

# New polymer-supported ion-complexing agents: Design, preparation and metal ion affinities of immobilized ligands

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## Abstract

Polymer-supported reagents are comprised of crosslinked polymer networks that have been modified with ligands capable of selective metal ion complexation. Applications of these polymers are in environmental remediation, ion chromatography, sensor technology, and hydrometallurgy. Bifunctional polymers with diphosphonate/sulfonate ligands have a high selectivity for actinide ions. The distribution coefficient for the uranyl ion from 1 M nitric acid is 70,000, compared to 900 for the monophosphonate/sulfonate polymer and 200 for the sulfonic acid ion-exchange resin. A bifunctional trihexyl/triethylammonium polymer has a high affinity and selectivity for pertechnetate and perchlorate anions from groundwater. In one example, its distribution coefficient for perchlorate ions in the presence of competing anions is 3,300,000, compared to 203,180 for a commercially available anion-exchange resin. Polystyrene modified with *N*-methyl-*D*-glucamine ligands is capable of selectively complexing arsenate from groundwater. It complexes 99% of the arsenate present in a solution of 100 mg/L arsenate with 560 mg/L sulfate ions. Its selectivity is retained even in the presence of 400 mg/L phosphate. There is no affinity for arsenate above pH 9, allowing for the polymer to be regenerated with moderate alkali solution. In studies aimed at developing a Hg(II)-selective resin, simple amine resins were found to have a high Hg(II) affinity and that affinity is dependent upon the solution pH and the counterion.

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## 1. Introduction

Polymer-supported reagents oftentimes consist of polystyrene or poly(glycidyl methacrylate) beads crosslinked with divinylbenzene that have been modified with ligands designed to function as reagents, catalysts, or ion-selective complexants. The beads are prepared by suspension polymerization. When the polymer is to be used as a selective complexant, the objective is to design new ligands for separations applied to environmental remediation, ion chromatography, sensor technology, and hydrometallurgy. Such ligands include amines, thiols, hydroxamic acids, and macrocycles [1]. This paper is a synopsis of the research in the author's laboratory; a complete literature review is included in the cited references.

## 2. Dual mechanism bifunctional polymers

Polymers applied to metal ion recovery are substituted with a given ligand [2]. Dual mechanism bifunctional poly-

mers (DMBPs) were developed to give ionic selectivity with rapid rates of reaction following the principle of reactive ion exchange described by Helfferich [3] wherein an ion-selective reaction is superimposed on the ion exchange process. The three classes of the DMBPs are ion exchange/reduction, coordination, and precipitation resins (Fig. 1). The ion exchange/reduction resin has phosphinic acid ligands and is capable of reducing Hg(II), Ag(I), and Cu(II) to the free metal [4]; one example of the ion exchange/coordination resins has diester/monoacid ligands and has a high affinity for silver ions [5]; and the ion exchange/precipitation resins have phosphonic acid/quaternary ammonium ligands which display a high Ag(I) affinity when the counterion in the polymer is the chloride ion [6].

## 3. Bifunctional diphosphonate/sulfonate resins

Vinylidene-1,1-diphosphonic acid (VDPA) is a water-soluble compound with a high affinity for actinide ions [7]. Its immobilization within a polymer support was expected to yield a solid reagent that could be used for the selective complexation of actinide ions from highly acidic solutions. Poly-

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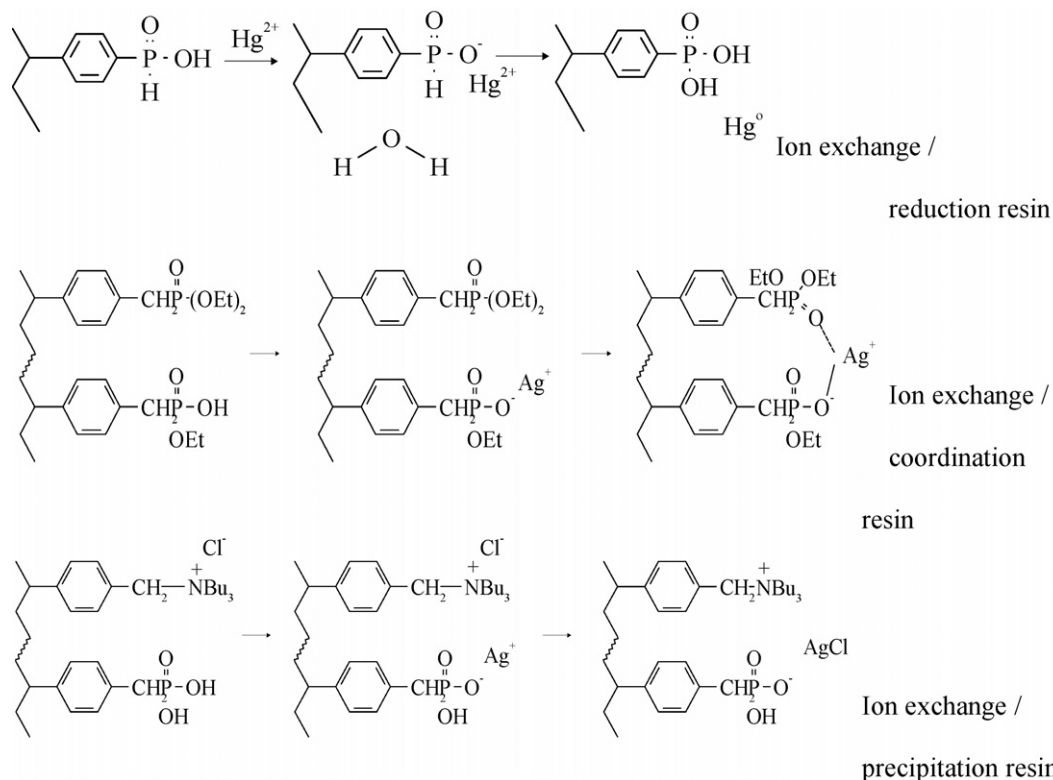


Fig. 1. The three classes of dual mechanism bifunctional polymers.

merization was achieved by using styrene, acrylonitrile, and divinylbenzene as co-monomers. The level of complexation remained low due to the polymer's hydrophobicity until the aromatic rings were sulfonated to give the final form of the bifunctional polymer, which was commercialized as Diphonix (Fig. 2). An example of its high metal ion affinity is indicated by results from 1 M HNO<sub>3</sub>: the distribution coefficient for Diphonix for UO<sub>2</sub><sup>2+</sup> is 70,000, compared to 900 for the corresponding monophosphonate resin and 200 for the sulfonic acid resin.

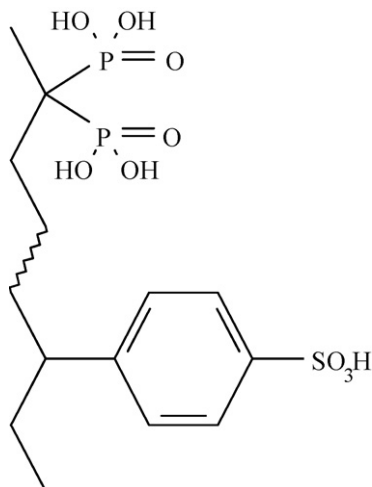
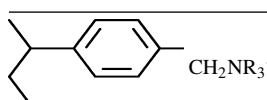


Fig. 2. Bifunctional diphosphonic acid/sulfonic acid resin.

#### 4. Biquaternary trihexylamine/triethylamine resins

Pertechnetate (TcO<sub>4</sub><sup>-</sup>) and perchlorate (ClO<sub>4</sub><sup>-</sup>) ions are contaminants in groundwater in different parts of the world [8,9]. Both are large, polarizable anions and their selective removal was found to occur with resins bearing large, polarizable quaternary ammonium sites. Using groundwater test solution, the results with a series of quaternary amine resins (Table 1) show that as the bulkiness of the amine group increases, the distribution coefficient for pertechnetate also increases up to tributyl, at which point it decreases precipitously. However, this was found to be due to kinetics, not the thermodynamic stability of the complex. The preparation of a bifunctional resin with both trihexyl and triethyl groups gave a resin with a distribution coefficient

Table 1  
Distribution coefficients for pertechnetate by different monofunctional amine resins

 CH <sub>2</sub> NR <sub>3</sub> <sup>+</sup>	D(TcO <sub>4</sub> <sup>-</sup> )
-CH <sub>2</sub> N(CH <sub>3</sub> ) <sub>3</sub>	6350
-CH <sub>2</sub> N(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub>	16200
-CH <sub>2</sub> N(C <sub>3</sub> H <sub>7</sub> ) <sub>3</sub>	22300
-CH <sub>2</sub> N(C <sub>4</sub> H <sub>9</sub> ) <sub>3</sub>	31800
-CH <sub>2</sub> N(C <sub>6</sub> H <sub>13</sub> ) <sub>3</sub>	1540
Amberlite IRA-900	2460
Purolite A-520E	12800
Reillex HPQ	4540

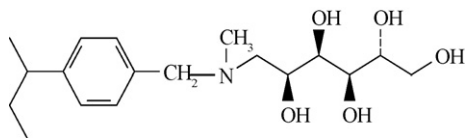


Fig. 3. *N*-methyl-D-glucamine resin.

of 37,300 [10]. The resin has been commercialized as BiQuat. In the treatment of contaminated groundwater, it shows 1% breakthrough at 580,000 bed volumes, compared to 105,000 bed volumes with PuroLite A-520E. In the treatment of groundwater contaminated with perchlorate, BiQuat shows breakthrough at 100,000 bed volumes, compared to 20,000 bed volumes for A-520E.

### 5. Arsenic-selective resin

The *N*-methyl-D-glucamine resin (NMDG) is well known for its high affinity for the borate ion under alkaline conditions (Fig. 3). In studies examining its affinity for other anions, it was found to have a high affinity and selectivity for the arsenate ion from aqueous solutions at neutral pH [11]. The percent removal of arsenate from an aqueous solution of 100 mg/L arsenate and 560 mg/L sulfate for the NMDG resin, Amberlite IRA-900, Reillex HPQ, BiQuat, Alcoa CPN, Apyron XP, and Apyron MP is 99%, 43%, 22%, 25%, 42%, 50%, and 56%, respectively. Complexation is unaffected by the presence of phosphate ions. The NMDG resin has no affinity for arsenate when the solution pH exceeds 9.0, indicating that it can be regenerated with alkaline solution after arsenate loading. It was determined that the key variable in its selectivity is that the resin has to be protonated prior to contact with the aqueous solution: the sorbitol moiety forms a stable complex with As(V) while the amine moiety maintains an acidic microenvironment within the resin.

### 6. Amine resins for the complexation of mercury(II)

The removal of mercury from water in the environment has been the subject of much research due to the metal's toxicity and its ability to bioaccumulate within living tissue. In a study of three simple polystyrene-bound amines with primary amine  $-\text{CH}_2\text{NH}_2$ , dimethylamine  $-\text{CH}_2\text{N}(\text{CH}_3)_2$ , and diethanolamine  $-\text{CH}_2\text{N}(\text{CH}_2\text{CH}_2\text{OH})_2$  ligands, it was determined that the resins have a significant affinity for Hg(II) by complexation through the nitrogen [12]. Solution pH is an important variable. When vials with 10 mL of  $10^{-4}\text{N}$   $\text{Hg}(\text{NO}_3)_2$  are contacted with 0.10 g of each of the three resins with the solution acidity within the range 0.0001–2 M  $\text{HNO}_3$ , the resins display different affinities. At pH 3.3 and greater, >98% of the Hg(II) is complexed by the three resins. Their affinities decrease as the solution acidity increases, but the decrease is less pronounced with the  $-\text{CH}_2\text{N}(\text{CH}_2\text{CH}_2\text{OH})_2$  (DEA) resin than it is with either the  $-\text{CH}_2\text{N}(\text{CH}_3)_2$  (DMA) or  $-\text{CH}_2\text{NH}_2$  (PA) resins: thus, at pH 1, the %Hg(II) complexed is 82%, 61%, and 40% for the DEA, DMA, and PA resins, respectively. The extent of complexation increases when the acid is changed from  $\text{HNO}_3$  to HCl: the DMA resin complexes Hg(II) nearly quantitatively even at pH  $-0.5$

(3 M HCl); 92% is complexed from 5 M HCl. The affinity of the resins for Hg(II) from nitrate solutions is  $\text{DEA} > \text{DMA} > \text{PA}$  while from chloride solutions it is  $\text{DMA} > \text{DEA} > \text{PA}$ . Under the conditions of these experiments, the resins show no affinity for Pb(II), Cd(II), Cu(II), Zn(II), and Ca(II). In studying the reason for the different behavior of the resins in the different solutions, the results in HCl may reflect that  $\text{HgCl}_2$  is the dominant species and that complexation increases as the electron density at the nitrogen increases. In  $\text{HNO}_3$ , the DEA resin may have the highest affinity for mercury because the ionic form of Hg(II) dominates and the  $-\text{OH}$  moiety may enter into the complexation.

### 7. Conclusion

Polymer-supported reagents will continue to gain emphasis in research as problems in groundwater remediation and wastewater treatment gain ever-increasing priority. As indicated in this brief review, the modification of a polymer as simple as polystyrene results in reagents with a wide range of selectivities depending on the covalently bound ligand. Actinide and mercury recovery from wastewater and the removal of pertechnetate, perchlorate, and arsenate from groundwater are only a few of the important problems that are being addressed. In this laboratory, research is now focused on modifying polystyrene with scaffolds and then modifying the scaffolds with ion-selective ligands, the advantage to this approach being that the ligands are in known stereochemical arrangements. This results in increased selectivity for the phosphate ligand [13]. Additional studies on the mechanism of interaction between polymer-supported reagents and the lanthanide ions are also in progress [14].

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