ABSTRACT

The importance of multi-functionality in the preparation of ion-selective polymers is evident from the structure of enzymes where specific metal ions are bound through cooperative interactions among different amino acids. In synthetic polymers, ionic selectivity is enhanced when a chemical reaction is superimposed on an 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 reduction, coordination or precipitation reactions as determined by various covalently-bound ligands. Development of three classes of dual mechanism bifunctional polymers, a new series of bifunctional diphosphonate polymers, and novel bifunctional ion-selective polymers with enhanced ionic accessibility will be presented. Bifunctional anion-selective polymers, interpenetrating polymer networks, and high-stability solvent impregnated resins will also be examined.
DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.
DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.
I. INTRODUCTION

The cooperativity of amino acid ligands in binding metal ions has been the subject of extensive research and is an important factor in their selectivity. For example, the zinc ion in carbonic anhydrase II (CAII) is bound by three separate histidine residues in the enzyme (1). This has led to CAII being used in fluorescence-based biosensors for the detection of zinc ions in solutions (2) with concentrations as low as the picomolar range (3). The microenvironment around the ligands is an additional factor in the ionic selectivity of the enzyme: amino acids with aromatic moieties near the binding site enhance the selectivity for zinc ions (4) by influencing the rigidity of the groups available for binding (5). It is this multifunctionality of enzymes that allows for selective metal ion interactions and which becomes the central theme in our research aimed at designing highly selective polymer-supported reagents.

II. ION EXCHANGE RESINS AND THE DEVELOPMENT OF ION-SELECTIVE POLYMERS

The widely available polystyrene-based sulfonic acid resin has very similar affinities for a wide range of cations (6) due to similar free energy of reactions (7). This ion exchange resin can be used to remove metal ions such as copper from solutions but only when the level of competing ions such as calcium and iron are low (8). The need for ion-selective polymer-supported complexants has thus long been recognized.

A. Reactive Ion Exchange

Helfferich proposed that selectivity is possible when ion exchange occurs along with a chemical reaction involving the metal ion (9). Eleven examples of ion exchange coupled
with chemical reactions were subdivided into four categories: in type I processes, counterions from the ion exchanger reacted with co-ions in solution (this included neutralization reactions); in type II processes, solution counterions reacted with immobilized exchange sites on the polymer; in type III processes, undissociated exchange sites were ionized by reaction with solution co-ions (this would include salt formation reactions); and in type IV processes, undissociated exchange sites were changed from one undissociated form to another by reaction with the solution co-ions. A reaction thus occurs which results in the exchanging ions no longer retaining their original chemical properties. This was later defined as reactive ion exchange which involved the exchange of ions between phases coupled with reactions that yield new products or otherwise alter initially present species allowing for complete removal of the target ion from its originating phase (10). Three methods were proposed in which ions could be chemically changed: (i) the charge on the ion is increased or decreased while retaining its original sign; (ii) the charge on the ion is decreased or increased to the opposite sign; and (iii) the charge on the ion is eliminated to give a zerovalent species. These concepts were applied and extended in the development of reactive polymers, to be detailed in section III.

B. Soluble Phosphorus-Based Metal Ion Complexants

An understanding of the development of polymer-supported reagents within the context of reactive ion exchange requires an overview of the soluble organophilic complexants used in solvent extraction processes. Solvent extraction is a popular technique due to its versatility, rapid rates of complexation, high selectivity and the extensive library of complexants that has been synthesized (11). Organophilic metal ion complexants used in solvent extraction processes have been prepared with a wide array
of functional groups. Particularly versatile are those complexants with phosphorus-based ligands, including phosphoric acids, phosphonic acids, phosphate esters and phosphine oxides. They have been studied over many years (12) and are still in current use.

Organophosphorus acids have significant affinities for rare earth and transition metal ions. Di(2-ethylhexyl)phosphoric acid (DEHPA) is an important complexant used under different conditions. A solution in hexane is able to remove trace levels of neodymium(III) from acidic solutions of varying pH where the ionic strength is kept constant at 0.1 M with sodium nitrate (13). A kerosene solution complexes yttrium(III) from highly acidic solutions (14) and iron(III) from aqueous chloride solutions (15). A kerosene solution of DEHPA which has been partially converted to its sodium salt with base becomes a more effective complexant for americium(III) from nitric acid solutions (16). A comparative study of partially neutralized phosphoric, phosphonic, and phosphinic acids dissolved in kerosene showed that the type of phosphorus acid was important to determining the affinity towards cobalt and nickel ions from acidic solutions, with the organophilic phosphinic acid being most effective (17).

Neutral organophosphorus complexants are another class of compounds that have been extensively studied. Tri-n-octyl phosphine oxide (TOPO) is one such compound. It has, for example, high affinities for both beryllium(II) and aluminum(III) and can be used to separate the former from the latter by adjusting the pH of the aqueous phase (18). Dihexyl-N,N-diethycarbamoylmethylphosphonate and octylphenyl-N,N-diisobutylcarbamoylmethylphosphonate are two compounds with the general structure \( R_2'P(O)CH_2C(O)NR_2 \) that are very effective actinide complexants from highly acidic solutions (19). From less acidic solutions, 2-(dihexylphosphino)-pyridine N,P-dioxide is a promising complexant
which is more selective for europium(III) than ytterbium(III) or cerium(III) (20).

It is the ability of phosphorus to form both ion exchange and neutral coordinating ligands with affinities for different metal ions that depend on their specific structural characteristics which became most important in our development of ion-selective polymer-supported reagents (vide infra).

C. Synergistic Interaction Between Ligands

Under certain conditions, solvent extraction with an organic solution of two different complexants yields a much greater level of extraction than would be expected from the behavior of each complexant alone. This phenomenon was termed synergistic extraction. An early observation involved the extraction of uranyl ions from acidic solutions when a complexant capable of ion exchange such as DEHPA was combined with a neutral coordinating complexant such as TOPO or tributyl phosphate (TBP) (21). Synergism has been identified in the extraction of lithium when an aqueous solution is contacted with DEHPA and TBP in kerosene (22): when the solution containing low (ppm) levels of lithium, sodium, potassium, magnesium and calcium ions, is contacted with an organic phase containing DEHPA alone, the affinity series is Ca(II)>Mg(II)>Li(I)>K(I)>Na(I) with 42.6% of the lithium being complexed; when the organic phase consists of both DEHPA and TBP, the amount of lithium complexed increases to 76.1% while complexation of the other metal ions is unchanged. The same combination of DEHPA and TBP is synergistic in the extraction of iron(III) from aqueous chloride solutions (23). Diaryldithiophosphinic acids and TOPO are synergistic in their complexation of americium(III) and europium(III) from nitric acid solutions as concentrated as 1 M whereas the phosphinic acids have no affinity for either ion when used alone (24).
Synergism is also evident when the neutral coordinating compound is a crown ether rather than an organophosphate. There is a synergistic interaction when dialkylphosphoric acids are combined with stereoisomers of dicyclohexano-18-crown-6 in the complexation of strontium and barium ions, but not calcium ions (25). In another example, the combination of dibenzo-18-crown-6 with 8-hydroxyquinoline in chloroform is synergistic for the extraction of cobalt(II) from aqueous solutions (26).

The concept of synergistic combinations between ligands with acid sites and neutral coordinating ligands to augment the extent of metal ion complexation, when combined with the concept of reactive ion exchange, led to the design and development of polymer-supported reagents with cooperative ligand interactions for enhanced metal ion affinities and selectivities. These cooperative interactions were tailored to produce a chemical or coordinative reaction.

III. BIFUNCTIONAL ION-SELECTIVE POLYMER-SUPPORTED REAGENTS

A. Dual Mechanism Bifunctional Polymers

Bifunctional polymers were synthesized with two different ligands immobilized onto a polymer support in order to determine whether synergistic interactions between the ligands could lead to enhanced metal ion affinities and selectivities. These polymers were collectively categorized as dual mechanism bifunctional polymers (DMBPs). The underlying theme is that one ligand acts through a relatively aspecific mechanism to allow metal ions access into the polymer matrix, followed by a selective recognition mechanism acting on the targeted metal ion (27). The DMBPs are divided into three classes: ion exchange is the access mechanism in each class because the ligand's hydrophilicity
makes it compatible with the metal ion's hydration shell; the recognition mechanism then
defines the selective reaction of each class.

Class I DMBPs. The first class of DMBPs consists of a reduction reaction as the
recognition mechanism combined with ion exchange for rapid access into the polymer
matrix. The Class I DMBPs focus on the synthesis of primary and secondary phosphinic
acid ligands on polystyrene (Figure 1). The resin is an effective ion exchanger for
transition metal ions, as seen in studies with Zn(II) in the presence of a large excess of
sodium ions (28, 29). The redox mechanism becomes operative when the resin is
contacted with Hg(II) or Ag(I) ions. In these reactions, the metal ion enters the matrix by
ion exchange, followed by its reduction to the zerovalent metallic state once it approaches
the P-H bond (which is the source of electrons in the reduction reaction). The primary
phosphinic acid reduces Hg(II) with a 1:1 stoichiometric ratio (Figure 2) and Ag(I) with a 1:2
ratio (Figure 3). Reduction of Hg(II) is more rapid than Ag(I) since only one Hg(II) ion must
be proximate to the P-H bond for reduction to occur. The primary phosphinic acid ligand
is then oxidized to phosphonic acid (30). The resin is stable in 4 M nitric acid at ambient
temperature. The minimum metal ion reduction potential that still allows for reduction by
phosphinic acid is approximately 0.3 V (31).

In the absence of cations capable of undergoing reduction (Ag(I), Hg(I), Hg(II), and
Cu(II)), the phosphinic acid resin was found to ion exchange in the order Pb(II)>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)
(32). Its ability to complex lanthanides and actinides was compared to the sulfonic acid
resin and quantified by the distribution coefficient, D, defined as mmol M\textsuperscript{II+} per g\textsubscript{dry resin} /
mmol M\textsuperscript{II+} per mL\textsubscript{soln} (33). A correlation of log D vs. pH for uptake of europium and
americium from nitric acid solutions shows that when the acidity is varied from 4 M to 0.25 M, the slopes of the lines for both ions with the phosphinic acid resin are 1.75 while the slopes for the sulfonic acid resin are 3.0. This indicates that the sulfonic acid exchanges with the trivalent ions while the phosphinic acid exchanges with the metal nitrate complexes (Figure 4). When sodium nitrate is added in an amount to give a constant 4 M nitrate background in all solutions of varying pH, the uptake for the phosphinic acid resin remains almost unchanged, as do the slopes of the log D vs. pH correlation (1.90 and 1.97 for Eu(III) and Am(III), respectively), while the uptake for the sulfonic acid resin falls to negligible levels and the slopes are near zero for both metal ions. This underscores the greater selectivity of the phosphinic acid resin over a wide range of solution conditions since the sulfonic acid resin exchanges for the sodium ions present in large excess which decreases the distribution coefficients for the targeted metal ions. The phosphinic acid resin was also superior in its uptake of both uranium and thorium at high acid concentrations and of plutonium at all acid concentrations in the presence of sodium ions.

In order to better understand metal ion uptake kinetics by the phosphinic acid resin, Ni(II) was studied in solutions of constant pH at 2° and 60°C (34). Equilibrium was reached in 1 h at the lower temperature and less than 15 min at the higher temperature. Ion exchange was the only mechanism operative as determined by reanalysis of the acid capacity after uptake and regeneration (a redox reaction gives an acid capacity higher than the original value). The amount of Ag(I) removed from aqueous solutions also increased as a function of temperature; the resin acid capacity after regeneration confirmed activity of the redox reaction.
Class II DMBPs. The second class of DMBPs couples ion exchange as the access mechanism with coordination as the recognition mechanism, the objective being to determine whether synergism could be observed when ligands were immobilized on a polymer support. Examples of Class II DMBPs are those with phosphonate monoethyl / diethyl ester ligands, phosphonic acid / tertiary amine ligands and carboxylic acid / pseudocrown ether ligands (Figure 5) (35, 36). In studies with the monoethyl /diethyl ester resin and americium nitrate, it was found that metal ion uptake in high levels of sodium nitrate is dependant on the percentage of diester, monoester, and diacid ligands on the phosphoryl groups (35): the monofunctional phosphonate monoethyl ester resin gave the highest Am(III) uptake of all resins studied, followed by resins with varying amounts of monoethyl /diethyl ester ligands, while resins with monoester / diacid ligands gave lower results that were similar to those of the monofunctional phosphonic acid resin. The phosphonate diethyl ester resin had almost no affinity for the americium ions. These results are in contrast to those found with silver ions which show clear evidence of synergism with the bifunctional resin (see section below on comparative study).

Class III DMBPs. The third class of DMBPs couples a precipitation reaction as the recognition mechanism with ion exchange for enhanced metal ion access (Figure 6) (37). A phosphonic acid ligand allows for ion exchange and a quaternary amine ligand leads to precipitation via its associated anion once the targeted metal ion exchanges into the resin. This results in both specificity and removal of the metal ion from solution by intra-resin precipitation which isolates the precipitated salt within the bead (Figure 7). Different cation selectivities are found depending on whether the associated anion is sulfate, thiocyanate, or iodate. The metal can be recovered by solubilizing the salt with the appropriate eluents.
Comparative study of DMBP metal ion affinities. A study of the ionic affinities displayed by a series of resins was completed in order to gain a better understanding of the mechanisms by which DMBPs interact with metal ions (38). Ten resins (viz., sulfonic acid, phosphinic acid, phosphonic acid, dimethylamine, phosphonic acid / dimethylamine, phosphonate monoethyl ester, dimethyl ester, diethyl ester, dibutyl ester, and monoethyl / diethyl ester) were contacted with 10^{-4} N solutions of five different metals (viz., Fe(III), Hg(II), Ag(I), Mn(II), and Zn(II)), each in four different concentrations of nitric acid (0.2, 1.0, 2.0, and 4.0 M) with the ionic strength maintained at a constant 4 M through the addition of sodium nitrate.

The sulfonic acid resin complexed low levels of all the transition metal ions because its ion exchange sites were saturated with the sodium ions present in much higher concentrations or inoperative (in the 4 M nitric acid solution) because the acid strength was far greater than the sites' pKa. On the other hand, the phosphinic acid resin was far more selective and displayed a series of Fe>Hg>>Ag>Mn>Zn in all solutions. Its affinity for Fe(III) and Hg(II) is significantly higher than for other metals: while the high affinity for mercury was expected due to intervention by the reduction reaction, the affinity for Fe(III) was less expected and later understood to be due to coordination through the phosphoryl oxygen. This ability to convert from an ion exchange to a coordination mechanism for certain ions, especially in solutions of high acidity, is an important property of resins with phosphoryl ligands. The phosphonic acid resin has the same general trend as the phosphinic acid resin except for a large decrease in uptake of mercuric ions due to the absence of the reduction mechanism; the high affinity for Fe(III) is retained due, again, to coordination by the phosphoryl oxygen.
The dimethylamine resin complexed moderate levels of only Hg(II) and Ag(I) while the bifunctional acid / amine resin gave results similar to those of the phosphonic acid resin. In this case, the ligands on the bifunctional resin behave independently and the distribution coefficients are seen to be reliable indicators of the extent to which ligands cooperate in the binding of metal ions. This conclusion became particularly important in results with the ester resins.

The phosphonate monoethyl ester resin performs like the phosphonic acid resin except for its higher affinity for Ag(I). The three dialkyl ester resins all retain a high affinity for Ag(I), especially from the more acidic solutions, and show an affinity series of Ag>>Hg>Fe>>Zn~Mn. Most importantly, the bifunctional monoethyl / diethyl ester resin had the highest affinity for Ag(I) of all the resins studied. Its level of complexation was much greater than could be expected from results with the monofunctional analogues; e.g., from the 4 M HNO₃ solution, the distribution coefficients for the monoethyl / diethyl, monoethyl, and diethyl resins were 2980, 500, and 550, respectively. The results thus clearly indicate participation of a supported ligand synergistic interaction. The basis for this mechanism is a compatibility between the metal ion and the ligands based on the principles of hard-soft acid-base theory with superimposed steric constraints from the coordinating ligand.

B. A General Method of Enhancing Ionic Accessibility in Crosslinked Polymers

The metal ion affinities of monofunctional resins with coordinating ligands such as the phosphonate diester resins indicate that while such resins can be selective in their ionic interactions, consistent with the behavior of soluble analogues, the kinetics of complexation can be slow due to diffusional limitations into the polymer matrix. A general method for enhancing the kinetics of complexation was thus developed that could be applied to a wide
range of coordinating ligands immobilized on crosslinked polymer supports. This was accomplished by utilizing the sulfonic acid ligand as the principal access ligand, based on the observation that the sulfonic acid resin is highly hydrophilic and has rapid ion exchange kinetics under different conditions.

Monofunctional phosphonic acid resins crosslinked with 2 and 12% divinylbenzene (DVB) were found to quantitatively complex 0.0001 N Eu(III) in 0.01 and 0.10 M nitric acid, but this decreased significantly as the acidity of the background solution increased to 0.50 and 1.0 M nitric acid (39). The reason typically given for this behavior was that the complexation mechanism changes from ion exchange to coordination at the phosphoryl oxygen as the solution pH falls below the pKa of the acid ligand and this gives a lower metal ion affinity due to competition by protons in solution for \( \text{P=O} \) sites. However, an alternative explanation would be that the polymer does not remain hydrated in low pH (high ionic strength) solutions and this prevents metal ion access due to collapse of the matrix.

When the resin was sulfonated to give a bifunctional sulfonic / phosphonic acid resin (Figure 8), complexation of Eu(III) increased to 95-100% for all solutions. The inherently hydrophilic sulfonic acid ligand thus hydrates the resin and this prevents the matrix from collapsing in highly acidic solutions. The same results were found when 0.40 M sodium nitrate was added to each of the four acid solutions, indicating that the high levels of Eu(III) complexation in the bifunctional resin are not due to exchange with the sulfonic acid ligand since it will have exchanged with the sodium ions present in large excess. The sulfonic acid ligand thus allows for access of all ions into the matrix while the phosphonic acid ligand complexes the target ion through a coordinative mechanism when solution conditions are unfavorable for ion exchange.
The effect of bifunctionality is especially pronounced as matrix crosslinking increases and contact with the ion-containing solution decreases (40). When phosphonic acid resins with crosslinking at 5, 12 and 20% DVB are contacted with a dilute solution of europium nitrate in 1 M nitric acid for 0.5 h, the amount complexed decreases from 31% to 0.61%. On the other hand, the bifunctional sulfonic / phosphonic acid resins complex 94-95% Eu(III) under the same conditions. Bifunctionality thus enhances accessibility even into highly crosslinked resins and does so to a much greater extent than by making the monofunctional resins macroporous (40).

Sulfonation may be accomplished at low temperatures with chlorosulfonic acid after the ion-selective ligand has been immobilized. It does not require the presence of unsubstituted phenyl rings since the electrophilic substitution reaction occurs on rings that have been phosphorylated (39). Additionally, it is not necessary to sulfonate all of the aromatic rings in order to increase the complexation rate. Sulfonating 20% of the aromatic rings in a fully functionalized phosphinic acid resin increased the distribution coefficient of Eu(III) in a 1 M nitric acid solution from 61 to 220 at a 0.5 h contact time (41).

IV. A New Family of Selective Polymers Based on the gem-Diphosphonate Ligand

Hydroxyethane-1,1-diphosphonic acid is known to be an effective complexant for a variety of metal ions, even from acidic solutions (42). As a result, it was decided to convert it to vinylidene-1,1-diphosphonic acid and prepare its polymerized analogue. While the monomer was too sterically hindered to homopolymerize with a free radical initiator, formation of the tetraester allowed for free radical copolymerization with acrylonitrile, styrene and DVB. After hydrolysis of the ester to the diphosphonic acid, it was found that
the polymer had slow rates of complexation. However, immobilizing sulfonic acid groups on the phenyl rings provided by incorporating styrene gave a bifunctional polymer whose ionic selectivity is coupled with rapid complexation rates (43). This polymer has been commercialized as Diphonix® ion exchange resin (Figure 9).

**Diphonix.** Diphonix forms highly stable metal complexes with tetra- and hexavalent actinides in acidic solutions by chelating the actinides with the gem-diphosphoryl group (44). The distribution coefficients for U(VI) and the tetravalent actinides (Th(IV), Np(IV), and Pu(IV)) fall within the remarkably high range of $10^4$ to $10^7$ in solutions with nitric acid concentrations up to 10 M (45). The slopes of the log $D$ vs. pH correlation are all significantly less than expected from the ionic charge, thus indicating a dominant coordinative component to the interaction. Only Am(III) uptake shows a slope indicating exchange with the trivalent ion. Comparing the kinetics of Am(III) uptake between Diphonix and its unsulfonated analogue confirms the importance of the sulfonate ligand to the rapid rates of complexation (45): Diphonix reaches 99.9% of its equilibrium uptake value at a 10 min contact time while the unsulfonated analogue requires days to reach equilibrium.

A comparative study of the log $D$ vs pH correlations with Am(III), U(VI) and Pu(IV) ions involving Diphonix, its monophosphonic acid analogue, and the sulfonic acid resin, highlights the unique ability of Diphonix to complex very high levels of metal ions due to the geminal arrangement of the diphosphoryl groups. Diphonix significantly outperforms the other resins in the complexation of uranium and plutonium ions; for example, in 10 M nitric acid, the Pu(IV) distribution coefficients for Diphonix, the monophosphonic acid resin and the sulfonic acid resin are 17000, 1000, and 20, respectively. Interestingly, Diphonix and the sulfonic acid resin behave identically towards the trivalent americium ion in
solutions less acidic than 4 M HNO₃, though as the acid concentration increases from 4 M, the sulfonic acid resin continues to complex less Am(III) while Diphonix stays constant at the level found at 4 M acid. The monophosphonic acid resin complexes the least amount of Am(III) at all acid concentrations, indicating that it is both a far less effective coordinator than Diphonix and less effective at ion exchange (46). The presence of high concentrations of sodium and calcium ions does not affect the uptake by Diphonix of tri-, tetra- and hexavalent actinides, which can allow for decontamination of numerous types of solutions (47).

A study of the uptake of transition metal ions shows that Diphonix strongly coordinates Fe(II) over the range of 0.02 to 10 M HNO₃ with a maximum at approximately 0.1 to 5 M HNO₃ (48). Over the same range of acidity, Ca(II), Co(II), and Zn(II) are complexed by Diphonix with a slope of 2 in the log D / pH correlation indicating that ion exchange is the sole sorption mechanism. From solutions at a pH between 5 and 8, Diphonix has a much higher affinity than the sulfonic acid resin for Cr(III), Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), and Pb(II) and similar affinities for Al(III), Hg(II), Sn(II), and Sb(II). Rate experiments with Co(II) in 0.05 M HNO₃, Zn(II) in 0.10 M HNO₃, Fe(III) in 1 M HNO₃, and Co(II) in pH 6 aqueous solution show that Diphonix has very fast rates of complexation for transition metal ions (45).

Diphonix has a high affinity for indium from solutions of 1 M H₂SO₄, even in the presence of 0.1 M Na₂SO₄ (49). Additionally, approximately 96% of the indium is complexed from 1 M H₂SO₄ solutions containing 1mM In(III) and 1mM Zn(II) or Cu(II). The resin displayed rapid rates of complexation under both batch and continuous flow conditions.
Diphonix II. An alternate preparation of polymers with immobilized gem-diphosphonate ligands was developed by functionalizing poly(vinylbenzyl chloride) with tetraisopropyl methylene-diphosphonate (Figure 10) (50). A gel copolymer crosslinked with 2% DVB gives 55% substitution with the diphosphonate ligand while a crosslinked vinylbenzyl chloride (VBC) - styrene copolymer (2:1 molar ratio) gives 72% functionalization, indicating that the bulky tetraisopropyl ligands sterically hinder complete reaction. When the crosslink level of the VBC-styrene copolymer increases to 5% DVB, functionalization decreases to 25%; this value is sensitive to the surface area of the copolymer since the macroporous analogue reaches 45% functionalization. Macroporosity influences metal ion uptake by the monofunctional diphosphonate resin: at a 0.5 h contact time, the 5% DVB gel resin complexes 11.4% Eu(III) from a 1 M HNO₃ solution while the macroporous resin complexes 69.2%. However, converting the gel to a bifunctional sulfonic / diphosphonic acid resin increases the Eu(III) uptake from 11.4% to 100%, again pointing to the importance of adding an access ligand to the resin.

Diphonix-A. A modified Diphonix was successfully synthesized that had an affinity for both cations and anions, which can be important to the treatment of nuclear wastes that contain both transuranium ions and ⁹⁹Tc (present as the pertechnetate anion) (51). This analogue, labeled Diphonix-A, was prepared by replacing the sulfonic acid ligand with either a quaternary trialkylammonium group (Diphonix-A, Type 1) (Figure 11) or an alkylated pyridinium group (Diphonix-A, Type 2) (Figure 12). Both Type 1 and Type 2 resins have a high affinity for TcO₄⁻, reaching equilibrium within five minutes. The Type 1 resins, however, have an apparently decreased affinity for actinide ions, which is actually due to slow complexation kinetics, while the Type 2 resins retain the rapid equilibration rate
expected from the behavior of Diphonix and an apparent high affinity for actinide ions. It is concluded that the trialkylammonium ligand interacts electrostatically with the diphosphonate ligand and this interaction needs to be broken before complexation with the actinide ions can occur; the rapid equilibration rates with the Type 2 resins indicate that this interaction is absent between the pyridinium and diphosphonate ligands. Diphonix-A, Type 2 resins may thus have an important role in radionuclide separations given an affinity for Tc\textsuperscript{O}_{4}^{-} from acidic solutions that is comparable to that of commercial anion exchange resins and an affinity for actinide ions that is comparable to Diphonix.

**Diphosil.** An inorganic analogue of Diphonix has been prepared by immobilizing the diphosphonate ligands on silica gel (52). Vinylbenzyl chloride was grafted on to silica gel after modifying the latter with a toluene solution of trichloroethylsilane and trichlorovinylsilane; reaction with tetraisopropyl methylenediphosphonate and subsequent hydrolysis gave Diphonix on silica, or Diphosil (Figure 13). It may be treated as solid waste after use in actinide separations since only 10% of its total weight is organic which results in minimal generation of gaseous by-products due to radiolytic decomposition.

While Diphosil has a lower phosphorus capacity than Diphonix (0.68 vs. 1.64 mmol / g, respectively, for two typical batches), the former has its capacity entirely on the surface layer provided by the porous silica support while the latter has its capacity distributed throughout the gel polymer bead. Diphosil thus has a higher surface capacity of ion-binding ligands on the surface than does Diphonix which obviates the need for Diphosil to have a sulfonic acid ligand for enhanced access. This is supported by rate experiments with solutions of Am(III), U(VI), Th(IV), and Fe(III) which show that both polymers reach 99% of the equilibrium value of the distribution coefficient within ten minutes of contact.
Both polymers have comparable affinities for Am(III) and U(VI) while Diphosil shows a much higher affinity for Pu(IV); for example, the Pu(IV) distribution coefficients in 1 M HNO₃ are $10^6$ and $10^6$ for Diphonix and Diphosil, respectively. The affinity for Th(IV) is very high for both polymers with the distribution coefficient being $10^6$ for both in 3 M HNO₃; results with Diphosil are less dependent on solution acidity with the effect that its distribution coefficients are greater than Diphonix in solutions more acidic than 3 M and lower than Diphonix in solutions less acidic than 3 M.

**Diphonix-CS.** The alkaline liquid portion in high-level nuclear waste storage tanks contains high levels of $^{137}$Cs and $^{90}$Sr. While Diphonix has a high affinity for Sr(II) from alkaline solutions, it has a relatively low affinity for Cs(I). Combining both cesium and strontium selectivity on a single resin would facilitate treatment of the alkaline supernate for waste minimization. In another example of how coupling the diphosphonate ligand with a second ion-selective ligand extends the conditions under which Diphonix may be applied, polyphenolic groups were immobilized alongside the diphosphonate ligand (Figure 14) (53). Tetraisopropyl vinylidene diphosphonate was first copolymerized with vinylbenzyl chloride, the -CH₂Cl groups converted to aldehyde moieties, and the polyphenolic ligands grafted there by reaction with phenol and formaldehyde. The resin prepared in this manner, referred to as Diphonix-CS, did not require sulfonation since it is to be used under alkaline conditions wherein the diphosphonate ligands are ionized, thus swelling the resin and enhancing ionic accessibility. Its affinity for both cesium and strontium is very high: from 1 M NaOH, the distribution coefficients are 3000 and 15000 for Cs(I) and Sr(II), respectively, while the corresponding values for Diphonix are 10 and 25000, respectively. Results are consistent with the two ligands in Diphonix-CS acting independently in their
complexation of Cs(I) and Sr(II) ions.

Diphonix is thus found to be a versatile resin wherein the conditions under which it can be utilized may be extended by modifying either the support or ligand structure.

V. Intra-Ligand Cooperation: Polymers with Immobilized Ketophosphonate Ligands

The metal ion affinities displayed by Diphonix are much higher than those found with other immobilized ligands and may be attributed to intra-ligand cooperation wherein the ligating sites are connected through a common atom, allowing for chelate formation with the substrate. This is in contrast to the Class II DMBPs where inter-ligand cooperation is responsible for the supported ligand synergistic interaction described earlier. Inter-ligand cooperation effects a significant increase in metal ion affinities relative to results in its absence, but intra-ligand cooperation may permit still greater affinities.

In order to more fully explore the general concept of intra-ligand cooperation, a series of polymers with immobilized ketophosphonate ligands were synthesized. The carbonyl and phosphoryl moieties were positioned adjacent to each other in the α-ketophosphonate and then separated by one and two methylene moieties to give the β- and γ-ketophosphonates, respectively (Figure 15) (54). The metal ion affinities were also compared to the monophosphonate ligand, for which intra-ligand cooperation is not possible.

Metal ion affinities with the four polymers for Pb(II), Cu(II), Cd(II), Co(II), Ag(I), and Eu(III) were quantified from solutions of 0.01, 0.10, and 1.0 M nitric acid. In each case where a trend is evident, the α-ketophosphonate outperforms the β-ketophosphonate which, in turn, is far more effective than the γ-ketophosphonate; the γ-ligand is comparable
to the monophosphonate. The results with Pb(II) and Cu(II) are representative: from 0.10 M nitric acid, the Pb(II) distribution coefficients for the α-, β-, γ- and monophosphonate ligands are 1060, 366, 40.8, and 59.8, respectively (97.5%, 90.7%, 53.1%, and 55.6% complexed) while for Cu(II) the values are 224, 64, 15.1, and 18.3 (89.5%, 63.0%, 29.6%, and 27.8% complexed).

The results are consistent with the absence of a significant interaction between the carbonyl and phosphoryl moieties in the γ-ketophosphonate, given that it behaves similarly to the monophosphonate ligand, due to an unacceptably large loss in entropy upon formation of the seven-membered ring which would result if the groups cooperated in binding the metal ion. However, interaction between the carbonyl and phosphoryl moieties clearly occurs in the α- and β-ketophosphonates to form five- and six-membered rings, respectively, with the former being somewhat favored because of the smaller loss in rotational entropy. Inter-ligand cooperation is thus an important concept for application to selective metal ion complexation studies. The ketophosphonates and diphosphonates offer a range of ionic affinities for application to metal ion separations under different solution conditions and are an important set of polymer-supported reagents for continued study.

VI. Bifunctional Anion-Selective Polymer-Supported Reagents

The design of polymer-supported reagents that are selective for metal oxyanions in the presence of common anions such as chloride, nitrate, and sulfate presents a unique challenge. An important application of a suitable resin would be removal of the radioactive pertechnetate anion from groundwater with which it is contaminated in certain areas at a
concentration that is four to five orders of magnitude less than that of other anions naturally found in groundwater (55). Commercially available anion exchange resins, including Purolite A-520-E, Ionac SR-6, Reillex HPQ, Dowex 1-X8, and Amberlite IRA-904, are not sufficiently selective for this application (55).

Metal oxyanions such as TcO₄⁻ are characterized by a single negative charge that is delocalized over a number of atomic centers resulting in a species that is highly polarizable with a low charge to volume ratio. It is reasonable to expect, based on the principles of hard-soft acid base theory (56), that a polymer-supported reagent with polarizable ligands of the opposite charge would be selective for the metal oxyanion. Since quaternary ammonium ion ligands can be prepared with a low charge to volume ratio by increasing the size of the groups on the nitrogen, trihexylamine was immobilized on poly(vinylbenzyl chloride) beads to give the trihexylammonium ion ligand which has a single positive charge associated with a very large ligand. Contact studies showed the resin to be selective for TcO₄⁻ but with a low exchange rate due to the ligand's hydrophobicity (55). While the trimethyl or triethylammonium resins reach equilibrium within 24 h (distribution coefficients of 1690 and 5690, respectively), the resin with trihexylammonium ligands does not reach equilibrium even after a contact time of 336 h, though the distribution coefficient of 28000 at that point indicates a very high affinity for the pertechnetate ion. Given the selectivity of the trihexylammonium ion ligand toward TcO₄⁻, it was evident that coupling that ligand with an access ligand could allow for rapid and selective complexation of oxyanions and thus give the first anionic analogue of the dual mechanism bifunctional polymers. Studies undertaken to combine the selectivity of the longer alkyl ammonium ligands with hydrophilic (and aspecific) ammonium ligands having
less bulky alkyl groups found that the bifunctional anion exchange resin that best combined TcO$_4^-$ selectivity with rapid rates of complexation was formed by successive reactions of macroporous beads with trihexylamine and then with triethylamine (Figure 18). This resin had a TcO$_4^-$ distribution coefficient at 24 h of 15810, compared to 1570 for the pure trihexylamine resin. Field tests under continuous conditions at the site of contaminated groundwater showed the bifunctional resin to perform approximately five times better than one of the best commercially available resins, Purolite A-520-E: at 1% breakthrough of pertechnetate, the bifunctional resin had treated 580,000 bed volumes while the Purolite resin had treated only 105,000 bed volumes (57). This behavior was confirmed with other monovalent oxyanions and established the generality of the concept of access/recognition in dual mechanism bifunctional polymers by extending it to anions.

VII. Bifunctional Interpenetrating Polymer Networks

Interpenetrating polymer networks (IPNs) are formed when the properties of one polymer are modified by the addition of a second polymer (58). In one synthetic method, an initially formed crosslinked polymer sorbs a monomer which is subsequently polymerized to form a second network that is entangled within it but not bonded to it. Including a crosslinking agent with the second monomer crosslinks the second network and prevents any phase separation that could occur between the two networks.

IPNs offer a novel means of preparing bifunctional polymers and probing for supported ligand synergistic interactions. An ion-complexing ligand, L$_1$, can be immobilized on an initially formed network and a second ligand, L$_2$, can be immobilized on the second network (Figure 17A). The resulting affinities can be contrasted with results from the
isolated $L_1$ and $L_2$ polymers. If the first network consists of non-binding groups $A_1$ and the second network is formed with ion-binding ligands $L_1$, then the effect of the microenvironment formed by network $A_1$ on the metal ion affinity of ligand $L_1$ can be quantified. The microenvironmental effect can be varied with different non-binding groups ($A_2, A_3, \ldots$) as well as by forming the second network with different ratios of $L_1$ and another non-binding group $B_1$ (Figure 17B). The non-binding groups ($A_n, B_n$) are able to modify the ion-binding affinities of ligand $L_1$ by varying the polymer's polarity or hydrophilicity. If the second network formed within the non-binding network $A_1$ consists of two binding ligands, $L_1$ and $L_2$, then the microenvironmental effect can be superimposed on any supported ligand synergistic interaction (Figure 17C).

In studying IPNs where the microenvironment of ligand $L_1$ was varied by introducing differing amounts of non-binding group $B_1$ within an initial $A_1$ network, N-vinylimidazole (VI) and ethyl acrylate (EA) were polymerized within an initial network of crosslinked polystyrene (59). Five IPNs were prepared with final VI / EA ratios of 100:0, 77:23, 53:47, 27:73, and 0:100. Imidazole was thus the ion-binding ligand and its microenvironment within the non-polar polystyrene was modified with the carboethoxy group - a moiety with no significant ionic affinity. The microenvironmental effect on the binding of Cu(II) and Co(II) was quantified from solutions buffered to pH 5 with acetate ion. This effect was evident from the experimentally determined binding constants: for Cu(II), the values were 3130, 4134, 8203, 3108, and 0 N$^{-1}$ for the IPNs with 100%, 77%, 53%, 27%, and 0% VI, respectively, while the corresponding values for Co(II) were 294, 270, 86, 129, and 0 N$^{-1}$, respectively. The results show that increasing the ester group content around the imidazole ligands up to an equimolar amount increases that ligand's affinity for Cu(II), after
which point the affinity decreases. Conversely, the affinity of the imidazole ligand for Co(II) is low and gets lower as the ester group content increases. The ester group alone, as expected, has no affinity for either metal ion and acts only to vary the polarity within the IPN. There is, therefore, an optimum microenvironment in which imidazole’s affinity for Cu(II) is maximized, probably due to an increased compatibility between the copper salt which is sorbed into the IPN and the IPN itself. The microenvironmental effect within IPNs can thus be an important means of enhancing a ligand’s affinity and selectivity for a targeted metal ion.

The influence of bifunctionality on metal ion affinities was studied by forming IPNs within polystyrene beads of 4-vinylpyridine (VP), EA, and an equimolar ratio of VP:EA followed by hydrolyzing the ester-containing IPNs to give carboxylic acid ligands (60). The IPNs were contacted with dilute (10^{-4} M) metal ion solutions of Eu(III), Ni(II), Co(II), Zn(II), Cu(II), Hg(II), and Cd(II) in 0.10 M HNO_3. The Ni(II) distribution coefficients for the VP, acid, and VP/acid IPNs are 105, 129, and 589, respectively, indicating that a supported ligand synergistic interaction is operative. Similar results are found with Co(II) and Zn(II). Synergism is not evident with Cu(II), Hg(II), and Cd(II): for example, the Cd(II) distribution coefficients are 10, 2344, and 2399 for the VP, acid, and VP/acid IPNs, respectively, indicating that the carboxylic acid ligand is solely responsible for the sorption process. With Eu(III), another effect was identified: the distribution coefficients for the IPNs as listed above are 3, 2042, and 22, respectively. In this case, bifunctionality leads to antagonism, not synergism. As confirmed by FTIR, there is hydrogen bonding between the pyridyl and carboxylic acid moieties and Eu(III) binding is not sufficiently strong to overcome it. Ions such as Cd(II) overcome the hydrogen bonding for binding to occur to one of the ligands,
while ions such as Ni(II) overcome the hydrogen bonding and bind more strongly to both ligands than to either one alone. IPNs are therefore an effective means of defining the conditions under which both the microenvironmental effect and supported ligand synergistic interaction can be effectively utilized for greater metal ion affinities and selectivities.

VIII. Bifunctional Solvent Impregnated Resins

The versatility of solvent extraction and the operational simplicity of ion exchange resins may be combined in the utilization of solvent impregnated resins (SIRs). In this technique, an organophilic complexant is sorbed within macroporous copolymer beads and the combined unit then handled as a polymer-supported reagent. Any complexant or combination of complexants may be used to form SIRs allowing a straightforward study of possible synergistic pairings without the need to develop immobilization strategies for new bifunctional immobilized polymers. In one of many examples, a SIR was prepared by combining DEHPA with TOPO and sorbing both into a macroporous support, Amberlite XAD-2 (61). The solution with an equimolar ratio of the two complexants allowed for better separation of Zn(II)/Cu(II) and Zn(II)/Cd(II) mixtures. A bifunctional complexant, O-methyl-dihexyl-phosphine-oxide O'-hexyl-2-ethyl phosphoric acid, was also sorbed within Amberlite XAD-2 (62). Zn(II), Cu(II), and Cd(II) were all complexed to a significant extent from 0.1 M NaNO₃ with the extent of complexation increasing as the solution pH increased.

A new bifunctional SIR was introduced in which ion-exchange ligands were immobilized on the macroporous support and an organophilic soluble coordinating complexant was sorbed into the polymer (63). The key advantage of solvent extraction -
flexibility in choosing among a large variety of selective soluble complexants - is retained and combined with the ease of synthesizing a monofunctional ion exchange resin. In this case, sulfonic acid ligands were immobilized on to macroporous polystyrene beads and tetrathia-14-crown-4 was sorbed into the beads. The degree of sulfonation of the polystyrene was a critical variable, with a lower degree of functionalization providing the most favorable results due to its compatibility with the organophilic crown. The crown ether itself dissolved in toluene or sorbed within non-functionalized polystyrene beads had no affinity for Cu(II) from sulfuric acid solutions. However, the crown/sulfonated SIR showed a synergistic enhancement of up to two orders of magnitude in the amount of Cu(II) complexed from sulfuric acid solution, which is perhaps the first observation of synergism in a functionalized SIR.

An important disadvantage of SIRS is the loss through aqueous phase solubility of the sorbed complexant. This is a significant problem and precludes their adaption to preparative scale applications. In order to obviate this loss of complexant, a new SIR has been prepared wherein a thin membrane coating is formed around each bead (64). This coating is hydrophilic thus preventing transport of the hydrophobic complexant out of the bead while permitting transport of the hydrophilic metal ion into the bead. The method by which this was accomplished involved: (1) converting the -CH₂Cl groups on the surface of macroporous crosslinked poly(vinylbenzy1 chloride) beads to phosphonate groups through an Arbusov reaction and then to vinyl groups through a Wadsworth-Emmons reaction; (2) sorbing the complexant into the beads; and (3) forming a thin membrane coating that is anchored to the surface of the beads from a 2% aqueous solution of glycidyl methacrylate / bis(acrylamide) in a 75/25 weight ratio. After DEHPA was encapsulated in this manner,
the beads were contacted with a solution of $10^{-4}$ M Cu(NO$_3$)$_2$ buffered to pH 8.4 in an ammonia/ammonium nitrate solution and found to complex 96% of the Cu(II) present. Most importantly, this level of complexation remained constant after five cycles of regeneration with 1 M HNO$_3$ and contact with fresh solution. By comparison, the standard SIR prepared in the same manner but without coat formation complexed the same amount of Cu(II) as the coated SIR in the first contact, but dropped to 23.2% Cu(II) after the first regeneration and 11.2% Cu(II) after the second regeneration. The hydrophilic membrane coating thus successfully retained the complexant within the pores of the beads without impeding the kinetics of metal ion transport and complex formation. The development of these high stability SIRs holds significant potential for long-term applications where soluble complexants with a targeted ionic selectivity have been identified.

IX. Current Developments

Research in our laboratory continues with bifunctional polymers involving a wide array of ligands, including aminophosphonate, phosphonoacetate, and phosphopyridyl. As will be reported in an upcoming publication, we have also synthesized a polymer-supported calixarene (65). The immobilized calix[4]arene has a high affinity for cesium ions from alkaline solutions and has the potential for being an important probe of intraligand cooperative effects since ion-complexing ligands can be placed around the ring at either the aromatic or phenolic ends. In one example, the calixarene ring in the cone conformation was substituted with phosphate groups at two of the phenolic sites (Figure 18). The order of affinity was Fe(III) > Pb(II) > Cu(II) > Ni(II) with quantitative complexation of Fe(III) and Pb(II) from 0.01 M HNO$_3$ solution. The unsubstituted calixarene,
poly(hydroxystyrene), and phosphate-substituted polystyrene had no affinity for any of the ions. It may be concluded that the high metal ion affinities and selectivities were due to a combination of the calixarene ring and the ion-complexing ligands in a conformation that permitted intra-ligand cooperation.

X. Conclusion

The design and development of ion-selective polymer-supported reagents is an important challenge for the 21st century. Bifunctional polymers in the form of beads, membranes, and high stability SIRS are exceptionally promising in their ability to enhance our understanding of metal ion coordination chemistry as well as in their application to environmental remediation, water purification, chromatographic separations, and sensor technology. Target selectivities will be best achieved with structures that maximize intra-ligand cooperation, such as immobilized macrocycles. Further breakthroughs from leading laboratories around the world are anticipated.

XI. Acknowledgments

We are grateful for the long-standing support we have received from the U.S. Department of Energy, Office of Basic Energy Sciences. Additionally, we have had productive collaborations with colleagues at the Oak Ridge National Laboratory (Drs. Bruce Moyer and Gilbert Brown have been principal collaborators), Argonne National Laboratory (it was the close cooperation with Dr. Phil Horwitz that led to Diphonix), and Los Alamos National Laboratory (Dr. Gordon Jarvinen has been a valued collaborator there). The graduate students who have worked with so much enthusiasm on this research are noted as co-authors in the publications cited. A special thanks goes to Dr. Robert Ober for compiling the references used in this report.
REFERENCES

46. E.P. Horwitz, R. Chiarizia, H. Diamond, R.C. Gatrone, S.D. Alexandratos, A.W.


Figure Captions

Figure 1. Class I DMBP with primary and secondary phosphinic acid ligands

Figure 2. Reduction of Hg(II) by the primary phosphinic acid ligand in aqueous solution

Figure 3. Reduction of Ag(I) by the primary phosphinic acid ligand in aqueous solution

Figure 4. Complexation of metal nitrate by the phosphinic acid resin

Figure 5. Class II DMBPs with phosphonate monoester / diester, phosphonic acid / phosphonate monoester, phosphonic acid / tertiary amine, and carboxylic acid / pseudocrown ether ligands

Figure 6. Class III DMBP with phosphonic acid / quaternary amine ligands

Figure 7. Ion exchange / precipitation reaction of the Class III DMBP with silver ions in aqueous solution

Figure 8. Sulfonation of polystyrene-supported phosphonic acid

Figure 9. Synthesis of Diphonix

Figure 10. Synthesis of Diphonix II

Figure 11. Diphonix-A, Type 1 resin

Figure 12. Diphonix-A, Type 2 resin

Figure 13. Diphosil

Figure 14. Diphonix-CS

Figure 15. Ketophosphonate resins used in the study of intra-ligand cooperation

Figure 16. Synthesis of an anion-selective dual mechanism bifunctional polymer

Figure 17. Schematic representation of interpenetrating polymer networks

Figure 18. Polystyrene-supported calix[4]arene
\[
\text{Phenylphosphonic acid} + [\text{M(NO}_3\text{)}_n]^{3-n} \rightarrow \\
\text{Phenylphosphinate} \quad [\text{M(NO}_3\text{)}_n]^{3-n}
\]
\[
\begin{align*}
\text{HO} & \quad \text{OH} \\
\text{P} & \quad \text{=O} \\
\text{P} & \quad \text{=O} \\
\text{HO} & \quad \text{OH}
\end{align*}
\]

\[
\begin{align*}
\text{CH}_2 & \quad \text{CH}_2 \quad (\text{CH}_2)_{4} \quad \text{OH} \\
\text{OH}
\end{align*}
\]
DESIGN AND DEVELOPMENT OF SELECTIVE
POLYMER-SUPPORTED REAGENTS:
APPLICATION TO IONIC SEPARATIONS AND ORGANIC REACTIONS

Triennial Performance Report
August 1, 1998 - October 31, 2001
(extended to October 31, 2002)

Spiro D. Alexandratos

May 2002

PREPARED FOR THE U.S. DEPARTMENT OF ENERGY
UNDER GRANT NUMBER DE-FG05-86ER13591

I. Introduction

The design and synthesis of polymer-supported reagents modified with ligands displaying high ionic affinity and selectivity continues to be an important area of research. The need to remove toxic transition metal ions and radionuclides dissolved in environmental water as well as waste treatment facilities is well known. Ion-selective polymers incorporate ligands capable of chelating or coordinating with a target metal ion. Such ligands include, amines (e.g., poly(ethylene-imine)s, piperazines, imidazoles, and amidoximes), carboxylic acids, crown ethers, phenols, and phosphonates. Polystyrene is a widely used support because of its versatility but poly(glycidyl methacrylate) is seeing increased use because of its greater compatibility with aqueous solution and polar reagents. The polymers are prepared by suspension polymerization to produce beads of appropriate size (usually 100 - 250 μm).

The most commonly available polymers used to complex metal ions from aqueous solutions are the cation exchange resins (consisting of sulfonic or carboxylic acid ligands) and the anion exchange resins (consisting of dimethyl- or trimethylamine ligands). Amphoteric ion exchange resins (with both acidic and basic functional groups) and chelating resins (with functional groups such as iminodiacetic acid) are also known. Phosphorus-based ion exchange and chelating resins, though less widely available, deserve increased emphasis given that their versatility and applicability

*The papers cited in this Progress Report are only to our publications during the current period. Appropriate review of the literature may be found in those publications.
to a wide range of conditions has been detailed in the area of solvent extraction. Di(2-ethylhexyl) phosphoric acid, tributyl phosphate and trioctylphosphine oxide are only three of a multitude of ligands that have been found to have high ionic affinities under a wide range of conditions.

Our research has focused on polymer-supported reagents with phosphorus ligands and we have emphasized bifunctional polymers prepared with two different ligands immobilized onto a polymer support in order to determine whether synergistic interactions between the ligands can lead to enhanced metal ion affinities and selectivities. These polymers are collectively categorized as dual mechanism bifunctional polymers (DMBPs). The underlying theme is that one ligand acts through a relatively aspecific mechanism to allow metal ions access into the polymer matrix, followed by a selective recognition mechanism acting on the targeted metal ion. The DMBPs are divided into three classes: ion exchange is the access mechanism in each class because the ligand's hydrophilicity makes it compatible with the metal ion's hydration shell; the recognition mechanism then defines the selective reaction of each class. The reactions studied to date are metal ion reduction, coordination and precipitation.

The versatility of polymer-supported reagents extends to their applicability as catalysts and reactants in organic synthesis. The polymers have been used as acid catalysts, phase transfer catalysts, reductants, oxidants, and halogenating agents. We have used them as reactants in the Mitsunobu reaction and as catalysts in the Prins reaction (see section VI below).

II. Polymer-Supported Reagents with Enhanced Ionic Affinities

The immobilized diphosphonic acid ligand displays high ionic affinities on a wide variety of polymer supports. The Diphonix® class of ion exchange resins has thus been developed in
collaboration with the Separations Science Group at Argonne National Laboratory (Dr. E. P. Horwitz (ret.), Group Leader). The original version of the resin had the gem-diphosphonic acid groups bonded within a polystyrene matrix. The preparation of the starting tetraalkyl vinylidene diphosphonate monomer has been patented. Later versions modified the resin to include anion exchange groups and bonding to a silica matrix. A resin with selectivity for both cesium and strontium was prepared by bonding both diphosphonate and oligophenolic ligands onto the polystyrene support (Figure 1). Diphonix-CS can remove cesium, and strontium ions from alkaline solutions through the combined action of the two ligands. For example, the distribution coefficients from 2 M NaOH are 2400 for cesium and 2400 for strontium. (Indications are that the resin will complex actinides from basic solutions, but this has not been thoroughly examined.)

Diphonix-CS as the tetraisopropyl ester, rather than the diphosphonic acid shown in Figure 1, has been found to display significant potential as a cesium-selective sensor when bonded to plastic scintillation fibers. Its performance was compared with that of a conventional ion exchange resin, Amberlite IRP-69, where the latter was ground to a size comparable to the Diphonix-CS and coated on to the fiber. Both Diphonix-CS(ester) and the Amberlite performed comparably when complexing cesium from a level of 1600 nCi/mL in 1M NaOH. However, when contacted with tank waste...
simulant containing cesium at 1600 nCi/mL, the fiber with IRP-69 retained only 2% of the original signal detected from 1M NaOH solution while signal retention was seven-fold greater from the fiber with Diphonix-CS(ester), thus indicating its enhanced selectivity and feasibility as a cesium-sensor.

In general, chelating and other selective resins have not been widely utilized because of slow rates of complexation with the targeted ions. In the earlier project period, we have shown that introducing a sulfonic acid ligand into a polymeric matrix bearing an ion-selective ligand can dramatically increase the rate of complexation while retaining the expected selectivity. This has allowed for the commercialization of Diphonix and its acceptance in industrial applications. Research during the current performance period has extended this concept. The monofunctional phosphonic acid and bifunctional phosphonic/ sulfonic acid resins have been prepared (Figure 2) and their performance compared. Over a wide range of crosslinking (2 - 25% divinylbenzene (DVB)), the bifunctional resin far outperforms the monofunctional resin. For example, in complexing Eu(III) from a 10^{-4} N solution in 1M HNO_3, using polymer supports crosslinked with 12% DVB, the monofunctional resin complexes 7% Eu(III) while the bifunctional resin complexes >99%.

The results are the identical when the solution also contains 0.40N NaNO_3, indicating
that it is not the non-selective sulfonic acid group that is responsible for the high levels of complexation. The sulfonic acid ligand must function to hydrate the matrix, making it compatible with the hydrated metal ions in solution and allowing the phosphonic acid ligands to rapidly complex the metal ions as they diffuse into the matrix; additionally, the more hydrophilic matrix is less prone to collapse in solutions with high ionic strength.\textsuperscript{12}

Results with the bifunctional resins allow us to propose a principle of bifunctionality: polymer-supported reagents with enhanced metal ion complexation kinetics require the presence of an access ligand along with a recognition ligand for targeted ionic selectivity.\textsuperscript{13} A defining study entailed studying the effect of increasing matrix rigidity on the extent of complexation. Poly(VBC) beads crosslinked with 5, 12 and 20\% DVB were prepared and functionalized with phosphonic acid and phosphonic/sulfonic acid ligands. Complexation with the phosphonic acid resins decreased from 97.7\% to 3.60\% Eu(III) at a 0.5 h contact time from $10^{-4}$ N Eu(NO$_3$)$_3$ / 0.10 N HNO$_3$ solution as the crosslink level in the gel resins changed from 5\% to 20\% DVB. Making the support macroporous increased the amount of Eu(III) complexed, but only marginally (for example, complexation by the 20\% DVB resin increased from 3.60\% to 31.2\% Eu(III)). However, immobilizing sulfonic acid groups on the aromatic rings bearing the phosphonic acid ligands allowed the level of complexation to exceed 99\% Eu(III) for all resins studied. Similarly large increases in complexation were observed from 1 N HNO$_3$ solutions where the sulfonic acid group participates minimally in ion exchange. Other studies in which the target ion is in the presence of a large excess of sodium ions confirm that enhanced complexation by the bifunctional resin is due to the influence of the sulfonic acid group on the resins' hydrophilicity and not on its participation in exchange of the target ion.
An alternative method to gaining rapid rates of complexation may be the preparation of functionalized foams. In research performed in collaboration with Los Alamos National Laboratory, foams were prepared from VBC and functionalized to give phosphonic and diphosphonic acid ligands. Contacting gel beads, macroporous beads and foam functionalized with phosphonic acid ligands, each crosslinked with 20% DVB, with a solution of $10^{-4} \text{N } \text{Fe(NO}_3\text{)}_3$ in 0.04 N HNO$_3$ at a 0.5 h contact time, showed the amount complexed as 9.98%, 62.41% and 98.05% Fe(III), respectively. The enhanced complexation kinetics displayed by the foam are attributed to the foams’ greater porosity and water content relative to the beads.

Given the high ionic affinities displayed by Diphonix due to intra-ligand cooperation by the gem-diphosphonate ligand, a set of $\alpha$-, $\beta$-, and $\gamma$-ketophosphonates were prepared and their metal ion affinities determined (Figure 3). The Perkow reaction was used in the synthesis of the $\alpha$-ketophosphonate while the Arbusov reaction was used for the $\beta$- and $\gamma$-ketophosphonates. The results with Eu(III) complexation from a 1 N HNO$_3$ solution are representative: the level of complexation for the $\alpha$-, $\beta$-, and $\gamma$-resins is 98.7%, 88.6%, and 40.5%, respectively. The monophosphonic acid resin (see Figure 2) complexes 16.5% Eu(III) under the same conditions. In general, the $\alpha$-ketophosphonate complexes greater levels of metal ions than the $\beta$-ketophosphonate and both complex far greater levels of ions than the $\gamma$-ketophosphonate resin. The latter gives results

![Chemical structures](image.png)

Figure 3.$\alpha$-, $\beta$-, and $\gamma$-ketophosphonic acid resins
comparable to the monophosphonic acid resin. Intra-ligand cooperation, now between the carbonyl and phosphoryl moieties, is again found to be critical to high ionic affinities.

Immobilization of ligands on to crosslinked polymer supports requires reactions that proceed with negligible levels of side reactions so that the final resin has a well-defined structure. In certain cases, this is not possible, especially when multiple steps are required to achieve a targeted ligand. Solvent-impregnated resins (SIRs) are an alternative functionalization technique. With SIRs, a soluble complexant (including, in some cases, an inert organic solvent acting as a diluent) is sorbed into crosslinked macroporous copolymer beads (usually polystyrene). Losses of complexants into the aqueous phase due to their small but finite solubility hinder acceptance of this technique. In this research, a copolymer comprised of glycidyl methacrylate and N,N-methylenebis(acrylamide) has been developed that can coat the SIRs. The copolymer was chosen to be hydrophilic so that the monomers would not be sorbed within the hydrophobic macroporous beads and the copolymer, once formed as a coating, would permit the metal ions to enter from the aqueous solution but would not permit the hydrophobic sorbed complexant from diffusing out of the pores. Additionally, the coating was anchored onto the SIR bead through vinyl groups formed on the surface prior to sorption of the complexant (Figure 4). Metal ion studies confirm the ability of the coating to yield a highly stable SIR. Uncoated and coated SIRs (prepared with di(2-ethylhexyl)phosphoric acid) were contacted

![Figure 4. Reaction to form vinyl groups on the surface of SIR beads](image-url)
with $10^{-4}$ N Cu(NO$_3$)$_2$ solutions buffered to pH 8.4. More than 95% Cu(II) is complexed after the first contact period. The amount complexed by the coated SIR remained constant through five cycles (each cycle consisted of a 24-h contact time with fresh solution followed by decomplexation of the copper ions from the SIR and regeneration of the complexant by 2 h contact with 1 N HNO$_3$).

In contrast to this, the amount complexed by the uncoated SIR decreased to 23.2% by the second cycle and 11.2% at the third cycle, after which point the contact was terminated. The coating alone has no affinity for copper ions. Additionally, initial studies show that the rate of complexation through the coating is very rapid. High stability SIRS are thus a promising alternative to polymers with covalently bound ligands.

III. Bifunctional Anion Exchange Resins

The Principle of Bifunctionality has now been extended to anionic recognition with an application to groundwater remediation. In collaboration with the Separations Science Group at the Oak Ridge National Laboratory, a new class of bifunctional anion exchange resins with high selectivity and rapid kinetics for removing pertechnetate from contaminated groundwater has been developed. The bifunctional resin consists of two quaternary ammonium groups: an organophilic trihexylammonium ligand yields higher TcO$_4^-$ selectivity and a hydrophilic triethylammonium ligand allows for enhanced kinetics. The affinity of the former ligand for pertechnetate was reasoned from hard-soft acid-base theory given that the anion is large and polarizable and would thus be expected to complex with a cation whose charge is diffuse (the bulky trialkyl groups prevent anions from becoming

\[
\text{CH}_3\text{N(C}_2\text{H}_5)_3, \quad \text{access ligand (rapid kinetics, low selectivity)}
\]

\[
\text{CH}_3\text{N(C}_2\text{H}_5)_3, \quad \text{recognition ligand}
\]
proximate to the positive charge on the nitrogen, making that positive charge only weakly felt). Column breakthrough experiments with TcO₄⁻ show that the bifunctional resin achieves 10% breakthrough at 1730 bed volumes while one of the best commercially available resins for this application, Purolite A-520E, shows breakthrough at less than 50 bed volumes. The resin's selectivity for the pertechnetate ion is further seen by the distribution coefficients determined after a 24 h contact time: the values for trialkylammonium resins with ligands trimethyl, triethyl, tripropyl, tributyl, trihexyl, and trihexyl/triethyl are 6350, 16200, 22300, 31800, 1540, and 37300, respectively. The bifunctional resin has been patented and licensed to a major ion exchange manufacturer. The resin has also been shown to have an affinity for the perchlorate ion, another soft anion that is a problem in the environment.

IV. Immobilization of Calixarenes on to Crosslinked Polymers

Calixarenes are macrocyclic compounds with four to eight repeat units formed by the condensation of p-alkylated phenols with formaldehyde. Substitution with ion-complexing ligands can allow for the synthesis of a wide array of selective coordinating compounds. Since phosphorus-containing ligands have been found to complex a large number of metal ions, with selectivity being determined by the precise ligand structure, the coordination chemistry that results when calixarenes are phosphorylated are expected to have unique potential for selective metal ion separations and in ion sensor technology. Calixarenes substituted at the -OH group with diphenylphosphinate ligands have been evaluated as actinide complexants. Cooperativity among the ligating groups after substitution at all -OH groups within the macrocycle can influence ionic affinities. We have now immobilized calix[4]arene onto polystyrene beads with well-defined crosslink levels and
microenvironments and then modified them with phosphate ligands in positions that allow a comparative study of intra- and inter-ligand cooperation.

Immobilization of the calixarene to polystyrene beads was successfully accomplished through an etherification reaction (Figure 5). The supported calixarene complexes 96.7% Cs(I) from a $10^{-4}$ N solution in 1 M NaOH. Poly(hydroxystyrene) complexes 36.5% Cs(I) from the same solution. Immobilization of the calixarene onto a polymer support thus does not affect its inherently high affinity for cesium ions. Substituting two of the three remaining hydroxyl groups on the calixarene with diethoxyphosphoryl moieties leads to quantitative complexation of Fe(III) and Pb(II) ions from 0.01 M HNO$_3$ solutions. The unsubstituted calixarene complexes 6.00% Fe(III) and 7.36% Pb(II) while diethoxyphosphoryl-substituted poly(hydroxystyrene) complexes 10.0% Fe(III) and 3.76% Pb(II). The calixarene therefore acts as a scaffold on which ligands can be immobilized in close enough proximity to permit cooperative binding of metal ions.

V. Synthesis and Characterization of Bifunctional Phosphonate-Substituted Polyamines

Studies with bifunctional polymers have been continued in order to determine the conditions under which supported ligand synergistic interaction can be observed. Amines are an important class
of complexants because of their ability to coordinate metal ions through the lone pair electrons. They also undergo a variety of derivatization reactions. In the latest study, the Mannich reaction was applied to the phosphorylation of resins with monoamine, ethylenediamine, diethylenetriamine, and tetraethylenepentamine ligands to give a series of bifunctional aminomethylphosphonic acid resins. The microenvironment around each ligand was varied by preparing fully functionalized resins (Figure 6), then a set with 82 mol% phenyl groups in the polymer, and a third set with 82 mol% carbomethoxy groups. The affinity of the resins for Cu(II), Cd(II), Pb(II), and Eu(III) was evaluated from solutions buffered at pH 5. Synergism was observed under certain conditions where both groups operating together complexed more metal ion than either one alone. Synergistic complexation of Cd(II) by all bifunctional aminomethylphosphonate resins (regardless of microenvironment) and of all metal ions by all bifunctional resins within the carbomethoxy microenvironment was quantified: for example, 26% Cd(II) is complexed by the ethylenediamine resin (distribution coefficient of 26), and 49% Cd(II) is complexed by the phosphonic acid resin (distribution coefficient of 48), but the bifunctional aminomethylphosphonic acid resin complexed 98% Cd(II) (distribution coefficient of 2300), which far exceeds the combined distribution coefficients of the monofunctional resins. Results are consistent with the conclusion that ion exchange by the phosphonate portion of the ligand and coordination by the amine portion cooperate as a dual mechanism for metal ion complexation.

Figure 6. Mannich reaction on immobilized diethylenetriamine resin
VI. Polymer-Supported Reagents in Organic Chemistry

In addition to their use in separations science, functionalized polymers have also been used as catalysts and reagents in many organic syntheses. In a study performed during the current budget period, the Prins reaction between formaldehyde and styrene was probed with immobilized sulfonic acid ligands as the catalyst (Figure 7) in order to examine the microenvironmental effect, i.e., the influence of groups around a catalyst ligand that do not take part in the reaction but can affect the polar character of the area around the ligand.25 Cross-linked polystyrene beads were sulfonated to varying degrees of substitution. Styrene was also copolymerized with butyl methacrylate and methyl methacrylate followed by complete sulfonation of the phenyl rings. The microenvironmental effect in polymer-supported catalysts was thus quantified by correlating the reaction kinetics with the neighboring group content, defined as the mole percent of neighboring groups (i.e., phenyl, carbobutoxy, or carbomethoxy) relative to the total sites (neighboring and sulfonic acid) in the polymer. Increasing the phenyl group content from 0 to 25% (i.e., decreasing the degree of substitution from 100 to 75%), increased the rate constant from 23.1 to 56.2 M⁻¹ s⁻¹ while a further increase lowered the rate constant. The carbobutoxy and carbomethoxy groups showed the same trend but the neighboring group content at which the maximum rate constant is observed (i.e., the critical neighboring group
content, CNGC) shifted to 15 and 10%, respectively. The rate constants were lower at the CNGC when phenyl groups were replaced by ester groups. When the neighboring group content increased from 20% to 55%, the rate constant decreased 3-fold with phenyl groups, 5.5-fold with carbobutoxy groups, and 12-fold with carbomethoxy groups. These results were rationalized by the hypothesis that a less ionic microenvironment may allow for a higher concentration of styrene within the polymer and lead to an immediate reaction with protonated formaldehyde. When sulfonation dropped below a given level, product formation decreased due to slower formation of protonated formaldehyde. The critical neighboring group content can thus be an important variable in tuning the performance of a catalyst for a given reaction through an optimum microenvironmental effect.

1. Polymer-Supported Reagents for the Selective Complexation of Metal Ions: An Overview
   R.A. Beauvais and S.D. Alexandratos
   Reactive and Functional Polymers, 36, 113-123 (1998)

2. Ion-Selective Polymer-Supported Reagents
   S.S. Smith and S.D. Alexandratos
   Solvent Extraction & Ion Exchange, 18, 779-807 (2000)

3. Design of Novel Polymer-Supported Metal Ion Chelating Agents
   S.D. Alexandratos and L.A. Hussain

4. Polymer-Supported Phosphorus Containing Ligands for Selective Metal Ion Complexation
   S.D. Alexandratos and K.E. Ripperger
   In “Adsorption and its Application in Industry and Environmental Protection”

5. Polymer-Supported Reagents: The Role of Bifunctionality in Ion-Selective Complexants
   S.D. Alexandratos
   In “Ion Exchange and Solvent Extraction”, vol 14, A. SenGupta, Y. Marcus Eds.,

6. Polymer-Supported Reagents: Synthesis and Application to Organic Reactions
   S.D. Alexandratos and D.H.J. Miller
   In “Advanced Functional Molecules and Polymers”, H.S. Nalwa, Ed.,

7. Recent Advances in the Chemistry and Applications of the Diphonix Resins
   E.P. Horwitz, R. Chiarizia, S.D. Alexandratos and M. Gula

8. Synthesis of Tetraalkyl Vinylidene Diphosphonate Monomer
   S.D. Alexandratos
   European Patent 600,519 (September 16, 1998)

9. Diphonix-Cs: A Novel Combined Cesium and Strontium Selective Ion Exchange Resin
   R. Chiarizia, E.P. Horwitz, R.A. Beauvais and S.D. Alexandratos

10. Chelating Scintillation Fibers for Measurements of $^{137}$Cs
    J. Headrick, M. Sepaniak, S.D. Alexandratos and P. Datskos

-15-
11. A Mechanism for Enhancing Ionic Accessibility into Selective Ion Exchange Resins
S.D. Alexandratos, C.A. Shelley, E.P. Horwitz and R. Chiarizia

12. Bifunctional Phenyl Monophosphonic / Sulfonic Acid Ion Exchange Resin
S.D. Alexandratos, C.A. Shelley and E.P. Horwitz
United States Patent 6,232,353 (May 15, 2001)

13. Ion-Selective Polymer-Supported Reagents: The Principle of Bifunctionality
S.D. Alexandratos and S. Natesan

14. Functionalized Polymer Foams as Metal Ion Chelating Agents with Rapid Complexation Kinetics
S.D. Alexandratos, R.A. Beauvais, J.R. Duke and B.S. Jorgensen

15. Synthesis of α, β, and γ-Ketophosphonate Polymer-Supported Reagents: The Role of Intra-Ligand Cooperation in the Complexation of Metal Ions
S.D. Alexandratos and L.A. Hussain

S.D. Alexandratos and K.P. Ripperger
Industrial & Engineering Chemistry Research, 37, 4756-4760 (1998)

17. Development of Novel Bifunctional Anion Exchange Resins with Improved Selectivity for Pertechnetate Sorption from Contaminated Groundwater
Environmental Science and Technology, 34, 1075-1080 (2000)

Environmental Science and Technology, 34, in press (2000)

S.D. Alexandratos, G.M. Brown, P.V. Bonnesen and B.A. Moyer
United States Patent 6,059,975 (May 9, 2000)

20. The Design of Selective Resins for the Removal of Pertechnetate and Perchlorate
21. Efficient Treatment of Perchlorate-Contaminated Groundwater with Bifunctional Resins

22. Coordination Chemistry of Phosphorylated Calixarenes and Their Application to Separations
Science
S.D. Alexandratos and S. Natesan

S.D. Alexandratos and S. Natesan
Macromolecules, 34, 206-210 (2001)

24. Enhanced Metal Ion Affinities by Supported Ligand Synergistic Interaction in Bifunctional Polymer-Supported Aminomethylphosphonates
S.D. Alexandratos and M.J. Hong
Separation Science and Technology, 37, 2587-2605 (2002)

25. Microenvironmental Effect in Polymer-Supported Reagents. 2. The Prins Reaction and the Influence of Neighboring Group Content on Catalytic Efficiency
S.D. Alexandratos and D.H.J. Miller

-17-