flask. The flask is then placed on a rotary evaporator and the beads are dried at 50°C. The amount of extractant present in the beads after being dried is determined by elemental analysis depending on the type of extractant being used. The extractant most used for the research is DEHPA. The phosphorus capacity after impregnation for this extractant was usually within the range of 1.9-2.2 mmol/g

Encapsulation[97]

The SIR beads (3.2g) are placed in a 250 mL round bottom flask equipped with a condenser, an overhead stirrer (set at a stir speed of 262 rpm), a stir paddle of a size of 4.5 cm, a thermometer, and gas inlet/outlet. A 2% aqueous solution of glycidyl methacrylate (1.55g)/ N,N'-methylenebisacrylamide (0.51g) is made in a 150 mL beaker using 99.94g of nanopure water with 0.06g(3% of monomer phase) of potassium persulfate as an initiator. The beaker is placed in an ice water bath and stirred until all the reactants are dissolved. The solution is sparged with nitrogen for ten minutes, added to the beads, and heated to 50°C for 8 hours while under a nitrogen sweep. After completion, the beads are washed four times with nanopure water and then placed on a 200 mesh sieve and washed with nanopure water. The beads are then placed in a 60°C oven overnight. After drying, 40 mL of nanopure water is added to the beads and placed on a shaker for 17 hours. The beads are placed on a 200 mesh sieve and washed with nanopure water. The beads are dried in a 60°C oven overnight. The beads are characterized by nitrogen capacity for the coating and by phosphorus capacity to ensure no loss of extractant. The nitrogen capacity is usually in the range of 0.9-1.2 mmol/g, whereas the phosphorus capacity is in the range of 1.7-2.0 mmol/g.

Modification of Encapsulation

The encapsulation procedure was modified due to the SIR beads adhering to the sides of the round bottom flask preventing the encapsulation of the SIR. The modified method solves the problem of adhesion of the SIR to the sides of the round bottom flask. A 2% aqueous solution of glycidyl methacrylate (1.55g)/ N,N'-methylenebisacrylamide (0.51g) made with 99.94 g of nanopure water without the initiator is placed in a 250 mL round bottom equipped with a condenser, an overhead stirrer (set at a stir speed of 262 rpm), a stir paddle of a size of 4.5 cm, a thermometer, and gas inlet/outlet. The solution is stirred until all the reactants are dissolved, while in an ice water bath. Once the reactants are dissolved the initiator (0.06g potassium persulfate) is added and stirred until dissolved. The solution is then sparged with nitrogen for ten minutes. The beads are added to the stirring solution and heated to 50°C for 8 hours while under a nitrogen sweep. After completion, the beads are washed four times with nanopure water, placed on a 200 mesh sieve and washed with nanopure water. The beads are dried in a 60°C oven overnight. After drying, 40 mL of nanopure water is added to the beads and placed on a shaker for 17 hours. The beads are placed on a 200 mesh sieve, washed with nanopure water, and dried in a 60°C oven overnight. After drying, the beads are characterized by nitrogen capacity for the coating and phosphorus capacity to ensure no loss of extractant. The nitrogen capacity is usually in the range of 0.9-1.2 mmol/g, whereas the phosphorus capacity is in the range of 1.7-2.0 mmol/g.

Metal Ion Studies

The SIR beads and the coated SIR beads are studied for their ability to complex Cu(II) in pH 8.4 buffer. The metal ion studies are carried out by general procedure as described in Chapter 5. The beads go through a cycle of contact/regeneration six times. The contact solution is 10 mL of the Cu(II) in pH 8.4 buffer for a specific contact time, followed by a 1 hour regeneration with 10 mL of 1 N HNO_3 and shaking for 15 min in pH 8.4 NH_3/NH_4NO_3. The data is plotted and compared. After the last regeneration the beads are shaken with nanopure water for 15 min and dried in a 60°C oven overnight. After drying, the beads are reanalyzed by nitrogen and phosphorus elemental analysis to determine if there is any loss of extractant or of coating. This will be discussed in more detail further in the chapter.

Kinetic Studies

The SIR beads and the coated SIR beads were contacted with the copper solution in pH 8.4 buffer for various times to determine the amount of time necessary to get complete complexation. Results at 24 hours are reported in Table 4.1.[97] The beads underwent a cycle of contact/regeneration with the copper solution a total of five times. The data was then graphed for easier analysis (Figure 4.10).[97] As seen by the graph the coated beads have a consistent absorbance of over 90% complexed, whereas the uncoated beads goes from over 90% complexing with the first cycle to 20% complexed with the

Table 4.1. Percent Cu(II) complexed from pH 8.4 buffer over 24 hour contact period

CONTACT	RESIN A UNCOATED[97]	RESIN B COATED[97]
1	98%	98%
2	21%	98%
3	10%	98%
4	[A]	98%
5	[A]	98%

[A] The uncoated resin was discontinued after the third cycle due to the significant drop in the percent complexation

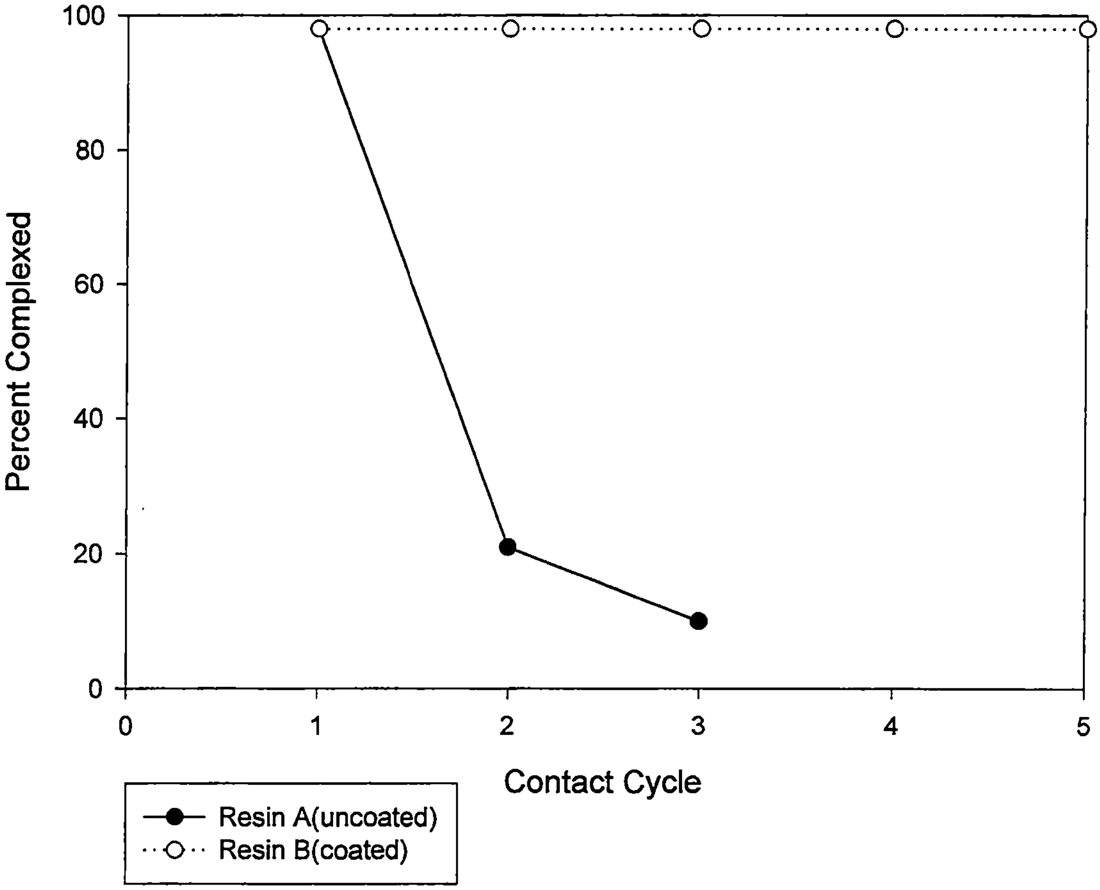


Figure 4.10. Graph of data from 24 hour contact period from Table 4.1

second cycle and the final cycle for the uncoated SIR complexed <20%. The loss of complexing ability of the uncoated beads seems to be due to loss of extractant. This appears to confirm the theory that a semi-permeable membrane can help maintain the longevity of the SIR. Even though the coated beads appear to maintain complexing ability at 24 hours, the test is to see if the contact time can be lowered and still maintain the high complexing ability. The beads used for the remaining studies were uncoated SIRs (SS-03-011 and SS-03-136) and coated SIR (SS-03-013 and SS-03-154). Two different resins of each type were used to demonstrate reproducibility. The contact time was dropped to 2 hours to study the effect on the uncoated and coated SIR beads. The data from this study is given in Table 4.2. For easier analysis and comparison to the 24 hour study the data was graphed (Figure 4.11 and Figure 4.12). The coated resin complexed consistently over 90% of the copper. The uncoated resin complexes >90% over the first cycles but at the second, third, and fourth cycle the amount complexed falls to about 50%. Unlike the 24 hour study, the uncoated SIR can go through the full six cycles even though the fifth and sixth cycle give a complexing of only 10-20%. The contact time appears to affect the rate at which the extractant is lost from the uncoated SIR even though it does not affect the complexing ability of the coated SIR. The final contact time studied was at 15 minutes (Table 4.3). As seen before, the graph (Figure 4.13 and Figure 4.14) shows the coated SIR gives over 90% complexed consistently over the six cycles with the exception of SS-03-013 at the sixth cycle. The reason behind this unclear. As seen with the 2 hour contact, the uncoated SIR maintains a complexing ability over 90% for the first three cycles. At the fourth cycle the percent complexed

Table 4.2. Percent Cu(II) complexed from pH 8.4 buffer over 2 hour contact period

CONTACT	SS-03-011[A] UNCOATED	SS-03-013[B] COATED	SS-03-136[C] UNCOATED	SS-03-154[D] COATED
1	100.0%	93.3%	95.9%	92.5%
2	97.4%	97.4%	56.9%	95.9%
3	52.7%	93.8%	57.3%	96.5%
4	51.0%	93.8%	41.0%	96.1%
5	10.5%	96.3%	22.0%	97.6%
6	7.7%	96.3%	18.4%	97.6%

[A] Phosphorus Capacity = 2.22mmol/g

[B] Phosphorus Capacity = 2.22mmol/g Nitrogen Capacity = 1.01 mmol/g

[C] Phosphorus Capacity = 2.36 mmol/g

[D] Phosphorus Capacity = 1.51 mmol/g Nitrogen Capacity = 0.91 mmol/g

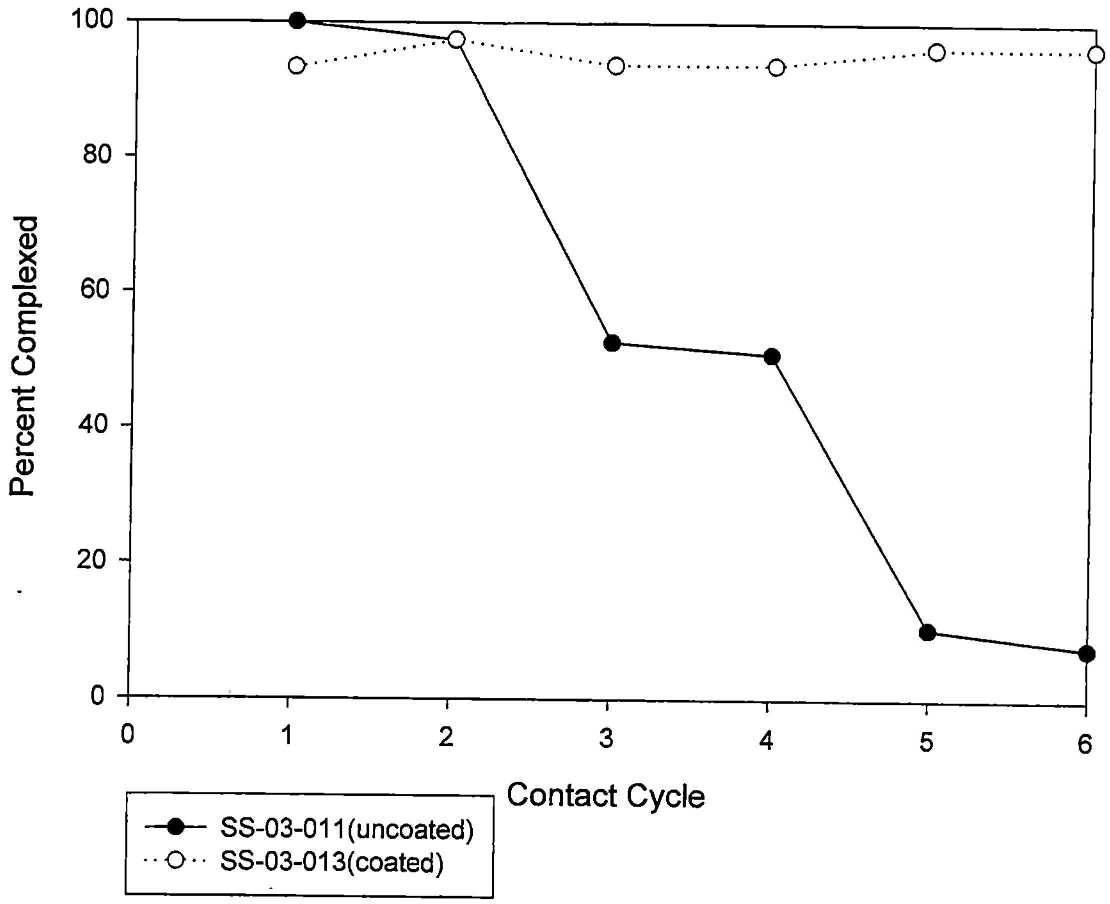


Figure 4.11. Graph of data from 2 hour contact period from Table 4.2

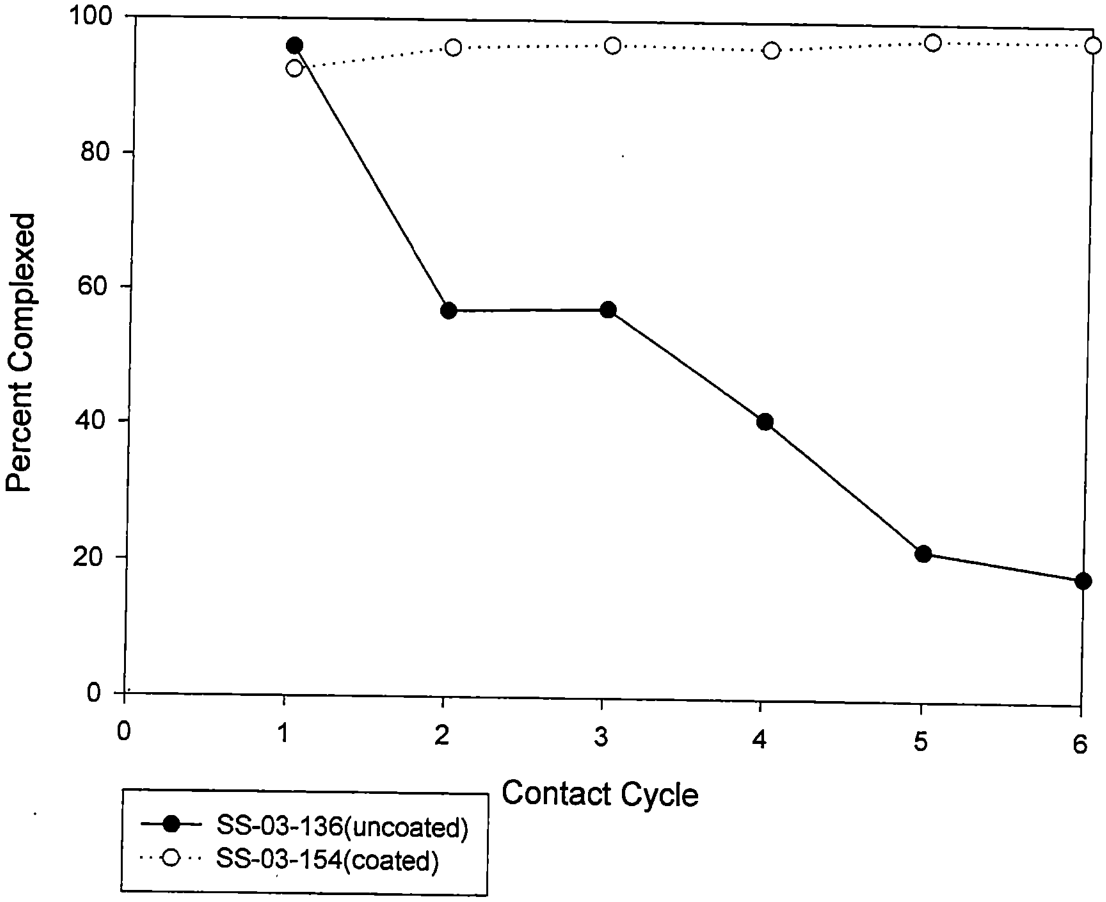


Figure 4.12. Graph of data from 2 hour contact period from Table 4.2

Table 4.3. Percent Cu(II) complexed from pH 8.4 buffer over 15 min contact period

CONTACT	SS-03-011[A] UNCOATED	SS-03-013[B] COATED	SS-03-136[C] UNCOATED	SS-03-154[D] COATED
1	99.5%	90.9%	97.7%	94.0%
2	98.7%	93.9%	95.2%	97.7%
3	97.7%	94.1%	93.3%	96.9%
4	94.0%	93.2%	32.5%	95.7%
5	28.8%	96.0%	9.9%	95.7%
6	36.3%	57.6%	11.1%	94.1%

[A] Phosphorus Capacity = 2.22 mmol/g

[B] Phosphorus Capacity = 1.895 mmol/g Nitrogen Capacity = 1.01 mmol/g

[C] Phosphorus Capacity = 2.36 mmol/g

[D] Phosphorus Capacity = 1.51 mmol/g Nitrogen Capacity = 0.91 mmol/g

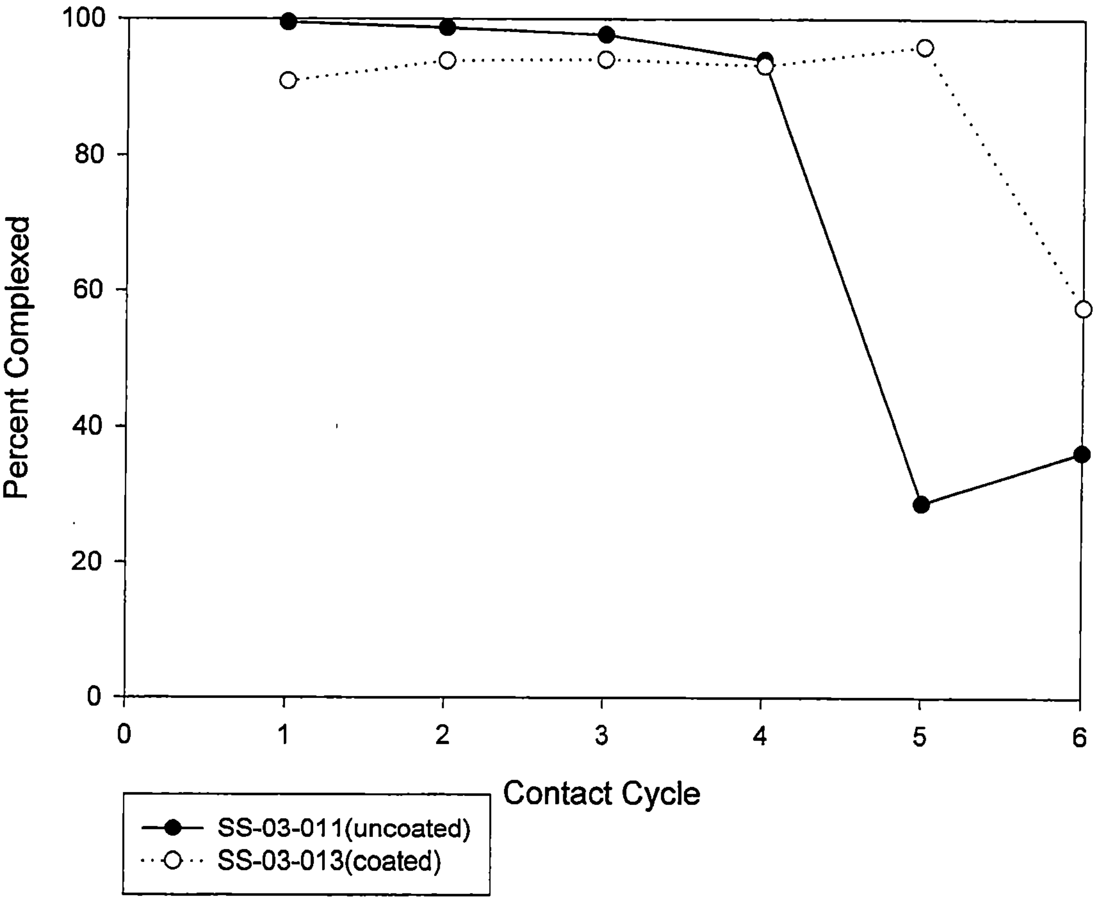


Figure 4.13. Graph of data from 15 min contact period from Table 4.3

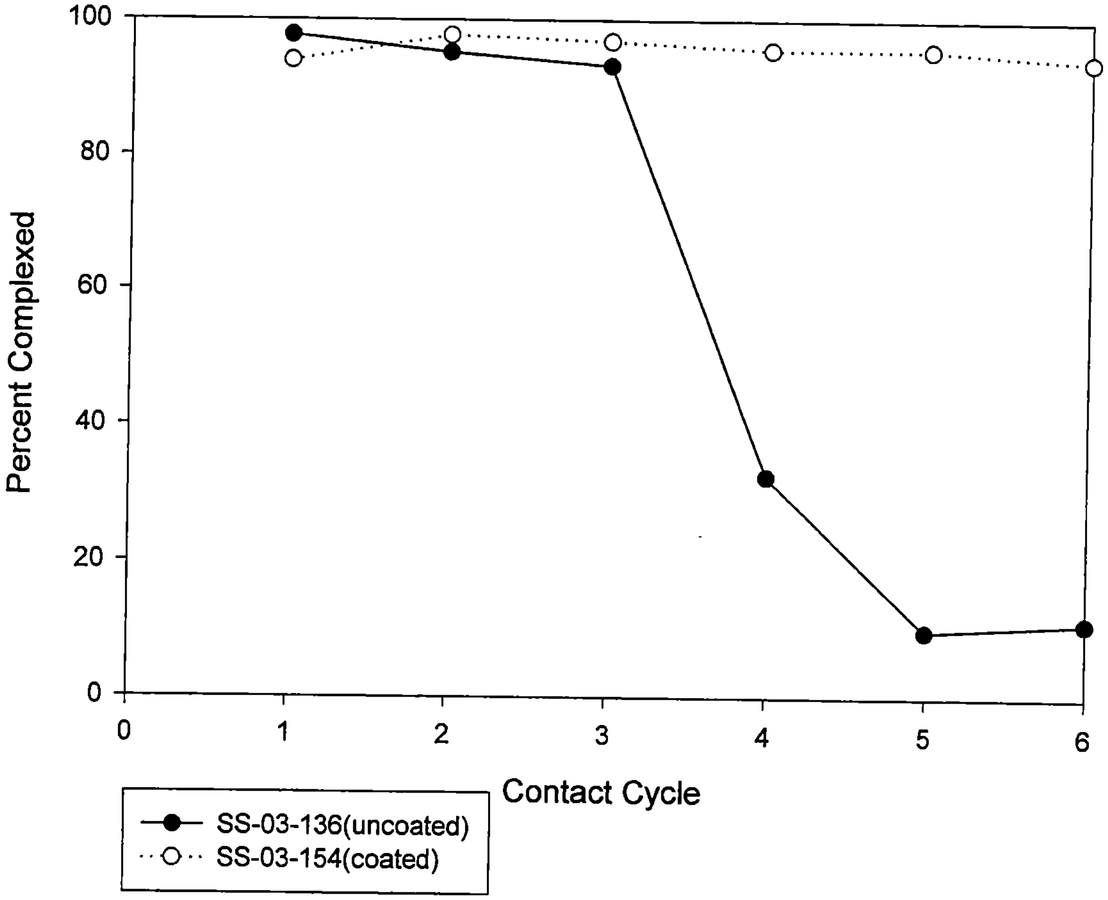


Figure 4.14. Graph of data from 15 min contact period from Table 4.3

drops significantly to 32.5% for SS-03-136 and 26.8% for SS-03-011 at the fifth cycle. The final contacts maintain a low level of complexation. This seems to support the theory of extractant loss from the uncoated SIR over the contact/regeneration cycle. The contact time appears to affect the uncoated SIR but not the coated SIR. This shows there is rapid diffusion of the metal into the coated SIR.

After each regeneration, regardless of the contact time, there appears to be oil droplets in the 1 N HNO_3 of the uncoated SIR. Attempts were made to isolate the oil droplets for analysis to determine if it was the extractant being lost. The only method to isolate the oil droplets in a large enough amount for analysis was to acidify the contact solution with concentrated HNO_3. The oil was analyzed by phosphorus capacity but a value of 0.1 mmol/g was obtained. The droplet was analyzed by IR and phosphorus NMR but the results showed no distinct presence of phosphorus. After the final cycle, the resins were shaken with nanopure water to remove any nitric acid present in the matrices of the uncoated and coated SIRs. The resins were placed in a 60°C oven overnight in order to be dry for analysis to determine the loss of extractant and whether or not the coating remained intact. The data from this analysis is in Table 4.4. Interestingly, there is a loss of only about 0.2-0.5 mmol/g of the extractant. This does not support the theory that the loss of extractant is the cause of the lowering in complexation for the uncoated SIR. The nitrogen capacity of the coated SIR demonstrates that the coating remains intact throughout the contact/regeneration cycles even though the nitrogen capacity is increasing by 0.2-0.6 mmol/g. This could be due to a small amount of HNO_3 still present in the polymer matrix. Further studies need to be done to determine the

Table 4.4. Data from reanalysis of uncoated and coated SIRs after the 6 contact/regeneration cycles

RESIN	PHOSPHORUS CAPACITY BEFORE CYCLE (mmol/g)	PHOSPHORUS CAPACITY AFTER CYCLE (mmol/g)	NITROGEN CAPACITY BEFORE CYCLE (mmol/g)	NITROGEN CAPACITY AFTER CYCLE (mmol/g)
SS-03-011 (uncoated)	2.22	1.90		
SS-03-013 (coated)	1.90	1.42	1.01	1.66
SS-03-136 (uncoated)	2.36	2.00		
SS-03-154 (coated)	1.51	1.93	0.91	1.45

reason for the loss in complexation of the uncoated resin, even though the phosphorus capacity has not been reduced a large amount. The composition of the oil droplets needs to be determined conclusively. At this time, the analysis attempted to determine the composition has been unsuccessful.

Porosity Studies

The porosity of the polymer support was varied to determine the affect of porosity on the uncoated and coated SIRs. The porosities studied were 25%, 50% (standard polymer support for all other studies), 60%, 75% MRs and gel beads. The first attempt to alter the porosity was with the 25% polymer support. The beads were surface modified and solvent impregnated by standard methods. The data from the analysis of the resin is given in Table 4.5. The decrease in porosity does not greatly affect the ability to impregnate with the extractant or to coat the SIR (SS-03-011, uncoated, phosphorus capacity = 2.22 mmol/g; SS-04-058, uncoated, phosphorus capacity = 1.81 mmol/g). The uncoated and coated SIRs were used in the standard metal ion study of the six contact/regeneration cycle. The contact time was 2 hours (Table 4.6) and the graph (Figure 4.15) shows the same results as demonstrated with the 50% porous polymer supports used in the kinetics studies. The regardless of porosity coated SIR gives a complexation of >90% whereas, the uncoated SIR has a complexation of >90% for the first three cycles but drops to <40% for the remaining contacts. The contact time was then changed to 15 minutes (Table 4.7) and as before the graph (Figure 4.16) demonstrates the same amount of complexation as seen by the polymer support with a porosity of 50% with the exception of the uncoated beads. The coated beads behave as

Table 4.5. Data from analysis of beads with a porosity of 25%

ELEMENTAL ANALYSIS	**SS-04-058[A] (uncoated)**	**SS-04-071[B] (coated)**	**SS-04-133[C] (uncoated)**	**SS-04-146[D] (coated)**
Phosphorus Capacity (mmol/g)	1.81	1.21	1.78	1.44
Nitrogen Capacity (mmol/g)		1.52		1.51

[A] Phosphorus Capacity after 6 cycles = 0.95 mmol/g

[B] Phosphorus Capacity after 6 cycles = 1.14 mmol/g

Nitrogen Capacity after 6 cycles = 2.01 mmol/g

[C] Phosphorus Capacity after 6 cycles = 1.06 mmol/g

[D] Phosphorus Capacity after 6 cycles = 1.27 mmol/g

Nitrogen Capacity after 6 cycles = 1.63 mmol/g

Table 4.6. Percent Cu(II) complexed from pH 8.4 buffer over 2 hour contact period

CONTACT	SS-04-133 UNCOATED	SS-04-146 COATED
1	96.1%	100.0%
2	98.3%	98.3%
3	98.3%	98.3%
4	36.3%	96.4%
5	15.1%	96.2%
6	1.5%	94.5%

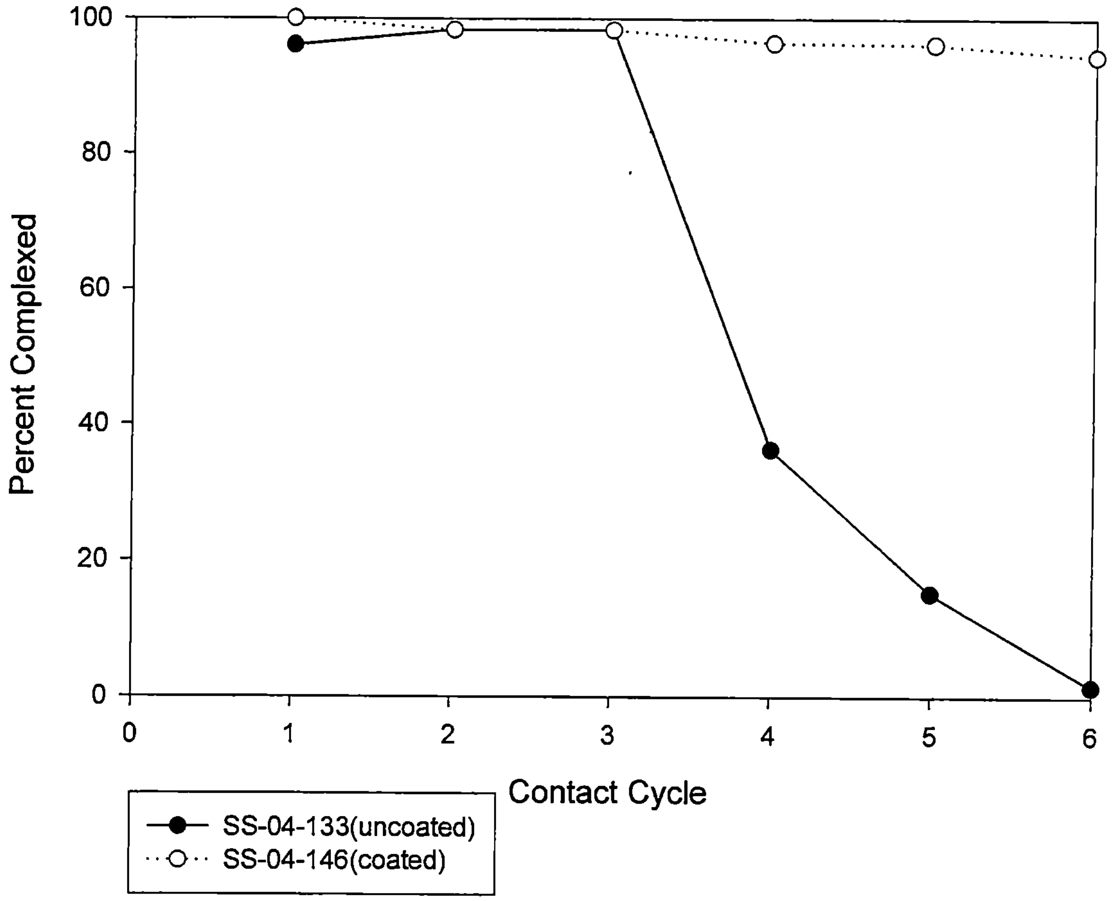


Figure 4.15. Graph of data from 2 hour contact period from Table 4.6

Table 4.7. Percent Cu(II) complexed from pH 8.4 buffer over 15 min contact period

CONTACT	**SS-04-133 UNCOATED**	**SS-04-146 COATED**
1	94.5%	93.3%
2	74.2%	94.9%
3	49.4%	95.2%
4	30.9%	94.1%
5	12.3%	94.1%
6	11.2%	94.1%

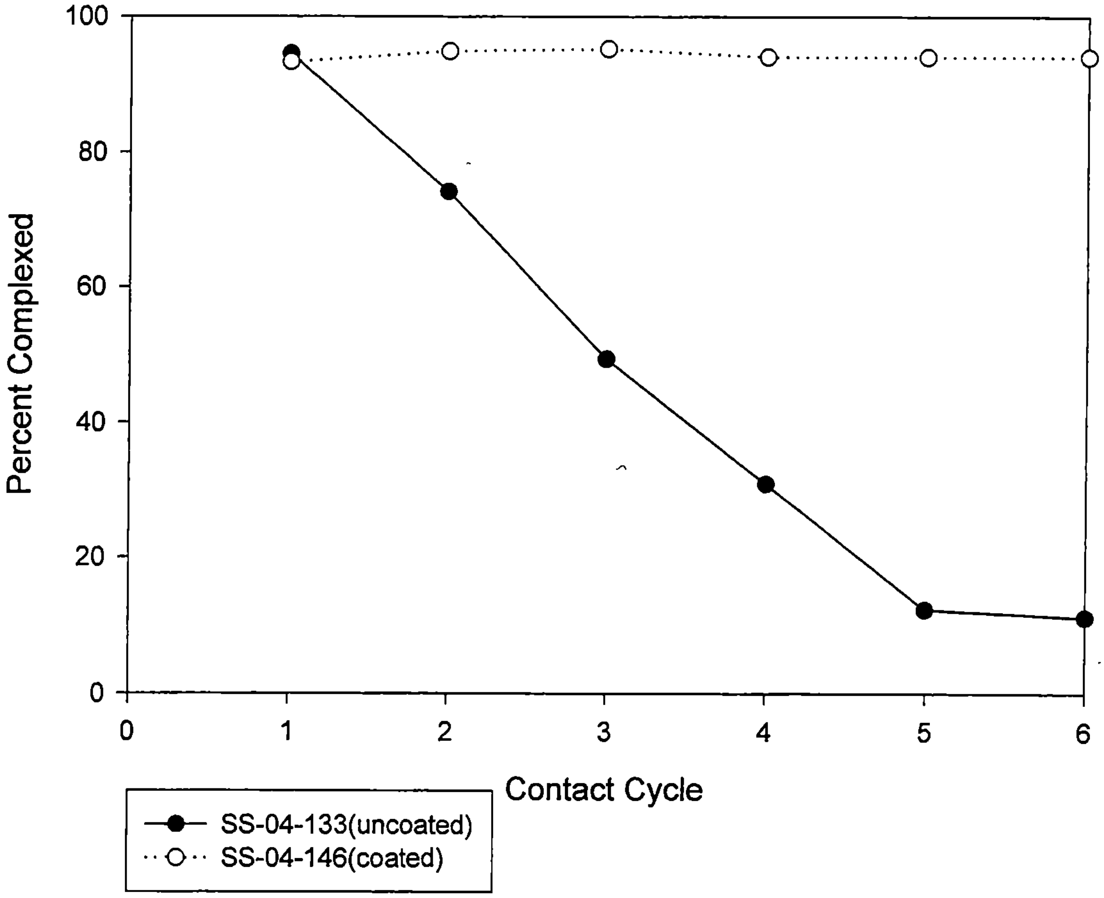


Figure 4.16. Graph of data from 15 min contact period from Table 4.7

expected with a complexation of >90% whereas the uncoated begins to have a loss of complexation after the first cycle which is a change from the trends seen previously with the 2 hour contact. The reason for the sudden decrease in complexing ability of the uncoated SIR may be the short contact time coupled with the decreased porosity. However, this theory seems not possible due to the first contact compexing >90%. Another possible explanation could be the decrease in porosity allows for more difficulty for the metal ion to diffuse through the polymer matrix. The reason behind the decrease in complexing ability is unclear and needs to be studied further for a concrete reason to be found for an explanation. The decrease in porosity has no affect on the complexing ability of the coated SIRs. The next attempt was to increase the porosity of the support to 75%. This was attempted by standard suspension polymerization of MR beads. Unfortunately, no beads were synthesized. The reaction was attempted again for reproducibility and the same results occurred. The porosity was too high to make a stable polymer support bead. The next attempt was to make a bead with a porosity of 60%. The synthesis worked to make beads, but once the beads were subjected to the surface Arbusov the beads fell apart into a powder. The modification was attempted various times but the powdering of the beads continued to occur. A porosity of 50% appears to be the highest porosity that can be synthesized for workable reactions.

Gel beads were also synthesized to determine if porosity is necessary to the SIRs. The beads would undergo the Arbusov reaction but would not form double bonds through the Wadsworth-Emmons reaction. The amount of phenyllithium was doubled as was the time, but the reaction would still not occur. The beads after analysis of each reaction, including the reactions with the variables changed, showed no change in phosphorus capacity (Table 4.8). Even with the phosphorus capacities remaining unchanged after the Wadsworth-Emmons reaction, the beads were impregnated and encapsulation was attempted (Table 4.9). The SIR was synthesized, but only a small amount of extractant done, in order to determine the cause of the inability to modify the surface and the inability to encapsulate the SIR.

Other Extractants

The idea of encapsulating other extractants into the 50% porous polymer support was studied extensively to see if the coating procedure can be used universally for other extractants. The first extractant attempted was tricaprylylmethyl ammonium chloride (Aliquat 336®) (Figure 4.17). The extractant was too viscous even after decreasing the normality to 0.5. Another extractant attempted was 2,2' dipyridyl (Figure 4.18). The problem that occurred with the extractant was the fact that its physical state is a solid. The extractant dissolved in toluene but once in contact with the beads to swell for 17 hours the extractant precipitated making it impossible to use as an SIR. Two other extractants were attempted; 4-sec-butyl-2-(α-methylbenzyl) phenol (BAMBP) (Figure 4.19) and caproic acid (Figure 4.20). Of the two extractants the only one that could be coated was the caproic acid (nitrogen capacity = 1.65 mmol/g). The problem with the caproic acid is there is no distinct analysis to confirm the amount, if any, present in the SIR and the encapsulated SIR. Acid capacity analysis was attempted but the beads completely powdered and could not be separated from the solution even with centrifuging.

Table 4.8. Data from analysis of attempts to modify gel beads

RESIN	PREVIOUS RESIN	REACTION	PHOSPHORUS CAPACITY (mmol/g)
SS-04-116	SS-04-109	Arbusov	0.47
SS-04-122	SS-04-116	Wadsworth-Emmons	0.47
SS-04-156	SS-04-122	2nd Wadsworth-Emmons	0.52
SS-04-186	SS-04-109	Arbusov	0.48
SS-04-193	SS-04-186	Wadsworth-Emmons	0.45
SS-05-107	SS-04-109	Arbusov	0.47
SS-05-127	SS-05-107	Wadsworth-Emmons	0.45
SS-05-147	SS-05-127	2nd Wadsworth-Emmons	*
SS-05-159	SS-05-147	3rd Wadsworth-Emmons	0.45
SS-05-182	SS-05-159	4th Wadsworth-Emmons (twice the amount of phenyllithium)	0.52
SS-05-192	SS-05-159	Arbusov (contact time changed to 2 hours)	0.83
SS-05-198	SS-05-192	Wadsworth-Emmons	0.94

* Phenyl lithium was inactive

Table 4.9. Data from the analysis of the formation of SIRs and encapsulated SIRs from gel beads

RESIN	**PREVIOUS RESIN**	**SYNTHESIS TYPE**	**PHOSPHORUS CAPACITY (mmol/g)**	**NITROGEN CAPACITY (mmol/g)**
SS-04-212	SS-04-193	SIR	1.15	
SS-04-226	SS-04-212	Encapsulation	*	*
SS-04-231	SS-04-193	SIR	1.13	
SS-04-238	SS-04-231	Encapsulation	*	*
SS-04-243	SS-04-193	SIR	1.24	
SS-05-095	SS-04-243	Encapsulation	*	*
SS-05-194	SS-05-182	SIR	1.15	
SS-05-207	SS-05-194	Encapsulation	*	*
SS-05-214	SS-05-198	SIR	1.38	
SS-05-220	SS-05-214	Encapsulation[A]	0.58	0.72
SS-05-229	SS-04-109	SIR[B]	0.78	
SS-04-212	SS-04-212	Encapsulation	*	*

* coating did not work

[A] the encapsulation was attempted after shaking the SIR with 75% ethanol for 4 secs.

[B] the support was unmodified before forming the SIR

$$CH_3N[(CH_2)_7CH_3]_3Cl$$

Figure 4.17. Aliquat 336®

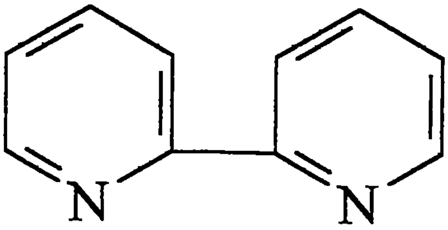


Figure 4.18. 2,2'-dipyridyl

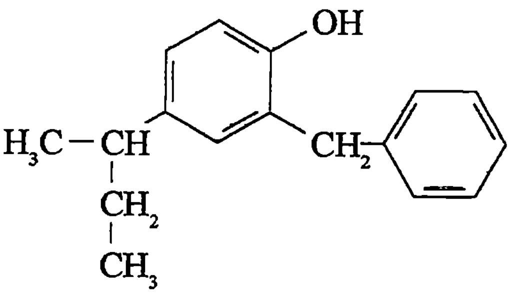


Figure 4.19. BAMBP

$$CH_3(CH_2)_4CO_2H$$

Figure 4.20. Caproic Acid

Controls have been done to determine whether the caproic acid SIRs can complex metal ions. The beads were first contacted with Zn(II), but they did not complex the metal ion. Due to a limited amount of resin, the remaining controls were done with liquid caproic acid at different normalities (Table 4.10). The only metal that seems to be complexed by the caproic acid is Fe(III) with a counter ion of chloride. This discovery needs to be further studied before any conclusive decision can be made concerning the use of caproic acid as a viable extractant for this type of procedure.

Conclusions

The combination of the two types of separation methods can be done successfully with encapsulated SIRs. The contact time for the SIR and encapsulated SIR does not affect the complexing ability of the resins. The encapsulated SIR removes>90% of Cu(II) regardless of the contact time. This shows the semi-permeable membrane has fast diffusion for the metal ion while keeping the extractant within the bead. Both 25% and 50% macroporous supports were applicable to this procedure. The complexing abilities of the encapsulated SIRs with both porosities were very similar. In order to have a maximum complexation with the 25% macroporous SIRs, the contact period needs to be increased. Other extractants need to be investigated in order to determine which can be solvent impregnated and then encapsulated.

Table 4.10. Controls for caproic acid with a 2 hour contact period

SAMPLE	**Li^+ in pH 10 SOLUTION**	**$Cu(NO_3)_2$ in pH 6 ACETATE BUFFER**	**$CuCl_2$ in pH 6 ACETATE BUFFER**	**$FeCl_3$ in NANOPURE WATER**
2N Caproic Acid	1.8%			
1N Caproic Acid		2.7%	0.0%	100.0%
0.5N Caproic Acid/0.5N TBP			0.0%	

CHAPTER 5

EXPERIMENTAL PROCEDURES

The chemicals used for all procedures were obtained commercially and used as received unless otherwise noted. The glassware used was Class A glassware. Reactions requiring a specific temperature were regulated with Therm-o-watch temperature control devices (Instruments for Research and Industry).

Synthesis

Copolymer Synthesis[98]

By using suspension polymerization, copolymer beads can be prepared as either gels or MRs. The amount of divinylbenzene can be varied to give a desired crosslinking level. An example of the procedure for copolymer synthesis by suspension polymerization to make 150 g poly(vinylbenzyl chloride) beads with a crosslinking level of 2% divinylbenzene is discussed.

The suspension polymerization is made up of two phases. An organic phase contains the monomer, crosslinking agent and the initiator while an aqueous phase contains water, a suspending agent and stabilizer. The organic phase is comprised of 143.1 g (0.938 mol) vinylbenzyl chloride (VBC), 5.4 g (0.0754 mol) divinylbenzene (at 55.4% purity) and 1.5 g (1% of solution) benzoyl peroxide, mixed thoroughly in a stoppered 250 erlenmeyer flask. The aqueous phase consists of 1.44 g Pharmagel dissolved in 158.3 mL water by heating to 50°C. Another solution consisting of 17.9 g polydiallyldimethylammonium chloride (PADMAC; Calgon Corp.) and 9.5 g (0.1536 mol) boric acid, dissolved in 316.5 mL water. The two aqueous solutions were combined and mixed thoroughly before adjusting the pH of the solution to 10.3 by adding 50% NaOH solution. Both phases were sparged with nitrogen for 10 minutes. The aqueous phase was poured into a 1L three neck round bottom flask equipped with a condenser, stir paddle and shaft attached to an overhead digital stirrer, nitrogen inlet and thermometer. The stir shaft was adjusted so the paddle was just immersed in the aqueous phase. The organic phase was added and the solution was stirred for 2 minutes, at the end of which time no separation of phases should occur. To obtain a specific size of beads, the stir speed was set accordingly. The reaction was slowly raised to 80°C over a 2 hour period (7°C every 15 min) with a heat lamp and a therm-o-watch. This temperature was maintained for 10 hours while under a continuous nitrogen sweep. After the 10 hours, 100 mL of distilled water is added and the mixture is refluxed for 2 hours. The excess solution is removed and the beads are washed once with 10^{-4} N HCl and then three times with distilled water. The beads are extracted in a soxhlet with toluene for 17 hours to remove any remaining oligomers, and oven dried at 60°C until dry. The beads are then sieved to obtain the desired size using U.S standard screens. Macroporous beads (MR) can be obtained by a similar procedure with the exception that 50% of the organic phase is replaced by 4-methyl-2-pentanol as the diluent.

Functionalized Foams

Synthesis of Monophosphonic Acid[99]

For every 1 gram of foam used, 100ml of triisopropyl phosphite was added to the reactor. A vacuum was pulled for 10 minutes to remove all the air from the foam. The reaction was then left to reflux for 17 hours. After refluxing, the resin was washed twice with acetone and twice with 0.1 N HCl for 15 minutes each. An excess of concentrated hydrochloric acid was added and set to reflux for 24 hours. The 15% cross linked 75/25 poly(VBC)/polystyrene and the 8% cross linked 75/25 poly(VBC)/polystyrene were both used to synthesize this resin.

Synthesis of Diphosphonic Acid[100]

To a 500 ml round bottom flask, 68.66 g of tetraisopropyl methylene diphosphonate(MDA) and 300 ml of dry toluene was added. 5.62 g (0.244 mol) of sodium metal was added to the solution under a nitrogen sweep while stirring. This was left to stir overnight under nitrogen. 3.2863 g (0.0161 mol) of the foam was placed in a reactor under a nitrogen sweep. The deprotonated MDA solution was transferred to the reactor through a double tipped needle . The reaction was allowed to reflux for 24 hours under nitrogen. After the reaction was complete, the foam was washed twice with ethanol and twice with distilled water for 15 minutes each. Hydrolysis of the ligands was carried out by adding an excess of concentrated hydrochloric acid to the foam and refluxing for 24 hours. The 15% cross linked 75/25 poly(VBC)/polystyrene and the 8% cross linked 75/25 poly(VBC)/polystyrene were both used to synthesize this resin.

Synthesis of α-ketophosphonic Acid[80]

To 5.1353 g (0.0252 mol) of the foam, 350 ml of dimethyl sulfoxide was added in a reactor. The reaction was allowed to reflux for 8 hours after adding 34.57 g (0.411 mol) of sodium bicarbonate. The washing cycle after the reaction was three times with ethanol and twice with hot distilled water for 15 minutes each. The foam was then swelled in 200 ml of dioxane for thirty minutes. After thirty minutes, 150 ml of 3N nitric acid was added and the reaction was set to reflux for 17 hours. Resin was washed twice with dioxane. Then 100 ml of dioxane and 260 ml of 30% hydrogen peroxide was added to the foam and it was refluxed for 17 hours. The resin was washed four times with acetone and soxhlet extracted with dioxane for 17 hours to remove all the water. The foam was dried in the vacuum oven for 4 hours at 40°C, placed back into a dry reactor and 300 ml of thionyl chloride added under a nitrogen sweep, then refluxed for 17 hours. The foam was washed four times with toluene for 15 minutes each. 300 ml of triethyl phosphite was added and refluxed for 17 hours. Washing afterwards included twice with acetone and twice with dilute hydrochloric acid (4 wt %) for 15 minutes each. Hydrolysis was done by adding an excess of concentrated hydrochloric acid and refluxing for 24 hours. The 15% cross linked 75/25 poly(VBC)/polystyrene and the 8% cross linked 75/25 poly(VBC)/polystyrene were both used to synthesize this resin.

Synthesis of β-ketophosphonic Acid[80]

In a reactor was added 2.9021 g (0.0279 mol) of the 8% cross linked polystyrene foam and swelled for 1 hour in 250 ml of carbon disulfide. The reactor was place in an ice bath before adding 10.91 g (81.75mmol) of $AlCl_3$, 4 ml (38.46mmol) of bromoacetyl bromide and 50 ml of carbon disulfide and left to stir for 48 hours. The ice bath can be removed after the first hour to let the reaction stir at room temperature. The resin was then quenched by adding a mixture of ethanol and ice (40/60) twice to the foam followed by washing with water, 10% acetic acid, and ethanol. The foam was then placed in the vacuum oven overnight at 70°C. After removing the foam from the oven, it was placed back in the reactor with 300 ml of triethyl phosphite and refluxed for 24 hours. The washing afterwards included twice with acetone and twice with dilute hydrochloric acid

(4 wt. %) for 15 minutes each. Hydrolysis was done by adding 300 mL of concentrated hydrochloric acid and refluxing for 24 hours.

Sulfonation of a-ketophosphonic Acid[80]

The resin was washed 4 times with acetone before soxhlet extracting with dioxane for 17 hours. The foam was dried in the vacuum oven for 4 hours at 40°C.

The amount of foam used for the reaction was 1.4630g. This was placed in a reactor with 200 ml of ethylene dichloride to swell for 1 hour. In an addition funnel, 16.5ml of chlorosulfonic acid and 66 ml of ethylene dichloride was placed. The mixture was dripped slowly into the reactor while stirring in an ice bath. The reaction was left stirring for 48 hours.

Functionalized Resins

Synthesis of Monophosphonic Acid[99]

The poly(vinylbenzyl chloride) beads at both porosities and particle sizes were funtionalized by refluxing 10 g (0.0655 mol) of beads with 300ml of triethyl phosphite for 24 hours. The beads were washed twice with acetone and twice with dilute HCl (4 wt. %). The reaction was followed by hydrolysis with 250ml of concentrated HCl (24 h reflux).

Synthesis of Phosphonoacetic Acid[101]

Triethyl phosphonoacetate, 31.60 g (0.1397 mol), was added to 150 ml of dry dioxane and 3.67 g (0.1596 mol) Na metal and left to stir overnight under a N_2 sweep. Poly(vinylbenzyl chloride) beads at both particle sizes, 10.00 g (0.0655 mol), was added to deprotonated triethyl phosphonoacetate and refluxed for 24 h. The beads were washed four times with toluene and then dried *in vacuo* at 60°C for 17 h, swelled in $CHCl_3$ for 1 h under a N_2 sweep, refluxed with 27 ml of Me_3SiBr for 24 h, and washed twice with dioxane and twice with water. The beads were then refluxed with 150 ml of 3N NaOH for 24 h.

Synthesis of β-KetophosphonicAcid[80]

The polystyrene beads of both porosities and particle sizes were functionalized by placing 10g of the polymer support with 200 ml of CS_2 to swell for 1 h while in an ice water bath. In 65 ml of CS_2, 40g of $AlCl_3$ was dissolved, added to stirring beads and left to stir for 2 h. 40.4 g of bromoacetyl bromide was added to an addition funnel with 10 ml of CS_2. The solution was added drop wise to beads and allowed to stir for 48 h while under a N_2 sweep. After 48 h, the solution was removed with a fritted glass filter and the beads were washed with dioxane until the solution remained clear. Beads are then washed with a mixture of dioxane/water (100/0 – 0/100) changing the ratio of dioxane to water until the beads are just washed in water, twice with ethanol, and twice with acetone, then dried *in vacuo* at 70°C for 4 h. The beads are refluxed for 24 h with 100 ml of triethyl phosphite. After refluxing, the beads are washed twice with acetone and twice with dilute HCl. The reaction was followed by hydrolysis with 250ml of concentrated HCl (24 h reflux).

Synthesis of Sulfonated Analogues of Functionalized Resins[80]

Each resin (~10.0 g) at a particle size of 250-425μm after functionalization was dried by azeotropic distillation with heptane and then placed in 500 ml round bottom flask and stirred for 1 hr with ethylene dichloride (EDC; 200ml). In an addition funnel, 65 ml of EDC was added to 16.5 ml of chlorosulfonic acid and added drop wise slowly to the stirring beads. The mixture was stirred at room temperature for 48 h. The beads was then washed with a mixture of dioxane/water (100/0 – 0/100) changing the ratio of dioxane to water until the beads are just washed in water.

High Stability SIR Synthesis

Surface Modification of the Beads[97]

The beads (10g) are surface modified in preparation for the encapsulation via two reactions. The first reaction is a surface Arbusov. Triethyl phosphite in excess (100 mL) is brought to reflux in a 250 mL round bottom flask equipped with an overhead stirrer, condenser and stopper. The beads are added to the refluxing solution while stirring and allowed to react for 40 min. Removing the heat and placing the round bottom flask in an ice water bath stops the reaction. Once cooled, the triethyl phosphite is removed and the beads are washed twice with acetone, four times with toluene, and dried overnight in a 60°C oven.

The second reaction is a Wadsworth-Emmons reaction. The beads are placed in a 250 mL round bottom flask equipped with an overhead stirrer, gas inlet and addition funnel. The beads are swelled for 1 hour at room temperature with 100 mL N,N'-dimethylformamide (DMF). The round bottom flask is then placed in an ice water bath for 1 hour while under a nitrogen sweep. Phenyllithium (50 mL of 1.8 N solution in ether) was added to the addition funnel via syringe and added dropwise slowly to the stirring beads. The reaction was allowed to go at room temperature for 24 hours. The beads were washed with 100 mL of dioxane, toluene, and water and then placed in a 60°C oven overnight.

Solvent Impregnation[97]

The modified beads (3.2g) are swelled in 25 mL of 2N extractant/solvent for 17 hours. The excess solution is removed from the beads and placed in a 50 mL one-neck round bottom flask. The flask is then placed on a rotary evaporator and the beads are dried at 50°C. The amount of extractant present in the beads after being dried is determined by elemental analysis depending on the type of extractant being used. The extractant most used for the research is DEHPA. The phosphorus capacity after impregnation for this extractant was usually within the range of 1.9-2.2 mmol/g

Encapsulation[97]

The SIR beads (3.2g) are placed in a 250 mL round bottom flask equipped with a condenser, an overhead stirrer (set at a stir speed of 262 rpm), a stir paddle of a size of 4.5 cm, a thermometer, and gas inlet/outlet. A 2% aqueous solution of glycidyl methacrylate (1.55g)/ N,N'-methylenebisacrylamide (0.51g) is made in a 150 mL beaker using 99.94g of nanopure water with 0.06g(3% of monomer phase) of potassium persulfate as an initiator. The beaker is placed in an ice water bath and stirred until all the reactants are dissolved. The solution is sparged with nitrogen for ten minutes, added to the beads, and heated to 50°C for 8 hours while under a nitrogen sweep. After completion, the beads are washed four times with nanopure water and then placed on a 200 mesh sieve and washed with nanopure water. The beads are then placed in a 60°C oven overnight. After drying, 40 mL of nanopure water is added to the beads and placed on a shaker for 17 hours. The beads are placed on a 200 mesh sieve and washed with nanopure water. The beads are dried in a 60°C oven overnight. The beads are characterized by nitrogen capacity for the coating and by phosphorus capacity to ensure no loss of extractant. The nitrogen capacity is usually in the range of 0.9-1.2 mmol/g, whereas the phosphorus capacity is in the range of 1.7-2.0 mmol/g.

Modification of Encapsulation

The encapsulation procedure was modified due to the SIR beads adhering to the sides of the round bottom flask which prevents the encapsulation of the SIR. The modified method solves the problem of adhesion of the SIR to the sides of the round bottom flask. A 2% aqueous solution of glycidyl methacrylate (1.55g)/ N,N'-methylenebisacrylamide (0.51g) made with 99.94 g of nanopure water without the initiator is placed in a 250 mL round bottom equipped with a condenser, an overhead stirrer (set at a stir speed of 262 rpm), a stir paddle of a size of 4.5 cm, a thermometer, and gas inlet/outlet. The solution is stirred until all the reactants are dissolved, while in an ice water bath. Once the reactants are dissolved the initiator (0.06g potassium persulfate) is added and stirred until dissolved. The solution is then sparged with nitrogen for ten minutes. The beads are added to the stirring solution and heated to 50°C for 8 hours while under a nitrogen sweep. After completion, the beads are washed four times with nanopure water, placed on a 200 mesh sieve and washed with nanopure water. The beads are dried in a 60°C oven overnight. After drying, 40 mL of nanopure water is added to the beads and placed on a shaker for 17 hours. The beads are placed on a 200 mesh sieve, washed with nanopure water, and dried in a 60°C oven overnight. After drying, the beads are characterized by nitrogen capacity for the coating and phosphorus capacity to ensure no loss of extractant. The nitrogen capacity is usually in the range of 0.9-1.2 mmol/g, whereas the phosphorus capacity is in the range of 1.7-2.0 mmol/g.

Characterization

Percent solids

All resins that were conditioned were kept under water. For analysis, the amount of water that remains in the beads must be obtained. The beads are Büchner dried to remove the excess water by placing the beads on a Büchner funnel and covered with a piece of latex that is held in place by a rubber band. A vacuum (710 mm Hg) is applied to the beads for 5 minutes. Approximately 1 g of resin is placed in a preweighed scintillation vial. The weights for the entire procedure are determined by an analytical balance. The resin is dried in a 110°C oven for 17 hours. The vial is then placed in a dessicator and allowed to cool. The mass of the resin after being dried is determined. The percent solids is calculated as:

$$\frac{(\text{Weight of the Büchner dried resin}) \times 100}{(\text{Weight of the oven dried resin})}$$

Total acid capacity

Büchner dried resin was accurately weighed (~ 1g) into a 250 mL Erlenmeyer flask using an analytical balance. To the Erlenmeyer flask, 200 mL of standardized 0.1N NaOH containing 5 wt% NaCl was added by a pipette, the flask was stoppered with a ground glass stopper and gently stirred for 17 hours at 350 rpm. The solution was removed from the beads without transferring any of the beads and two 50 mL aliquots are titrated with a standardized 0.1N HCl to a phenolphthalein end point. The total acid capacity is calculated as:

$$\frac{[(\text{Volume NaOH})(\text{N NaOH})]-[4(\text{Volume HCl})(\text{N HCl})]}{(\text{weight Büchner dried resin})(\%\text{ solids})}$$

Modified acid capacity procedure

100 ml of 0.0659N NaOH(5 wt% NaCl) was added to 1 g of Büchner dried resin in a 250 ml erlenmeyer flask and left to stir at 350 rpm for 17 hours after stoppering. Then 2 aliquots of 25 ml were titrated to the end point with 0.0652 N HCL using phenolphthalein as an indicator. The equation remains as above.

Phosphorus elemental analysis[101]

Approximately 20 mg of dried resin is accurately weighed into a 125 Erlenmeyer flask (experiment done in duplicate), 400 μL of 0.5 M $CuSO_4$ solution and 10 ml of concentrated H_2SO_4 is added. The mixture was then heated on a hot plate for 2-3 hours on a high setting until the solution is clear and the beads are completely digested. After cooling, 75 mL of distilled water and 2 g of potassium persulfate was added to the solution and heated for another 2 hours at a low setting. Once cooled, the solution is neutralized by first adding 50 wt% NaOH dropwise until the solution just turned brown. The solution is then brought to neutral by adding 2 wt% H_2SO_4 dropwise. The solution is allowed to cool before being transferred quantitatively to a 100 mL volumetric flask and diluted to the mark with distilled water. From this solution, a 25 mL aliquot is transferred via a pipette to a 50 mL volumetric flask and 10 mL of vanadate-molybdate solution (prepared by 2.5 g ammonium molybdate tetrahydrate, 0.13 g ammonium metavanadate, 33 mL of concentrated HCl and 67 g distilled water) added and diluted to the mark. A blank was prepared without the analyte in order to zero the instrument. The absorbance values were read on a Spec 21 at 470 nm after zeroing the instrument with the blank. The phosphorus capacity (in mmol/g) was determined using the formula:

$$\frac{4[(\text{Absorbance-intercept})/\text{slope}]}{[(30.974\text{mg/meq})(\text{g dry resin})]}$$

Nitrogen elemental analysis[102]

Approximately 0.2 g of dried resin was accurately weighed and placed into a three neck round bottom flask and 0.25 g $CuSO_4$, 10 g K_2SO_4, 25 mL of concentrated H_2SO_4, and a few boiling chips were added. Stoppers were placed in two of the necks of the flask while the middle neck had a long open end condenser attached. The mixture was heated gently for 1 hour and then vigoresly for 9 hours. After heating, a light clear blue solution should be obtained. The condenser was washed with a minimum of distilled water as were the two stoppers into the flask. One of the necks was equipped with an addition funnel containing 150 mL of NaOH and the middle neck was equipped with a distillation apparatus. On the end of the distillation apparatus, a plastic funnel was attached, the mouth of the funnel was just immersed in 50 mL of 0.1 N standardized HCl in a 600 mL beaker. The NaOH was added slowly dropwise while the solution was stirred. After the 150 mL is added (the solution should be brown), the solution is heated to distill ammoniacalwater into the acid (the nitrogen in the resin is converted to ammonia which is collected in the solution). Once the water coming across is no longer basic the distillation is complete. The distillation apparatus is dismantled and the solution obtained is transferred to a 250 mL volumetric flask. The flask is diluted to the mark with distilled water. Two 50 mL aliquots are titrated to a bromocresol green end point using standardized 0.1 N NaOH containing 5 wt% NaCl. The nitrogen capacity is calculated using the formula:

$$\frac{[(\text{Volume HCl})(\text{N HCl})]-[5(\text{Volume NaOH})(\text{N NaOH})]}{\text{g dry resin}}$$

Complexation Studies

Metal Ion Solutions

A 10^{-3} N stock solution is made using nanopure water and reagent grade metal salts and acids in a 1 L volumetric flask using the appropriate background for the study being done. Standards and contact solutions of a lower concentration are made from the stock solution by subsequent dilution in volumetric flasks. All contact solutions have a concentration of 10^{-4} N unless otherwise noted.

Some metal solutions are made in a buffer medium. The buffer is made at a specific normality for the study being done and then adjusted to the proper pH via a pH meter. An example would be the making of 0.6 N pH 8.4 NH_3/NH_4NO_3. The appropriate amount of NH_4OH (141.62 g) is weighed into a 2 L beaker. The NH_4OH is then diluted to 1600 mL with nanopure water. The solution is then buffered to the appropriate pH with 6N HNO_3. The solution is then placed in a 2 L volumetric and diluted to the mark with nanopure water. The lower concentration solutions are then diluted with the buffer solution.

Metal Ion Studies

One milliequivelent of Büchner dried resin weighed into a clean 20 mL scintillation vial. The resin is solvent exchanged four times with 10 mL of the medium solution for 15 min by placing on a wrist action shaker. After each 15 min, the solution is removed with a Pasteur pipette taking care not to remove any of the beads. After removal of the last exchange solution, the contact solution (10 mL) is added to the beads and placed on the shaker for the appropriate amount of time. The contact solution is removed via a Pasteur pipette and placed in a clean 20 mL scintillation vial for analysis on the Perkin-Elmer 3100 atomic absorption/emission spectrometer.

Atomic Absorption/Emission Spectroscopy

The contact solutions were analyzed by a Perkin-Elmer 3100 atomic absorption/emission spectrometer. Each metal has specific parameters, which are reported in Table 5.1. Europium solutions had to be spiked with 4000 ppm KCl before analysis on the instrument. The KCl prevents ionization of the metal ion solution.

Table 5.1 Atomic absorption/emission parameters

METAL ION	AA/AE	WAVELENGTH(nm)	FLAME
Cu(II)	AA	324.8	Air/acetylene
Pb(II)	AA	283.3	Air/acetylene
Cd(II)	AA	228.8	Air/acetylene
Zn(II)	AA	213.9	Air/acetylene
Fe(III)	AA	248.3	Air/acetylene
Eu(III)	AE	459.4	Nitrous oxide/acetylene

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