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I am submitting herewith a dissertation written by Robert Dean Ober entitled "Synthesis and Development of Selective Ion-Exchange Resins for the Removal of Toxic Metal Ions from Water in the Environment." I have examined the final 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

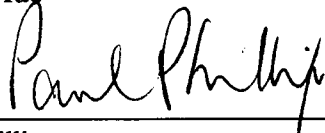
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Dean of the Graduate School

SYNTHESIS AND DEVELOPMENT OF SELECTIVE ION-EXCHANGE
RESINS FOR THE REMOVAL OF TOXIC METAL IONS FROM
WATER IN THE ENVIRONMENT

A Dissertation

Presented for the

Doctor of Philosophy

Degree

The University of Tennessee, Knoxville

Robert Dean Ober

December 1999

DEDICATION

This dissertation is dedicated

to my parents

Robert N. Ober and Nancy J. Ober

and my wife

Terri Thompson Ober

who have given me

support, encouragement, strength and the means to succeed

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ABSTRACT

A general synthesis for the formation of polymer bound phosphonate esters and phosphonamides has been devised and studied. Phosphonic acid resin was produced by an Arbuzov reaction and subsequent hydrolysis of a vinylbenzyl chloride-divinylbenzene copolymer. The phosphonic acid resin was reacted with thionyl chloride to form a reactive intermediate, phosphoryl dichloride resin. The phosphoryl dichloride resin was reacted with various alcohols and amines to form the aforementioned resins. Reaction time, reaction temperature, reaction solvent, pre-reaction work-up, and post-reaction work-up were all studied. A mechanism has been proposed to help explain the trends accompanying the reaction variables. The mechanism states that the weak base solvent, pyridine, can attack the functionality forming a salt with the phosphoryl moiety. If the salt formation is favorable, the amount of functionalization is reaction time and temperature dependent. If the salt formation is unfavorable, there is no dependence on the reaction time or the reaction temperature. The resins were analyzed for uptake of various divalent transition metals in a pH 2 nitrate solution with a large excess of competing sodium ions. Generally, the phosphonamides were an improvement for the metals studied upon comparison to phosphonic acid resin, the control. The phosphonate esters were, at best, as good as the phosphonic acid resin, but were usually much worse in removing the metals studied.

Combining long alkyl and short alkyl chain ligands to form a dual mechanism bifunctional polymer (DMBP) gives rise to a new type of anion exchange resin where one works as an

access ligand and the second works as a recognition ligand. Working with scientists at Oak Ridge National Laboratory (ORNL), the newly found polymers were analyzed for the uptake of the pertechnetate anion from groundwater samples. It was discovered that the ligand with the highest affinity for the TcO_4^- (but the slowest uptake time) is a quaternary ammonium ligand made from trihexylamine. The addition of a second quaternary ammonium ligand by amination with a smaller trialkylamine (triethylamine) to form a bifunctional quaternary ammonium exchange resin improved the uptake and kinetics of the resin made from amination with trihexylamine. The reaction procedure was stream-lined for use on an industrial scale.

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CHAPTER 1

INTRODUCTION

Summary

Ion-selective polymers can be prepared when a chemical reaction is superimposed on the ion-exchange process. The concept of “reactive ion exchange” has been extended through the synthesis of crosslinked polymers whose metal ion selectivity is a function of the precipitation, coordination and oxidation/reduction reactions carried out by different covalently bound ligands in the presence of various metal ions. Development of three classes of dual mechanism bifunctional polymers, a new diphosphonate polymer and its different derivatives, as well as various bifunctional polymers that enhance ionic accessibility will be discussed. A discussion of bifunctional anion-selective polymers, interpenetrating polymer networks, and high stability solvent impregnated resins will also be addressed.

Part I:

Ion-Selective Bifunctional Polymers with Phosphorus-Based Ligands

Dual Mechanism Bifunctional Polymers

Dual mechanism bifunctional polymers (DMBPs) are a category of ion exchange resins with enhanced recognition and selectivity over monofunctional ion-exchange polymers. These polymers are formed from functionalization of given polymer support with two groups that each perform a desired mechanism. One mechanism is relatively aspecific and

allows the metal ion access to the highly specific recognition mechanism ⁽¹⁾. The DMBPs are divided into three different classes. Ion exchange acts as the access mechanism in each class and the recognition mechanism defines the class.

Class I DMBPs

The first of the three classes of DMBPs consist of a redox component (recognition) combined with an ion exchange moiety (access). The Class I DMBPs focus on the synthesis of either primary phosphinic acid / secondary phosphine oxide or primary / secondary phosphinic acid ligands on polystyrene (Figure 1-1) ⁽²⁾. These resins were tested for their uptake of Zn(II) ions in a solution containing excess Na ions. These initial studies showed improved metal uptake when compared with sulfonic acid and carboxylic acid resins ⁽³⁾. The redox mechanism became apparent when the resin was contacted with Hg(II) and Ag(I) ions. The primary phosphinic acid ligand is oxidized to phosphonic acid while the metal is reduced to its zero valent state. The phosphonic acid ligand can sorb remaining metal ions by ion exchange ⁽⁴⁾. It was found that these resins are stable in solutions of 4 N nitric acid at ambient temperatures. Studies show that the minimum metal ion reduction potential that still allows for reduction by the phosphinic acid resin is approximately 0.3 V ⁽³⁾. The primary phosphinic acid reduces divalent cations with a 1:1 stoichiometric ratio (Figure 1-2) and monovalent cations with a 1:2 ratio (Figure 1-3). The resin thus reduces divalent ions more rapidly than monovalent ions due to the fact that two monovalent ions must be within close proximity to each other and the primary phosphinic acid ligand in order for reduction to take place.

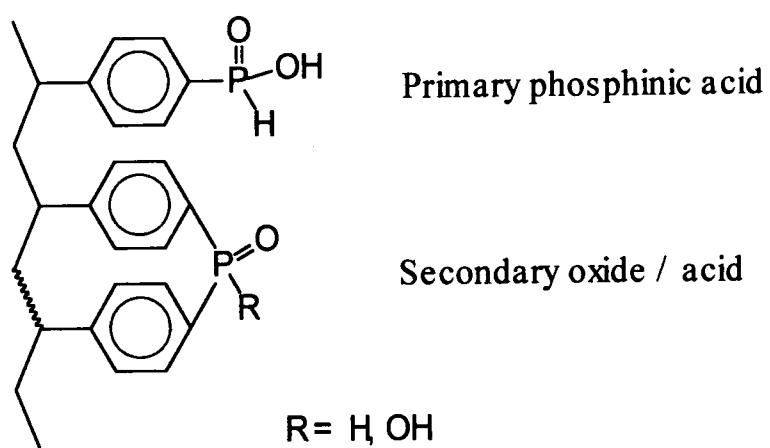


Figure 1-1. General structure of Class I DMBP

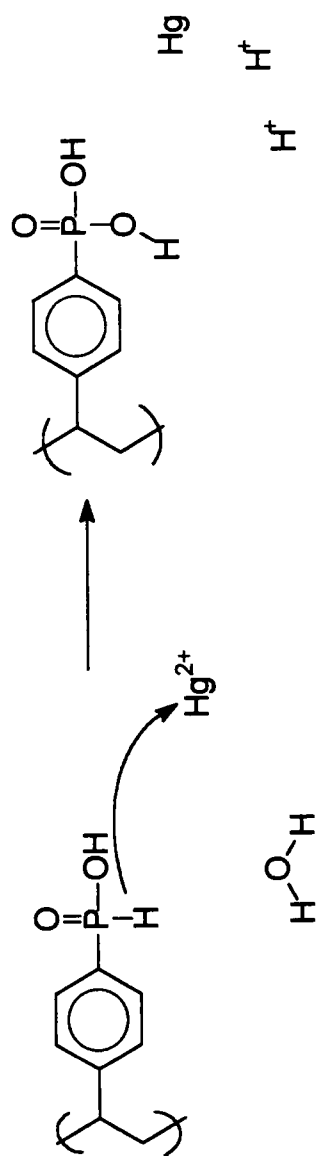


Figure 1-2. Mechanism of primary phosphinic acid reduction of Hg(II) in water

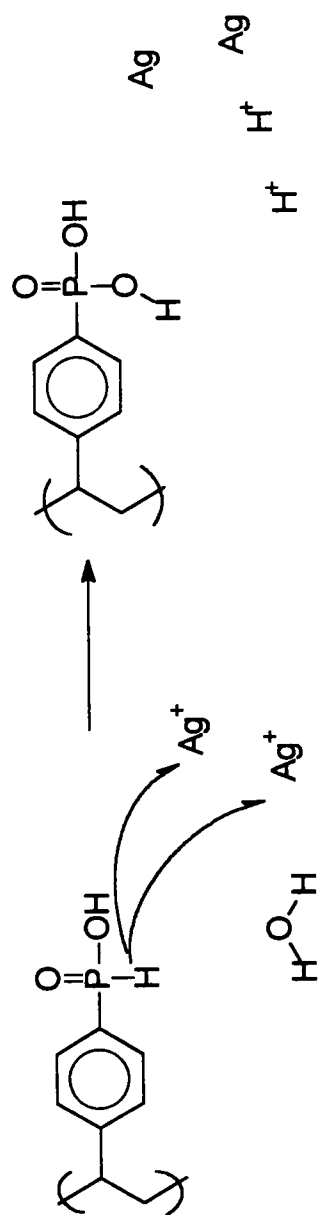


Figure 1-3. Mechanism of primary phosphonic acid reduction of Ag(I) in water

A cation affinity series for the primary/secondary phosphinic acid resin was done using a 10% crosslinked gel resin ⁽⁵⁾. A batch method was utilized for each determination at constant temperature (25 °C) for 24 hours to ensure equilibrium had been reached.

The resin was found to have an affinity for metal ions in the order: Pb(I) > Mn(II) >> Cd(II) > Ca(II) > Zn(II) > Mg(II) > Ni(II) > Ba(II) > Sr(II) > Co(II) >> Fe(III) >> Cs(I) >> Li(I) > Na(I) > Rb(I) in a solution of nitric acid. The series was set by the distribution coefficient, D, defined as the amount of metal on the resin per gram of resin divided by the amount of metal remaining in solution per mL of solution. Not included were Ag(I), Hg(I), Hg(II), and Cu(II) due to reduction of the metal ions. ⁽⁵⁾.

The primary/secondary phosphinic acid Class I resin was also studied for its uptake of various lanthanides and actinides and then compared with results from the sulfonic acid resin ⁽⁶⁾. A correlation of log D vs pH for uptake of both europium and americium from aqueous nitric acid (4 M to 0.2 M) shows that when the pH is varied, the slope of the line for the phosphinic acid resin is 1.75 and the slope for the sulfonic acid resin is 3.0. This shows that the sulfonic acid is utilizing an ion exchange mechanism while the phosphinic acid is complexing metal nitrate complexes (Figure 1-4). When sodium nitrate is added to maintain a constant 4 M nitrate ion concentration at varying pH, the phosphinic acid resin has nearly an identical uptake of the two metals (slope, Eu = 1.90; slope, Am = 1.97) whereas the slope for the sulfonic acid resin is near zero for both metal ions. Since the phosphinic acid resin utilizes a coordination mechanism instead of a pure ion exchange mechanism like the sulfonic acid resin, the addition of sodium ions does not affect the uptake of the desired metals by the phosphinic acid resin. The sulfonic acid resin, on the

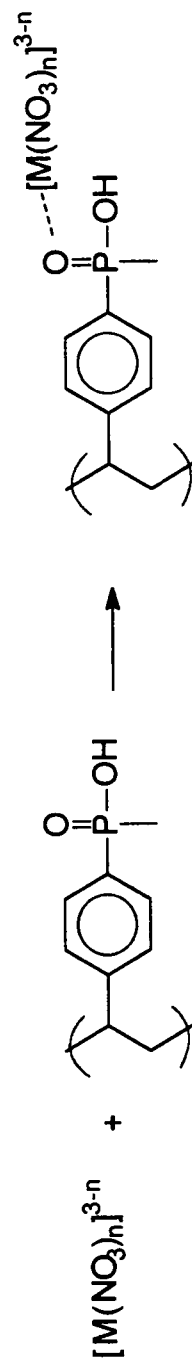


Figure 1-4. Complexation of metal nitrate with phosphonic acid resin

other hand, exchanges for the sodium ions present in large excess, decreasing the D values for the targeted metal ions. The phosphinic acid resin thus displays a much greater selectivity than the sulfonic acid resin. Comparisons were also made between the two resins for their uptake of uranium (as the UO_2^{2+} complex), thorium and plutonium. The phosphinic acid resin was superior in uptake of both uranium and thorium at high acid concentrations, and of plutonium at all acid concentrations studied as well as in the presence of excess sodium ions.

In order to get a better understanding of the metal ion uptake kinetics, Ni(II) was studied at a constant pH at both 2°C and 60°C. Equilibrium was reached in 1 hour at the lower temperature and less than 15 minutes at the higher temperature ⁽⁷⁾. It was also confirmed that ion exchange was the only operative mechanism by the phosphinic acid resin during Ni(II) uptake by reanalysis of the acid capacity after uptake and regeneration (a redox reaction gives an acid capacity higher than the original value). The temperature dependance was also studied for the uptake of Ag(I) ions. The acid capacity determination confirms the redox reaction. The temperature dependence found with the uptake of Ni(II) ions holds true with Ag(I).

Class II DMBPs

The second class of DMBPs consists of an ion-exchange (access) mechanism combined with a coordination (recognition) mechanism. The first example of class II DMBPs is a phosphonic acid/ phosphonate ethyl ester resin (Figure 1-5). In studies with americium nitrate, it was found that the uptake of Am(III) in excess sodium nitrate is highly

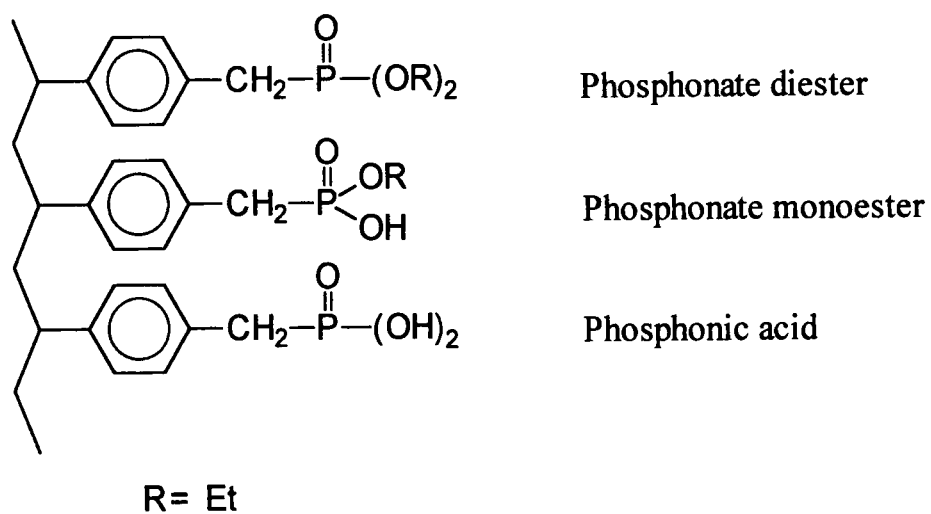


Figure 1-5. General structure of phosphonic acid/phosphonate ester Class II DMBP

dependant on the percentage of diester, monoester, and diacid ligands on the phosphoryl groups. The pure phosphonate monoethyl ester gave the best uptake of Am(III) for all of the resins, followed by the resins of various mixed diethyl ester and monoethyl ester ligands. The resins of various mixed monoethyl ester and diacid ligands gave almost identical results as the phosphonic acid control. The resin consisting of purely diester ligands gave essentially no uptake of americium in the solution studied ⁽⁸⁾.

The second example of a Class II DMBP is a phosphonic acid/ tertiary amine resin (Figure 1-6). This resin was also studied for uptake of americium in a solution of excess sodium nitrate and, like the pure diethyl ester resin, has a negligible uptake of americium.

The behavior of purely coordinating resins, such as that with diester ligands, can be expected to depend on the counterion in solution; results in the resence of chloride ions may be different than those in the resence of nitrate ions ⁽⁸⁾.

A third example of an ion exchange/coordination resin has ion exchange by a carboxylic acid ligand and coordination by a pseudocrown-ether ligand prepared with penta(ethylene glycol) [PEG] (Figure 1-7). This resin, along with its monofunctional counterparts, was tested for extraction of Group IA ions from a solution at pH 9.6. The resins were studied for the equilibrium uptake of potassium, rubidium, and cesium ions in separate solutions containing nitrate, sulfate, and phosphate anions. The bifunctional resin, has a slight preference for Cs over Rb and K ⁽⁹⁾.

Class III DMBPs

The third class of DMBPs consists of ion exchange (access) and precipitation

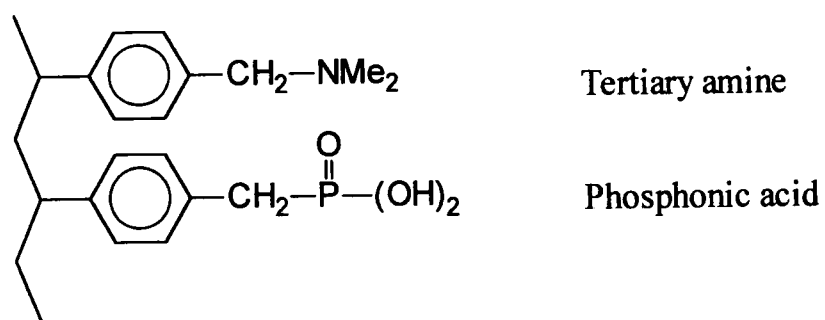


Figure 1-6. General structure of phosphonic acid/tertiary amine Class II DMBP

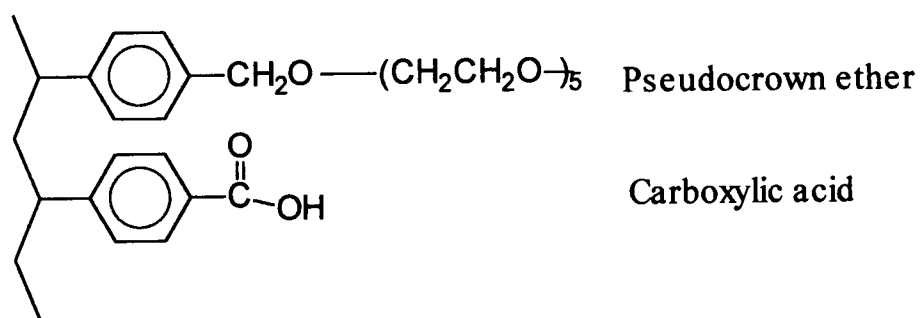


Figure 1-7. General structure of the pseudo-crown ether/ carboxylic acid Class II DMBP

(recognition) mechanisms (Figure 1-8). The phosphonic acid ligand is responsible for ion exchange and the quaternary amine ligand allows for precipitation to occur via its associated anion once the metal ion exchanges into the resin. This class allows for both specificity and removal of the selected metal ion from solutions by intra-resin precipitation which isolates the salt within the bead (Figure 1-9). The metal can be recovered by solubilizing the salt with appropriate eluents ⁽¹⁰⁾.

Determination of polymer ligand- metal ion affinities

A comprehensive study of the metal ion selectivities displayed by a series of polymers was completed in order to gain a better understanding of the selectivity in ion-polymer interactions ⁽¹¹⁾. Ten different resins were used (sulfonic acid, phosphinic acid, phosphonic acid, dimethylamine, amine/ phosphonic acid, monoethyl ester, dimethyl ester, diethyl ester, dibutyl ester, and 40%diethyl ester/60% monoethyl ester) in contact with five different metals (Fe(III), Hg(II), Ag(I), Mn(II), and Zn(II)) at a concentration of 10^{-4} N each in one of four different concentrations of nitric acid (4, 2, 1, and 0.2 N) all with excess (4 N) sodium ions.

The sulfonic acid resin displayed no selectivity as well as low levels of complexation for all of the transition metals studied. The phosphinic acid resin had a selectivity series of $\text{Fe} > \text{Hg} > \text{Ag} > \text{Mn} > \text{Zn}$ in high acid/high ionic strength solutions. The affinities for Fe and Hg are both significantly higher than the other metals; the affinity for mercury is due to its reduction reaction while that for iron(III) is due to coordination through the phosphoryl oxygen. The phosphonic acid resin has the same general trend as the phosphinic acid resin

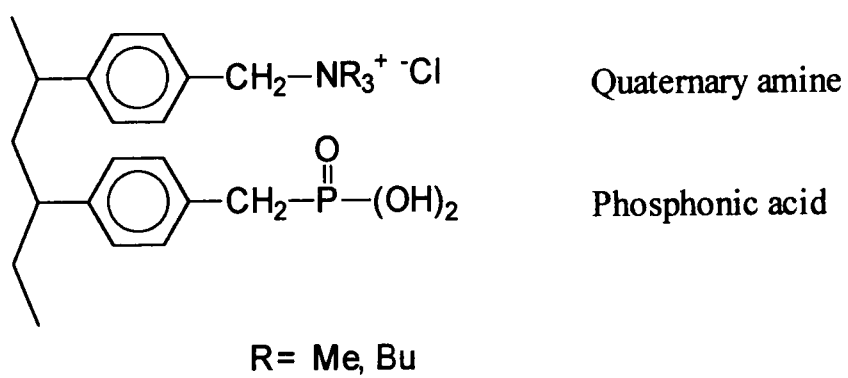


Figure 1-8. General structure of the Class III DMBP

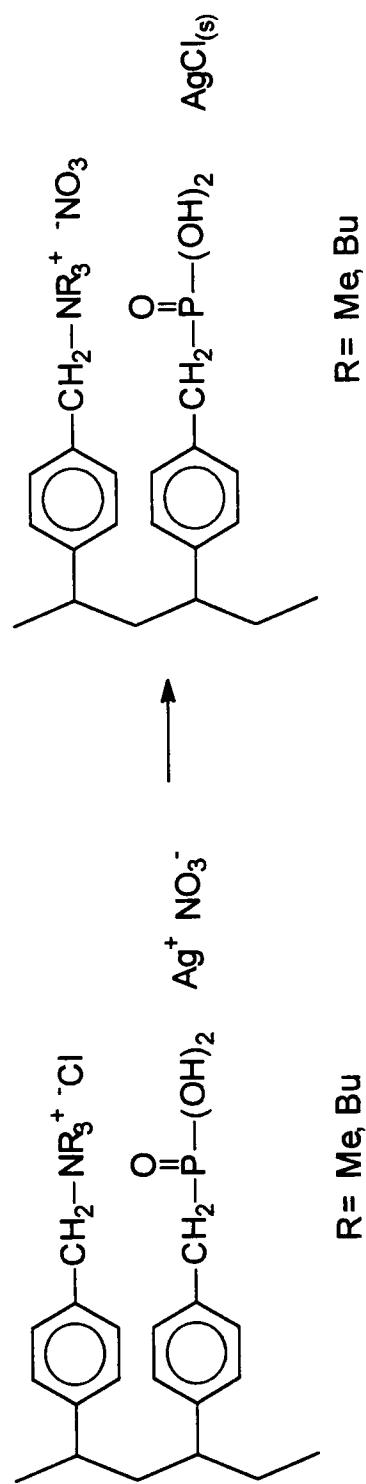


Figure 1-9. Reaction of Class III DMBP with a soluble silver salt

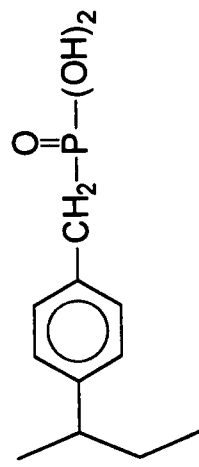
except for a large decrease in uptake of Hg(II) in all acid concentrations and a low selectivity between Mn(II) and Zn(II) due to competition between the H⁺ and all metals in the higher acidic solutions, except Fe(III) for which the phosphoryl oxygen retains a high affinity. The dimethylamine resin showed significant affinity for Hg(II), considering the acidity of the solutions, as well as a slight affinity for Ag(I), with the remaining metals all sorbed at very low levels. The mixed amine/acid resin operates through the acid ligand and gives the same selectivity series as the phosphonic acid resin. The phosphonate monoethyl ester resin coordinates Ag(I) at a much higher level than the phosphonic acid resin while the rest of the selectivity sequence remains the same. The phosphonate dialkyl ester resins give a vastly different selectivity series (Ag > Hg > Fe > Zn, 0% Mn). Another difference found was that the affinity for Ag decreases as the acid concentration decreases, drastically for the dimethyl ester resin and gradually flattening out as the alkyl chain increases in size. Of all the phosphonate ester resins studied, the 40% diethyl ester/60% monoethyl ester resin had the highest affinity for Ag(I) ion. This is an example of supported ligand synergistic interaction. The bifunctional diester/ monoester resin displays a higher affinity than the monoethyl ester resin, the diethyl ester resin, as well as a mixed bed of the monoester and diester ⁽¹¹⁾.

Bifunctional polymers with enhanced ionic accessibility

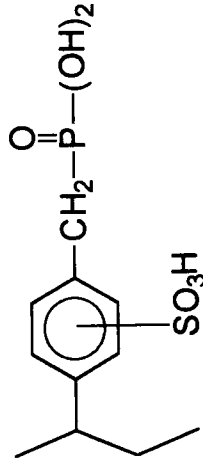
Enhancing ionic accessibility

Monofunctional phosphonic acid resins crosslinked with 2 and 12% DVB complex Eu(III)

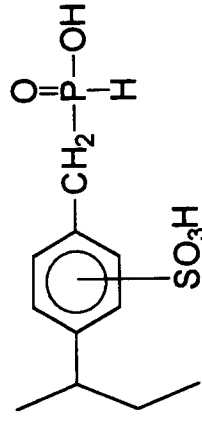
present in 0.01 N and 0.10 N nitric acid almost quantitatively. Complexation decreases significantly, however, as the acidity of the background solution increases to 0.50 N and 1.00 N nitric acid. While the reason conventionally given for this type of behavior is that the mechanism of complexation changes from ion exchange to coordination at the phosphoryl oxygen as the solution pH falls below the pK_a of the phosphorus acid ligand and this gives a lower metal ion affinity due to competition by the acid for phosphoryl oxygen sites, an alternative explanation was also offered: that the phosphonic acid ligands are insufficiently hydrophilic to remain hydrated in solutions where the pH is too low thus preventing metal ion access due to collapse of the matrix. Results are almost identical in the presence of 0.40 N sodium nitrate. If the alternative explanation is operative, then an increase in hydrophilicity of the resin should enhance the extent of complexation in more acidic solutions. For this reason, three phosphonic acid resins (2%, 12% and 25% DVB crosslinked) were sulfonated to give bifunctional resins (Figure 1-10). Complexation of Eu(III) was almost quantitative in all solutions. Thus, the sulfonic acid ligand hydrates the resin due to its inherent hydrophilicity and this hydration prevents even the flexible 2% DVB matrix from collapsing. Collapse is especially prone to happen when coordination, rather than ion exchange, is the mechanism of complexation and this is obviated with a hydrophilic ligand. The amount of Eu(III) complexed is unchanged in the presence of a large (12000:1) excess of sodium ions relative to protons. The sulfonic acid ligand thus allows for access of all ions into the matrix while the phosphonic acid ligand complexes the Eu(III) through a coordination mechanism ⁽¹²⁾.



Monophosphonic acid



Sulfonated monophosphonic acid



Sulfonated phosphinic acid

Figure 1-10. Various types of phosphorus acid bound polymers

Bifunctionality as alternative to macroporosity

Sulfonation of a phosphinic acid ion exchange resin greatly increases ionic accessibility which, in turn, enhances complexation kinetics and selectivity⁽¹³⁾. The amount of complexation of Eu(III) by polymer-bound phosphinic acid decreases as crosslinking increases for both gel (microporous) and MR (macroreticular) beads (10-fold and 3-fold, respectively). When comparing the distribution coefficients between the gel and the MR beads for a given amount of crosslinking, the MR beads are higher by 10- to 30-fold. The advantages of using gel over MR beads, including decreased friability and greater bed volume capacity, led to a search for other methods of enhancing the complexation of the targeted metal. By addition of a sulfonic acid ligand to the polymer matrix, a nonselective rapid access mechanism is added to the inherent recognition mechanism of Eu(III) coordination by the phosphoryl oxygen on the phosphinic acid ligand⁽¹³⁾. It was also determined that addition of the sulfonic acid ligand is not responsible for the increase in distribution coefficients.

Sulfonation of a phosphonic acid ion-exchange resin also enhanced complexation kinetics and selectivity. By the same ideas stated above with the phosphinic acid resin, the sulfonation gave quantitative uptake of Eu(III) as well as Fe(III) from 0.10 N nitric acid between a crosslink level of 5% and 20% DVB⁽¹⁴⁾.

Bifunctional gem-diphosphonate resins

Diphonix

Diphonix (Figure 1-11) is a multifunctional chelating ion exchange resin containing geminally disubstituted phosphonic acid ligands chemically bonded within a styrene-based matrix ⁽¹⁵⁾. Diphonix can be regarded as a dual mechanism polymer, with an aspecific sulfonic acid cation exchange group allowing for rapid uptake of ions into the polymer network, and the diphosphonic acid group responsible for metal ion specificity ⁽¹⁶⁾.

Diphonix exhibits strong affinity for actinides, especially in the tetra- and hexavalent oxidation states ⁽¹⁷⁾. The acidity of the diphosphonic acid group and its tendency to chelate actinides through the coordinative ability of the geminal phosphoryl groups, makes possible the formation of metal complexes of high stability under conditions too acidic for appreciable complexation by other ligands ⁽¹⁷⁾. Upon analysis of nitric acid dependencies of the distribution ratio, D , of U(VI), Am(III), Th(IV), Np(IV), and Pu(IV) with Diphonix, the most striking feature is the remarkably high retention of hexavalent uranium and tetravalent actinides in the whole acidity range-even up to 10 M nitric acid. A second important aspect of the data is the different acid dependency shown by the various actinide ions: (1) the uptake of Am(III) shows a strong negative dependence on the acid concentration, (2) the uptake of uranium and thorium shows at least some inverse hydrogen ion dependency [both of these are what would be expected for a cation-exchange resin], (3) the other tetravalent actinides exhibit an uptake curve going through a maximum in the range of 0.5 to 3 M acid, declining significantly only at the highest acidities ⁽¹⁸⁾.

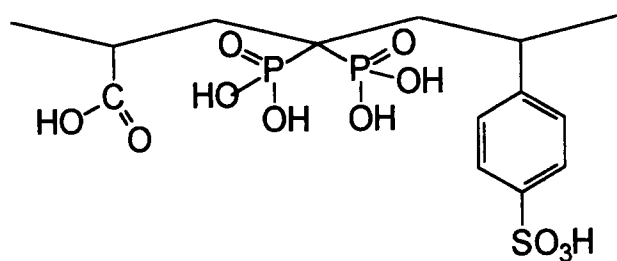


Figure 1-11. General structure of Diphonix

Acid dependencies have also been determined in hydrochloric acid. Major differences from nitric acid are encountered only with uranium, whose D values decline much more rapidly with increasing HCl concentration than they do in HNO_3 . It appears, with the exception of U(VI), the behavior of the acid dependencies in the two acids cannot be easily correlated to the complexing ability of chloride and nitrate anions toward actinides ⁽¹⁸⁾.

Am(III) was stripped from Diphonix using 1-hydroxyethane-1,1-diphosphonic acid (HEDPA), a liquid extractant that contains the same ligand groups as Diphonix. A 1 M HEDPA solution used in stripping Am(III) was found to rapidly remove the actinide from the resin. Only five minutes of contact are needed to remove 85% of the metal from the resin, and more than 95% of the metal is stripped from the resin in 30 minutes ⁽¹⁶⁾.

Upon comparison of Diphonix with monophosphonic and sulfonic acid resins, U(VI) and Pu(IV) uptake show that different mechanisms are operating for the three resins. The sulfonic acid resin clearly shows that sorption occurs solely by ion exchange. With the monophosphonic resin, on the other hand, the Pu(IV) data show a slope of about 0.5, indicating that the metal ion is also extracted through coordination with the phosphoryl group of the phosphonic acid. With Diphonix, the presence of a region with a slope between zero and minus one indicates that strong chelation of the metal ions to the diphosphonic acid group is the main factor for metal uptake ⁽¹⁸⁾.

The data clearly show the superiority of Diphonix with the uptake of actinide ions from acidic solutions in the presence of a very large excess of sodium ions. In 1 M nitric acid, the addition of 4 M sodium nitrate brings about a decrease of D values with the sulfonic

resin of more than three orders of magnitude, while, under the same conditions, the D value for the uptake of Am(III) by Diphonix decreases by only a factor of five, and still remains in a useful range for practical application ⁽¹⁸⁾. The presence of Al(III) strongly interferes with the sorption of Am(III) , but addition of HF solves this problem because aluminum is more strongly complexed by fluoride ion than Am(III) , allowing the Am(III) to be complexed by the resin ⁽¹⁹⁾.

The study of the uptake of transition and alkaline earth metal ions from acid solutions by Diphonix is important because these cations may interfere with the uptake of actinide ions. The most noteworthy feature is the behavior of Fe(III) . Its behavior most strongly resembles the curve for Pu(IV) and Np(IV) , with a plateau in the intermediate acid range and D values declining for lower acidities. Analysis of the plot of $\log D$ vs nitric acid concentration shows that Ca(II) is exchanged by ion exchange while Fe(III) is sorbed predominantly through coordination to the phosphoryl groups without release of protons by the resin, thus explaining the near-zero slope up to very high acidities ⁽²⁰⁾. Though the presence of Fe(III) can decrease complexation of the actinides, it must be present in relatively high amounts before the effect is significant. Additionally, converting the Fe(III) to Fe(II) via reduction obviates any interference ⁽¹⁹⁾.

The behavior of the other trivalent cations Bi , Eu , Al , and Cr , shows an unusual feature: there is a complete reversal of selectivity over the acidity range from dilute to concentrated acid. Also, for these same trivalent cations, the higher the distribution ratio at low acidity, the lower the distribution ratio at high acid concentration. The acid dependency of Eu(III) closely follows the one reported for Am(III) , with slightly higher D

values for Eu(III) ⁽²⁰⁾.

The divalent ions Ca(II), Co(II), and Zn(II) behave similarly and with completely different behavior from that of Fe(III), indicating the displacement of protons as the metal uptake proceeds. The data of Sb(III) and Hg(II) roughly parallel the curve for Ag(I), although with lower D values. Because this behavior is also exhibited with the sulfonic and monophosphonic acid resins, it is evidently due to the chemistry of the ions in solution and not to a particular type of interaction with Diphonix ⁽²⁰⁾.

The complexing properties of Diphonix toward In(III) and Ga(III) were investigated in sulfuric acid solutions up to 2 M concentration. The complexing properties were also studied with a large excess of sodium ions relative to the metal ion concentration. For all studies, the uptake of In(III) and Ga(III) was quantitative within a relatively short contact time. Ga(III) complexation was found to be more strongly dependant on solution pH than indium ⁽²¹⁾. This difference in resin behavior can be explained by the hardness of the In(III) cation which makes it less sensitive to changes in solution acidity ⁽²²⁾.

Polymers with immobilized gem-diphosphonic acid ligands formed from functionalization of VBC-styrene-divinylbenzene copolymers with tetraisopropyl methylene diphosphonate were also studied for uptake of Eu(III) from acidic solutions ⁽²³⁾. A crosslinked copolymer of VBC and styrene was chosen because studies with only crosslinked VBC copolymer gave only 55% functionalization with the gem-diphosphonate compared with 72% functionalization of a crosslinked VBC-styrene copolymer prepared with a 2:1 molar ratio. This is due to the increased steric hindrance of complete functionalization by the bulky tetraisopropyl ligands with the VBC copolymer. Going from a gel resin to a MR resin

increases the percent functionalization from 25% to 45% for a 5% crosslinked VBC-styrene (2:1 ratio) resin, but the uptake of Eu(III) is increased from 13.6% to 91.7% at a 30 minute contact time in a background solution of 1 M nitric acid/ 4 M sodium nitrate. In the same contact solution, the gel resin after sulfonation to form a bifunctional ion exchange resin increased its Eu(III) uptake from 13.6% to 94.1%, while the bifunctional MR resin decreased from 91.7% to 65.7%. Once the amount of crosslinking in the MR bifunctional resin was increased, an extra 2.5% , 5%, and 7.5%, the uptake of Eu(III) was back to 94.5%, 97.4%, and 95.8%, respectively. This is another example of selective complexation through a dual access/recognition mechanism explained earlier ⁽²³⁾.

Diphonix A-Type 1 and Type 2 resins

Diphonix resin can be used for the separation of TRU elements from stored nuclear wastes. Among the fission products present in nuclear wastes, whose separation from the bulk of the waste would be desirable, is ⁹⁹Tc, characterized by a high fission yield and a very long half life (2.13×10^5 years). Because technetium exists in the wastes as the pertechnetate anion, TcO_4^- , its separation requires materials exhibiting affinity for anionic species. For this purpose, Diphonix-analogues were synthesized where the sulfonic acid groups were replaced by either aliphatic (Type 1) or pyridinium (Type 2) quaternary ammonium groups (Figures 1-12 and 1-13). The resins have been named Diphonix-A, for anionic Diphonix ⁽²⁴⁾.

Type 1 Diphonix-A resins bring about a remarkable decline in actinide uptake by comparison with Diphonix. This effect is evident with both methyl and ethyl quaternary

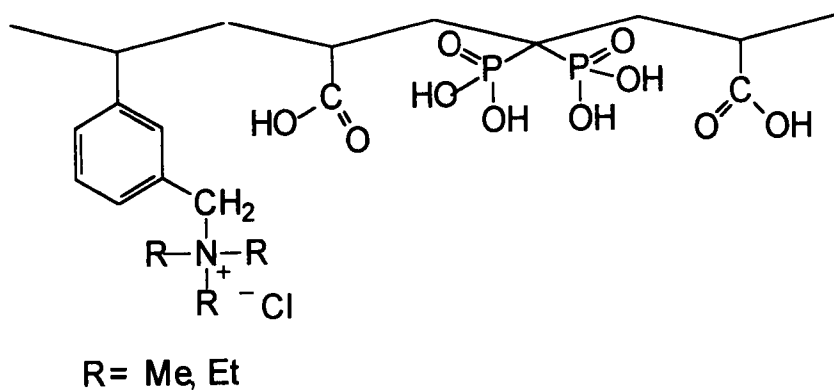


Figure 1-12. General structure of Diphonix-A, Type 1

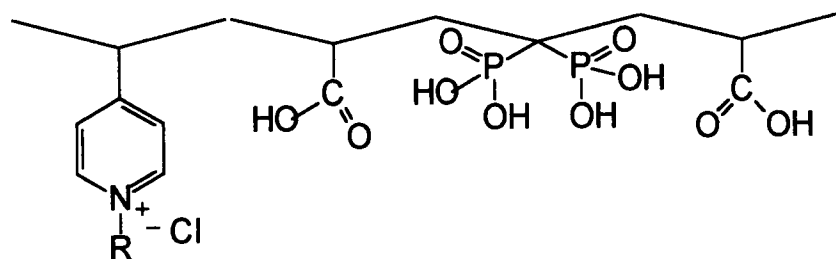


Figure 1-13. General structure of Diphonix-A, Type 2

ammonium groups although it is more pronounced with the ethyl derivative. Type 2 Diphonix-A resins do not have significant differences in actinide uptake relative to Diphonix. With Th(IV), the uptake at high nitric acid concentrations by the Type 2 resin is even higher than by Diphonix. The Th(IV) distribution ratio at high acidity is probably a composite that includes the contribution of the chelating diphosphonic acid group and the pyridinium quaternary ammonium group to the total metal ion uptake. Both Type 1 and Type 2 resins exhibit similar uptake of pertechnetate anion as compared with commercially available anion exchange resins. Type 2 Diphonix-A exhibits a gradual increase in anion uptake in the 2 to 10 M nitric acid range while Type 1 Diphonix-A and commercially available anion exchange resins show a decrease in pertechnetate anion uptake ⁽²⁴⁾.

Diphosil

The actinides are so strongly retained by Diphonix that the only effective stripping agents are compounds belonging to the family of aqueous soluble diphosphonic acids which contain the same ligand group as the resin. Because of this, it may be preferable in some cases to leave the actinides on the resin and treat them as solid waste. In this case, some or all of the polymeric resin matrix should be replaced by an inorganic material, to avoid possible generation of gases due to slow radiolytic degradation of the organic polymer. Therefore, a new version of Diphonix was prepared where the chelating diphosphonic acid groups are grafted to a silica support (Figure 1-14) ⁽²⁵⁾.

Due to the structure of the silica support, the diphosphonic acid groups are concentrated in a surface area where the ligands are much more closely packed. It can be calculated

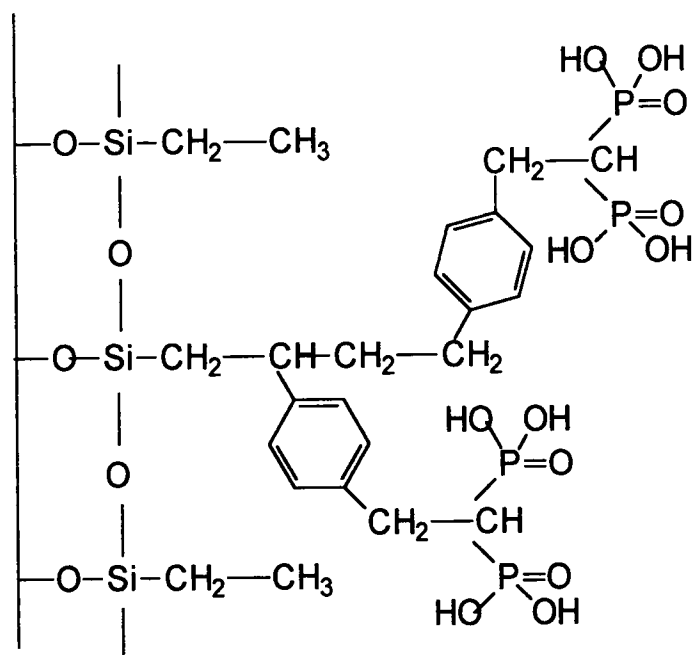


Figure 1-14. General structure of Diphosil

that the concentration of the diphosphonic acid groups in the surface layer would be at least one order of magnitude larger than the average concentration of ligands in a Diphonix resin bead.

Am(III) and U(VI) data show little change in going from Diphonix to Diphosil, with the former exhibiting slightly higher values. The uptake of tetravalent actinides, such as Pu(IV), is clearly higher for Diphosil. The Th(IV) data show that uptake by Diphosil is much less sensitive to acidity than with Diphonix. The behavior of Eu(III) with the two resins is much the same as that of Am(III). Diphosil exhibits a much higher affinity for trivalent iron and a much lower affinity for aluminum relative to Diphonix. All three investigated divalent cations, Ca(II), Zn(II), and Co(II), exhibit substantially lower D-values with Diphosil as compared to Diphonix. Based on the above results, Diphosil appears particularly well suited for those cases where the recovery and further processing of the sorbed actinides is not required and the loaded resin can be considered a solid waste. Because about 90% of the Diphosil weight is silica, the problem of possible generation of gaseous compounds is minimized ⁽²⁵⁾.

Diphonix-CS

Diphonix has been shown to have a high uptake of Sr from alkaline media, but data indicate that its selectivity for Cs ion is not significant. The presence of a large excess of sodium ions, as is normally the case in alkaline high-level waste, would likely prevent the sorption of cesium. To efficiently, selectively, and rapidly remove actinide species, Sr and Cs simultaneously from alkaline waste solutions, functional groups exhibiting selectivity

for Cs(I) ions needed to be attached to the Diphonix polymer. This new form of Diphonix (Figure 1-15) contains the diphosphonic acid groups (for actinides and Sr) and phenolic groups (for Cs) ⁽²⁶⁾.

The Diphonix-CS resin retains cesium ions with D-values over one hundred times greater than Diphonix. By comparing the cesium and strontium NaOH dependancies it appears that although the D-value of Sr is initially higher than that for Cs, it decreases rapidly as the concentration of NaOH increases showing that the two cations are complexed by different functional groups in the resin phase. Because the concentration of Cs in alkaline supernate is higher than that of Sr, a higher degree of removal of cesium than strontium is required. Therefore, the decrease of Sr uptake below that of Cs above 3M NaOH is not a serious problem. However, Diphonix-CS does have a problem with removal of Sr and Am(III) from alkaline waste simulants containing significant concentrations of organic chelating agents such as EDTA and similar compounds ⁽²⁸⁾.

Polymers with immobilized ketophosphonate ligands

The high metal ion affinity of bifunctional polymers such as the Class II phosphonate monoester/diester resin is attributed to inter-ligand cooperation between two different functional groups in binding a given metal ion such as Ag(I). The high metal ion affinity displayed by Diphonix is an example of intra-ligand cooperation between the geminal phosphoryl groups. Intra-ligand cooperation allows for ionic affinities much higher than would be possible with inter--ligand cooperation alone due to chelate formation ⁽²⁷⁾.

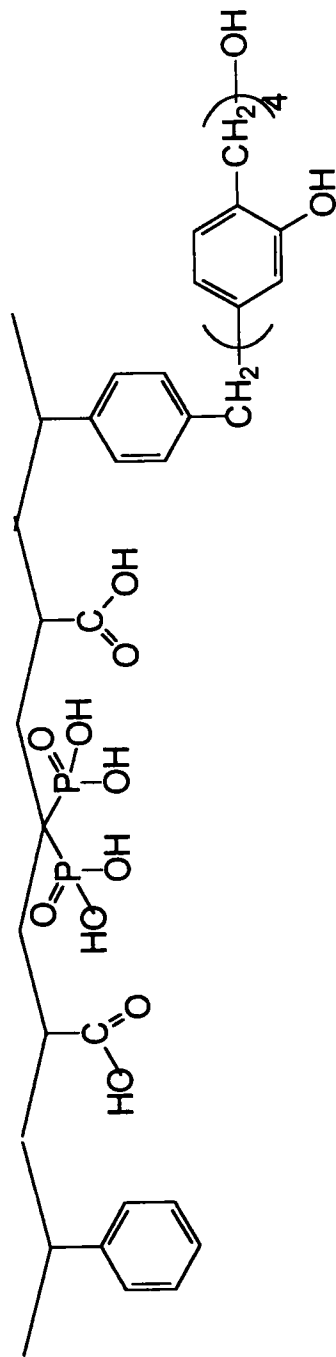
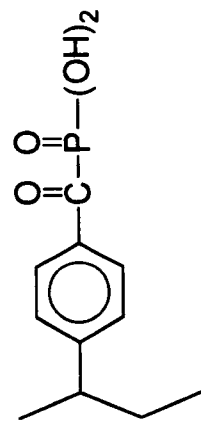


Figure 1-15. General structure of Diphonix-CS

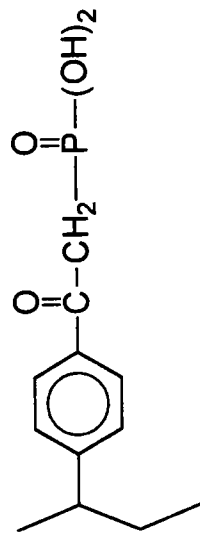
The ability of diphosphonates and ketophosphonates to act as strong ion-complexing agents through a chelation mechanism has been studied ⁽²⁸⁾. Styrene-based α -, β -, and γ -ketophosphonate polymers were thus developed to more fully explore ionic selectivities through intra-ligand cooperation. By increasing the distance between binding sites (i.e. the carbonyl and phosphoryl groups), the extent of intra-ligand cooperation is varied systematically while keeping other variables constant (Figure 1-16). Since the ligands are also capable of ion exchange, it was important to define solution conditions where the background acidity was high enough to counter the ion-exchange mechanism but low enough so that the ligands were not coordinated to the protons in solution. As a result, the ion complexation studies of Eu(III), Cu(II), Pb(II), Cd(II), Co(II) and Ag(I) were performed in 0.01, 0.10, and 1.0 N nitric acid solutions ⁽²⁷⁾.

All polymers, including a phosphonic acid resin control, complexed metal ions nearly quantitatively from 0.01 N nitric acid solutions. The important differences in Eu(III) affinities become evident from 1.0 N nitric acid, where ionic complexation is expected to occur by coordination rather than ion-exchange: the D-value is greatest for the α -ketophosphonate (2057 (98.7% complexed)) followed by the β -ketophosphonate (291 (88.6% complexed)). The phosphonic acid resin and the γ -ketophosphonate polymer show low affinities (9.43 and 21.8 (16.5% and 40.5% complexed) respectively). The same trend is observed for the other metal ions, from 0.10 N nitric acid. All polymers show low affinities for these ions from 1.0 N nitric acid solutions ⁽²⁷⁾.

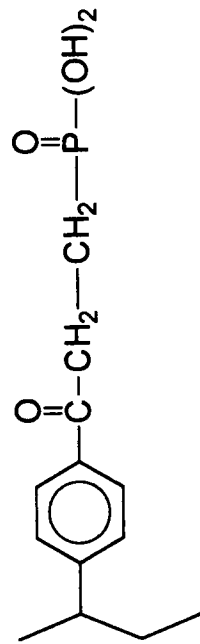
These ionic affinities can be explained in terms of intra-ligand cooperation and the stability of the rings formed upon chelation. The high ionic affinity of the α -ketophosphonate



alpha-ketophosphonic acid



beta-ketophosphonic acid



gamma-ketophosphonic acid

Figure 1-16. Ketophosphonate resins used in the intra-ligand studies

ligand can be attributed to the formation of a stable five-membered ring coupled with a relatively low loss of entropy upon chelation. This is consistent with the results obtained with the β -ketophosphonate ligand where a six-membered ring is formed but with a higher loss of rotational entropy, thus leading to a lower level of complexation. The γ -ketophosphonate ligand is much less likely to form a stable seven-membered chelate ring and so displays ionic affinities much like the phosphonic acid resin. The low metal ion affinities of the latter two ligands may thus be due to the absence of intra-ligand cooperation through a single site (the phosphoryl oxygen) for each ligand ⁽²⁷⁾.

Part II:

Bifunctional Anion-Selective Polymers

Background

Commercially available anion exchange resin, Purolite A-520E, made from functionalizing chloromethylated styrene-divinylbenzene copolymer with triethylamine has been used for the removal of anions from contaminated groundwater. A more specific contaminant in the environment is the radionuclide technetium (Tc-99) as the pertechnetate anion (TcO_4^-), which can be present in concentrations that are 4 to 5 orders of magnitude lower than those for other anions commonly found in groundwater, such as chloride, sulfate, and nitrate ⁽²⁹⁾. Purolite A-520 E, along with Sybron Ionac SR-6, Reillex HPQ, Dowex 1-X8, and Amberlite IRA-904, sorb the pertechnetate anion but are insufficiently selective when the anion is in low concentrations in the presence of other anions ⁽²⁹⁾.

Technetium-selective polymers

The goal was to find an anion exchange resin that could quantitatively complex TcO_4^- in the presence of competing anions. It was first determined that quaternary ammonium ligands containing longer alkyl chains are more selective for the pertechnetate anion, but at a low exchange rate. While trimethyl or triethylammonium-bound ligands would reach maximum capacity within an hour, resins containing the longer alkyl chains took up to a week or more. Combining anionic access and recognition ligands to form a dual mechanism bifunctional polymer gives rise to a new type of anion exchange resin. After finding that the trihexylammonium ligand has the highest affinity for the TcO_4^- (though maximum capacity is not reached until after 7 days), studies were undertaken to increase the resin's hydrophilicity by combining the selectivity of the longer alkyl ligands with shorter alkyl ligands.

The best biquaternary ammonium exchange resin was formed by amination of macroporous beads with trihexylamine followed by amination with triethylamine. This synthetic resin was compared with Purolite A-520E for sorption of pertechnetate anion in excess chloride, nitrate, and sulfate ions. After 1 hour, the hexyl/ethyl resin had a D-value of 14,400 while the Purolite resin had a D-value of 9,400. After 24 hours, the value for the hexyl/ethyl resins increased to 38,500 while the Purolite resin increased to only 12,800. The final analysis came after 168 hours (7 days). The hexyl/ethyl resin had a sorption value of 50,100 while the Purolite had a value of only 10,400. This shows that the Purolite resin had reached its capacity shortly after 1 hour and did not have a high

selectivity for the pertechnetate anion. The hexyl/ethyl resin did not reach its maximum capacity until well after 7 days and had almost a two-fold increase in selectivity over the commercial anion exchange resin after only 1 hour of contact time ⁽²⁹⁾.

Part III:

Bifunctional Interpenetrating Polymer Networks

Background

Interpenetrating polymer networks (IPNs) are an important category of polymers with properties which can be quite different from their component networks. One crosslinked network may be prepared in the presence of another with no covalent crosslinks binding them together. The physical entanglement which thus arises minimizes their phase separation since each network is independently crosslinked ⁽³⁰⁾.

Bifunctional IPNs

IPNs combining N-vinylimidazole with ethyl acrylate in varying ratios were formed in order to determine differences in cationic selectivity for Cu(II) and Co(II) as a function of the ligands' microenvironment ⁽³¹⁾. Metal ion affinities were measured from nitrate salts of Cu(II) and Co(II) buffered to pH 5 with acetate buffer at a concentration of 0.6 N and calculated as binding constants. The equimolar imidazole:ester IPN binds Cu(II) much more strongly than the IPN made purely of imidazole with binding constants of 8203 N^{-1}

and 3130 N^{-1} , respectively. While there was an increase in the Cu(II) affinity, the affinity for Co(II) decreased going from the imidazole IPN to the equimolar imidazole:ester IPN, 294 N^{-1} to 86 N^{-1} , respectively. The IPN made only with ester had no affinity for either metal studied ⁽³¹⁾. With the cations associated with the acetate ion (since it is present in large excess over the nitrate ion), the uptake of Cu(II) increases as more ester is added until an equimolar level of imidazole and ester sites is reached because the copper acetate enters into a more compatible microenvironment. Metal sorption decreases once past the equimolar ratio, probably due to the decrease in concentration of ligating sites. Although, this does not explain what happens with the uptake of Co(II), the change in the microenvironment must affect different ions in different ways ⁽³¹⁾.

IPNs containing two monomer pairs have been studied: N-vinyl imidazole (VI)/ethylacrylate (EA), VI/ acrylic acid (AA), 4-vinylpyridine (VP)/ EA and VP/ AA . It was found that the bifunctional IPNs offer a different binding environment to metal ions than the monofunctional analogues. Through the study of Co(II) and Cu(II) ion extraction, it was found that the bifunctional network is capable of distinguishing between different ions. The VI ligand has a binding constant that is 10 times greater for Cu(II) than for Co(II), and this selectivity is retained in the bifunctional IPN, though at a lower absolute value, which indicates different binding environments for the two IPNs. Under the conditions studied (the acetate-buffered solutions at pH 5) the ligands interact with the metal ions in a noncooperative manner, i.e. the relationship between ligand ratio and the metal's binding constant is linear ⁽³²⁾. Between the VP/AA ligands, it was concluded that complexation of Ni(II), Zn(II) and Co(II) occurs with a supported ligand synergistic

interaction. It was also shown that the IPN with AA ligands efficiently complexes Eu(III). However, combining the AA and VP ligands in the bifunctional resin decreases the distribution coefficient by nearly a factor of 100. This suggests that a new interaction plays an important role in the decreased metal ion affinity. Upon analysis by FTIR of the VP/AA bifunctional IPN, peaks were found representative of hydrogen bonding between pyridine and carboxylic acid ligands. It may thus be concluded that the affinity of the ligands for hard metal ions in the VP/AA bifunctional IPN is not strong enough to overcome their hydrogen bonding interaction ⁽³³⁾.

Part IV:

Bifunctional Solvent Impregnated Resins

Background

Solvent impregnated resins (SIRs) are a hybrid of solvent extraction and resin ion exchange systems that may (1) serve as a convenient vehicle to examine potential synergistic combinations of extractive functionalities, (2) permit the modification of the great variety of existing extractive resins, and (3) generally offer new possibilities for developing improved separations systems. The extraction reagents in SIRs are freely mobile within the bead and thus the extraction behavior of SIRs more closely resemble solvent extraction behavior than it does resin ion exchange ⁽³⁴⁾. From the literature, it may be concluded that essentially any solvent extractant as well as a combination of extractants may be employed in SIRs ⁽³⁵⁾.

Bifunctional SIRs

Bifunctional liquid extractants have also been impregnated into a macroporous styrene/divinylbenzene (DVB) support. Extraction resins of this type are important for the recovery and separation of metal ions, as they combine features of solvent extraction and ion exchange resins ⁽³⁶⁾. Extraction of Zn(II), Cu(II), and Cd(II) from 0.1 M sodium nitrate by impregnated resins containing a bifunctional organophosphorus extractant, O-methyl-diethyl-phosphine oxide O'-hexyl-2-ethyl phosphoric acid, has been accomplished. The extraction ability of the impregnated resin decreases, as a function of pH, in the order Cd(II) > Zn(II) > Cu(II) ⁽³⁷⁾. The extraction of these same three divalent metal ions from nitrate solutions was accomplished with an impregnated resin containing mixtures of di(2-ethylhexyl)phosphoric acid (DEHPA) and tri-n-octyl phosphine oxide (TOPO). With respect to the metal extraction, the impregnated resin shows a high performance for the extraction of Zn, Cu and Cd. The metal extraction shows a pH dependence with a general trend of increased extraction as the pH increases ⁽³⁸⁾. Impregnated resins have the same general inadequacies of liquid extraction, just not to the same degree. Since the extractant is not covalently bound to any type of support, the extractant will eventually leach out into the aqueous phase. The best method to prevent all of the problems with liquid extraction is to covalently bind the extractant to a solid support which allows the dispersal of the extractant throughout, usually a gel or macroporous resin.

A new class of SIRs was introduced in which one of the extractive functionalities was fixed to the polymer backbone as in traditional resins and the other extractive functionality was present in the form of a freely mobile extractant as in normal SIRs. Thus, one would

gain some of the advantages of solvent extraction, including selectivity and flexibility in choosing among a great variety of available reagents, and yet encompass some of the advantages of resin ion exchange. To test the notion of selective synergism in an SIR containing a functionalized support, the thia-macrocycle tetrathia-14-crown-4 (TT14C4) was chosen to sorb onto polystyrene-divinylbenzene copolymer functionalized with sulfonic acid ligands to obtain an SIR for extraction of Cu(II) from sulfuric acid solution. It was found that the resin system closely resembles the solvent extraction system in its essential chemical synergism combining cation exchange and metal ion coordination by the macrocycle ⁽³⁴⁾.

High-Stability SIRs

SIR still has some drawbacks when used in separations. Loss of the impregnated extractant(s) has still been enough of a problem to disallow large scale usage of these resins. Coating the SIR with paraffin and ethylcellulose has been done and utilized in drug delivery systems ^(39, 40), but these coatings are designed to slowly release the encapsulated compound. For ion removal, the coating must allow for rapid intake of the metal, but prevent the loss of the encapsulated compound as well as the newly formed complexant/metal species ⁽⁴¹⁾. Due to difficulty using ionically held and hydrogen-bonded anchors, a third approach using a covalently bound anchor was attempted. The surface -CH₂Cl end groups of the copolymer were modified into vinyl groups via an Arbuzov reaction followed by a Wadsworth-Emmons reaction. The beads were then coated with a 2% solution of glycidyl methacrylate (GMA)/ bis(acrylamide) in a 75/25 weight ratio. The

coating was added to the resin after encapsulation of di(2-ethylhexyl)phosphoric acid (DEHPA) and used in studies for the uptake of Cu(II). Metal ion studies were accomplished with 10^{-4} copper(II) nitrate solutions buffered to pH 8.4 with an ammonia/ammonium nitrate solution. The coating alone was analyzed for uptake of Cu(II) and gave a 0.4% uptake thus proving that the coating has no affinity for the metal. Both the uncoated and coated DEHPA encapsulated SIRs display an affinity for Cu(II) greater than 90% after the first contact period. The amount of Cu(II) complexed by the coated SIR remained constant at 96% through five cycles of the study. The amount complexed by the uncoated SIR, however, dropped precipitously to 23.2% by the second cycle and 11.2% at the third cycle, after which point further study was terminated. Therefore, the metal ion studies confirm the formation of a highly stable SIR ⁽⁴¹⁾.

CHAPTER 2

FORMATION OF PHOSPHONATE ESTER AND PHOSPHONAMIDE RESINS

Introduction

Several methods have been described in the literature for the preparation of phosphonic acid dichlorides and their use as reaction intermediates. Chlorination of soluble phosphonic acids or phosphonate esters with thionyl chloride ^(42, 43), oxalyl chloride ⁽⁴⁴⁾, phosphorus pentachloride ⁽⁴⁵⁾, or a mixture of phosphorus pentachloride and phosphorus oxychloride ⁽⁴⁶⁾ have been used under varying conditions all producing respectable yields. The phosphonic acid dichlorides have been used to form phosphonamidates and phosphonates for the possible use in both catalytic antibody research and protease or ligase enzyme research ⁽⁴⁵⁾. Phosphonate analogues of alkylphosphocholines have been used to help verify the relation between metabolism and antineoplastic activity ⁽⁴⁷⁾. Novel cyclophosphamide derivatives bearing a sugar structure were prepared as possible alkylation type anti-cancer agents with high biological activities ⁽⁴⁸⁾. A phosphonate diester in the form of a hapten compound was found to generate useful catalytic antibodies ⁽⁴⁹⁾. All of these procedures follow different reaction conditions using different reactants and catalysts.

The phosphonate esters and the phosphonamide compounds also have potential in removing metal contaminants from the environment. Early research had been done on the formation of polymer bound phosphonate ethyl esters and their use in the removal of metal ions from aqueous solutions, ⁽⁵⁰⁾ but no extensive study of other types of phosphonate

esters as well as phosphonamides had been done.

The goal of the present research is to devise a procedure that allows for the synthesis of a wide variety of ion-selective polymers from a common reactive intermediate using one simple, general procedure. The variables studied include: solvent, reaction temperature, reaction time, pre-reaction and post reaction conditions.

Experimental

Suspension copolymerization of vinylbenzyl chloride and divinylbenzene gel beads

The copolymer beads were prepared from vinylbenzyl chloride (VBC) and divinylbenzene (DVB) by suspension polymerization. Beads were prepared with 2 % DVB in microporous (gel) form. Beads that were used in the functionalization reactions had particle size in the range of 0.25 - 0.42 mm (-40 +60 mesh).

Synthesis of phosphonic acid resin

The VBC copolymer was reacted with triisopropyl phosphite at reflux temperature for 17 h. The excess solution was siphoned off. The ester form was hydrolyzed by refluxing the resin with conc. HCl for 24 h. The beads were washed with water and conditioned with 1 L each of water, 4 wt% NaOH, water, 4 wt% HCl and water. The resin was then extracted in a soxlet with water for 17 h, and the above-stated conditioning sequence was repeated.

Synthesis of phosphoryl dichloride resin

The phosphonic acid resin was buchner dried under slight vacuum (710 mm Hg) for 5 minutes in order to remove excess water. The buchner dried resin was placed in a small glass jar with ~50 mL of N,N'-dimethylformamide (DMF) capped, and placed on a wrist-action shaker for at least 15 minutes. The solution was siphoned off and the DMF wash was repeated two more times. The resin was solvent exchanged with dichloromethane three times. A thionyl chloride/ DMF solution was added dropwise to the resin/ dichloromethane mixture which was immersed in an ice-water bath. The new mixture was stirred at room temperature for 4 hours, after which time the solution was siphoned off. The chlorination step was repeated a second time at room temperature for 17 hours. The solution was siphoned off and the resin was washed with solutions of dichloromethane and toluene (both under a strong nitrogen sweep).

Synthesis of phosphonate ester resin

The toluene was siphoned off of the phosphoryl dichloride resin and replaced with pyridine. An excess of the desired alcohol reactant was added dropwise while a light nitrogen sweep passed through the apparatus. Once all of the alcohol was added, the mixture was heated to the reaction temperature and the reaction time was started. When the reaction was completed, the solution was immediately removed and the resin was washed with 75% aqueous 1,4-dioxane followed by a water wash. The resin was then conditioned and characterized for the appropriate elemental analyses.

Synthesis of phosphonamide resin

The toluene was siphoned off of the phosphoryl dichloride resin and replaced with pyridine. An excess of the desired amine reactant was added dropwise while a light nitrogen sweep passed through the apparatus. Once all of the amine was added, the mixture was heated to the reaction temperature and the reaction time was started. Once the reaction was complete, the solution was immediately removed and the resin was washed with 75% aqueous 1,4-dioxane followed by a water wash. The resin was then conditioned and characterized for the appropriate elemental analyses.

Metal ion studies

The metal ion studies were performed by contacting enough of the resins to give 1 mequiv of phosphorus ligands (based on the phosphorus capacity) with 10 mL of 10^{-4} N $\text{Cu}(\text{NO}_3)_2$, $\text{Pb}(\text{NO}_3)_2$, $\text{Ni}(\text{NO}_3)_2$, $\text{Zn}(\text{NO}_3)_2$, and $\text{Co}(\text{NO}_3)_2$ solutions in 0.010 N HNO_3 with 0.40 N NaNO_3 and then shaken for 24 hours (equilibrium). The amount of metal ion complexed was determined by atomic absorption.

Results

Removal of water from phosphonic acid resin

Three different drying methods were attempted followed by chlorination with thionyl chloride and functionalization with 2-aminopyridine. The first method began by azeotropically distilling the resin in heptane, followed by a solvent exchange with dichloromethane. This method yielded no functionalization with 2-aminopyridine, an (N)

capacity of -0.19 mequiv/g and an (OH) capacity of 9.63 mequiv/g. The second method for removal of latent water from within the pores utilized successive multiple washes with acetone. Once again, within experimental error, there was no observed functionalization with 2-aminopyridine, (N) capacity of 0.27 mequiv/g. The third drying method attempted washed the phosphonic acid resin multiple times with N,N'-dimethylformamide (DMF). This method of removing latent pore water yielded a respectable amount of functionalization using 2-aminopyridine, an (N) capacity of 3.31 mequiv/g and an acid capacity of 5.43 mequiv/g.

Functionalization solvent

After chlorination, the resin was washed with successive washes of methylene chloride and toluene under a strong nitrogen sweep to remove any latent thionyl chloride. The phosphoryl dichloride bound resin was then reacted with 3-dimethylamino-1-propanol at room temperature for 17 hours, once in toluene and once in pyridine. The resins were each washed, conditioned and characterized by elemental analysis (Table 2-1).

Conditioning of resin post-functionalization

The resin was put through a conditioning sequence. The sequence went in the order of water, sodium hydroxide, water, hydrochloric acid, and water. The strength of the acid and base elutions had to be determined. Traditionally, a 1.0 N solution of each is used. With these solutions, functionalization was being removed and replaced with an original acid site with all resins studied except for the phosphonate benzyl esters (Table 2-2).

Table 2-1. Determination of reaction solvent by functionalization of phosphoryl dichloride resin with 3-dimethylamino-1-propanol at room temperature for 17 hours

Solvent	% solids	(OH) capacity (mequiv/g)	(N) capacity (mequiv/g)	(P) capacity (mequiv/g)
toluene (RO-01-239)	67.12 %	7.97	0.72	4.74
pyridine (RO-01-228)	63.49 %	5.86	1.49	4.50

Table 2-2. Analysis of various functionalized resins, at a reaction temperature of 100°C for 17 hours (unless otherwise noted), each conditioned with multiple strengths of base and acid

resin	conditioning solution	% solids	(OH) capacity (mequiv/g)	(N) capacity (mequiv/g)	(P) capacity (mequiv/g)
3-pyridylcarbinol *					
RO-02-132	0.01 N	58.27 %	6.07	1.94	4.01
RO-02-110	1 N	57.82 %	7.94	1.32	4.27
3-dimethylamino-1-propanol					
RO-01-242	0.01 N	45.48 %	2.67	3.62	3.20
RO-02-193	0.1 N	43.91 %	3.35	3.29	3.22
ethanolamine					
RO-02-137	0.01 N	52.10 %	3.39	3.29	4.08
RO-02-196	1 N	45.99 %	5.82	2.37	3.95
benzyl alcohol **					
RO-01-148	0.01 N	86.18 %	0.27	-----	2.59
RO-01-148	1 N	85.77 %	0.34	-----	2.61
RO-01-148	4 N	85.98 %	0.28	-----	2.71

* Reaction time of 82 hours

** Reaction temperature at RT

Reaction atmosphere

Two different reaction atmospheres were tested. Either a light nitrogen sweep or an argon blanket was applied to the apparatus. If the argon blanket was used, the system was immediately sealed. These methods were tested using 2-pyridylcarbinol as the reactant (Table 2-3).

Reaction temperature during functionalization

Reaction temperature was studied in the formation of various phosphonate esters. It was found that as the temperature increased for the reaction with 3-dimethylamino-1-propanol the amount of functionalization increased (Table 2-4). As the temperature increased for the reaction with 2-pyridylcarbinol (Table 2-5) or benzyl alcohol (Table 2-6) the amount of functionalization decreased. As the temperature increased for the reaction with ethanol the amount of functionalization stayed essentially the same (Table 2-7).

Reaction time during functionalization

Studies of reaction time were done with both formation of phosphonate esters and phosphonamides. Functionalizations were either independent of reaction time or reaction time dependent. The description of the results were thus broken into these two sections. In order to equally compare elemental results of different functionalizations a common thread had to be devised. Since the functionalizations started as various phosphonic acid resin with distinct amounts of acid and phosphorus capacities, using the actual elemental values was not appropriate. Calculating percent functionalization for each resin gave the

Table 2-3. Analysis of functionalization atmosphere during reaction of phosphoryl dichloride resin with 2-pyridylcarbinol at 100°C and conditioning with 0.10 N solutions

Resin	atmos- phere	reaction time (hr)	% solids	(OH) capacity (mequiv/g)	(N) capacity (mequiv/g)	(P) capacity (mequiv/g)
RO-04-192	Ar blanket	0.50	57.83 %	1.77	4.37	3.04
RO-03-148	nitrogen sweep	0.50	62.53 %	1.67	4.04	2.78
RO-04-195	Ar blanket	75.25	53.05 %	7.54	0.95	4.46
RO-03-154	nitrogen sweep	75.00	58.28 %	5.82	1.96	3.88

Table 2-4. Determination of reaction temperature by functionalization of phosphoryl dichloride resin with 3-dimethylamino-1-propanol

resin	rxn temp (°C)	rxn time (hr)	% solids	(OH) capacity (mequiv/g)	(N) capacity (mequiv/g)	(P) capacity (mequiv/g)
RO-01-228	RT	17.00	63.49 %	5.86	1.49	4.50
RO-01-242	100	17.00	45.48 %	2.67	3.62	3.20
RO-01-245	RT	82.00	62.89 %	3.27	2.34	3.85
RO-01-248	100	82.00	45.69 %	2.81	3.57	3.46

Table 2-5. Determination of reaction temperature by functionalization of phosphoryl dichloride resin with 2-pyridylcarbinol

resin	rxn temp (°C)	rxn time (hr)	% solids	(OH) capacity (mequiv/g)	(N) capacity (mequiv/g)	(P) capacity (mequiv/g)
RO-04-223	RT	0.50	71.00 %	1.25	4.40	2.76
RO-03-187	100	0.50	62.32 %	1.83	3.92	2.73
RO-04-270	RT	75.00	63.04 %	1.31	4.47	2.92
RO-03-154	100	75.00	58.28 %	5.82	1.96	3.88

Table 2-6. Determination of reaction temperature by functionalization of phosphoryl dichloride resin with benzyl alcohol

resin	rxn temp (°C)	rxn time (hr)	% solids	(OH) capacity (mequiv/g)	(P) capacity (mequiv/g)
RO-04-211	RT	0.50	81.76 %	0.18	2.92
RO-04-217	77	0.50	81.36 %	0.32	2.93
RO-02-267	100	0.50	69.39 %	1.59	3.06
RO-04-239	RT	63.00	85.20 %	0.15	2.91
RO-04-236	77	63.00	67.92 %	3.87	3.85
RO-04-096	100	63.00	61.36 %	7.11	4.41

Table 2-7. Determination of reaction temperature by functionalization of phosphoryl dichloride resin with ethanol

resin	rxn temp (°C)	rxn time (hr)	% solids	(OH) capacity (mequiv/g)	(P) capacity (mequiv/g)
RO-04-214	RT	0.50	54.00 %	0.34	3.99
RO-04-093	77	0.50	69.29 %	0.30	3.77
RO-02-211	96	2.50	67.69 %	0.49	3.66
RO-04-208	RT	72.00	66.97 %	0.43	3.87
RO-04-118	77	72.00	69.62 %	0.67	3.91

desired common thread. For reactions with alcohols (Figure 2-1), % diester, % monoester and % diacid were calculated. For reactions with amines (Figure 2-2), % diamide, % monoamide and % diacid were calculated. Each of the two types of reactions can form one of two different possible combinations. The newly formed phosphonate ester is most likely to be either a combination of diester and monoester, or a combination of monoester and diacid. The newly formed phosphonamide can either be a combination of diamide and monoamide, or a combination of monoamide and diacid.

The phosphonate ester group where the R-group does not have nitrogen is broken into two sets of equations. If the acid capacity is less than the phosphorus capacity, this means that the resin is predominantly diester with the remaining as monoester. If the acid capacity is greater than the phosphorus capacity, this means that the resin is predominantly monoester with the remaining as diacid (Equations 2-1).

If the phosphonate ester contains a nitrogen within the ligand, a new set of equations is used (Equations 2-2). With the possibility of the nitrogen remaining protonated, the error for the acid capacity increases. Therefore, the acid capacity is not used due with addition of an amine on the ligand. Therefore, if the nitrogen capacity is less than the phosphorus capacity the resin contains the combination of monoester and diacid. If the nitrogen capacity is greater than the phosphorus capacity the resin contains the combination of diester and monoester.

The phosphonamide resin where the ligand does not contain a second nitrogen is broken down into two different sets of equations (Equations 2-3). If the nitrogen capacity is greater than the phosphorus capacity then the resin contains the combination of diamide

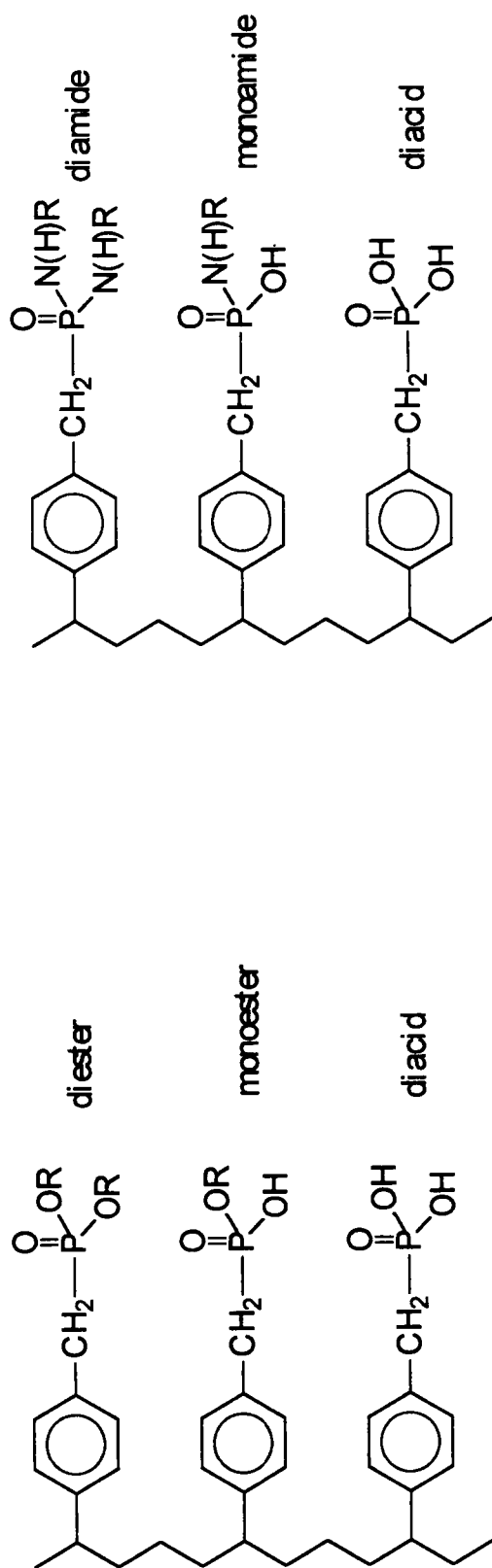


Figure 2-1. possible ligands on a phosphonate ester resin

Figure 2-2. Possible ligands on a phosphonamide resin

$$\text{OH} < \text{P}, \quad \% \text{ diester} = \frac{(\text{P} - \text{OH})}{\text{P}} \times 100\%$$

$$\% \text{ monoester} = \frac{\text{OH}}{\text{P}} \times 100\%$$

$$\text{OH} > \text{P}, \quad \% \text{ monoester} = \frac{2\text{P} - \text{OH}}{\text{P}} \times 100\%$$

$$\% \text{ diacid} = \frac{(\text{OH} - \text{P})}{\text{P}} \times 100\%$$

Equation 2-1. Calculations for phosphonate esters where the R-group does not contain nitrogen

$$\text{OH} < \text{P}, \quad \% \text{ diester} = \frac{(\text{P} - \text{OH})}{\text{P}} \times 100\%$$

$$\% \text{ monoester} = \frac{\text{OH}}{\text{P}} \times 100\%$$

can check the mass balance using the following:

$$\text{calculated N} = (2\text{P} - \text{OH})$$

$$\text{OH} > \text{P}, \quad \% \text{ monoester} = \frac{\text{N}}{\text{P}} \times 100\%$$

$$\% \text{ diacid} = \frac{(\text{P} - \text{N})}{\text{P}} \times 100\%$$

can check the mass balance using the following:

$$\text{calculated OH} = (2\text{P} - \text{N})$$

Equation 2-2. Calculations for phosphonate esters where the R-group contains nitrogen

$$N > P, \quad \% \text{ diamide} = \frac{(P - OH)}{P} \times 100\%$$

$$\% \text{ monoamide} = \frac{OH}{P} \times 100\%$$

can check the mass balance using the following:

$$\text{calculated } N = (2P - OH)$$

$$N < P, \quad \% \text{ monoamide} = \frac{N}{P} \times 100\%$$

$$\% \text{ diacid} = \frac{(P - N)}{P} \times 100\%$$

can check the mass balance using the following:

$$\text{calculated } OH = (2P - N)$$

Equation 2-3. Calculations for phosphonamides where the R-group does not contain a second nitrogen

and monoamide. The phosphonamide resin where the ligand contains a second nitrogen is also broken down into two sets of equations (Equations 2-4). If half of the nitrogen capacity is greater than the phosphorus capacity than the resin contains the combination of diamide and monoamide. If one half of the nitrogen capacity is less than the phosphorus capacity, the resin is the combination of monoamide with the remaining as diacid. Reactions at varying times at elevated temperature (100 °C or 8 degrees below the reactant's b.p, whichever was lower) using these calculations can be found in the next twelve tables.

Reaction time dependent functionalizations

All reactions were done at 100 °C and conditioned with 0.10 N elutions, unless otherwise noted. As shown in Tables 2-8 and 2-9, functionalization of the polymer bound phosphoryl dichloride with 2-pyridylcarbinol is reaction time dependant. At a reaction time of 30 minutes, there is almost a 50:50 mixture of diester and monoester, but even at a reaction time of 5½ hours the functionalization drops to almost pure monoester. As time is increased even more, the amount of diacid increases as the %monoester decreases. All of this shows a dependency on reaction time when all other variables are kept constant. Reactions using 3-pyridylcarbinol (Table 2-10 and 2-11) or 4-pyridylcarbinol (Table 2-12 and 2-13) both show the same general trend of reaction time dependency . The largest number of trials were done using 3-pyridylcarbinol. Depending on the particular reaction time, there were as few as one trial and as many as four.

The fourth reactant studied that showed a dependency for reaction time was benzyl

$$N > 2P, \quad \% \text{ diamide} = \frac{(P - OH)}{P} \times 100\%$$

$$\% \text{ monoamide} = \frac{OH}{P} \times 100\%$$

can check the mass balance using the following:

$$\text{calculated } N = 2 \times (2P - OH)$$

$$N < 2P, \quad \% \text{ monoamide} = \frac{N}{2P} \times 100\%$$

$$\% \text{ diacid} = \frac{(P - \frac{1}{2}N)}{P} \times 100\%$$

can check the mass balance using the following:

$$\text{calculated } OH = (2P - \frac{1}{2}N)$$

Equation 2-4. Calculations for phosphonamides where the R-group contains a second nitrogen

Table 2-8. Percent functionalization for reactions with 2-pyridylcarbinol at 100 °C

Resin	reaction time (hr)	% solids	(OH) capacity (mequiv/g)	(N) capacity (mequiv/g)	(P) capacity (mequiv/g)	% diester	% monoester	% diacid
RO-03-187	0.50	62.32	1.83	3.92	2.73	43.59	56.41	0.00
RO-03-148	0.50	62.53	1.67	4.04	2.78	45.32	54.68	0.00
RO-03-151	5.50	45.43	3.87	3.01	3.28	0.00	91.77	8.23
RO-03-193	17.00	54.42	4.26	2.41	3.36	0.00	71.73	28.27
RO-03-172	17.00	51.51	3.86	2.80	3.44	0.00	81.40	18.60
RO-03-154	75.00	58.28	5.82	1.96	3.88	0.00	50.52	49.48

Table 2-9. Averages of percent functionalization results in Table 2-8 (2-pyridylcarbinol)

reaction time (hr)	% diester	% monoester	% diacid
0.50	44.46	55.54	0.00
5.50	0.00	91.77	8.23
17.00	0.00	76.56	23.44
75.00	0.00	50.52	49.48

Table 2-10. Percent functionalization of reactions with 3-pyridylcarbinol at 100 °C *

Resin	reaction time (hr)	% solids	(OH) capacity (mequiv/g)	(N) capacity (mequiv/g)	(P) capacity (mequiv/g)	% diester	% monoester	% diacid
RO-02-184	0.50	50.72	3.06	3.29	3.24	1.54	98.46	0.00
RO-03-190	2.50	52.19	4.10	3.08	3.22	0.00	95.65	4.35
RO-02-172	2.50	50.00	3.62	3.01	3.32	0.00	90.66	9.34
RO-04-063	2.50	49.49	4.06	3.21	3.07	0.00	104.56	-4.56
RO-04-060	5.50	47.40	4.42	2.87	3.30	0.00	86.97	13.03
RO-02-143	5.50	51.37	3.79	2.75	3.56	0.00	77.25	22.75
RO-04-233	5.50	47.56	4.36	3.70	3.63	0.00	101.93	-1.93
RO-04-081	5.50	47.48	4.76	3.13	3.41	0.00	91.79	8.21
RO-04-245	11.00	52.47	5.12	3.17	3.88	0.00	81.70	18.30

* The second half of this table is on the following page

Table 2-10. Continued.

Resin	reaction time (hr)	% solids	(OH) capacity (mequiv/g)	(N) capacity (mequiv/g)	(P) capacity (mequiv/g)	% diester	% monoester	% diacid
RO-04-057	11.00	54.88	4.62	2.83	3.18	0.00	88.99	11.01
RO-01-302	17.00	58.60	4.23	2.58	3.63	0.00	71.07	28.93
RO-04-084	17.00	59.65	5.86	2.22	3.81	0.00	58.27	41.73
RO-04-054	17.00	51.24	5.01	2.38	3.37	0.00	70.62	29.38
RO-04-273	27.00	59.63	5.53	2.81	3.59	0.00	78.27	21.73
RO-04-046	27.00	60.19	5.69	2.06	3.79	0.00	54.35	45.65
RO-04-252	38.00	59.39	6.87	2.14	4.02	0.00	53.23	46.77
RO-04-059	38.00	60.82	5.90	2.24	3.77	0.00	59.42	40.58
RO-04-035	48.00	60.37	6.74	1.63	4.03	0.00	40.45	59.55
RO-02-174	82.00	65.86	6.76	1.29	3.92	0.00	32.91	67.09

Table 2-11. Averages of percent functionalization results in Table 2-10 (3-pyridylcarbinol)

reaction time (hr)	% diester	% monoester	% diacid
0.50	1.54	98.46	0.00
2.50	0.00	96.96	3.04
5.50	0.00	89.48	10.52
11.00	0.00	85.35	14.65
17.00	0.00	66.66	33.34
27.00	0.00	66.31	33.69
38.00	0.00	56.33	43.67
48.00	0.00	40.45	59.55
82.00	0.00	32.91	67.09

Table 2-12. Percent functionalization of reactions with 4-pyridylcarbinol at 100 °C

Resin	reaction time (hr)	% solids	(OH) capacity (mequiv/g)	(N) capacity (mequiv/g)	(P) capacity (mequiv/g)	% diester	% monoester	% diacid
RO-03-160	0.50	52.33	3.24	3.06	3.23	0.00	94.74	5.26
RO-03-198	5.50	53.89	4.78	2.42	3.58	0.00	67.60	32.40
RO-03-163	5.50	53.27	4.20	2.59	3.51	0.00	73.79	26.21
RO-03-201	17.00	58.76	5.02	2.31	3.67	0.00	62.94	37.06
RO-03-169	17.00	56.06	4.97	2.23	3.68	0.00	60.60	39.40
RO-03-166	59.00	60.10	6.38	1.58	4.10	0.00	38.54	61.46

Table 2-13. Averages of percent functionalization results in Table 2-12, (4-pyridylcarbinol)

reaction time (hr)	% diester	% monoester	% diacid
0.50	0.00	94.74	5.26
5.50	0.00	70.69	29.31
17.00	0.00	61.77	38.23
59.00	0.00	38.54	61.46

alcohol (Table 2-14). Here, the percent functionalization results mimic that found with 2-pyridylcarbinol. The functionalization starts out roughly as a 50:50 mixture of diester:monoester and quickly loses ligand functionality and forms diacid ligands. A final esterification reaction studied, although briefly, was the reaction with 4-methoxybenzyl alcohol. As shown in Table 2-15, the percent functionalization started as a 50:50 mixture of monoester:diacid at the 30 minute reaction time. After 72 hours, the resin was over 91% diacid with less than 9% remaining as monoester.

Reaction time independent functionalizations

The first reactant studied to mention from this group was benzyl amine (see Tables 2-16 and 2-17). Here one can see that about two-thirds of the functionalization at thirty minutes is made up of diamide with the remaining as monoamide. This trend stays predominantly constant through the entire study even as high as 83.5 hours. Reactions with 3-(aminomethyl)pyridine gave similar results (see Tables 2-18 and 2-19) showing a generally constant amount of functionalization (around 90% monoamide) from 30 minutes to 83.5 hours. As seen in Table 2-20, the formation of almost pure diester from reaction with ethanol occurs at 30 minutes and this remains constant up to the last time studied (72 hours).

Only two reactions were attempted with 4-methoxybenzyl amine, a 30 minute reaction and a 72 hour reaction (Table 2-21). Both were in good agreement of each other yielding 90% monoamide with the remaining as diacid. Various reactions were also attempted with n-butyl amine (Tables 2-22 and 2-23). Two different 30 minute reactions yielded

Table 2-14. Percent functionalization for reactions with benzyl alcohol at 100 °C

Resin	reaction time (hr)	% solids	(OH) capacity (mequiv/g)	(N) capacity (mequiv/g)	(P) capacity (mequiv/g)	% diester	% monoester	% diacid
RO-02-267	0.50	69.39	1.59	n/a	3.06	48.04	51.96	0.00
RO-02-208	2.50	77.37	2.75	n/a	3.21	14.33	85.67	0.00
RO-04-106	18.25	62.01	4.82	n/a	3.85	0.00	74.81	25.19
RO-04-096	63.00	61.36	7.11	n/a	4.41	0.00	38.78	61.22

Table 2-15. Percent functionalization for reactions with 4-methoxybenzyl alcohol at 100 °C

Resin	reaction time (hr)	% solids	(OH) capacity (mequiv/g)	(N) capacity (mequiv/g)	(P) capacity (mequiv/g)	% diester	% monoester	% diacid
RO-03-290	0.50	60.35	6.10	n/a	4.04	0.00	49.01	50.99
RO-04-025	72.00	54.98	8.91	n/a	4.66	0.00	8.80	91.20

Table 2-16. Percent functionalization of reactions with benzyl amine at 100 °C

Resin	reaction time (hr)	% solids	(OH) capacity (mequiv/g)	(N) capacity (mequiv/g)	(P) capacity (mequiv/g)	% diester	% monoester	% diacid
RO-03-026	0.50	75.41	0.57	4.35	2.90	50.00	50.00	0.00
RO-03-029	0.50	75.27	0.64	4.65	2.58	80.23	19.77	0.00
RO-04-166	2.50	76.44	0.22	4.91	2.87	71.08	28.92	0.00
RO-04-169	17.00	76.12	0.23	4.69	2.89	62.28	37.72	0.00
RO-04-172	83.50	74.27	0.32	4.91	2.89	69.90	30.10	0.00

Table 2-17. Averages of percent functionalization results in Table 2-16 (benzyl amine)

reaction time (hr)	% diamide	% monoamide	% diacid
0.50	65.12	34.88	0.00
2.50	71.08	28.92	0.00
17.00	62.28	37.72	0.00
83.50	69.90	30.10	0.00

Table 2-18. Percent functionalization of reactions with 3-(aminomethyl)pyridine at 68 °C

Resin	reaction time (hr)	% solids	(OH) capacity (mequiv/g)	(N) capacity (mequiv/g)	(P) capacity (mequiv/g)	% diamide	% monoamide	% diacid
RO-04-154	0.50	49.25	2.70	6.40	3.71	0.00	86.25	13.75
RO-04-157	17.00	58.81	2.72	5.98	3.60	0.00	83.06	16.94
RO-05-085	17.00	58.55	2.45	5.95	3.17	0.00	93.85	6.15
RO-04-175	83.50	55.75	2.61	6.72	3.52	0.00	95.45	4.55

Table 2-19. Averages of percent functionalization results in Table 2-18.
(3-(aminomethyl)pyridine)

reaction time (hr)	% diamide	% monoamide	% diacid
0.50	0.00	86.25	13.75
17.00	0.00	88.45	11.55
83.50	0.00	95.45	4.55

Table 2-20. Percent functionalization of reactions with ethanol at 77 °C

Resin	reaction time (hr)	% solids	(OH) capacity (mequiv/g)	(N) capacity (mequiv/g)	(P) capacity (mequiv/g)	% diester	% monoester	% diacid
RO-04-093	0.50	69.29	0.30	n/a	3.77	92.04	7.96	0.00
RO-02-264	2.50	70.74	0.62	n/a	3.70	93.24	16.76	0.00
RO-04-100	19.67	60.80	0.44	n/a	3.88	88.66	11.34	0.00
RO-04-118	72.00	69.62	0.67	n/a	3.91	82.86	17.14	0.00

Table 2-21. Percent functionalization of reactions with 4-methoxybenzyl amine at 100 °C

Resin	reaction time (hr)	% solids	(OH) capacity (mequiv/g)	(N) capacity (mequiv/g)	(P) capacity (mequiv/g)	% diester	% monoester	% diacid
RO-03-293	0.50	70.78	2.10	2.82	3.14	0.00	89.81	10.19
RO-04-022	72.00	69.04	2.10	2.79	3.09	0.00	90.29	9.71

Table 2-22. Percent functionalization of reactions with n-butyl amine at 73 °C

Resin	reaction time (hr)	% solids	(OH) capacity (mequiv/g)	(N) capacity (mequiv/g)	(P) capacity (mequiv/g)	% diester	% monoester	% diacid
RO-03-275	0.50	73.87	0.53	5.28	3.17	66.56	33.44	0.00
RO-04-090	0.50	75.46	0.31	5.22	3.26	60.12	39.88	0.00
RO-03-272	17.00	74.80	0.43	5.27	3.10	70.00	30.00	0.00
RO-04-121	72.00	73.09	0.32	5.26	3.44	52.91	47.09	0.00

Table 2-23. Averages of percent functionalization results in Table 2-22 (n-butyl amine)

reaction time (hr)	% diamide	% monoamide	% diacid
0.50	63.34	36.66	0.0
17.00	70.00	30.00	0.00
72.00	52.91	47.09	0.00

67% and 60% diamide with the remaining as monoamide, respectively. A 17 hour reaction and a 72 hour reaction were also done. These produced 70% and 53% diamide with remaining as monoamide, respectively. The final reaction to discuss utilized 4-(aminomethyl)pyridine as the reactant (Table 2-24). Studies from 30 minutes to 72 hours gave a minimum of 12% monoamide with the remaining 88% as diacid up to a maximum of 35% monoamide with the remaining 65% as diacid.

Reactivity difference between alcohol and amine

Early on in this project functionalizations were done using ethanolamine as the reactant with hopes of having a phosphonate ester with a free amine at the end of each ligand. Reactions were done at both room temperature and 100 °C as well as various times between 30 minutes and 82 hours at 100 °C (Table 2-25). No discernable trends were found in any of the studies. By combining set mixtures of benzyl alcohol and benzyl amine in the same reaction and then altering the reactant ratio with different reactions gave results to explain the ethanolamine reactions.

Formation of other phosphonate esters and phosphonamides

Many different functionalizations were attempted during the course of the project without extensively researching the dependance on the variables discussed above. Although, the products from these reactions were used in the studies for divalent metal ion uptake (vide infra). The first of these reactions to be discussed used 2-(aminomethyl)pyridine. Two different reactions were done, both at 77 °C (about eight degrees below the reactant's

Table 2-24. Percent functionalization of reactions with 4-(aminomethyl)pyridine at 100 °C

Resin	reaction time (hr)	% solids	(OH) capacity (mequiv/g)	(N) capacity (mequiv/g)	(P) capacity (mequiv/g)	% diester	% monoester	% diacid
RO-04-141	0.50	56.13	5.94	1.17	4.91	0.00	11.91	88.09
RO-04-144	2.50	58.78	5.10	1.97	4.90	0.00	20.10	79.90
RO-04-147	17.00	61.63	4.65	3.19	4.53	0.00	35.21	64.79
RO-04-160	72.00	61.35	4.46	1.51	4.32	0.00	17.48	82.52

Table 2-25. Elemental analysis of reactions with ethanolamine at 100 °C

Resin	rxn time (hr)	% solids	(OH) capacity (mequiv/g)	(N) capacity (mequiv/g)	(P) capacity (mequiv/g)
RO-02-187	0.50	55.27	3.74	3.81	3.95
RO-03-112	0.50	54.39	4.66	2.96	4.33
RO-03-23	0.50	54.46	4.54	3.22	3.85
RO-03-015	5.50	53.42	5.36	2.01	4.49
RO-03-127	5.50	56.51	5.01	2.79	4.12
RO-03-052	17.00	57.64	5.21	2.79	4.19
RO-03-018	82.00	51.98	4.80	2.74	4.04

boiling point), the first for a 30 minute reaction time and the second for 17 hours (Table 2-26).

Reactions with benzyl alcohol and benzylamine were extensively researched mechanistically as well as for uptake of various metal ions. In order to get a better understanding of the metal ion uptake studies, various para-substituted benzyl alcohols and benzylamines were formed. The 4-chloro- and the 4-methoxy- substituted reactants were studied (Tables 2-27 and 2-28).

In order to get a better understanding of the effect of the para- group on the aromatic ring of the reactant, reactions were done with phenol and various para-substituted phenols. As seen in Table 2-29, there is no loss of functionalization within each reaction and all reactions are at least 65% diester or better.

Up until now, the only type of amines that have been discussed have been primary amines. In order to get a better understanding of the reaction mechanism, reactions using a secondary amine as well as various tertiary amines were attempted. The secondary amine chosen was dibutylamine. This was done once at a 30 minute reaction time at 100 °C.

Upon elemental analysis, the resin had a nitrogen capacity nearly equivalent to the phosphorus capacity (3.16 mequiv/g to 3.06 mequiv/g, respectively). Although the acid capacity was below what it should have been according to the other elemental analyses (2.16 mequiv/g), using the calculated acid capacity from the mass balance equation, the reaction yielded a resin of 96.7% monoamide with the remaining 3.3% as diamide.

Reactions were also attempted with various tertiary amines. The first tertiary amine to be studied was N,N'-dimethylbutylamine. The most simple tertiary amine with a similar

Table 2-26. Elemental analysis and percent functionalization of 2-(aminomethyl)pyridine based reactions

Resin	reaction time (hr)	% solids	(OH) capacity (mequiv/g)	(N) capacity (mequiv/g)	(P) capacity (mequiv/g)	% diester	% monoester	% diacid
RO-05-090	0.50	57.82%	4.27	3.61	3.61	0.00 %	50.00 %	50.00 %
RO-05-082	17.00	60.18%	2.48	6.36	2.96	7.43 %	92.57 %	0.00 %

Table 2-27. Elemental analysis and percent functionalization of para-substituted benzyl amine reactions

Resin	reaction time (hr)	% solids	(OH) capacity (mequiv/g)	(N) capacity (mequiv/g)	(P) capacity (mequiv/g)	% diester	% monoester	% diacid
4-chloro-benzyl amine								
RO-3-278	0.50	72.91 %	0.32	3.75	2.32	61.64 %	38.36 %	0.00 %
4-methoxy-benzyl amine								
RO-3-293	0.50	70.78 %	2.10	2.82	3.46	0.00 %	89.91 %	10.19 %
RO-4-022	72.00	69.04 %	2.10	2.79	3.39	0.00 %	90.29 %	9.71 %

Table 2-28. Elemental analysis and percent functionalization of para-substituted benzyl alcohol reactions

Resin	reaction time (hr)	% solids	(OH) capacity (mequiv/g)	(N) capacity (mequiv/g)	(P) capacity (mequiv/g)	% diester	% monoester	% diacid
4-chloro-benzyl alcohol								
3-266	0.50	79.02 %	0.92	n/a	2.56	64.06 %	35.94 %	0.00 %
3-263	0.50	73.45 %	1.07	n/a	2.65	59.62 %	40.38 %	0.00 %
4-methoxy-benzyl alcohol								
3-290	0.50	60.35 %	6.10	n/a	4.04	0.00 %	49.01 %	50.99 %
4-025	72.00	54.98 %	8.91	n/a	4.66	0.00 %	8.80 %	91.20 %

Table 2-29. Elemental analysis and percent functionalization of phenol based reactions

Resin	reaction time (hr)	% solids	(OH) capacity (mequiv/g)	(N) capacity (mequiv/g)	(P) capacity (mequiv/g)	% diester	% monoester	% diacid
phenol								
RO-4-276	0.50	76.43%	0.76	n/a	2.96	74.32%	25.68%	0.00%
RO-4-279	72.00	82.90%	0.65	n/a	2.83	77.03%	22.97%	0.00%
4-chlorophenol								
RO-4-258	0.50	80.30%	0.76	n/a	2.45	68.98%	31.02%	0.00%
RO-4-264	72.00	79.25%	0.85	n/a	2.44	65.16%	34.84%	0.00%
4-methoxyphenol								
RO-4-032	0.50	74.71%	0.44	n/a	2.45	82.04%	17.96%	0.00%
RO-4-261	0.50	78.70%	0.89	n/a	2.52	64.68%	35.32%	0.00%
RO-4-267	72.00	76.27%	0.68	n/a	2.44	72.13%	27.87%	0.00%
4-nitrophenol								
RO-5-093	0.50	80.64%	0.48	n/a	2.24	78.57%	21.43%	0.00%

structure to n-butylamine, whose reactions were discussed earlier. Three different trials were attempted (Table 2-30), all for 30 minutes at 85 °C (around eight degrees below the boiling point of the reactant). A small amount of nitrogen capacity (around 0.5 mequiv/g for two of the three reactions and 1.2 mequiv/g for the third) was found in the reactions with N,N'-dimethylbutylamine, and the acid capacities were below what they should have been. Two reactions with triethylamine done at 80 °C were attempted (Table 2-30), one at 30 minutes and the second at extended time (74.5 hours). The 30 minute reaction was analyzed for elemental analyses and gave a nitrogen capacity of 0.34 mequiv/g. Although bordering a value considered within experimental error, the results led to even more confusion when the acid capacity was found to be 6.77 mequiv/g. The acid capacity of the starting phosphonic acid resin was 9.37 mequiv/g. The extended time reaction was also analyzed for elemental analysis. This resin had a slightly higher nitrogen capacity, 0.72 mequiv/g, but the acid capacity was even lower at 5.31 mequiv/g. The acid capacity of this starting phosphonic acid was 9.50 mequiv/g.

All of the above stated data led to various control reactions using no reactant and only solvent. After chlorination with thionyl chloride, the reaction was run with pyridine only at 100 °C for 72 hours. This control was done two separate times each yielding the same results (Table 2-31). The same study was done at room temperature instead of 100 °C (Table 2-31).

A final control was done with these resins. A sample from the reaction at room temperature was refluxed with concentrated hydrochloric acid for 24 hours, washed with water, and conditioned with 0.1 N elutions. This resin was characterized and compared

Table 2-30. Reaction conditions and characterization of reactions with tertiary amines

Resin	rxn time (hr)	rxn temp. (°C)	% solids	(OH) capacity (mequiv/g)	(N) capacity (mequiv/g)	(P) capacity (mequiv/g)
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N,N'-dimethyl-butylamine

RO-03-260	0.50	85	54.97 %	7.88	0.53	4.43
RO-03-257	0.50	85	60.68 %	7.72	0.48	4.40
RO-03-130	0.50	85	57.63 %	5.98	1.19	4.37

triethylamine

RO-03-299	0.50	80	57.71 %	6.77	0.34	4.52
RO-04-110	74.50	80	65.10 %	5.31	0.72	4.53

Table 2-31. Reaction conditions and characterization of solvent controls

Resin	rxn. temp. (°C)	rxn time (hr)	% solids	(OH) capacity (mequiv/g)	(N) capacity (mequiv/g)	(P) capacity (mequiv/g)
pyridine only						
RO-04-198	100	72.00	54.95 %	6.05	0.69	4.36
RO-04-286	100	72.00	57.88 %	6.12	0.55	4.13
RO-04-291	RT	72.00	58.52 %	7.31	0.33	4.46
triethylamine only						
RO-05-015	73	72.00	57.67 %	7.01	0.41	4.65
RO-05-010	RT	72.00	67.30 %	7.14	0.46	4.77
toluene only						
RO-05-025	95	49.75	56.15 %	8.35	0.10	4.73
RO-05-020	RT	50.00	50.68 %	8.43	0.28	4.69
acetic anhydride only						
RO-05-032	108	49.50	63.90 %	6.19	0.27	4.59

with the unrefluxed resin. to produced an acid capacity of 9.50 mequiv/g, a phosphorus capacity of 4.81 mequiv/g and a nitrogen capacity of 0.34 mequiv/g.

Similar control studies were done using triethylamine as well as toluene instead of pyridine. In the studies with triethylamine as the solvent at the elevated temperature reactions, the results generally the same as those found with pyridine but not as severe (Table 2-31). In the studies with toluene as the solvent, the results were even less severe (Table 2-31). A fourth and final control using acetic anhydride as the solvent was used. This control was done for just under 50 hours (Table 2-31).

Metal ion studies

The newly formed phosphonate ester and phosphonamide resins were used in studies for the uptake of various divalent metal ions in a background of competing sodium ions. Five different metals were used at a concentration of 1×10^{-4} N metal nitrate in a background solution of 0.01 N nitric acid along with 0.40 N sodium nitrate and the resin was shaken in these solutions to equilibrium (24 hours). Most of the newly formed resins were analyzed for the uptake of divalent ions lead, zinc, copper, nickel, and cobalt, and then compared to results found with phosphonic acid resin (starting material). The studies are separated into five different groups all dependant on the type of functionalization.

Group 1. Functionalizations containing only alkyl chains

As seen in Table 2-32, the phosphonamide resins gave comparable or improved uptake of all metals when compared to the phosphonic acid resin control (shown at the bottom of

Table 2-32. Metal ion study Group 1 results. All metal ion solutions were 1×10^{-4} N metal nitrate in a background of 0.01 N nitric acid and 0.40 N sodium nitrate, and shaken for 24 hours.

RO#	resin	Pb(II)			Zn(II)			Cu(II)			Ni(II)			Co(II)		
		%complexed	D		%complexed	D		%complexed	D		%complexed	D		%complexed	D	
4-093	ethanol	10.94	4.6		-1.86	0.0		8.83	4.2		-0.07	0.0		0.29	1.1	
2-187	ethanolamine	80.77	182.5		59.77	64.8		81.64	193.9		16.38	8.54		15.83	8.2	
3-275	n-butylamine	100.0	infinity		100.0	infinity		100.0	infinity		100.0	infinity		100.0	infinity	
5-096	dibutylamine	100.0	infinity		71.58	83.6		89.89	296.3		31.81	15.5		39.49	21.7	
2-283	3(dimethyl- amino)-1- propanol	2.83	0.8		0.00	0.0		0.98	0.3		0.17	0.1		0.00	0.0	
3-037	ethylene- diamine	100.0	infinity		100.0	infinity		100.0	infinity		95.42	724.9		84.45	188.8	
4-065	phosphonic acid	94.01	816.1		63.22	89.3		70.65	115.2		38.32	32.3		39.98	34.6	

the table). The phosphonamide resin formed from n-butylamine had a mixture of 67% diamide and 33% monoamide, and this resin showed complete complexation of all metals studied even with an excess of sodium ions. The other two phosphonamide resins, from a reaction with dibutylamine and from a reaction with ethylenediamine, did not have the same results across the board. The resin formed from ethylenediamine showed greater than 95% uptake for all but cobalt ions which still gave over a 2-fold improvement in percent complexation over phosphonic acid resin. The phosphonamide from dibutylamine, essentially a perfect monoamide, showed only a slight improvement for all metals except nickel which gave slightly poorer results than the phosphonic acid resin control. Functionalization with ethanolamine could be considered middle ground in this group, since there is a mix of phosphonamide and phosphonate ester with the reaction. The uptake of the metal ions varied upon the metal studied. There was a slight improvement over phosphonic acid resin with the uptake of copper, but this resin fell below phosphonic acid resin to varying degrees with the remaining metal ions studied. The remaining two resins gave very poor results. The phosphonate ester from ethanol, almost a complete diester (92%), showed a minuscule complexation with lead ion and copper ions, but gave zero complexation with the remaining three metals. The phosphonate ester from 3-dimethylamino-1-propanol gave essentially zero metal complexation for all metal studied.

Group 2. Functionalizations containing a pyridyl ring

This group can be separated into either functionalization with a pyridylcarbinol to form a phosphonate ester or with an (aminomethyl)pyridine to form a phosphonamide

(Table 2-33). The 2- isomer and the 3-isomer phosphonamides had a percent complexation above 98% for all metal ions studied, except cobalt ions. The 4-isomer did give an improvement over phosphonic acid resin for all metals, but not to the same extent as the other two isomers except for uptake of copper ion which gave quantitative complexation for copper ions.

Of the phosphonate esters from this group, only the functionalization with 4-pyridylcarbinol gave any substantial amount of complexation for the metals studied. The 2-isomer (except for uptake of copper) and the 3-isomer were both well below the amounts found with phosphonic acid resin.

Group 3. Functionalizations containing a benzyl ring

The third group contains functionalizations done with benzyl alcohol, benzyl amine, or any of the substituted versions of these two (Table 2-34). First, let's compare the phosphonamides versus the phosphonate esters in this group. Functionalizations from benzyl amine, a resin made up of 80% diamide and 20% monoamide, showed major improvements over both phosphonic acid resin which gave superior complexation values than the phosphonate ester formed from benzyl alcohol. Comparing the substituted reactants with the unsubstituted ones gave some interesting results. The 4-methoxy-substituted benzyl alcohol functionalization, a mixture of 49% monoester and 51% diacid, gave values superior to phosphonic acid resin with all but uptake of nickel and cobalt ions, and with these two metals the results were quite comparable. The 4-chloro-substituted benzyl alcohol functionalization, a mixture of 60% diester and 40% monoester, produced

Table 2-33. Metal ion study Group 2 results. All metal ion solutions were 1×10^{-4} N metal nitrate in a background of 0.01 N nitric acid and 0.40 N sodium nitrate, and shaken for 24 hours.

RO#	resin	Pb(II)		Zn(II)		Cu(II)		Ni(II)		Co(II)	
		%complexed	D	%complexed	D	%complexed	D	%complexed	D	%complexed	D
3-187	2-pyridyl carbinol	60.78	49.0	41.53	22.4	81.09	118.7	20.26	8.0	18.61	7.2
4-063	3-pyridyl carbinol	56.63	35.2	34.02	13.9	59.59	50.5	33.81	13.8	24.72	8.8
3-160	4-pyridyl carbinol	79.47	102.9	76.57	86.9	77.96	149.8	40.58	18.2	30.82	11.9
5-082	2-aminomethyl pyridine	100.0	infinity	100.0	infinity	100.0	infinity	98.84	2720.5	93.22	439.8
4-154	3-aminomethyl pyridine	98.16	1705.5	100.0	infinity	100.0	infinity	100.0	infinity	97.98	1550.7
4-147	4-aminomethyl pyridine	98.16	2384.8	89.08	365.0	100.0	infinity	56.39	57.9	67.45	92.8
4-065	phosphonic acid	94.01	816.1	63.22	89.3	70.65	115.2	38.32	32.3	39.98	34.6

Table 2-34. Metal ion study Group 3 results. All metal ion solutions were 1×10^{-4} N metal nitrate in a background of 0.01 N nitric acid and 0.40 N sodium nitrate, and shaken for 24 hours.

RO#	resin	Pb(II)		Zn(II)		Cu(II)		Ni(II)		Co(II)	
		%complexed	D	%complexed	D	%complexed	D	%complexed	D	%complexed	D
3-263	4-chloro-benzyl alcohol	14.34	4.2	4.07	1.1	11.60	33.4	0.00	0.0	0.00	0.0
2-267	benzyl alcohol	62.86	45.7	34.85	14.5	41.75	20.1	13.48	4.2	15.56	5.0
3-290	4-methoxy benzyl alcohol	94.48	653.0	80.44	155.8	93.16	469.2	38.32	23.9	40.77	26.3
3-278	4-chloro-benzyl amine	48.68	23.1	13.06	3.7	37.19	13.2	0.00	0.0	0.00	0.0
3-029	benzyl amine	98.16	1447.3	93.67	402.0	99.65	7182.3	60.90	42.3	70.51	64.8
3-293	4-methoxy benzyl amine	100.0	infinity	100.0	infinity	100.0	infinity	83.48	168.3	88.61	258.9
4-065	phosphonic acid	94.01	816.1	63.22	89.3	70.65	115.2	38.32	32.3	39.98	34.6

zero complexation values for all but lead and copper ion uptake (both of which were below 15% complexation). This trend was also found with the phosphonamides from the three benzylamines. The 4-methoxy-substituted amine, 90% monoamide and 10% diacid, was an improvement across the board and the 4-chloro-substituted amine, 62% diamide and 38% monoamide, gave values well below that of even phosphonic acid resin for all metal ions studied.

Group 4. Functionalization from a phenol compound

Four different resins were studied for the fourth group (Table 2-35). Functionalizations with phenol, and three different para-substituted phenols (nitro-, chloro- and methoxy-) were all studied for their uptake of the divalent metal ions. All resins were at least 69% diester with the remaining as monoester. Complexation values were well below that of phosphonic acid for all four resins, and all four resins gave essentially zero complexation of nickel and cobalt ions in the solution studied. The trend found in group 3 (4-methoxy- > unsubstituted > 4-chloro-), was directly the opposite for the three remaining metals that gave complexation. Here the 4-methoxy-substituted resin was essentially zero for all metals studied while the 4-chloro substituted resin gave the highest complexation for the remaining three metals studied. The p-nitro resin fell somewhere between unsubstituted and 4-methoxy- substituted.

Group 5. Reactants that should have been unreactive

The metal ion uptake results of the fifth and last group (Table 2-36) actually make the

Table 2-35. Metal ion study Group 4 results. All metal ion solutions were 1×10^{-4} N metal nitrate in a background of 0.01 N nitric acid and 0.40 N sodium nitrate, and shaken for 24 hours.

RO#	resin	Pb(II)			Zn(II)			Cu(II)			Ni(II)			Co(II)		
		%complexed	D		%complexed	D		%complexed	D		%complexed	D		%complexed	D	
5-093	4-nitrophenol	38.05	13.6		8.77	2.1		19.25	5.3		0.00	0.0		1.88	0.4	
4-258	4-chlorophenol	72.35	90.9		31.86	12.4		33.02	13.1		2.19	0.6		0.00	0.0	
4-276	phenol	49.18	27.0		11.39	3.57		12.03	3.8		0.00	0.0		0.00	0.0	
4-032	4-methoxy phenol	9.76	2.4		1.83	0.4		9.04	2.4		0.00	0.0		0.00	0.0	
4-065	phosphonic acid	94.01	816.1		63.22	89.3		70.65	115.2		38.32	32.3		39.98	34.6	

Table 2-36. Metal ion study Group 5 results. All metal ion solutions were 1×10^{-4} N metal nitrate in a background of 0.01 N nitric acid and 0.40 N sodium nitrate, and shaken for 24 hours.

RO#	resin	Pb(II)		Zn(II)		Cu(II)		Ni(II)		Co(II)	
		%complexed	D	%complexed	D	%complexed	D	%complexed	D	%complexed	D
3-257	N,N'-dimethyl-butylamine	96.08	90.4	79.49	142.0	100.0	infinity	47.35	33.2	55.24	45.3
4-110	triethylamine	100.0	infinity	92.84	571.5	100.0	infinity	63.16	75.4	73.56	122.1
4-065	phosphonic acid	94.01	816.1	63.22	89.3	70.65	115.2	38.32	32.3	39.98	34.6

resins their own group. Reactions with tertiary amines should have given back the phosphonic acid resin that was used to start the reaction since the amines are unreactive in the reaction. Resins with comparable phosphorus capacities but acid capacities well below the starting phosphonic acid resin led to the metal ion studies for these resins. If the results would have been the same as those for phosphonic acid resin, then one could try and come up with explanations for the altered characterization. But the complexation values were from equivalent to far better than those with phosphonic acid resin. The reaction with triethylamine that led to the largest drop in acid capacity gave metal uptake greater than 92% for Zn(II) ion and 100% complexation of Pb(II) and Cu(II) ions in the solutions studied. The uptake of Ni(II) ions and Co(II) ions by this resin was 63% and 74%, respectively while both fell below 40% with phosphonic acid resin.

Discussion

Formation of reactive intermediate (Chlorination of phosphonic acid resin)

The first hurdle was deciding what type of reactive intermediate should be used and how this intermediate would be formed. We wanted to start with the phosphonic acid resin, due to its ease of handling and its known ion exchange properties. Taking into consideration the examples discussed in the introduction, chlorination of the phosphonic acid resin with thionyl chloride was utilized.

Removal of water from phosphonic acid resin

The next procedural hurdle was to decide how to dry the phosphonic acid resin and remove any latent water trapped in the pores of the resin. Trapped water is detrimental to the water sensitive chlorination reaction. Any water remaining in the beads will react violently with the thionyl chloride. If this reaction with water would occur within the bead, the combination of the exotherm and the evolved gas would essentially explode the bead from within turning the beads into chaff. Three different drying methods were attempted followed by chlorination with thionyl chloride followed by functionalization with 2-aminopyridine. First, the resin was azeotropically distilled with heptane. This method yielded no functionalization with 2-aminopyridine. Heptane is a very non-polar solvent. Although azeotropic distillation is a successful method for the removal of water from within the resin, heptane cannot successfully solvate the phosphonic acid ligands. This caused the phosphonic acid to solvate itself and collapse within the bead. Upon chlorination with thionyl chloride in dichloromethane, the phosphonic acid ligands are not accessible for chlorination and thus cannot be further functionalized with 2-aminopyridine. The second method for removal of latent water from within the pores utilized successive multiple washes with acetone. Once again, there was no observed functionalization with 2-aminopyridine, within experimental error. Even though the acetone is much more polar than heptane, it is apparently not polar enough to allow for the solvation of the phosphonic acid.

The third drying method was washing the phosphonic acid resin three times with N,N'-dimethylformamide (DMF). This method of removing latent pore water yielded a

respectable amount of functionalization, around 41% monoamide with the remaining 59% as diacid. The DMF is a polar solvent and from the given results, solvates the phosphonic acid ligands on the resin. Therefore, the chosen method to remove the latent water from the pores of the phosphonic acid resin was multiple washes with DMF.

Functionalization solvent

Determining the solvent used during the formation of the phosphonate esters and phosphonamides was the next hurdle. Two solvents were studied, pyridine and toluene. The phosphoryl dichloride bound resin was reacted with 3-dimethylamino-1-propanol at room temperature for 17 hours, once in toluene and once in pyridine. The reaction with pyridine as the solvent yielded almost twice as much functionalization than the reaction with toluene as the solvent (Table 2-1). Toluene was chosen for its known solvation of styrenic based polymers. Pyridine has the same general solvation ability as toluene, but pyridine is a weak base which was proven beneficial for the capture of the hydrochloric acid side product during the reaction.

Washing of resin post-functionalization

Early on in the project we realized that a standard method of post reaction treatment was necessary. Since the solvent for functionalization chosen was pyridine, the washing cycle needs to be able to remove all of the pyridine as well as excess reactant from the resin pores. Any latent solvent or reactant would adversely affect the characterization values of the resin. Which in turn, would give false readings when determining the extent of

reaction. The washing cycle also needs to gently hydrolyze any unreacted phosphoryl dichloride. A 75% aqueous solution of 1,4-dioxane was chosen to simultaneously remove the pyridine and excess reactant as well as hydrolyze the unreacted ligands back to phosphonic acid sites.

Conditioning of resin post-functionalization

In order to remove any remaining excess solvent and/or reactant not removed during the washing cycle the resin was put through a conditioning sequence. The sequence went in the order of water, sodium hydroxide, water, hydrochloric acid, and water. The pH of the eluent was tested after each elution before moving on to the next elution. If the pH of the eluent was not what it should have been based on the elution just used, then a second elution, using the same volume of that solution, would be passed through the beads to ensure completeness. The sodium hydroxide came after the initial water elution because the beads swell when placed in a basic medium. Now that the beads are swollen the innermost pores are more accessible. Therefore, water was the next elution to wash out any latent contaminant from the swollen pores. This was followed by acid to re-protonate the acid sites. This was followed by a final water elution in order to remove the excess acid and bring the storage medium back to a neutral pH.

The strength of the acid and base elutions had to be determined. Traditionally, a 4 wt% solution (1.00 N) of acid and base are used. This was found to be too strong of an elution for most of the functionalized resins. Upon comparing the 1.0 N conditioning solutions with 0.01 N conditioning solutions, functionalization was being removed and replaced

with an original acid site using 1.0 N base and acid with all resins studied except for the phosphonate benzyl esters (Table 2-2). The three different functionalizations all had an increase in acid and phosphorus capacities with a drop in the nitrogen capacity.

Conditioning with the low normality (0.01 N) solutions would sometimes take more than one 1 L elution of either acid and/or base to reach the needed pH of eluent. The 0.01 N elutions did not have an adverse effect on the functionalization, but due to the added time it took to continually elute the resin with multiple liters of solution this concentration was undesirable as well. Elutions with 0.10 N base and acid were tested. It was found that relatively little functionalization was lost with the 0.10 N elutions compared to the 0.01 N elutions for the resin functionalized with 3-dimethylamino-1-propanol (Table 2-2). The 0.10 N elution procedure was more efficient than the 0.01 N elution sequence, and was not as detrimental to the ligand as 1.0 N elutions. Thus, the 0.10 N elutions were chosen for the conditioning method.

Reaction atmosphere

Due to the sensitivity of the formation of the reactive intermediate as well as the moisture sensitive intermediate used during the functionalization it was imperative that the reaction atmosphere be defined. During the formation of the phosphoryl dichloride a moisture free system had to be employed. During the chlorination the apparatus was connected to atmospheric conditions through a drying tube filled with fresh Drierite. While the reactant was being added to the phosphoryl dichloride resin a light nitrogen gas sweep was passed through the apparatus. The nitrogen sweep was to ensure that an inert system

continually filled the apparatus. At this point, two different reaction atmospheres were tested. In the first study, the nitrogen sweep was continued. The second study utilized an argon blanket applied to the apparatus followed by the system being sealed. These two methods were tested using 2-pyridylcarbinol as the reactant (Table 2-3). Reactions with 2-pyridylcarbinol are known to decrease in extent of functionalization as the reaction time increases (*vide infra*). The extent of functionalization for the two reactions at 30 minutes were within experimental error of each other. But after a 72 hour reaction time, the reaction method using an argon blanket had lost more functionalization (an increase in acid capacity from 1.77 to 7.54 mequiv/g and a drop in nitrogen capacity from 4.37 to 0.95 mequiv/g) than the method using a light nitrogen sweep (an increase in acid capacity from 1.67 to 5.82 mequiv/g and a drop in nitrogen capacity from 4.04 to 1.96 mequiv/g). At this point, a firm explanation of why the nitrogen sweep was not as detrimental as the argon blanket is unknown.

Reaction temperature during functionalization

The first of the remaining two variables studied most extensively is reaction temperature. Reaction temperature was studied for the formation of various phosphonate esters. An increase in extent of functionalization using 3-dimethylamino-1-propanol as the reaction time increased (Table 2-4) can be explained with reaction rate. The incorporation of this alcohol is quite slow at room temperature (a nitrogen capacity of 1.49 mequiv/g after 17 hours and 2.34 mequiv/g after 82 hours). At elevated temperature (100 °C) a higher amount of capacity is obtained at the shorter reaction time (17 hours) than the extended

time (82 hours) at room temperature, nitrogen capacities of 3.62 and 2.34 mequiv/g, respectively. The amount of functionalization stays roughly the same at 100 °C between 17 hours and 82 hours as indicated by the nitrogen capacities (3.62 and 3.57 mequiv/g, respectively). This shows that the reaction has reached its maximum amount of functionalization and remained constant.

As reaction temperature increased for the reaction with 2-pyridylcarbinol (Table 2-5) the amount of functionalization decreased. The difference is most evident at the extended reaction times, 75 hours. The nitrogen capacity drops from 4.47 to 1.96 mequiv/g when the reaction temperature increases from room temperature to 100 °C. This same trend was also found for reactions with benzyl alcohol (Table 2-6). Increasing the reaction temperature from room temperature to 77 °C to 100 °C at a reaction time of 63 hours increased the acid capacity from 0.15 to 3.87 to 7.11 mequiv/g, respectively. As the reaction temperature increased from room temperature to 77 °C at a reaction time of 72 hours for the reaction with ethanol (Table 2-7) the amount of functionalization stayed essentially the same (0.43 to 0.67 mequiv/g, respectively). These trends can be explained by the following proposed mechanism.

Proposed mechanism

The results lead us to propose a mechanistic explanation. According to our data, functionalizations can be placed in two general categories. Those that allow for the formation of a salt with pyridine (the solvent) and those that do not. The functionalizations that do allow for the formation of a pyridinium salt are reaction

temperature dependant. The functionalizations that do not form a pyridinium salt are independent of reaction temperature.

As one can see from Figure 2-3 (using a phosphonate mono ester with 2-pyridylcarbinol as the example), The electron withdrawing effect of the phosphoryl oxygen on one side of methylene carbon in the ester and the electron withdrawing effect of the aromatic (or pyridyl) ring on the other side causes the formation of a partial positive charge on the methylene carbon. The lone pair electrons of the nitrogen in pyridine now have an attack site. As long as the salt that forms is stable enough, this occurs due to the large excess of solvent used during the reaction. Therefore, at extended time, more pyridinium salt has a chance to form. This salt will be washed out with the aqueous washes and elutions that follow, being replaced by protons, i.e. reforming the phosphonic acid ligand. Thus, the higher the reaction temperature, the more pyridinium salt will form. The more salt that forms, more functionalization will be lost during the post-reaction treatment leading to an increase in phosphonic acid sites and a decrease in functionalization.

Figure 2-4 (using a phosphonate mono ester of ethanol as the example) shows the loss of functionalization is not possible if a partial positive charge on the methylene carbon is not formed. By this process, no matter what reaction temperature, there will be no attack by the pyridine lone pair of electrons, and functionalization will remain constant once it reaches its maximum amount of functionalization. This was also seen with the reaction using 3-dimethylamino-1-propanol. Once the reaction reached its stearic maximum amount of ligands bound to the phosphorus, that amount remained constant from that point, i.e. no loss of functionalization.

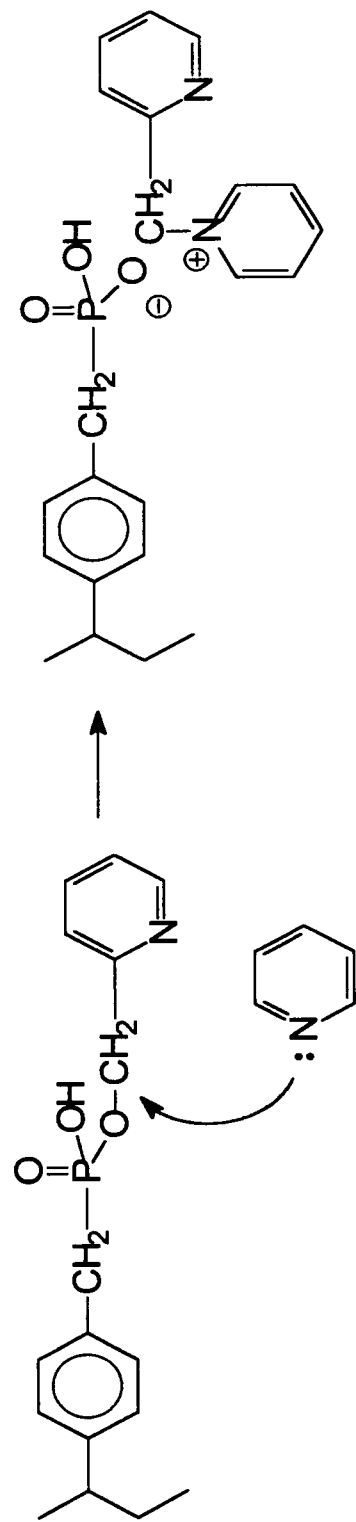


Figure 2-3. Formation of a pyridinium salt by reaction of pyridine with the polymer bound phosphonate ester of 2-pyridylcarbinol

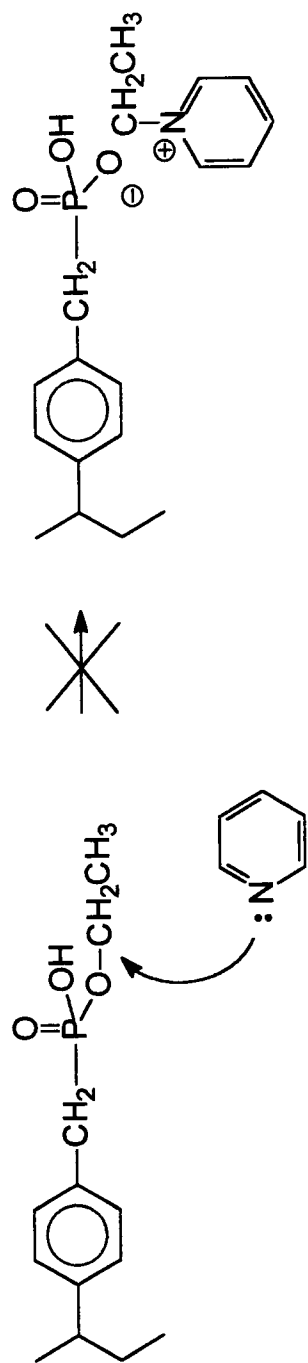


Figure 2-4. Theoretical formation of a pyridinium salt by reaction of pyridine with the polymer bound phosphonate ester of ethanol

Reaction time during functionalization

Studies of reaction time were done with both formation of phosphonate esters and phosphonamides. As stated in the previous section, there are two general categories of functionalizations for this procedure: those that form a pyridinium salt with the solvent and those that do not. By the same mechanism, the first category also has a dependency for reaction time as well. Those functionalizations that do not form pyridinium salts with the solvent are independent of reaction time. It was discovered that formation of phosphonamide bound resins fall in the second category. This is explained by the same mechanism. As seen in Figure 2-5, the mono phosphonamide formed from reaction with *n*-butylamine does not allow for the formation of a partial positive charge on the methylene carbon next to the nitrogen of the amide due to the electron donating effect of the remaining alkyl chain. Therefore, there will be no attack by the solvent and thus no loss of functionalization. A reaction time study was also done with a ligand that does form a partial positive charge on the methylene carbon next to the amide. As shown in Figure 2-6, the formation of a mono phosphonamide from functionalization with 3-(aminomethyl)pyridine will form the partial positive charge on the carbon. But if the pyridine attacks and tries to form a salt, the nitrogen will end up with a negative charge. This is highly unfavorable. Therefore, the salt formation due to excess pyridine (solvent) is overpowered by the formation of a nitrogen with a negative charge and no functionalization will be lost.

As shown in Figure 2-7 from the data in Table 2-9, functionalization of the polymer bound phosphoryl dichloride with 2-pyridylcarbinol is reaction time dependant. At a reaction

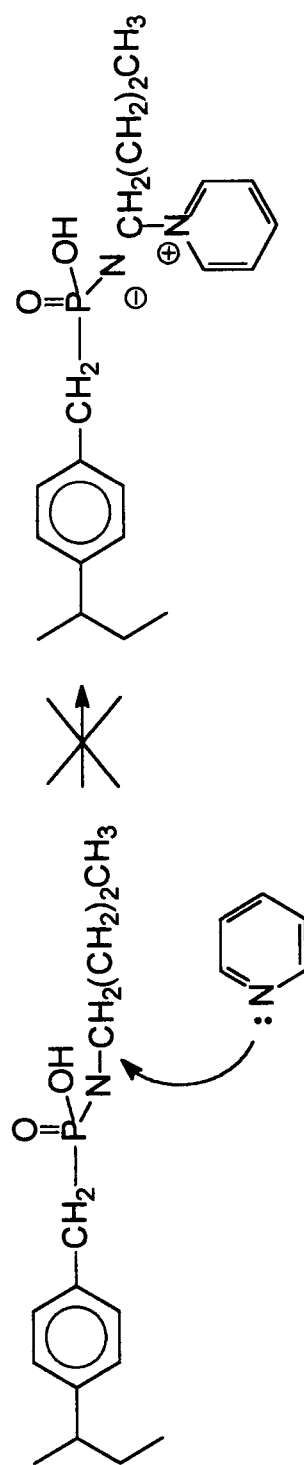


Figure 2-5. Theoretical formation of a pyridinium salt by reaction of pyridine with the polymer bound phosphonamide of n-butyl amine

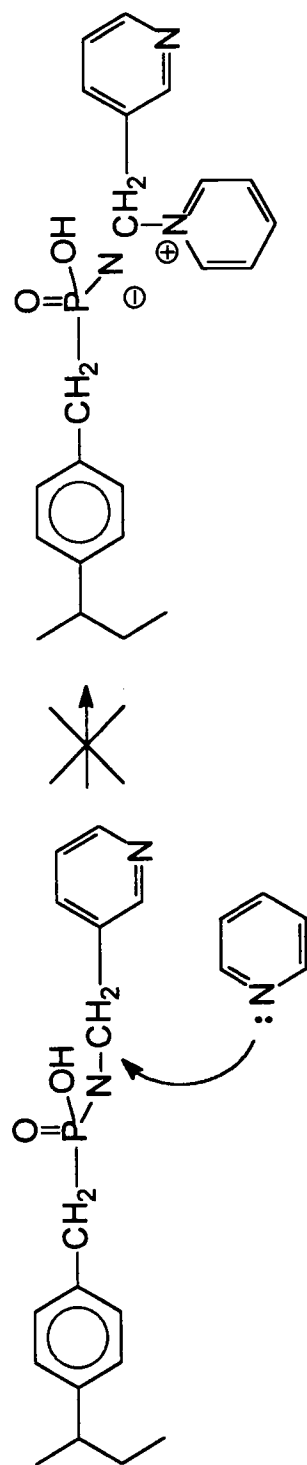


Figure 2-6. Theoretical formation of a pyridinium salt by reaction of pyridine with the polymer bound phosphonamide of 3-(aminomethyl)pyridine

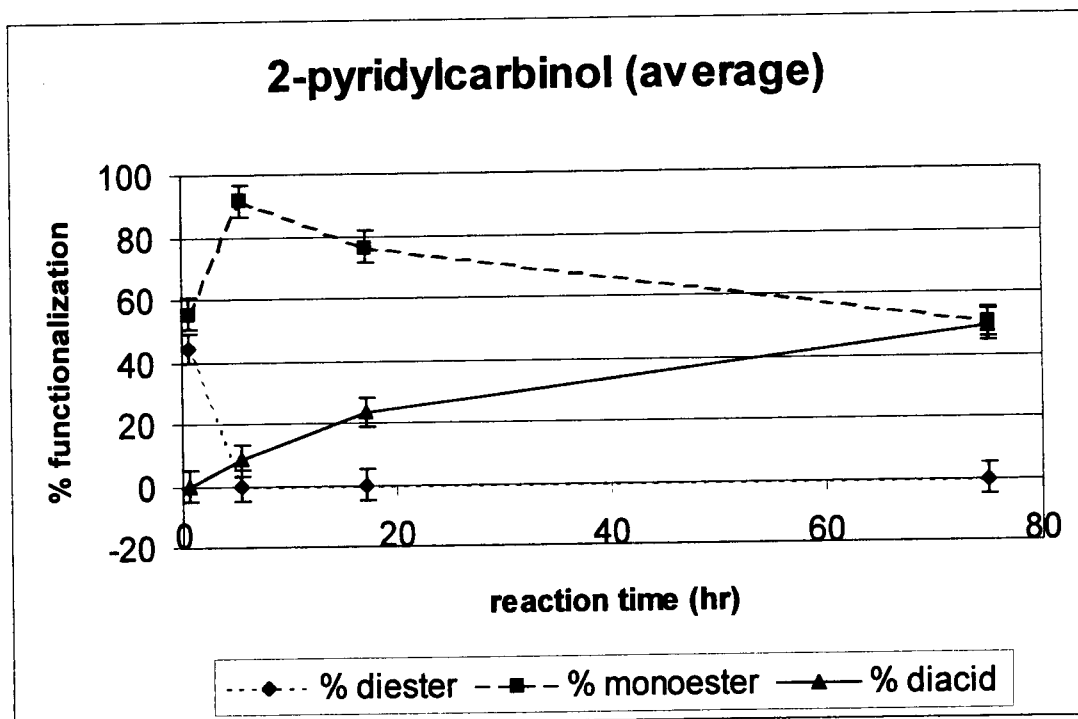


Figure 2-7. Percent functionalization versus reaction time for the phosphonate ester with 2-pyridylcarbinol

time of 30 minutes, there is almost a 50:50 mixture of diester and monoester and no diacid. As time is increased the amount of diacid increases (49.48% at 75 hours) as the %diester dissipates to 0% , i.e. the ligand is being lost and the resin is returning to the phosphonic acid form. All of this shows a dependency on reaction time when all other variables are kept constant.

Reactions using 4-pyridylcarbinol (data from Table 2-13) show the same general trend of reaction time dependency (Figure 2-8). Unlike the 2-isomer, functionalizations starts out as primarily monoester (94.74%, decreasing to 38.54% after 59 hours) instead of a mixture of diester and monoester.

This is probable due to steric constraints with the possible formation of the diester from reactions with 4-pyridylcarbinol. The pyridyl nitrogen and its lone pair of electrons will have more strain placed on them with the formation of a diester. The ester formed from reaction with 2-pyridylcarbinol will not have that problem due to the spacial placement of the pyridyl nitrogen.

Reactions using 3-pyridylcarbinol (Figure 2-9, from data in Table 2-11) have the largest number of trials for each reaction time (Table 2-10). The plot of these values is not a smooth one, but the overall trend of decreasing functionality as the reaction time increases at a constant, elevated reaction temperature is still evident. It is not known why there were discrepancies between trials at the same reaction time. An as yet unknown variable must be involved during the reaction. Reactions with benzyl alcohol (Figure 2-10, data from Table 2-14) mimic the results found with 2-pyridylcarbinol. The functionalization starts out roughly as a 50:50 mixture of diester:monoester and quickly loses diester

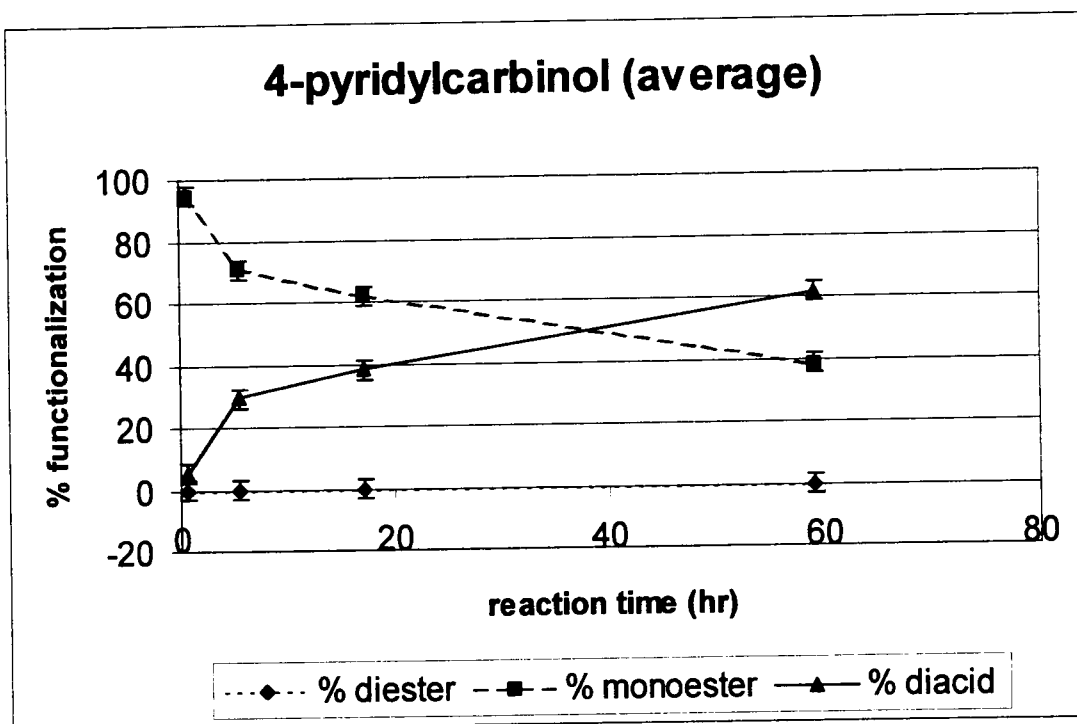


Figure 2-8. Percent functionalization versus reaction time for the phosphonate ester with 4-pyridylcarbinol

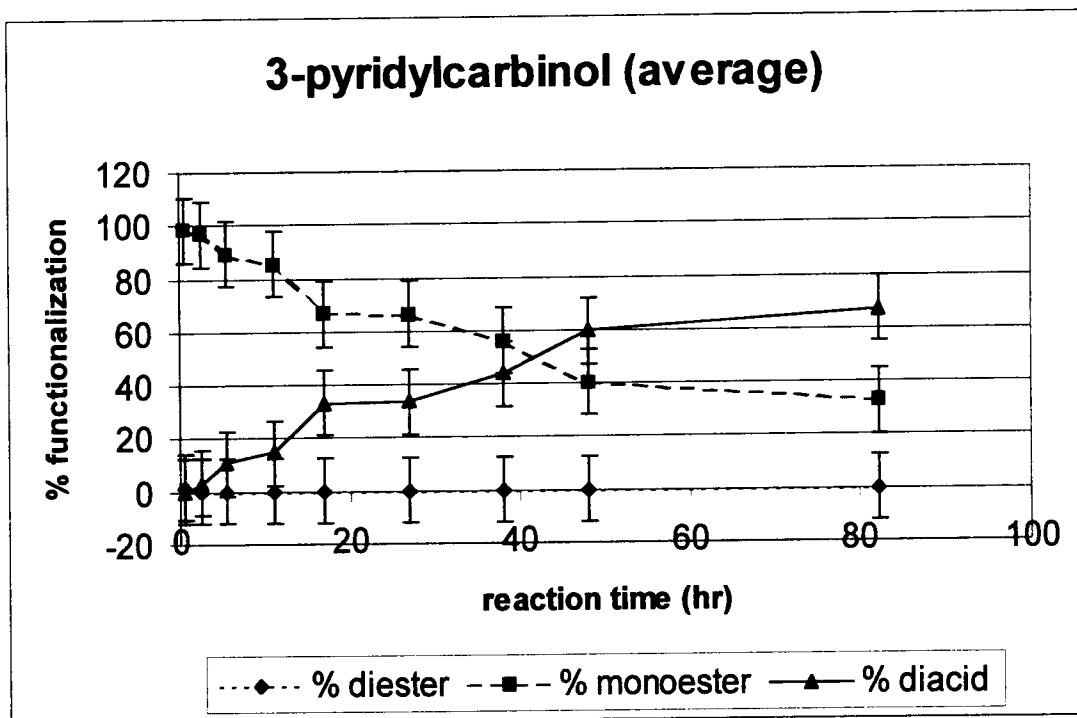


Figure 2-9. Percent functionalization versus reaction time for the phosphonate ester with 3-pyridylcarbinol

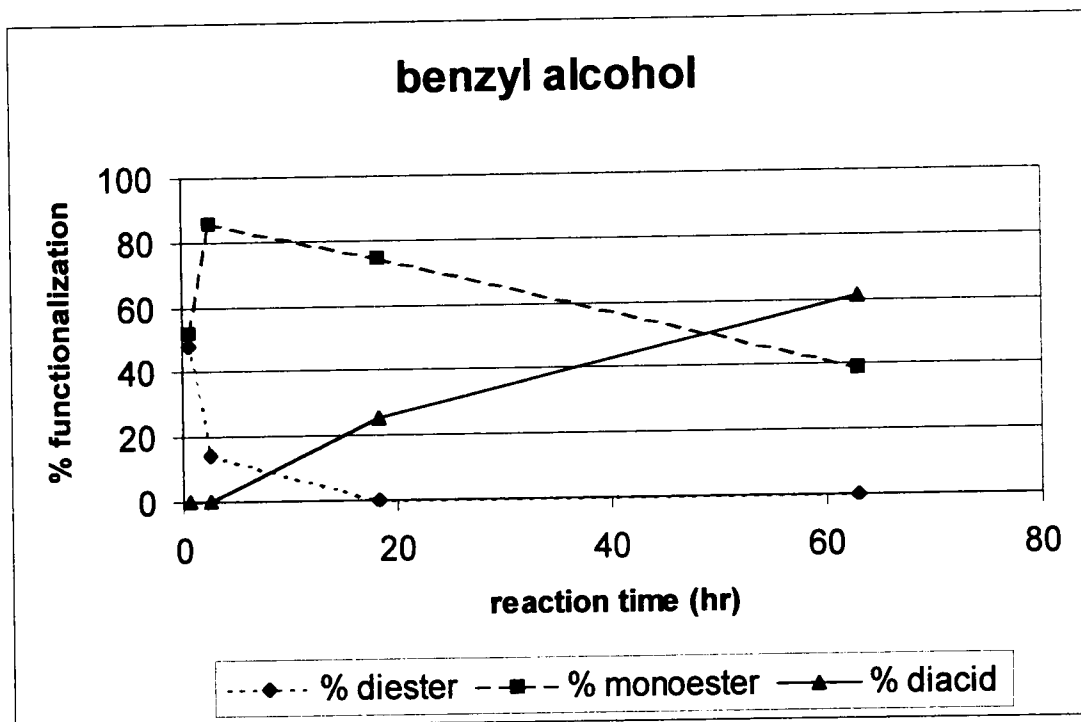


Figure 2-10. Percent functionalization versus reaction time for the phosphonate ester with benzyl alcohol

functionality and forms diacid ligands (61.22% after 63 hours). All four of these plots reinforce the mechanism proposed earlier. Since these reactants allow for the formation of a partial positive charge on the methylene carbon next to the ester oxygen as well as formation of a phosphonate anion, functionalization decreases as reaction time increases.

Reaction time independent functionalizations

Studies with benzyl amine and 3-(aminomethyl)pyridine Figure 2-11 and Figure 2-12, respectively, support the proposed mechanism for phosphonamide formation. For the reaction with benzyl amine (data from Table 2-17), about two-thirds of the functionalization at thirty minutes (65.12%) is made up of diamide with the remaining (34.88%) as monoamide. Why there are such large variances between the two trials that occur at thirty minutes is not completely known. Once again, it must indicate an inconsistency in a reaction variable that has so far gone unrecognized. The averaged trend stayed predominantly constant through the entire study even as high as 82 hours (69.90% diamide, 30.10% monoamide). Reactions with 3-(aminomethyl)pyridine (data from Table 2-19) produced a generally constant amount of functionalization from 30 minutes (86.25% monoamide) to 82 hours (95.45% monoamide). The differences between the extent of functionalization between these two reactions may be due to steric reasons. As seen in Figure 2-13 (data from Table 2-20), the formation of almost pure diester (92.04%) from reaction with ethanol occurs at 30 minutes and this remains relatively constant up to 82 hours (82.86%). Here, unlike with the formation of the phosphonamides, the phosphoryl oxygen can hold a negative charge in a salt, but in the

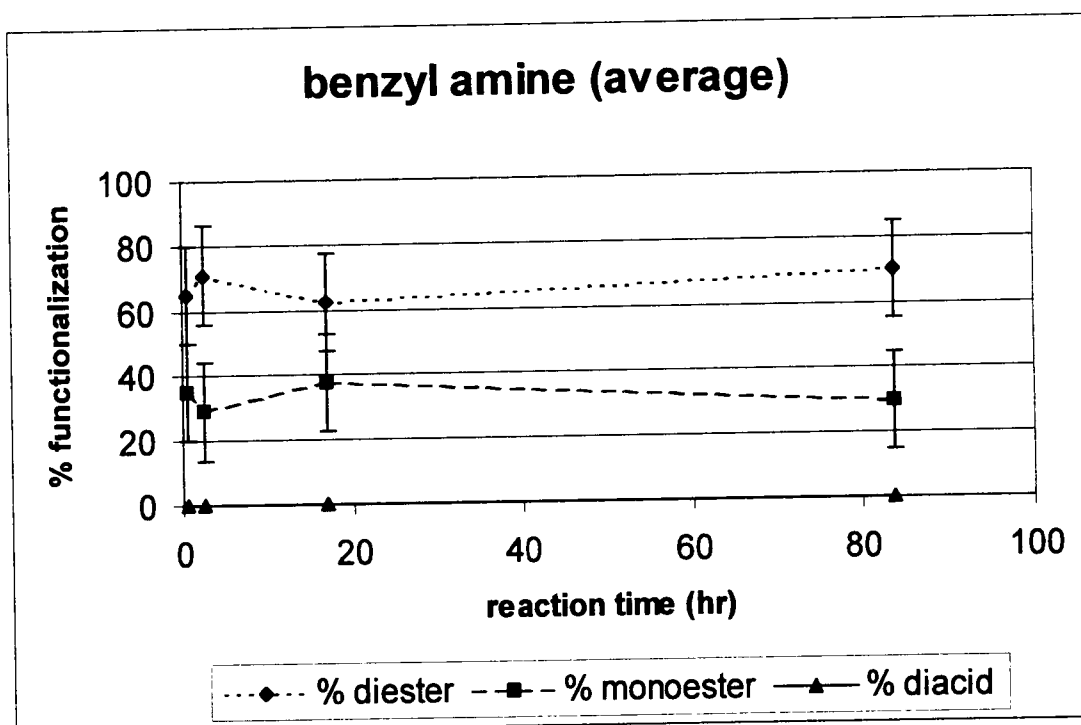


Figure 2-11. Percent functionalization versus reaction time for the phosphonamide with benzyl amine

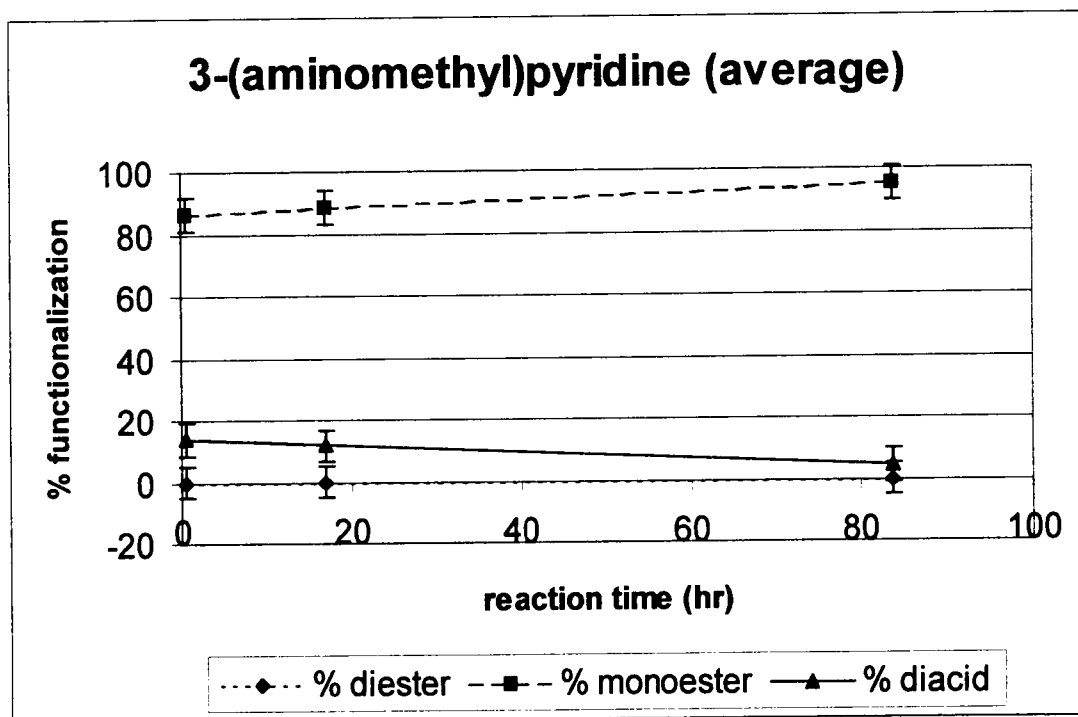


Figure 2-12. Percent functionalization versus reaction time for the phosphonamide with 3-(aminomethyl)pyridine

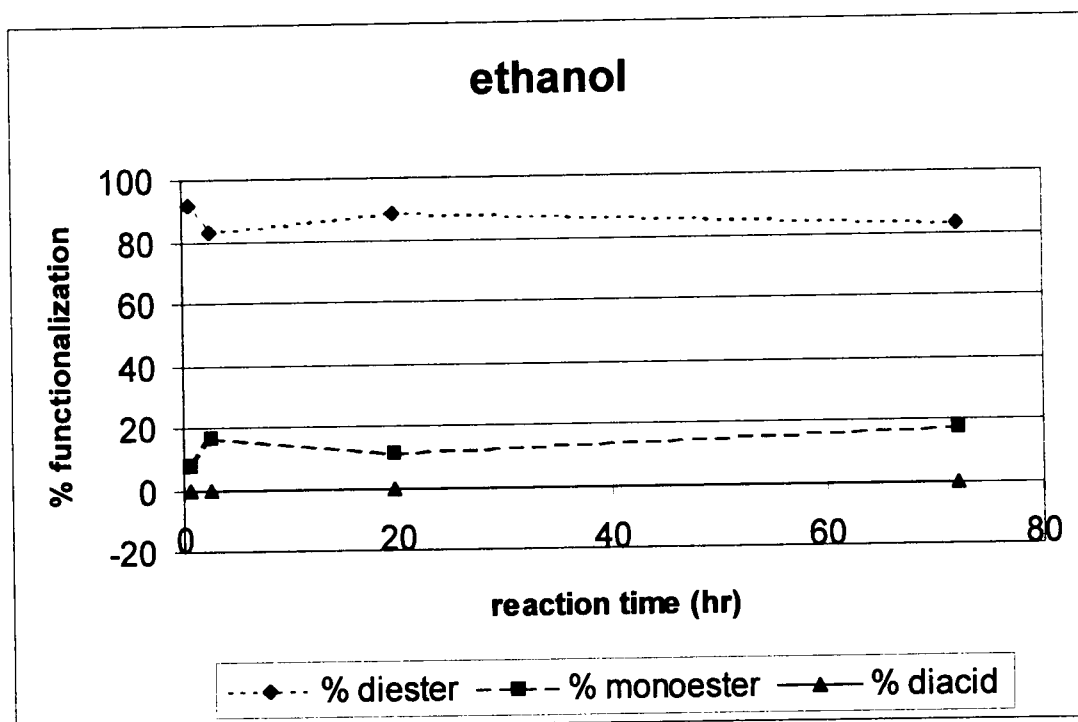


Figure 2-13. Percent functionalization versus reaction time for the phosphonate ester with ethanol

mechanism there must be a desirable attack site for the lone electrons of the pyridine.

With the formation of a phosphonate ester using ethanol there will be no formation of a partially positive carbon due to the electron donating effect of the remaining ethyl group.

Therefore, there is no loss of functionalization due to attack by pyridine which is what was found.

Figure 2-14 shows the percent functionalization trend for functionalization with n-butyl amine (data from Table 2-23). The trend is not as straight as reactions studied with other amines, but the general idea from the proposed mechanism still holds true. Reactions with 4-(aminomethyl)pyridine (Figure 2-15, data from Table 2-24) all but the 17 hour reaction show essentially no great amount of functionalization. The % monoester is 20% or below for reactions at 0.5 hours, 2.5 hours, and 72 hours with the remaining ligands diacid, but the 17 hour reaction produced 35.21% monoester.

Reactivity difference between alcohol and amine

A wide variety of reaction temperatures and reaction times were attempted with ethanolamine, but no discernable trends were found in between the studies. A second set of experiments were done by combining a mixture of a set ratio of benzyl alcohol and benzyl amine. The ratio was then altered and the reaction was done again. This procedure was repeated until a set of results led to the plot found in Figure 2-16. The increase in benzyl amine was linear with the increase in the nitrogen elemental. During this same series, the phosphorus elemental and the acid capacity stayed relatively linear. This shows that the phosphoryl dichloride has no preference when given a choice of alcohol or amine.

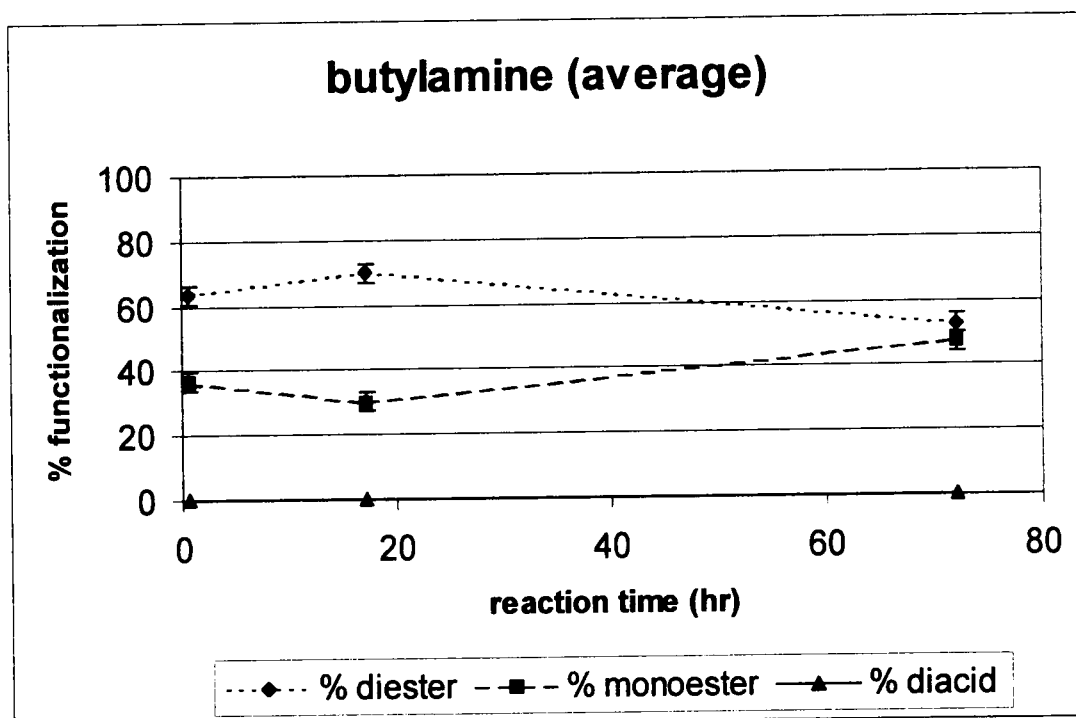


Figure 2-14. Percent functionalization versus reaction time for the phosphonamide with n-butylamine

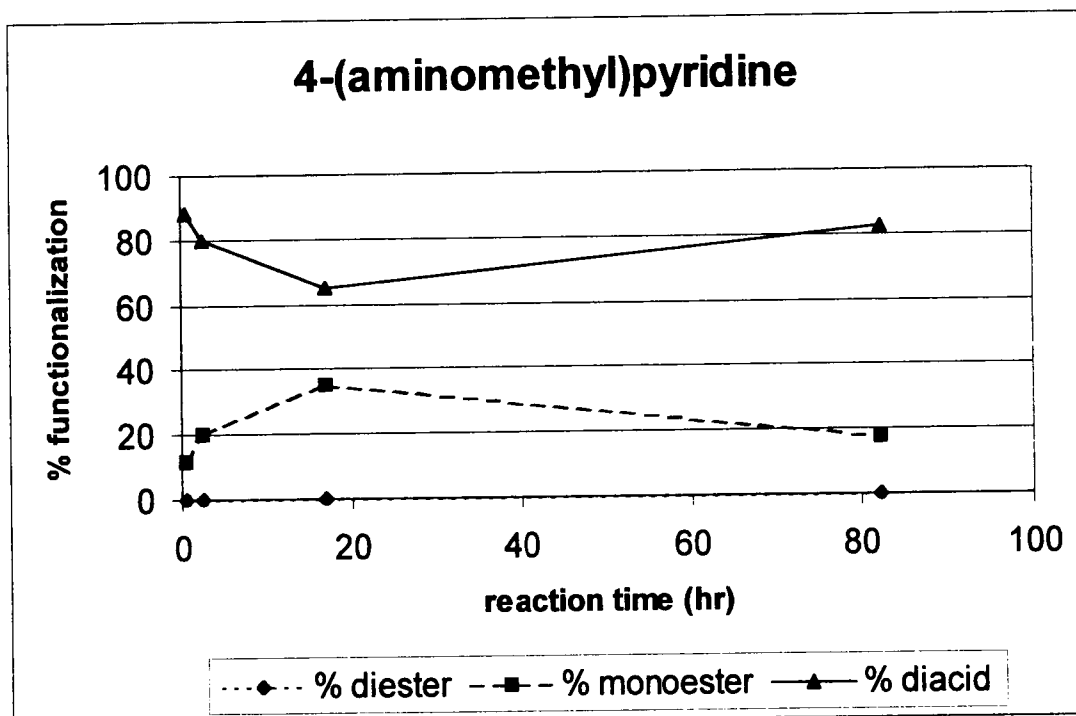


Figure 2-15. Percent functionalization versus reaction time for the phosphonamide with 4-(aminomethyl)pyridine

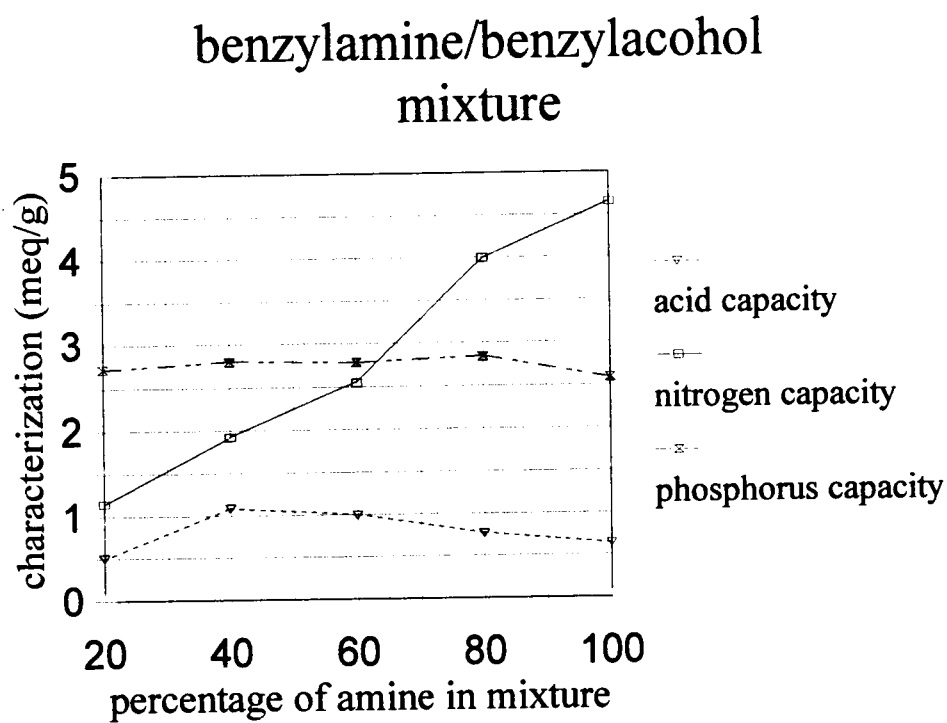


Figure 2-16. Elemental characterization versus percentage of benzyl amine in a mixture of benzyl amine/benzyl alcohol each reacted at 100 °C for a 30 minute reaction time

Knowing this fact helps to explain the randomness of the reactions with ethanolamine. A fifty/fifty mixture of phosphonamide and phosphonate ester from the same reactant invalidates the percent functionalization equations.

Formation of other phosphonate esters and phosphonamides

Many different functionalizations were attempted during the course of the project without extensively researching the dependence on the variables discussed above. Although the products from these reactions were used in the studies for divalent metal ion uptake (vide infra). The first of these reactions to be discussed used 2-(aminomethyl)pyridine. Two different reactions were done, both at 77 °C (about eight degrees below the reactant's boiling point), the first for a 30 minute reaction time and the second for 17 hours. After 30 minutes, the reaction produced resin with a mixture of 50.0 % monoamide and 50.0% diacid. After 17 hours, the reaction produced resin with a mixture of 7.4 % diamide and 92.6% monoamide. The combination of an amine with the nitrogen in the two position of the pyridine ring apparently slows down the rate of reaction, but does not hinder the formation of the phosphonamide.

Reactions with benzyl alcohol and benzyl amine were extensively researched mechanistically as well as for uptake of various metal ions. In order to get a better understanding of the metal ion uptake studies, reactions with the 4-chloro- and the 4-methoxy- substituted benzyl alcohols and benzyl amines were studied. For the 4-methoxy-substituted benzyl amine (Table 2-21), a 30 minute reaction and a 72 hour reaction were done. There is no difference upon comparing the % functionalization between each other.

Each has 90% monoamide with 10% diacid. When these values are compared with the un-substituted benzyl amine, the stark difference is found. Benzyl amine gives between 60% and 70% diamide with the remaining as monoamide, between the same two reaction times. For the 4-methoxy-substituted benzyl alcohol (Table 2-15), the same two reaction times were studied (30 minutes and 72 hours). There is a major difference between the two reactions. After 30 minutes, the reaction yielded a mixture of 49% monoester and 51% diacid. After 72 hours, the reaction yielded a mixture of 8.8% monoester with the remaining 91.2% as diacid. These values support the reaction mechanism, but are definitely more extreme than the unsubstituted benzyl alcohol. Benzyl alcohol after 30 minutes produced a 48:52 mixture of diester and monoester. The functionalization decreased to about 39% monoester and 61% diacid after 63 hours. These sets of reactions help to support the proposed reaction mechanism, and having the methoxy group para to the reactive site decreases the reactivity of the reactant. This decrease in reactivity can be attributed to the electron donation of the methoxy group to the aromatic ring. This in turn decreases the pull of the ring toward the methylene carbon between the ring and the alcohol reactivity. This decrease in pull on the methylene carbon will decrease the nucleophilicity of the alcohol oxygen, decreasing the extent of functionalization.

The 4-chloro-reactants were each just formed at a 30 minute reaction time at 100 °C. The 4-chloro-benzylamine (Table 2-27) produced a mixture of 61.6% diamide and 38.4% monoamide, comparing well with the unsubstituted counterpart. The 4-chloro-benzyl alcohol (Table 2-28) was done twice at 30 minutes. Each compared well with each other,

64.1% diester 35.9% monoester for the first reaction and 59.6% diester 40.4% monoester for the second reaction. These are both slightly higher than the unsubstituted reactant which gave a mixture of 48% diester and 52% monoester. Having the chloro group para to the reactive site did not truly effect the reactivity of the reactant at a 30 minute reaction time. Since longer reactions were not attempted, it is unsure if this was the maximum amount of functionalization for each reaction.

In order to get a better understanding of the effect of the para- group on the aromatic ring of the reactant, reactions were done with phenol and various para-substituted phenols (Table 2-29). There is no loss of functionalization within each reaction and all reactions are at least 65% diester or better. Once again, this supports the reaction mechanism. Since there is no methylene carbon to attack, the solvent (pyridine) cannot attack and remove ligand. Comparing individual substitutions shows that the 4-chloro substituted reactant gives the lowest amount of functionalization, and the 4-methoxy substituted reactant has no apparent change from the unsubstituted reactant. Just the opposite of the para substituted benzyl reactants.

Reactions with dibutyl amine

Up until now, the only type of amines that have been discussed have been primary amines. In order to get a better understanding of the reaction mechanism, reactions using secondary amines as well as various tertiary amines were attempted. The secondary amine chosen was dibutyl amine. This was done once at a 30 minute reaction time at 100 °C.

After the reaction was completed, very few beads were left. The majority of the beads had

formed fissures and broken into pieces during the reaction. This was observed by analyzing the polymer under a microscope. Upon elemental analysis, the resin had a nitrogen capacity nearly equivalent to the phosphorus capacity (3.16 mequiv/g to 3.06 mequiv/g, respectively). Although the acid capacity was below what it should have been according to the other elemental analyses (2.16 mequiv/g), using the calculated acid capacity from the mass balance equation, the reaction yielded a resin of 96.7% monoamide with the remaining 3.3% as diamide. Apparently, having half of the ligands as the highly hydrophobic dibutylamide and the other half as the hydrophilic phosphonic acid was too much for the matrix causing the beads to break apart into chaff.

Reactions with tertiary amines

Reactions were also attempted with various tertiary amines (Table 2-30), keeping in mind that these were set up as controls, and that we expected to get back the original phosphonic acid resin. The first tertiary amine to be studied was N,N'-dimethylbutylamine. The most simple tertiary amine with a similar structure to n-butylamine (studied somewhat extensively). Three different trials were attempted, all for 30 minutes at 85 °C (around eight degrees below the boiling point of the reactant). Based on the reaction mechanism, there must be a good leaving group in the reactant that will form with the chloride of the phosphoryl dichloride. Since this amine does not have a very good leaving group, there should not have been any functionalization during the reaction and the acid capacity should have stayed the same. A small amount of nitrogen capacity (around 0.5 mequiv/g for two of the three reactions and 1.2 mequiv/g for the third) was

found in the reactions with N,N'-dimethylbutylamine. Also, the acid capacities were below what they should have been. The drop in acid capacity posed the larger question. To try and get a better understanding of what was going on with the reaction using tertiary amines, two reactions with triethylamine done at 80 °C were attempted, one at 30 minutes and the second at extended time (74.5 hours). The 30 minute reaction yielded an acid capacity of 6.77 mequiv/g. Note that the initial phosphonic acid capacity was 9.37 mequiv/g. The extended time reaction had an even lower acid capacity at 5.31 mequiv/g. Another reaction was done early on in the project with 1-nitropropane. This was set up to be a control to test the reactivity of nitro-compounds. The reaction was done at room temperature for 17 hours and yielded a product where the phosphorus did not change from the starting phosphonic acid (4.71 mequiv/g to 4.75 mequiv/g), but the acid capacity dropped from 9.13 mequiv/g to 6.04 mequiv/g. This shows that a totally unreactive substance gives the same result as the tertiary amines leading one to believe that an unknown reaction is taking place (*vide infra*).

All of the above stated data led to various control reactions using no reactant and only solvent (Table 2-31). After chlorination with thionyl chloride, the reaction was run with pyridine only at 100 °C for 72 hours. The resin was washed with aqueous 1,4-dioxane and eluted as normal. This control was done two separate times each yielding the same results. This control should have given back the acid and phosphorus capacities of the starting phosphonic acid, but instead the samples gave resins with an acid capacity of 6.1 mequiv/g each time, a phosphorus capacity of 4.1 and 4.4 mequiv/g, and a nitrogen capacity of 0.6 and 0.7 mequiv/g. This same study was done at room temperature instead

of 100 °C. All that changed were the extremes of the numbers. The drop in acid capacity was still apparent. A final control was done with these resins. After aqueous washes from the reaction at room temperature the resin was refluxed with concentrated hydrochloric acid for 24 hours to see if the resin could give back the same elemental analysis as the starting phosphonic acid resin. The sample produced an acid capacity of 9.50 mequiv/g, a phosphorus capacity of 4.81 mequiv/g and a nitrogen capacity of 0.34 mequiv/g. This proves that the original acid capacity of the phosphonic acid can be regained and that whatever change is going on is a real change.

After these findings, similar control studies were done using triethylamine as well as toluene instead of pyridine. In the studies with triethylamine as the solvent, the results were the same as those with pyridine, just not as severe. Instead of the acid capacity dropping to 6.1 mequiv/g, the drop was only to 7.1 mequiv/g. In the studies with toluene as the solvent, the results were even less severe. The drop was only to 8.4 mequiv/g and there was no analysis of nitrogen capacity. The trialkylamine almost surely does not react with the phosphoryl dichloride ligand to produce a salt ⁽⁴⁹⁾.

A fourth and final control was attempted. Instead of using pyridine as the solvent during the control, acetic anhydride was used. This control was done for just under 50 hours. After aqueous washes, the resin gave an acid capacity of 6.19 mequiv/g, and a phosphorus capacity relatively unchanged at 4.59 mequiv/g. All of this proves that a byproduct during the reaction is formed and this byproduct is stable enough to be detected when no other reactant is present. Since the results were found without the addition of pyridine, although the results were enhanced with pyridine, the by-product is occurring during the

chlorination step. It is believed that a possible anhydride like structure between two phosphorus is forming during the chlorination (Figure 2-17). This anhydride is stable in an unreactive surrounding, but likely breaks apart when a reactive enough substance, such as an alcohol or an amine, is added to the system. The formation of a pyrophosphonate anhydride was recently found to be a by-product during the chlorination of soluble phosphonate monoesters with thionyl chloride ⁽⁴⁹⁾. The anhydrides reacted readily with alcohols, and only sluggishly, if at all, with amines ⁽⁴⁹⁾.

Metal ion studies

The newly formed phosphonate ester and phosphonamide resin were used in a study for the uptake of various divalent metal ions in a background of competing sodium ions. All but a few of the functionalizations attempted were analyzed for the uptake of divalent ions lead, zinc, copper, nickel, and cobalt, and then compared to results found with phosphonic acid resin (starting material). The studies are separated into five different groups all dependant on the type of functionalization.

Group 1. Functionalizations containing only alkyl chains

As seen in Table 2-32, the phosphonamide resins gave comparable or improved uptake of all metals when compared to the phosphonic acid resin control (shown at the bottom of the table). The phosphonamide resin formed from n-butylamine had a mixture of 67% diamide and 33% monoamide, and this resin showed complete complexation of all metals

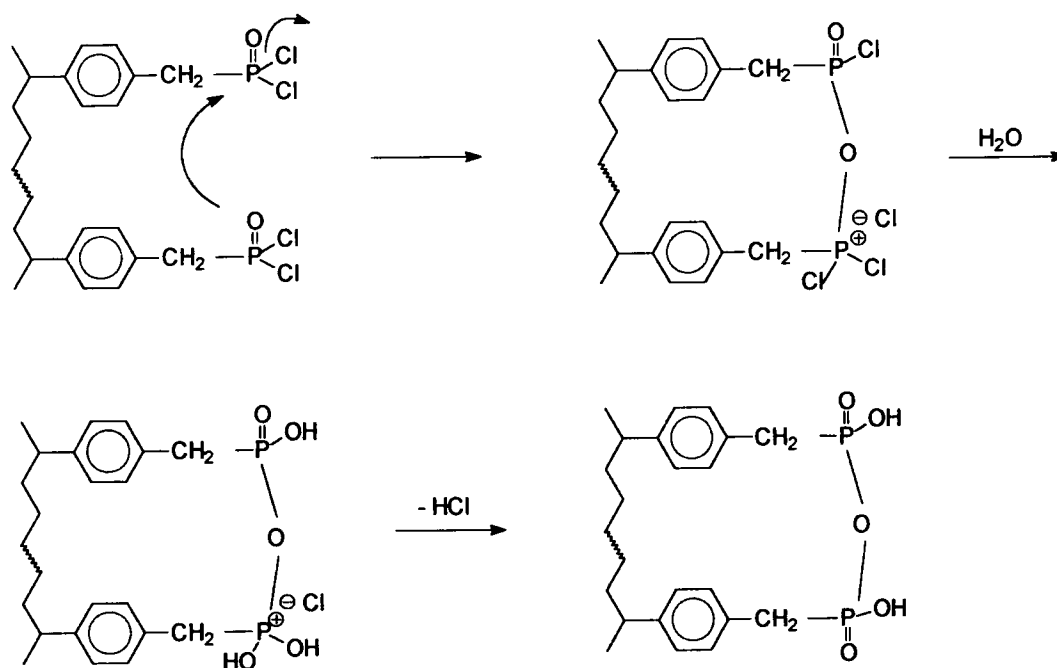


Figure 2-17. Formation of phosphono anhydride during chlorination reaction of phosphonic acid resin with thionyl chloride

studied even with an excess of sodium ions. The other two phosphonamide resins, from a reaction with dibutylamine and from a reaction with ethylenediamine, did not have the same results across the board. The resin formed from ethylenediamine showed greater than 95% uptake for all but cobalt ions which still gave over a 2-fold improvement in percent complexation than phosphonic acid resin. The phosphonamide from dibutylamine, essentially a perfect monoamide, showed only a slight improvement for all metals except nickel which gave slightly poorer results than the phosphonic acid resin control.

Functionalization with ethanolamine could be considered middle ground in this group, since there is a mix of phosphonamide and phosphonate ester with the reaction. The uptake of the metal ions varied upon the metal studied. There was a slight improvement over phosphonic acid resin with the uptake of copper, but this resin fell below phosphonic acid resin to varying degrees with the remaining metal ions studied.

The remaining two functionalizations, both phosphonate esters, gave very poor results.

The phosphonate ester from ethanol, almost a complete diester (92%), showed a minuscule amount of complexation with lead ion and copper ions, but gave zero complexation with the remaining three metals. The phosphonate ester from 3-dimethylamino-1-propanol gave essentially zero metal complexation for all metal studied. This may have to do with the formation of a free alkyl-ammonium ion (as opposed to a free pyridinium ion) on the ligand. Since the background solution is acidic, the free amine will have some amount of protonation. This positively charged species will repel the positive metal ions that are trying to be complexed by the resin.

Group 2. Functionalizations containing a pyridyl ring

This group can be separated into either functionalization with a pyridylcarbinol to form a phosphonate ester or with an (aminomethyl)pyridine to form a phosphonamide (Table 2-33). Of this group, the phosphonamides had a percent complexation above 98% (except for cobalt ions) for the 2-isomer and the 3-isomer. The 4-isomer did give an improvement over phosphonic acid resin for all metals, and gave quantitative complexation for copper ions. But the complexation of nickel and cobalt fell well behind the other two isomers. A possible explanation for these differences may be due to the amount of functionalization in each resin. The 4-isomer only had about 35% monoamide with the remaining as diacid. The 3- and 2-isomers were both predominantly monoamide with the 2-isomer having 9% diamide and the 3-isomer having 14% diacid as the remaining ligands. Since the 4-isomer was predominantly phosphonic acid, it would be expected to act more like phosphonic acid than not. A percent functionalization of 35% monoamide was the highest extent of functionalization for any resin made from 4-(aminomethyl)pyridine. Based upon results found with the three isomers of pyridylcarbinol (*vide infra*), the phosphonamide from the 4-isomer in this group should have been equaled if not better than complexation using the other two isomers if the extent of reaction was constant between the resins.

Of the phosphonate esters from this group, only the functionalization with 4-pyridylcarbinol gave any substantial amount of complexation for the metals studied. The 2-isomer (except for uptake of copper) and the 3-isomer were both well below the amounts found with phosphonic acid resin. Both the 3- and the 4-isomers were above 95% monoester and the 2-isomer contained a mixture of 44% diester and 56% monoester.

Overall, once again, the phosphonamides gave much better complexation results than the phosphonate esters.

Group 3. Functionalizations containing a benzyl ring

The third group contains functionalizations done with benzyl alcohol, benzyl amine, or any of the substituted versions of these two (Table 2-34). First, let's compare the phosphonamides versus the phosphonate esters in this group. Functionalizations from benzyl amide, a resin made up of 80% diamide and 20% monoamide, showed major improvements over both phosphonic acid resin which gave superior complexation values compared to the phosphonate ester formed from benzyl alcohol. Considering results from the first two groups, this was not a large surprise. Comparing the substituted reactants with the unsubstituted ones gave some interesting results. The 4-methoxy-substituted benzyl alcohol functionalization, a mixture of 49% monoester and 51% diacid, gave values superior to phosphonic acid resin with all but uptake of nickel and cobalt ions, and with these two metals the results were quite comparable. The 4-chloro-substituted benzyl alcohol functionalization, a mixture of 60% diester and 40% monoester, produced complexation values below 5% for all but lead and copper ion uptake (both of which were below 15% complexation). This trend was also found with the phosphonamide from the three benzylamines. The 4-methoxy-substituted amine, 90% monoamide and 10% diacid, was an improvement across the board and the 4-chloro-substituted amine, 62% diamide and 38% monoamide, gave values well below that of even phosphonic acid resin for all metal ions studied. The amount of functionalization of each resin may play some part, but

the benzyl alcohol functionalization studied had very similar amounts as the 4-chloro-substituted functionalization when there was such a stark difference in the metal uptake. Also, there was more diamide in the unsubstituted benzylamine functionalization than the 4-chloro-substituted and the 4-methoxy-substituted was primarily monoamide with a small amount of diacid. From these results, it can be stated that the substitution plays a major role in the complexation of the metal ion, but the precise role of the substituents in affecting the electron density at the ligating site is still unclear.

Group 4. Functionalization from a phenol compound

Four different resins were studied for the fourth group (Table 2-35). Functionalizations with phenol, and three different para-substituted phenols (nitro-, chloro- and methoxy-) were all studied for their uptake of the divalent metal ions. All resins were at least 69% diester with the remaining as monoester. Complexation values were well below that of phosphonic acid for all four resins, and all four resins gave essentially zero complexation of nickel and cobalt ions in the solution studied. The trend found in group 3 (4-methoxy- > unsubstituted > 4-chloro-), was directly the opposite for the three remaining metals that gave complexation. Here the 4-methoxy-substituted resin was essentially zero for all metals studied. The complexation values for the 4-nitro-substituted phosphonate ester did not fall into the trend where initially theorized. It was believed that the stronger electron withdrawing effect of the nitro substitution compared to that of chloro would give greater complexation values. Experimentally, the resin fell somewhere between unsubstituted and 4-methoxy- substituted. Once again, there are still unanswered question here.

Group 5. Reactants that should have been unreactive

The metal ion uptake results of the fifth and last group (Table 2-36) actually make the resins their own group. Reactions with tertiary amines should have given back the phosphonic acid resin that was used to start the reaction since the amines are unreactive in the reaction. Resins with comparable phosphorus capacities but acid capacities well below the starting phosphonic acid resin led to the metal ion studies for these resins. If the results would have been the same as those for phosphonic acid resin, then one could try and come up with explanations for the altered characterization. But the complexation values were from equivalent to far better than those with phosphonic acid resin. The metal uptake values helped to explain the formation of a phosphonamide functionality during the chlorination reaction. The anhydride has vast differences in the sharing of electrons than phosphonic acid resin which leads to improved complexation through the phosphoryl oxygen.

Conclusions

Chlorination of a 2% crosslinked phosphonic acid resin using thionyl chloride successfully forms a stable, yet reactive intermediate for the formation of a large library of polymer bound ligands through a nucleophilic attack by an alcohol or amine. The procedure uses pyridine as the solvent which can attack the newly formed functionalization causing possible reaction time and reaction temperature dependence for functionalizations with certain alcohols. A mechanism has been proposed to explain the attack and the above stated variable dependencies where the lone electrons on the pyridine nitrogen attack a

partially positive methylene carbon of phosphonate esters. With the formation of a stable salt after attack of this methylene carbon by the solvent, the functionality is lost over time, and the loss is heightened with increasing reaction temperature.

During the chlorination procedure, it is postulated that a phosphoanhydride forms between two phosphorus on the phosphoryl dichloride resin. The anhydride remains as long as no nucleophilic reactant is added to the system. The resin can be hydrolyzed to form a resin made of a combination of phosphonic acid and the above stated phosphoanhydride. The newly formed phosphonate ester resins, phosphonamide resins, and phosphoanhydride resins were analyzed for their metal ion complexation abilities with various divalent transition metal ions in pH 2 nitric acid and 0.4 N sodium nitrate where the sodium ion acts as competition. These results were compared with the complexation results found for phosphonic acid resin. Overall the phosphonamide resins were at least comparable if not a major improvement in metal uptake over that of phosphonic acid resin. Altering the substitution as well as the percent functionality greatly alters the complexation results. The phosphonate esters studied as a whole were not good complexers of the divalent metal ions studied. Finally, the phosphoanhydride resins showed great promise in complexation of the metal ions. These resins gave greater than 90% complexation for all of the metals studied except Ni(II) ions and Co(II) ions.

Future Work

Many questions with this project have yet to be answered. Early in the project, the reaction solvent was decided upon between only pyridine and toluene. Towards the end

of the project, it was determined that triethylamine may have been a better choice (less phosphoanhydride formation with triethylamine). Reactions with triethylamine as the reaction solvent should be done, followed by analysis for phosphoanhydride and metal ion studies to determine if any differences are apparent. To help determine the resin's molecular structure, IR spectroscopy and ^{18}O - NMR spectroscopy should be used. Once the proposed mechanism is confirmed qualitatively, the amount of phosphoanhydride for a given chlorination should be determined quantitatively. After this proves successful, the quantitative amount of phosphoanhydride should be determine after various reactions. This will shed light on the stability of the phosphoanhydride ligand. If results show that phosphoanhydride remains after some reactions, the metal ion studies should be redone with resin free from phosphoanhydride ligand. This will give a much clearer resin order with respect to selectivity for a given metal ion.

To prove that the pore size within the bead is not playing any role during the reaction, MR copolymer should be used to form the phosphonic acid starting material. Followed by reactions with larger and smaller reactants. The subsequent results can be compared to the resins formed from gel copolymer. An independence with respect to bead size was assumed based upon past work within the research group. Phosphonic acid resin from small copolymer (-200 mesh) and larger copolymer (-20 +40 mesh) should be chlorinated and reacted with both a large reactant and a small reactant. This will help determine if the reaction is truly independent of bead size.

CHAPTER 3

FORMATION OF BIFUNCTIONAL QUATERNARY AMMONIUM EXCHANGE RESINS

Introduction

Selectivity of the resin is of particular concern when the ion of interest exists in low solution concentrations compared with other ions in solution. Resin selectivity is important to minimizing cost associated with many applications, including the purification of groundwater, contaminated with radioactive ions. One of the most dangerous radioactive pollutants found in the groundwater near fission plants is technetium ⁽⁵¹⁾. Because of its nuclear instability, technetium is not found naturally on earth. However, it has been produced in kilogram quantities from other elements by nuclear reaction ⁽⁵¹⁾. Tc-99, one of the isotopes of technetium with a half-life of 2.14×10^5 yrs, is easily oxidized into pertechnetate (TcO_4^-) anion which forms highly soluble salts. This causes the radionuclide to spread out over a wide area. Contaminated aquifers also have high concentrations of other anions such as sulfate, nitrate and chloride at a concentration of 10^6 times greater than pertechnetate ⁽⁵²⁾. Commercially available quaternary ammonium exchange resins have a rapid exchange rate but the selectivity for the desired anion is low, especially in high concentrations of the other anions ⁽⁵³⁾. These polymers generally contain trimethyl or triethyl ammonium ligands as the active site. It was discovered that quaternary ammonium ligands containing longer alkyl chains are higher in selectivity for pertechnetate anion ⁽⁵²⁾. Unfortunately, this is at the cost of the exchange rate. Where the trimethyl or triethyl ammonium bound ligands would reach maximum capacity within an

hour, the exchange resins containing the longer alkyl chains can take up to a week and sometimes more ⁽⁵²⁾.

For this process to be taken to the next level, changes were necessary. The procedure in its original form was not feasible on an industrial level. Thus, drastic methodology changes with pre-reaction procedure, reaction time, and post-reaction work up were all altered in some form. The changes were successful and produced an improved anion exchange resin for pertechnetate that could be made on a large scale.

Experimental

Suspension copolymerization of vinylbenzyl chloride and divinylbenzene macroporous beads

The copolymer beads are prepared from vinylbenzyl chloride (VBC) and divinylbenzene (DVB) by suspension polymerization. Macroreticular (MR) beads are prepared with 5 % or 10% DVB using 4-methyl-2-pentanol as the poragen. Beads used in the amination reactions have particle size in the range of 0.25-0.42 mm (-40+60 mesh).

Suspension copolymerization of vinylbenzyl chloride, styrene and divinylbenzene xerogel beads

The copolymer beads are prepared from VBC, styrene and DVB by suspension polymerization with toluene as the diluent. Beads are prepared with 2% DVB in xerogel form. Beads that are used in the amination reactions have a particle size in the range of 0.25 to 0.42 mm (-40+60 mesh).

Synthesis of monofunctional quaternary ammonium exchange resin

The copolymer is initially swollen in solvent (1,4-dioxane) overnight to ensure complete swelling, ascertained when the beads have sunk to the bottom of the round bottom flask. The trialkylamine along with additional solvent and a small amount of distilled water are added to the round bottom flask and the mixture is heated to reflux temperature while stirring for seventeen to nineteen hours. The solution is removed and the resin is washed with fresh 1,4-dioxane, ethanol, aqueous ethanol followed by water. Finally, the resin is conditioned with solutions in the order: water, 1 N sodium hydroxide, water, 1 N hydrochloric acid, water.

Synthesis of bifunctional quaternary ammonium exchange resin

The first half of this procedure follows the synthesis of monofunctional quaternary amine resin up to the washing sequence. At this point, the solution is removed, replaced with fresh solvent (1,4-dioxane) along with the second trialkylamine and a small amount of water. The reaction is heated to reflux temperature once again for an additional 17 to 19 hours. The solution is removed and the resin is washed and conditioned as described in the synthesis of monofunctional quaternary amine resin.

Industrially-compatible synthesis of monofunctional quaternary ammonium exchange resin

The copolymer is initially swollen in solvent (methylal or toluene) by stirring at reflux

temperature for a minimum of four hours. The trialkylamine along with additional solvent and a small amount of distilled water are added to the round bottom flask and the mixture is heated to reflux temperature while stirring for four hours. The solution is removed and the resin is washed with ethanol, aqueous ethanol followed by water. Finally, the resin is conditioned with solutions in the order: water, 1 N sodium hydroxide, water, 1 N hydrochloric acid, water.

Industrially-compatible synthesis of bifunctional quaternary ammonium exchange resin

The first half of this procedure follows the industrially-compatible synthesis of monofunctional quaternary amine resin up to the washing sequence. At this point, the solution is removed, replaced with fresh solvent along with the second trialkylamine and a small amount of water. The reaction is heated to reflux temperature once again for an additional four hour minimum with overhead stirring. The solution is removed and the resin is washed and conditioned as described in the synthesis of industrially-compatible monofunctional quaternary amine resin.

Metal ion studies with TcO_4^- using test solution; batch studies

Metal ion studies of the resins were done at ORNL by Peter Bonnesen and colleagues.

One and twenty-four hour batch studies for all resins were performed. The analysis of contaminated ground water from an environmental site revealed the concentration of technetium to be on the range of 0.3 to 2.2 nanomolar compared to a concentration of the

most abundant anions, chloride, nitrate and sulfate, in the range of 0.56 to 0.90, 0.04 to 0.15 and 0.10 to 0.26 millimolar, respectively ⁽⁵²⁾. To simulate the performance on a large scale, the concentration of each of these ions was kept approximately 10⁵ times higher in the working test solution used during these studies. Prior to the complexation experiments, each resin (initially in the chloride form) was equilibrated with the test solution without technetium. The resin was then buchner dried and contacted with the test solution containing the technetium for the desired contact time. The beads were filtered out and the solution was tested for Tc-99 activity on a Tricarb counter using the standard liquid scintillation method. The amount of Tc complexed by the resin was determined by subtracting the Tc activity in the equilibrium solution from the total Tc activity in the starting solution. The distribution ratio (K'_d) in mL/g was determined by the following equation ⁽⁵²⁾.

$$K'_d = \frac{\text{Pertechmetate sorbed on resin (mg/g)}}{\text{Pertechmetate in solution (mg/mL)}}$$

Metal ion studies with TcO_4^- using test solution; column studies

Standard groundwater test solution was prepared and dripped through columns containing 3.0 mL of resin (bed volume). The first fraction of eluent was collected at 100mL followed by every 200 mL of eluent. The Tc-99 activity was determined by standard liquid scintillation to determine breakthrough at 0.1%, 1.0%, and 10.0% as well as distribution ratio, K'_d .

Results

Enhancing the accessibility of the trihexyl ammonium ligand

A 10 % crosslinked copolymer made of a 25:75 ratio of VBC to styrene was chosen for this experiment. The first copolymer was a macroreticular (MR) structure made by adding a diluent (4-methyl-2-pentanol) during the suspension polymerization. The second copolymer of the same monomer ratio was a xerogel bead made by adding an organic solvent (toluene) during the suspension polymerization. Both of these copolymers were used in amination reactions with trihexylamine. The post-reaction characterization is found in Table 3-1.

A sulfonic acid ligand was bonded to the xerogel-based quaternary ammonium resins to increase the hydrophilicity of the beads by a sulfonation reaction. Two different types of sulfonation were attempted. The first method was a sulfonation with chlorosulfonic acid in ethylene dichloride (EDC), at room temperature as well as 80 °C, all for short reaction times. The second method used concentrated sulfuric acid at 80 °C for short reaction times. Each of the two methods decreased the hydrophobicity of the xerogel quaternary ammonium resin, but had varying effects on the total anion exchange capacity (TAEC) (Table 3-2). All of these resins were tested at ORNL for the uptake of pertechnetate anion (Table 3-3).

Addition of a second quaternary ammonium ligand

By combining the trihexylammonium ligand with smaller alkyl chain quaternary ammonium ligands instead of the sulfonic acid ligand, the hydrophilicity could still be increased while

Table 3-1. Characterization of amination reactions with trihexylamine and VBC:Styrene (25:75 molar ratio) copolymer
(Theoretical nitrogen capacity, chlorine capacity and TAEC for MR = 1.11 mequiv/g and Xerogel = 1.31 mequiv/g)

resin	copolymer structure	% DVB	% solids	nitrogen capacity (mequiv/g)	chlorine capacity (mequiv/g)	TAEC (mequiv/g)
RO-1-260	MR	10	32.46 %	1.14	-----	-----
RO-1-289	xerogel	2	73.70 %	1.61	1.72	0.49
RO-2-024	xerogel	2	67.97 %	1.49	1.79	0.83

Table 3-2. Characterization of sulfonated xerogel trihexyl ammonium exchange resins

resin	pre-sulfonation numbers			sulfonation	post-sulfonation numbers		
	% solids	nitrogen capacity (mequiv/g)	TAEC (mequiv/g)		% solids	nitrogen capacity (mequiv/g)	TAEC (mequiv/g)
RO-2-013	74.51	1.64	0.57	chlorosulfonic acid 4 hr/ RT	29.38	1.35	0.87
RO-2-016	72.60	1.68	0.98	chlorosulfonic acid 1 hr/ RT	27.76	1.05	0.90
RO-2-048	-----	-----	-----	chlorosulfonic acid 1 hr/ 80 °C	27.22	1.00	1.49
RO-2-025	67.97	1.49	0.83	sulfuric acid 4 hr/ 80 °C	64.79	1.53	1.03
RO-2-028	83.09	1.60	0.54	sulfuric acid 1 hr/ 80 °C	68.53	1.23	0.94

Table 3-3. Batch studies for uptake of pertechnetate anion by bifunctional quaternary ammonium/ sulfonic acid exchange resin

resin	sulfonation	K'd (eq) (1 hr) (mL/equiv)	K'd(eq) (2 hr) (mL/equiv)	K'd (eq) (4 hr) (mL/equiv)	K'd (eq) (6 hr) (mL/equiv)	K'd (eq) (24 hr) (mL/equiv)
RO-2-016	chlorosulfonic acid 1 hr/ RT	-----	90	-----	80	100
RO-2-048	chlorosulfonic acid 1 hr/80 °C	90	-----	70	-----	80
RO-2-025	sulfuric acid 4 hr/ 80 °C	40	-----	50	-----	70
RO-2-028	sulfuric acid 1 hr/80 °C	60	-----	70	-----	160

the intake of pertechnetate would be enhanced (Table 3-4) ⁽⁵²⁾. A 5% crosslinked MR bead of poly(vinylbenzyl chloride) was chosen as the starting copolymer (Table 3-5) ⁽⁵²⁾. A biquaternary ammonium resin was formed from amination with a longer trialkyl amine followed by amination with a shorter trialkylamine (Figure 3-1). Various combinations of biquaternary ammonium resins were formed and then analyzed for uptake of pertechnetate anion (Table 3-6). Table 3-7 shows column study results using three synthetic biquaternary ammonium resins.

Using crosslinked VBC copolymer is not feasible on an industrial scale. Due to economics, industries prefer to use chloromethylated polystyrene as the starting crosslinked copolymer. Therefore, 4.5 % crosslinked chloromethylated polystyrene copolymer was obtained from Sybron and used in the above stated amination reactions followed by analysis of uptake of pertechnetate anion to determine any differences. From Table 3-6, the elemental characterizations are the same, but from the remaining analyses it is apparent that there are stark differences between the two starting copolymers. The percent solids are higher and the distribution coefficients at both 1 hour and 24 hours are vastly lower. In order to improve these results, a 3% crosslinked chloromethylated polystyrene was obtained from Sybron and functionalized to form the biquaternary ammonium exchange resin. However, this commercially available lightly crosslinked copolymer was only available in gel form. As shown in Table 3-6, the more lightly crosslinked Sybron resin is a major improvement over the resin using the higher crosslinked Sybron copolymer in uptake of the pertechnetate anion after 24 hours. In fact, the lightly crosslinked Sybron resin is almost at the level of the VBC copolymer at this

Table 3-4. Characterization and distribution coefficient for uptake of pertechnetate anion of monoquaternary and biquaternary ammonium exchange resins. All resins were from 5% DVB VBC copolymer (-40+60 mesh size) ⁽⁵²⁾

resin	functionality (in Cl form)	% solids	TAEC (mequiv/g)	K'd (24 hr) (mL/g)
VP-02-109	trihexyl	56.38	1.02	9000
VP-02-131	tripropyl	41.30	2.58	20000
VP-02-165	trihexyl/tripropyl	43.10	2.13	40000
VP-02-261	trihexyl/tributyl	49.61	1.76	39000
VP-02-258	trihexyl/triethyl	44.47	2.36	37000

Table 3-5. Characterization of resins derived from differently crosslinked VBC/DVB copolymer and tripropylamine ⁽⁵²⁾

% DVB	% solids	TAEC (mequiv/g)	chlorine capacity (mequiv/g)	nitrogen capacity (mequiv/g)
5	34.73	2.58	2.24	1.99
10	29.98	1.73	3.25	1.70
15	28.96	1.58	2.21	1.40
25	30.05	1.32	2.23	1.28
40	30.29	0.48	1.35	0.46

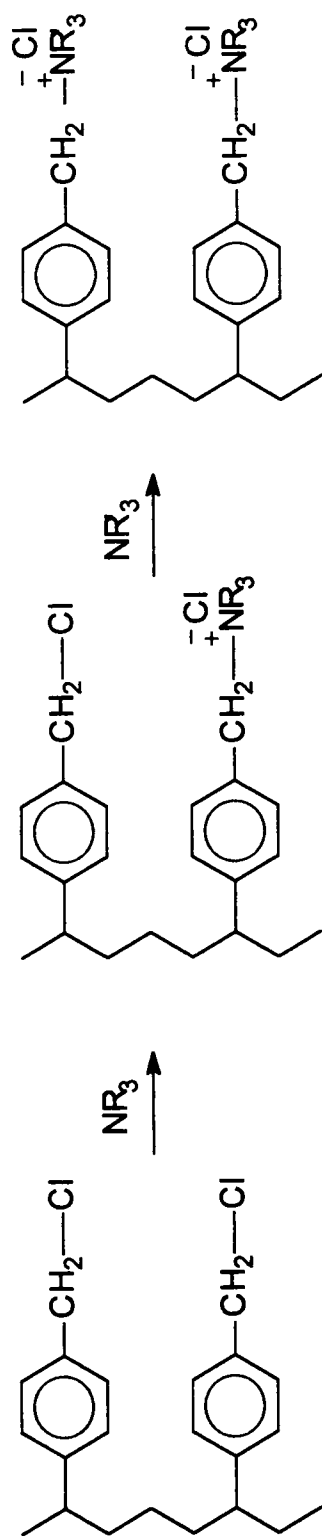


Figure 3-1. formation of biquaternary ammonium anion exchange resin from starting copolymer

Table 3-6. Various biquaternary ammonium anion exchange resins: characterization and distribution coefficients for uptake of pertechnetate anion (* batch equilibrium result at stated time; all values have a +/- 5% uncertainty)

resin	amine #1	amine #2	% solids	nitrogen capacity (mequiv/g)	TAEC (mequiv/g)	K'd * (1hr) (mL/g)	K'd * (24 hr) (mL/g)
5% crosslinked VBC MR resin							
RO-2-074	triethyl	triethyl	40.49	2.36	2.07	1.7×10^4	4.0×10^4
RO-2-061	triethyl	tripropyl	44.79	2.24	2.40	1.1×10^4	3.8×10^4
RO-2-084	tripentyl	tripropyl	42.43	2.13	2.11	9.9×10^3	2.5×10^4
4.5% crosslinked chloromethylated polystyrene MR resin (Sybron)							
RO-2-076	triethyl	triethyl	50.23	2.11	1.93	1.1×10^4	3.3×10^4
RO-2-063	triethyl	tripropyl	54.80	2.25	1.79	7.4×10^3	2.6×10^4
RO-2-087	tripentyl	tripropyl	51.48	1.94	1.96	6.7×10^3	2.1×10^4
3% crosslinked chloromethylated polystyrene gel resin (Sybron)							
RO-2-244	triethyl	triethyl	63.68	2.10	2.10	9.7×10^3	4.0×10^4

Table 3-7. Results of column study for biquaternary ammonium exchange resins ⁽⁵²⁾

resin	amine #1	amine #2	flow rate (BV/min)	Bed volume for breakthrough		
				0.1%	1.0%	10.0%
VP-02-261	hexyl	butyl	3.40	40	240	1370
VP-02-165	hexyl	propyl	3.89	66	400	1950
VP-02-258	hexyl	ethyl	3.42	140	800	0

* 10% breakthrough was not reached by 1800BV. 4% breakthrough was achieved at 1730 BV.

time. Unfortunately the slower kinetics found at 1 hour discourages its use. Three different sulfonation methods were attempted on the hexyl/ethyl biquaternary ammonium exchange resin from 3% crosslinked chloromethylated polystyrene from Sybron. Sulfonation with concentrated sulfuric acid at 128 °C, with chlorosulfonic acid at room temperature and finally with fuming sulfuric acid at room temperature were all attempted. A 15 minute contact time with fuming sulfuric acid at room temperature was the only method that lowered the percent solids (from 68.54 % to 54.53 %). The resin was characterized after sulfonation to produce an acid capacity of 1.27 mequiv/g. This capacity was too high for our purpose and the addition of a sulfonate ligand was no longer pursued.

Scale-up of procedure for formation of bifunctional ammonium resin

The entire procedure for formation of the biquaternary ammonium exchange resin had to be streamlined in order to be used on an industrial scale including the pre-reaction swell, reaction time, and post-reaction treatment (Table 3-8). The solvent also had to be changed because 1,4-dioxane cannot be used in production facilities due to its believed mutagenicity. Two other solvents were tried, toluene and methylal, using amination times of 17 hours. The resin formed in toluene gave results comparable to the best resins formed in 1,4-dioxane at contact times below 24 hours at which point it has reached an equilibrium much like the results from the streamlined procedure before altering the solvent. Reactions with methylal proved to be too bothersome. The methylal proved to be too volatile for our condensers. Each trial with methylal had only resin and

Table 3-8. Procedure changes for formation of trihexylamine / triethylamine resin and following resin characterization

resin	pre-reaction swell time/temp	rxn time: trihexylamine (°C)	1,4-dioxane wash before 2 nd reaction	rxn time: triethylamine (°C)	washes after 2 nd amine rxn	% solids	N capacity (mequiv/g)	TAEC (mequiv/g)
RO-02-074	17 hr / RT	17 hr	yes	17 hr	organic*	41.65 %	2.23	3.04
RO-03-089	17 hr / RT	4 hr	yes	4 hr	organic*	26.05 %	2.78	3.01
RO-03-113	12 hr / RT	4 hr	no	4 hr (with balloon)	aqueous**	27.16 %	3.15	2.88
RO-03-124	4 hr/ reflux	4 hr	no	4 hr (with balloon)	aqueous**	25.55 %	3.10	3.15

* denotes a washing sequence consisting of 1,4-dioxane, ethanol, aqueous ethanol, and water

** denotes a washing sequence consisting of aqueous ethanol and water only

Table 3-9. Characterization and distribution coefficients for uptake of pertechnetate anion using trihexyl/triethyl biquaternary ammonium exchange resin formed from various procedural methods.

resin	functionalization method	% solids	nitrogen capacity (mequiv/g)	K'd (1 hr) (mL/g)	K'd (24 hr) (mL/g)
RO-02-074	original	41.65	2.23	1.5×10^4	3.8×10^4
RO-04-012	streamlined in 1,4-dioxane	43.65	2.60	1.9×10^4	3.5×10^4
RO-04-126	streamlined in toluene*	23.69	2.40	2.1×10^4	3.7×10^4
RO-04-132	streamlined in methylal**	34.84	1.77**	5.4×10^1	1.0×10^3

* The amination reactions went for 17 hours instead of 4 hours

** The resin was near full functionalization after the amination with trihexylamine, which may explain the low distribution coefficients

triethylamine in the round-bottom flask at the end of the reaction. The resin was analyzed after the triethylamine reaction and the nitrogen capacity was 1.97 mequiv/g. The resin was reacted with triethylamine in methylal and produced a resin containing a nitrogen capacity of 1.77 mequiv/g.

All of the changes led to a resin with a lower percent solids than the resin produced by the original procedure. This led to a higher uptake of TcO_4^- at 1 hour (see Table 3-9). At this point, the procedure was passed along to an industrial partner for large scale synthesis and analysis.

Discussion

Enhancing the accessibility of the triethyl ammonium ligand

It was found that the quaternary ammonium exchange resin made from triethylamine has a high selectivity for the pertechnetate anion, but a very slow exchange rate⁽⁵²⁾. Enhancing the access of the anion to the exchange site was the first goal. A lightly crosslinked copolymer made of a 25:75 ratio of VBC to styrene was chosen for this experiment. The first copolymer was a macroreticular (MR) bead made by adding a diluent (4-methyl-2-pentanol) during the suspension polymerization. The monomers are soluble in 4-methyl-2-pentanol (4M2P), but the polymer is insoluble. Macrochannels and pores are formed throughout the polymer beads, allowing for a much larger surface area over gel beads. The second copolymer of the same ratio stated above was a xerogel bead made by adding an organic solvent (toluene) during the suspension polymerization. Both the monomer and polymer are soluble in toluene, allowing for a swollen crosslinked matrix formed during

the polymerization. The matrix can be expanded and contracted depending on the solvent allowing for a much larger swelling ratio. Both of these copolymers were used in amination reactions with trihexylamine. The post-reaction characterizations are found in Table 3-1. Both of the resins were within the theoretical nitrogen capacities for their respective starting copolymer, but the xerogel resins' percent solids were too high for the intended applications. The high percent solids can be attributed to the increased ability of the xerogel matrix to collapse due to the hydrophobicity of the trihexylammonium ligand. When this happens, the pore water content is going to be low. With a low pore water content (high percent solids), the metal ion in the aqueous solution will not be able to diffuse into the bead, causing a low percent uptake.

In order to overcome the high percent solids of the xerogels, an access mechanism was added to the system. The hydrophilic ligand chosen was the sulfonic acid ligand in hopes that sulfonation would open up the matrix, as it does with cation exchange resins, and increase the kinetics of the exchange. This was done despite expectations that the Donnan potential may dominate and prevent significant anion exchange. The ligand was bonded by sulfonation of the quaternary ammonium resin. Two different types of sulfonation were attempted. The first method was a sulfonation with chlorosulfonic acid in ethylene dichloride (EDC) at room temperature as well as one attempted at 80 °C, all for short reaction times. The second method used concentrated sulfuric acid at an elevated temperature (80 °C) for short reaction times. Each of the two methods had a positive effect on the hydrophilicity of the quaternary ammonium resin (Table 3-2). Sulfonation with chlorosulfonic acid at room temperature greatly dropped the percent solids, from

over 70% to below 30%, values below that of the 10% crosslinked MR resin, but the total anion exchange capacity (TAEC) of the now bifunctional resin was not greatly increased, except for the chlorosulfonation done at 80 °C. Sulfonation with concentrated sulfuric acid at 80 °C did not greatly affect either the percent solids or the TAEC. All of these resins were tested at ORNL for the uptake of pertechnetate anion. Unfortunately, sulfonation appears to retard uptake of pertechnetate anion removal (Table 3-3). Probably due to the increase in negative charge around the quaternary ammonium ligand from the sulfonate group. It is also possible that a significant number of the sulfate groups ionically bind with the ammonium ions, and this association may not be easily broken.

Addition of a second quaternary ammonium ligand

Previous work done within our research group ⁽⁵²⁾ showed that addition of a second quaternary ammonium ligand using a smaller trialkyl amine decreases the hydrophobicity (decreased percent solids) and enhances the uptake of pertechnetate anion. All functionalizations were done on a 5% crosslinked VBC/DVB MR copolymer. As seen in Table 3-5, Patel discovered that even though the percent solids are slightly higher in the 5% DVB resin compared to the 10% crosslinked copolymer and higher, the amount of functionalization and the TAEC were both maximized with the 5% crosslinked copolymer. Therefore, an MR bead of VBC, 5% crosslinked with DVB, was the starting copolymer used to form a biquaternary ammonium exchange resin from amination with a longer trialkyl amine followed by amination with a shorter trialkylamine (Figure 3-1). Various combinations were tried (Table 3-6). From Table 3-6, it is seen that the three biquaternary

ammonium exchange resins formed all had comparable amounts of functionalization, but differences were found upon analysis for uptake of pertechnetate anion at both 1 hour and 24 hours. The resin containing tripentyl ligands as the larger trialkylamine (RO-02-084) has lower K'_d values than the resins containing trihexyl ligands as the larger trialkylamine. The resin containing triethyl ligands as the smaller alkylamine (RO-02-074) has better results at both 1 hour and 24 hours when compared to the resin containing tripropyl ligands (RO-02-061). This led to the amination of the VBC/DVB copolymer with trihexylamine followed by amination using triethylamine on a large scale. Due to economics, industries prefer to use chloromethylated polystyrene rather than a crosslinked VBC copolymer as the starting crosslinked copolymer. Thus, 4.5 % crosslinked chloromethylated polystyrene copolymer was obtained from Sybron and used in the above stated amination reactions followed by analysis of uptake of pertechnetate anion to determine any differences. Comparing the first three entries to the second three entries in Table 3-6, it is seen that elemental characterizations of the resin starting from Sybron copolymer and the resin starting from VBC copolymer are within experimental error of each other, but from the remaining analyses it is apparent that there are stark differences between the two starting copolymers. The percent solids are higher and the distribution coefficients at both 1 hour and 24 hours are vastly lower for the resin starting from Sybron copolymer. These two concepts likely go hand in hand with each other. If the percent solids are higher, then the accessibility within the polymer has decreased. This in turn, would decrease the uptake of the anion. This may be explained by secondary crosslinking that takes place during chloromethylation (Figure 3-2). This would increase the

crosslinking level of the MR resin past that of its original level, here 4.5%. Thus a 3% crosslinked chloromethylated polystyrene was obtained from Sybron and functionalized to form the biquaternary ammonium exchange resin. However, this commercially available lightly crosslinked copolymer was only available in gel form. As shown in Table 3-5, the lighter crosslinked Sybron resin is a major improvement over the higher crosslinked copolymer in uptake of the pertechnetate anion after 24 hours. In fact, the lighter crosslinked Sybron resin is almost to the level of the VBC copolymer at 24 hours. Unfortunately the slower kinetics as implied by the 1 hour study makes the resin unusable. In order to decrease the percent solids, the 3% crosslinked Sybron resin was lightly sulfonated after formation of the biquaternary ammonium ligands. Three different sulfonation methods were attempted on the hexyl/ethyl biquaternary ammonium exchange resin. Sulfonation with concentrated sulfuric acid at 128 °C, with chlorosulfonic acid at room temperature and finally with fuming sulfuric acid at room temperature were all attempted. A 15 minute contact time with fuming sulfuric acid at room temperature was the only method that lowered the percent solids, from 68.54 % to 54.53 %. The resin was characterized after sulfonation to produce an acid capacity of 1.27 meq/g. This capacity was too high for our purpose and the addition of a sulfonate ligand was no longer pursued.

Scale-up of procedure for formation of bifunctional ammonium resin

With the original amination procedure, the swelling time was overnight at room



Figure 3-2. Secondary crosslinking during chloromethylation of crosslinked polystyrene

temperature and both of the amination times were for 17 hours. A washing sequence was used between the first and second amination followed by an extensive washing sequence after the second amination. None of these procedural intricacies are feasible on an industrial setting. Therefore, the entire procedure for formation of the biquaternary ammonium exchange resin had to be streamlined yet retain the resin's characteristics. The amination procedure was the first to be improved upon. Instead of a 17 hr reaction time at reflux, the same results were found with a 4 hour reaction time at reflux (Table 3-8). The swelling procedure was then altered. Increasing the swelling temperature to the reflux temperature with stirring afforded a decrease from 17 hours down to 4 hours (Table 3-8). The washing sequence between the two aminations was discarded and the washing sequence after the second amination was simplified to three aqueous ethanol washes and a water wash. Also, it was found that triethylamine was escaping during the amination reaction. Thus a balloon was added to the end of the condenser to allow for variation in pressure but keeping all of the reactant in the reaction. None of these changes hampered the resin characteristics (Table 3-8).

The solvent was also changed. Use of 1,4-dioxane was not permissible on an industrial level. Two other solvents were tried, toluene as well as methylal, using amination times of 17 hours. The resin formed in toluene gave quite comparable results (Table 3-9) to the best resins formed in 1,4-dioxane at contact times 24 hours and below at which point it has reached an equilibrium much like the results from the streamlined procedure in 1,4-dioxane.

All of the changes led to a resin with a lower percent solids than found using the original

procedure. This led to a higher uptake at 1 hour (20670 versus 14600 mL/g) but the final distribution coefficient was higher for the resin prepared by the original procedure: using the original procedure, the distribution coefficient reached between 46000 and 50000 mL/g after 7 days of contact time. Interestingly, at 4 hr, the resin formed from the streamlined procedure reached its equilibrium value at 25000 mL/g, which was equivalent to the 4 hour contact time value with the original procedure resin. This decrease in kinetics is probably due to decrease in matrix flexibility from secondary crosslinking during the chloromethylation of the polystyrene resin.

Conclusions

A biquaternary ammonium anion exchange resin has been formed that is selective for pertechnetate anion at low concentration levels in high concentrations of anions commonly found in groundwater such as chloride, sulfate and nitrate. The resin has also shown improvement in kinetics over the present commercially available anion exchange resins. The resin described was created from reacting trialkylamines with lightly crosslinked macroporous VBC copolymer. Using two different trialkylamines, one with long alkyl chains followed by amination with a trialkylamine having short alkyl chains. Tests were conducted by Oak Ridge National Laboratory to determine the amount of uptake of pertechnetate anion in simulated contaminated groundwater. The most successful exchange resin formed was from reactions with trihexylamine followed by reaction with triethylamine. The procedure to form this biquaternary ammonium resin was successfully streamlined for production on an industrial scale.

CHAPTER 4

EXPERIMENTAL PROCEDURES

All chemicals were used without further purification, except for those dried over 4A molecular sieves, and were obtained from common chemical companies. Metal ion solutions for contact studied were prepared using Class A glass pipettes and volumetric flasks.

Synthesis

Copolymer synthesis ⁽⁵⁴⁾

Copolymer beads were prepared either as gels or MRs by suspension polymerization. The percent crosslinking with divinylbenzene (DVB) was varied according to needs. A representative procedure for the synthesis of 300 g poly(vinylbenzyl chloride) beads crosslinked with 2% divinylbenzene by suspension copolymerization follows.

The aqueous phase was prepared by adding 1.44 g Pharmagel to 158.25 g distilled water and heating to 50 °C with stirring until the gelatin dissolves. The gelatin solution was added to a second aqueous phase comprised of 17.85 g poly(diallyldimethylammonium chloride) (PADMAC), 9.495 g boric acid and 316.5 g distilled water. This mixture was stirred and the pH was adjusted to 10.3 with 50 wt% NaOH. The aqueous phase was added to a 1 L three-neck round-bottom flask and sparged with nitrogen gas for at least 8 minutes. A Friedrich's condenser, a thermometer, and a single-paddle stir shaft with stir bearing attached to an overhead motor with digital

readout were added to the 1 L round-bottom flask.

The organic phase was made separately in a 500 mL Erlenmeyer flask with a ground glass top. To the flask, 286.10 g vinylbenzyl chloride (VBC), 10.91 g divinylbenzene (DVB) (technical grade, 55.4% pure), and 3.0 g benzoyl peroxide were added. The mixture stirred until the solid peroxide dissolved, usually taking 5 minutes. The organic phase was sparged with nitrogen for at least 5 minutes and added to the 1 L round-bottom flask containing the aqueous phase. The placement of the stir shaft was adjusted so that the top of the stir paddle was at the phase interface. Using gas inlet adapters, a light nitrogen sweep was passed through the apparatus from this point.

A start-up period was used to suspend the organic droplets throughout the aqueous phase by turning the stirrer on for two minutes, and then off for 1 minute; done three times total. As long as bead formation persisted, the stirrer was set for the appropriate speed to produce the desired bead size, and the suspension was heated to 80 °C at a rate of 7 °C per 15 minutes. The temperature was maintained at 80 °C for 10 hours. To the suspension, 200 mL of distilled water was added and the mixture stirred for 2 hours at reflux. This was the finish off period. The solution was removed and the copolymer was washed once with 10^{-4} N HCl, followed by three water washes. The copolymer was filtered from the solution with a Buchner funnel and extracted with toluene for 17 hours with a soxlet extractor. The beads were removed from the extractor and dried in a large glass dish in a 60 °C oven. The dry beads were sieved and separated by size using U.S. Standard screens.

MR copolymer beads were prepared in a similar manner, but 50 mass percent of

the organic phase was replaced with the 4-methyl-2-pentanol. The finish off period was also replaced with a 6 hour distillation using a Dean-Stark trap and enough additional water to remove the 4-methyl-2-pentanol. When forming a copolymer containing styrene, the desired monomer ratios were used to recalculate initial monomer masses.

Xerogel beads were synthesized by replacing 40% by mass of the organic phase with toluene. The beads were stored under acetone until just before use at which point the beads were dried at room temperature.

Phosphonic acid resin synthesis

Thirty grams of 2% DVB crosslinked poly(vinylbenzyl chloride) resin were transferred to a 500 mL three-neck round-bottom flask equipped with a Friedrich's condenser, a single-paddle stir shaft with stir bearing attached to an overhead motor, and a ground glass stopper. Two hundred and fifty milliliters of triisopropyl phosphite was added to the copolymer and the mixture stirred at reflux for 17 hours. The solution was removed via a gas dispersion tube connected to a vacuum, and replaced with 300 mL of concentrated HCl. The new mixture was slowly brought to a vigorous reflux (decreases bumping of resin into the condenser) at which point the mixture stirred for 24 hours. The solution was removed and the resin was washed with 300 mL of 50 percent by volume HCl for 20 minutes, followed by two additional washes with 300 mL of distilled water. The resin was conditioned by eluting in a fritted glass column with 1 liter each of water, 4 wt% NaOH, water, 4 wt% HCl, and water at a rate of 1 liter per hour. The resin was extracted with distilled water for 17 hours with a Soxlet extractor. The resin was

conditioned in the same manner as previously done.

Chlorination of phosphonic acid resin

Phosphonic acid resin was placed in a Buchner funnel and covered with a sheet of latex rubber which was held firmly in place by a rubber band. A vacuum (710 mm Hg) was applied to the resin for 5 minutes to remove excess water. Phosphonic acid resin (10.0 g) was added to a small glass jar along with about 35 mL of N,N'-dimethylformamide (DMF) and capped with a solvent proof cap. The jar was placed on a wrist-action shaker for 15 minutes at which point the solution was removed and replaced with fresh 35 mL of DMF. The resin was once again placed on the wrist-action shaker for 15 minutes, and this was repeated one more time. The resin-DMF mixture was added to a 500 mL three-neck round-bottom flask equipped with two ground glass stoppers and a single-paddle stir shaft with stir bearing attached to an overhead motor. The solution was removed and the resin was solvent exchanged with dry dichloromethane (dried over 4A molecular sieves for at least 8 hours) three times. Fifty milliliters of fresh, dry dichloromethane was added to the resin and an addition funnel with a pressure equalization arm was added to the round-bottom flask. To the addition funnel, 5.5 milliliters of DMF and 50 mL of thionyl chloride were added. This mixture dripped into the round-bottom flask over a thirty minute period while the round-bottom flask was immersed in an ice / water bath. The bath was removed and the reaction was stirred at room temperature for 4 hours. The solution was removed and replaced with 50 mL of fresh, dry dichloromethane. Another 5.5 mL DMF / 50 mL thionyl chloride mixture was

added to the addition funnel. This was once again added in the same manner to the round-bottom flask and the reaction stirred at room temperature for 17 hours. The solution was removed and replaced with 50 mL of dry dichloromethane. The mixture was stirred for 15 minutes with a strong nitrogen gas sweep passing through the apparatus. The wash was removed and replaced with 50 mL of dry toluene. This stirred for 15 minutes with a strong nitrogen sweep.

Formation of phosphonate ester resin

To the three-neck round-bottom flask containing the phosphoryl dichloride resin in toluene with a nitrogen sweep, the following work was continued. The toluene was removed and replaced with 75 mL of dry pyridine (dried over 4A molecular sieves for at least 8 hours). The mixture stirred for about 10 minutes under a light nitrogen sweep. An addition funnel with a pressure equalization arm, a thermometer with 24/40 adaptor, and a Claisen adapter were added to the apparatus. A twenty molar excess of reacting alcohol relative to the moles of phosphorus in the resin was added to the addition funnel. The alcohol dripped into the flask between 5 and 25 minutes while the mixture stirred depending on the amount of alcohol in the funnel. The system was heated to the desired temperature (eight degrees below the alcohol's b.p. or 100 °C, whichever temperature was lower) with a heat lamp and aluminum foil wrapping. The reaction stirred for the set amount of time once at the desired temperature. The system was cooled to room temperature, the nitrogen sweep was removed, and the solution was removed using a glass dispersion tube and suction. The resin was washed four times each for 15 minutes with

1000 mL of 75% aqueous 1,4-dioxane. The resin was then washed once with 200 mL of distilled water. The resin was then conditioned by eluting in a fritted glass column with 1 liter each of water, NaOH, water, HCl, and water at a rate of 1 liter per hour. Concentrations of elutions were varied.

Formation of phosphonamide resin

To the three-neck round-bottom flask containing the phosphoryl dichloride resin in toluene with a nitrogen sweep, the following work was continued. The toluene was removed and replaced with 75 mL of dry pyridine (dried over 4A molecular sieves for at least 8 hours). The mixture stirred for about 10 minutes under a light nitrogen sweep. An addition funnel with a pressure equalization arm, a thermometer with 24/40 adaptor, and a Claisen adapter were added to the apparatus. A twenty molar excess of reacting amine relative to the moles of phosphorus in the resin was added to the addition funnel. The alcohol dripped into the flask between 5 and 25 minutes while the mixture stirred depending on the amount of amine in the addition funnel. The system was heated to the desired temperature (eight degrees below the amine's b.p. or 100 °C, whichever temperature was lower) with a heat lamp and aluminum foil wrapping. The reaction stirred for the set amount of time once at the desired temperature. The system was cooled to room temperature, the nitrogen sweep was removed, and the solution was removed using a glass dispersion tube and suction. The resin was washed four times each for 15 minutes with 1000 mL of 75% aqueous 1,4-dioxane. The resin was then washed once with 200 mL of distilled water. The resin was then conditioned by eluting in a fritted

glass column with 1 liter each of water, NaOH, water, HCl, and water at a rate of 1 liter per hour. Concentrations of elutions were varied.

Synthesis of monofunctional quaternary ammonium exchange resin

To a 500 mL three-neck round-bottom flask, 10.0 g of 5% crosslinked MR poly(vinylbenzyl chloride) beads were added along with 100 mL of 1,4-dioxane. Each of the three necks were covered with parafilm to prevent loss of solvent. The beads were allowed to completely swell in the solvent at least 15 hours and generally overnight. Trialkylamine (trihexylamine, 65 mL), an additional 50 mL of 1,4-dioxane, and 10 mL of distilled water were added to the round-bottom flask equipped with a Friedrich's condenser, a single-paddle stir shaft with stir bearing attached to an overhead motor, and a ground glass stopper. The mixture was heated to reflux with a heat lamp and continued to stir for 17 hours.

If the resin was to be aminated with a second trialkylamine, the solution was removed, the resin was washed with 100 mL of fresh 1,4-dioxane for 15 minutes, and the new reaction was started. If no more reactions were to take place, the resin was washed with 100 mL per wash, each for 15 minutes, as follows: 1, 4-dioxane, 95% aqueous ethanol, 50% aqueous ethanol, 1 N hydrochloric acid, water. The resin was then conditioned by eluting in a fritted glass column with 1 liter each of water, 4 wt% NaOH, water, 4 wt% HCl, and water at a rate of 1 liter per hour.

Synthesis of bifunctional quaternary ammonium exchange resin

Once the solution was removed from the monofunctional quaternary ammonium resin formed above and washed with 100 mL of 1,4-dioxane, the second trialkylamine (triethylamine, 60 mL), 150 mL of 1,4-dioxane, and 10 mL of distilled water were added to the round-bottom flask. The reaction was heated to reflux with a heat lamp and stirred for 17 hours. The solution was removed, and the resin was washed with 100 mL per wash, each for 15 minutes, as follows: 1,4-dioxane, 95% aqueous ethanol, 50% aqueous ethanol, 1 N hydrochloric acid, water. The resin was then conditioned by eluting in a fritted glass column with 1 liter each of water, 4 wt% NaOH, water, 4 wt% HCl, and water at a rate of 1 liter per hour.

Industrially compatible synthesis of monofunctional quaternary ammonium exchange resin

To a 500 mL three-neck round-bottom flask, 10.0 g of 5% crosslinked MR poly(vinylbenzyl chloride) beads were added along with 100 mL of 1,4-dioxane. A Friedrich's condenser, a single-paddle stir shaft with stir bearing attached to an overhead motor, and a ground glass stopper were added to the round-bottom flask and the mixture was heated to reflux with a heat lamp for 4 hours. The mixture was cooled to room temperature. Sixty-five milliliters trihexylamine, an additional 50 mL of 1,4-dioxane, and 10 mL of distilled water were added to the round-bottom flask. The mixture was heated to reflux with a heat lamp and continued to stir for 4 hours.

Industrially compatible synthesis of bifunctional quaternary ammonium exchange resin

Once the solution was removed from the monofunctional quaternary ammonium resin formed above, 60 mL triethylamine, 150 mL of 1,4-dioxane, and 10 mL of distilled water were added to the round-bottom flask. A balloon was added to the outlet of the condenser to prevent loss of unreacted amine. The reaction was heated to reflux with a heat lamp and stirred for 4 hours. The solution was removed, and the resin was washed with 100 mL per wash, each for 15 minutes, as follows: 95% aqueous ethanol, 75% aqueous ethanol, 50% aqueous ethanol, water, water. The resin was then conditioned by eluting in a fritted glass column with 1 liter each of water, 4 wt% NaOH, water, 4 wt% HCl, and water at a rate of 1 liter per hour.

Characterization

Percent solids

All conditioned resins were stored under water. For characterization and metal ion complexation studies, the excess water over the resin was removed by suction filtration using a Buchner funnel. This process is referred to as Buchner drying. The resin stored under water is placed in a Buchner funnel and covered with a sheet of latex rubber which is held firmly in place by a rubber band. A vacuum (710 mm Hg) was applied to the resin for 5 minutes. The resin is now referred to as wet resin. Wet resin was placed in a pre-weighed glass scintillation vial and accurately weighed to four decimal places with an

analytical balance. The resin containing vial was allowed to dry in a 110 °C oven for 17 hours. The vial was removed, allowed to cool in a dessicator, and the now dry resin in the scintillation vial was weighed once again with an analytical balance. The percent solids was calculated with the following equation.

$$\% \text{ Solids} = \frac{(\text{Weight of oven dried resin})}{(\text{Weight of Buchner dried resin})} \times 100\%$$

Total acid capacity

Into a 250 mL Erlenmeyer flask with a ground glass joint, 1.0 to 1.2 grams of Buchner dried resin (accurately weighed with an analytical balance) was added along with a small stirring bar. To the same Erlenmeyer flask, 200 mL of standardized 0.10 N NaOH containing 5 wt% NaCl was transferred using a Class A glass pipette. The Erlenmeyer flask was sealed with a plastic cap and stirred for 17 hours at 350 rpms. The resin was allowed to settle and the solution was removed. Two to three 50 mL aliquots were titrated to a phenolphthalein end point with a standardized 0.10 N HCl solution. The total acid capacity in mequiv/g was calculated with the following equation.

$$\text{OH capacity} = \frac{[(\text{Volume of NaOH}) \times (\text{N of NaOH})] - [4 \times (\text{Volume of HCl}) \times (\text{N of HCl})]}{[(\text{Weight of Buchner dried resin}) \times (\text{Percent solids})]}$$

Phosphorus elemental analysis

All glassware in this procedure was cleaned with aa non-soap product so as not to

introduce outside phosphorus contaminants. The Bauche and Lomb Spectrometer 21 was calibrated every four to six weeks using four standard potassium phosphate monobasic solutions obtained from a calibration stock solution. The slope and y-intercept of this line was used in determining the phosphorus content as long as the linear correlation was at least 0.998.

Samples were analyzed in duplicate. Twenty to twenty-five milligrams of 110 °C oven dried resin was weighed into a 125 mL Erlenmeyer flask. Four hundred micro liters of 0.5 M copper sulfate solution and 10 mL of concentrated sulfuric acid were added to each flask and heated on a hot plate on a medium-high setting for about 2 hours or until the solution was pale-yellow to colorless. In order to prevent the flask from going dry, a watch glass was sometimes placed on the top of the flask. The solution was cooled to room temperature. Two grams of potassium persulfate and about 75 mL of distilled water were added to the flask and heated on a low-medium setting for two hours. The solution was cooled to room temperature. The solution was made basic (color changed to brown) with a 50% sodium hydroxide solution and then neutralized (color change to a pale blue to clear) with 2% sulfuric acid solution. The cool solution is transferred to a 100 mL volumetric flask and diluted to the mark with distilled water. A 25 mL aliquot was pipetted into a 50 mL volumetric solution. Ten milliliters of molybdate/vanadate developing solution (prepared with 25 g ammonium molybdate tetrahydrate, 1.28 g ammonium vanadate, 330 mL concentrated hydrochloric acid and 670 mL distilled water in a 1L volumetric flask) was pipetted into the flask and diluted to the mark with distilled water. A blank was also prepared by adding 10 mL of the developing solution into a 50

mL volumetric flask diluted to the mark with distilled water. After a development time of fifteen to twenty minutes, the absorbances of the solutions and blank were analyzed using a Bauche and Lomb Spectrometer 21 with a wavelength of 470 nm. The phosphorus capacity in mequiv/g was calculated with the following equation.

$$\text{P capacity} = \frac{4[(\text{absorbance} - \text{y-intercept}) / \text{slope}]}{(30.974) (\text{weight of dry resin})}$$

Nitrogen elemental analysis ⁽⁵⁵⁾

Between 200 and 250 mg of 110 °C oven dried resin was accurately weighed into a 500 mL three-neck round-bottom flask. Ten grams potassium sulfate, 0.25 g copper(II) sulfate, a few dark grey boiling chips, and 25 mL concentrated sulfuric acid was added to the round-bottom flask. The round-bottom flask was fitted with two ground glass stoppers and a standard 14 inch water jacket condenser. Using a heating mantle, the round-bottom flask was gently heated (veriac setting of 50) for 45 minutes. The contents were then heated strongly (veriac setting of 85) at least 8 hours. After cooling to room temperature, the condenser and one of the stoppers were removed and rinsed back into the round-bottom flask with about 25 mL of distilled water. A magnetic stir bar and an additional 100 mL of distilled water were added to the round-bottom flask. A distillation condenser with a plastic funnel attached with a piece of tygon tubing by the funnel neck was added to the middle neck of the round-bottom flask. A 250 mL stoppered addition funnel with a pressure equalization arm containing 150 mL of 6 N sodium hydroxide was added to the remaining open neck of the round-bottom flask. Fifty milliliters of

standardized 0.1 N hydrochloric acid was pipetted into a 600 mL beaker at which point the bell of the attached funnel was submerged in the acid but not flat against the bottom of the beaker. All seals were checked and the sodium hydroxide was dripped into the round-bottom flask over a 2 minute period while the mixture stirred. The mixture was heated (veriac setting at 94) and the round bottom flask was wrapped in aluminum foil to prevent heat loss. The mixture was distilled into the acid until the distillate was neutral and the volume in the beaker was approximately 200 mL. The acid solution was quantitatively transferred to a 250 mL volumetric flask and diluted to the mark with distilled water. Fifty milliliter aliquots were titrated with standardized 0.1 N sodium hydroxide containing 5 wt% sodium chloride using bromocresol green as the indicator. The nitrogen capacity in mequiv/g was calculated with the following equation.

$$\text{N capacity} = \frac{[(50.0 \text{ mL HCl})(\text{Normality of HCl})] - [5(\text{Vol. NaOH})(\text{Normality of NaOH})]}{\text{Weight of dry resin}}$$

Chlorine elemental analysis

Nanopure water was used throughout this entire procedure due to a detectable amount of chlorine in distilled water. All inner surfaces of a Parr bomb were thoroughly cleaned and rinsed with nanopure water prior to use. The inner surface of the bomb cylinder was wetted with 5 mL of 5 wt% sodium carbonate. The 110 °C oven dried resin and silicon oil (masses determined via Table 4.1) were accurately weighed into a stainless steel capsule and placed into the bomb holder. Ten centimeters nickel alloy fuse wire was threaded through the bomb holder stem holes and secured so that the fuse wire did not

touch the metal of the capsule and hovered just over the oil/resin mixture. The bomb was assembled and secured. The bomb was purged with 30 atm O₂ twice, and then filled with 30 atm of O₂. The bomb was submerged in a water bath, the wire leads were attached to the bomb, and the fuse wire ignited. After five minutes maximum in the water bath, the pressure inside the bomb was allowed to slowly bleed out. The inner surface of the bomb was quantitatively scrubbed with a rubber policeman and nanopure water, and the contents were placed into a dry 400 mL beaker. The solution was filtered into a 250 mL volumetric flask and diluted to the mark. Two 25 mL aliquots were pipetted into separate 125 mL Erlenmeyer flasks; ~ 2 mL 2 N nitric acid solution was added to each flask to remove the carbonate. Ten milliliters 0.0500 N silver nitrate was pipetted into the flasks and the samples were heated to boiling on a hot plate. Using the same 10 mL pipette, two blanks were prepared. The heated samples were then allowed to cool to room temperature in a dark place. These samples are filtered with pre-folded filter paper into clean, dry 125 mL Erlenmeyer flasks and washed with 1 to 2 small pipets of 0.01 N nitric acid. Three milliliters of ferric ammonium sulfate in 2 N nitric acid was added to each flask, including the blanks. The blanks were titrated via a 10 mL buret with 0.05 N ammonium thiocyanate until the first trace of the brick red end point was visible (best seen by stopping the stirrer to allow the white silver chloride precipitate to slightly settle). Now that the titrant has been standardized, the resin samples were titrated in the same manner. The chlorine capacity in mequiv/g was calculated with the following equation.

$$\text{Cl capacity} = \frac{(10) \times [(\text{normality of AgNO}_3)(\text{vol. AgNO}_3)] - [(\text{normality of NH}_4\text{SCN})(\text{vol. NH}_4\text{SCN})]}{\text{weight of dry resin}}$$

Table 4.1. Sample mass for chlorine elemental analysis

% Cl by wt	sample mass (g)	oil mass (g)
Less than 2	0.8	0.0
2 - 5	0.4	0.4
5 - 10	0.2	0.6
10 - 20	0.1	0.7
20 - 50	0.05	0.75

Total anion exchange capacity

Nanopure water was used throughout this entire procedure. A percent solids was set up as discussed earlier. To a tarred glass vial, 2.5 to 3.0 g of the same buchner dried resin was accurately weighed. The resin was quantitatively transferred to a glass fritted column using nanopure water and all solution was forced out of the column. The resin was eluted with 250.0 mL of 1.0 N sodium nitrate solution (volumetrically measured) over a 1 hour period into a 250 mL volumetric flask. Two 50 mL aliquots were pipetted into 125 mL Erlenmeyer flasks; 3 drops of methyl orange indicator were added to each flask; 1 drop of concentrated nitric acid was added to each flask change the color if the solution from yellow to pink. A dilute sodium hydroxide solution (0.01 N) was used to neutralize each sample (just returning the color of solution back to yellow); 3 more drops of methyl orange were added; ~ 2 mL potassium chromate solution was added to each flask changing the solution color to a bright yellow. Each sample was titrated with 0.05 N silver nitrate to the first constant color change (bright yellow to a pale orange). The total anion exchange capacity (TAEC) in mequiv/g was calculated with the following equation.

$$\text{TAEC} = \frac{5 \times (\text{Normality of AgNO}_3)(\text{vol. AgNO}_3)}{\text{weight of dry resin}}$$

Complexation studies

Contact solutions

All contact solutions were prepared with nanopure water along with reagent grade

metal salts and acids. Stock solutions of the metal ion were prepared in concentrations of 10^{-3} N in a 500 mL volumetric flask using an appropriate matrix. Lower concentrations were prepared with appropriate dilution solutions. All contact solutions containing the appropriate metal nitrate had a concentration of 10^{-4} N prepared by pipetting 10 mL of the stock solution into a 100 mL volumetric flask and diluting to the mark with the appropriate matrix.

Metal ion studies

One milliequivalent (based upon the phosphorus capacity) of buchner dried resin was accurately weighed into a clean, dry 20 mL scintillation vial. The resin was pre-equilibrated with roughly 10 mL of the appropriate matrix for 15 minutes on a Burrell wrist-action shaker. The solution was removed using a Pasteur pipet and suction. The procedure was repeated three more times. Ten milliliters of the contact solutions was pipetted into the vial and the resin shaken for 24 hours. The contact solution was removed from the resin with a clean Pasteur pipet and analyzed using a Perkin-Elmer atomic absorption (AA) spectrometer with an air/acetylene flame. The appropriate parameters used for each metal ion studied are reported in Table 4.2.

Anionic batch studies ⁽⁵²⁾

Prior to the complexation experiments for technetium, each resin (initially in the chloride form) was equilibrated with the appropriate test solution without technetium. The resin was then buchner dried and contacted with the test solution containing the

technetium for the desired contact time. The beads were filtered out and the solution was tested for Tc-99 activity on a Tricarb counter using the standard liquid scintillation method. The amount of Tc complexed by the resin was determined by subtracting the Tc activity in the equilibrium solution from the total Tc activity in the starting solution.

Anionic column studies ⁽⁵²⁾

Standard groundwater test solution was prepared and dripped through columns containing 3.0 mL of resin (bed volume). The first fraction of eluent was collected at 100mL followed by every 200 mL of eluent. The Tc-99 activity was determined by standard liquid scintillation to determine breakthrough at 0.1%, 1.0%, and 10.0%.

Table 4.2. Atomic absorption parameters

Metal ion	Wavelength (nm)
Pb(II)	283.3
Cu(II)	324.8
Zn(II)	213.9
Ni(II)	232.0
Cd(II)	228.8

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